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STUDIES OF THE METAL-BINDING SITES IN MACROCYCLIC QUADRIDENTATE LIGANDS

A thesis submitted to the Council
for National Academic Awards in
partial fulfilment of the requirements
for the degree of Doctor of Philosophy
by

Daljit Kaur Uppal

January 1986

The work described in this thesis was carried out in the School of Chemistry, The Polytechnic of North London in collaboration with I.C.I. Organics Division.

STUDIES OF THE METAL-BINDING SITES IN MACROCYCLIC QUADRIDENTATE LIGANDS

by DALJIT KAUR UPPAL

Abstract

The preparations of quadridentate macrocyclic ligands with N_4-, O_2N_2- and S_2N_2-donor-sets are described. 10-Methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane (I) and 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane (II) have been prepared via Schiff base condensation reactions of linear diamines with 2-methyl-3-ethoxyacrolein followed by high pressure hydrogenation. The Co(II), Ni(II) and Cu(II) complexes of II and a copper(II) complex of I are reported. A novel synthetic route has been devised for the analogous S_2N_2-macrocycle, 8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane (III), involving the tosylation of 1,3-Bis(*o*-aminophenylthio)-propane followed by cyclisation with propan-1,3-ditosylate in the presence of anhydrous potassium carbonate. Detosylation to yield III was carried out using sodium napthalenide. The problems incurred in the purification of III are discussed and the best separation from other impurities was achieved using gel filtration techniques with Sephadex LH-20, eluting with halogenated alkanes. This synthetic route was adapted to cyclise six ditosylated macrocycles of varying ring sizes (13 to 16), which have alkyl chain of different lengths between the heteroatoms. The related O_2N_2-macrocycle 8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane (IV) and a pentadentate S_2N_3-macrocycle, 8,11,14-triaza-1,5-dithio-6,7:13,14-dibenzocyclohexadecane, (V) were obtained by this method after detosylation. The preparation of the copper(II) complex of III is reported. Two new macrocyclic S_2N_2-complexes have been isolated via metal template syntheses; [(8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane-9,11-dienato)nickel(II)] monotetrafluoroborate (VI) and [(8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradeca-9,11-dionato)nickel(II)] (VII). Protonation constants and metal complex stability constant data for I, II and their linear analogues are reported and compared with those of analogous 14-membered macrocycles. High resolution ^1H nmr spectra of these two macrocycles indicate that the macrocycles are relatively rigid and that the methyl substituent adopts an equatorial location in a pseudo-chair conformation of the propane linkages between the anilino nitrogen atoms. The X-ray structures of II and its low- and high-spin nickel(II) complexes $[Ni(II)](BF_4)_2$ and $[Ni(II)(NCS)_2]$ respectively are described and the goodness-of-fit of the high-and low-spin Ni^{2+} ion for the ligand cavities are compared for other 14-membered tetra-azamacrocycles. Preliminary molecular mechanics calculations for these structures are also included and also suggest that equatorial siting of the methyl substituent is energetically more favourable than axial siting.

Preface

While registered as a canditate for the degree for which submission is made the author has not been a registered canditate for another award of the CNAA or of a University. The results and conclusions presented in this thesis represent original work by the author unless specific reference is made to the contrary.

In partial fulfilment of the requirements of the degree the author completed the following courses

(a) Kinetics of Metal Complexes

(b) Organometallic reagents in Organic Syntheses.

To my parents

Acknowledgements

I would like to thank the following people who have given advice and help over the past three years.

My supervisor, Dr Peter A Tasker, for his encouragement, advice, patience and continuous help.

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Dr L F Lindoy and his research team at James Cook University for obtaining the protonation constants and metal complex stability data for my ligands. Thanks are also due to Mr Larry Brigden for performing molecular mechanics calculations referred to in this work.

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My family for being so supportive and understanding throughout this period.

The Science Research Council, for providing the funds to support this SERC/CASE award.

Abbreviations

Å	Angstrom 10^{-10} metre
AcOH	Acetic Acid
b	Broad
cm	Centimetre
^{13}C nmr	Broad-Band Noise Proton Decoupled Carbon-13 nmr
d	Doublet
dm	decimetre
DMA	Dimethylacetamide
DMF	Dimethylformamide
Et	Ethyl
ET_2O	Diethylether
EtOH	Ethanol
F_c	Calculated Structure Factor
F_o	Observed Structure Factor
g	Grams
glc	Gas Liquid Chromatography
^{1}H nmr	Proton Nuclear Magnetic Resonance
J	Coupling Constant (Hz)
L	Ligand
l	litre
M	Metal Ion
M^*	Molecular Ion
mc	Multiplet Component
Me	Methyl
MeOH	Methanol
mmol	Millimoles

M_r	Relative Molecular Mass
m/z	Mass to Charge Ratio
nmr	Nuclear Magnetic Resonance
o-	ortho
OAc	Acetate
p-	para
p	Pentet
Ph	Phenyl
R	Alkyl
R	Residual Index in Crystallography
ROH	Alcohol
R_w	Weighted Residual Index
s	Singlet
t	Triplet
THF	Tetrahydrofuran
tlc	Thin Layer Chromatography
TMS	Tetramethylsilane
TsO	Tosylate (4-toluenesulfonate)
TsOH	4-Toluenesulfonic Acid
δ	Chemical Shifts in ppm
ν	Stretching Frequency of Bond (cm^{-1})
w	Weak

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CHAPTER 2: Preparation of the Ligands

CHAPTER 3: Properties of X_2N_2-Macrocycles

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CHAPTER 1: Introduction

CHAPTER 1: Introduction

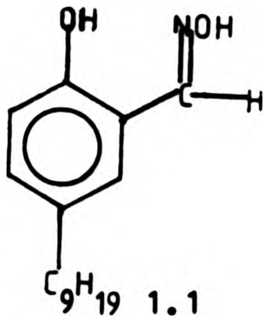
The project involved the investigation of routes to new classes of quadridentate macrocyclic ligands based on relatively inexpensive aromatic precursors. The macrocycles had variable donor sets and as a result, were thought to show a wide range of complexing abilities. The development of selective ligating agents for base metal ions is of current interest to the Mining Chemicals Group in the collaborating institution.

1.1 Pyrometallurgy and Hydrometallurgy

It is only within the last 30 years, that there has been significant use of hydrometallurgical methods for winning of base metals. Pyrometallurgy involves the extraction of metals by the application and action of heat. Previously only pyrometallurgical methods were used exclusively for metal separation from ores. Pyrometallurgical methods are becoming less viable due to rising energy costs, environmental problems and the depletion of the high grade ores which are needed for smelting processes.

In hydrometallurgy involving solvent extraction a ligand is often used to selectively extract one type of metal ion from an aqueous mixture. The ligand imparts a lipophilic solubility on the resulting complex which can then be extracted into an organic phase[1]. The first metal to be extracted commercially in this way was uranium in the 1940's[1]. During the 1960's the method was applied to extraction of base metals such as copper, cobalt, nickel and zinc.

I.C.I.'s 5-nonyl-2-hydroxybenzaldoxime (1.1) has become a successful extractant for copper in an aqueous medium (see scheme 1.1).

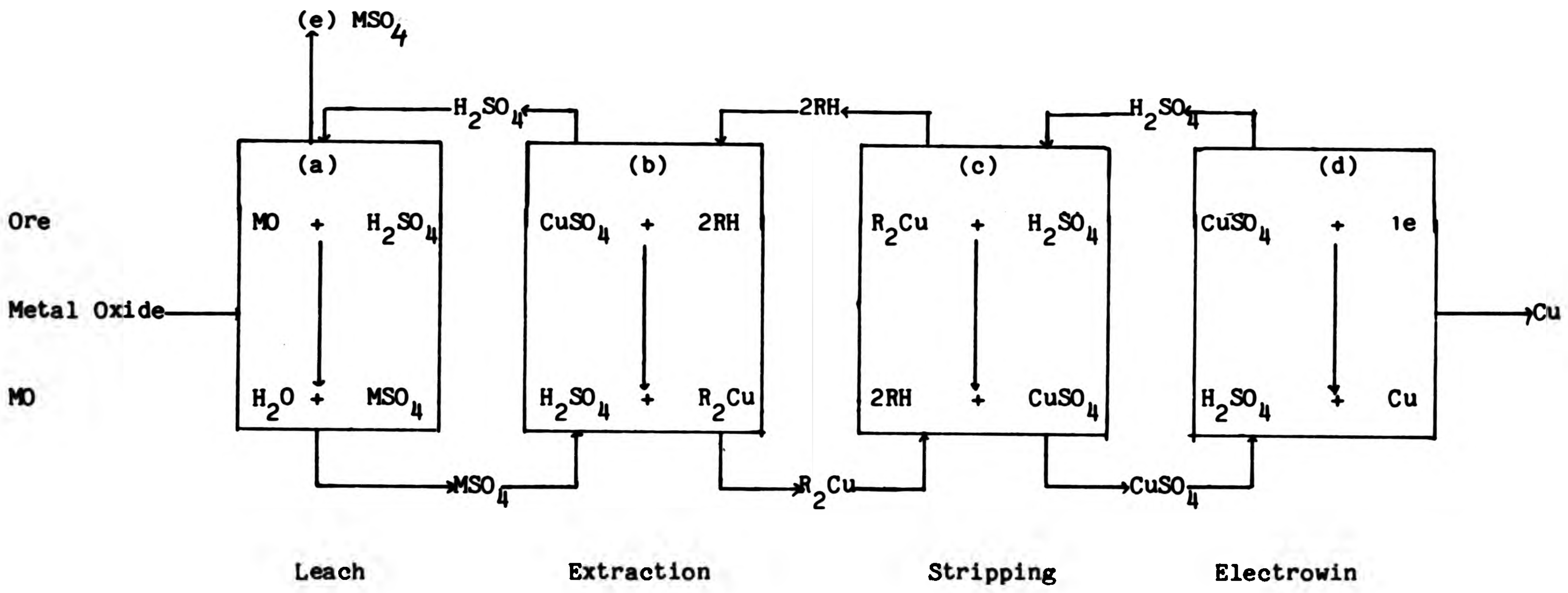


1.1

Copper is now obtained in large quantities by solvent extraction with oxime reagents (see below). For both base and rare metals, extraction is more difficult due to lack of suitable extractant ligands. Research at I.C.I Organics Division is being carried out to develop new solvent extraction agents. Some of the work undertaken in this project was related to this problem by considering the design and synthesis of ligands likely to show metal-ion discrimination.

Scheme 1.1

Extraction of Copper from an Aqueous Solution by an Organic Long Alkyl Chain Solvent Extractant



(a) Leaching takes place here in an aqueous medium. H_2SO_4 is used to form the copper sulphate from the ore.

(b) Extraction takes place in a mixer-settler where the organic (kerosene) and aqueous phases are beaten together to transfer the copper ions from the aqueous phase to the organic phase as the copper complex. The two phases are then separated and collected.

(c) In the stripping process a stronger sulphuric acid solution is used to remove the copper from the organic phase back into an aqueous phase.

(d) In the electrowin step pure copper is removed from the aqueous phase by an electrochemical process (usually electrolysis).

(e) A bleed stream is maintained to remove metal sulphates other than copper to prevent large concentrations of metal sulphates accumulating in the extractor.

1.2 Criteria of a Good Solvent Extractant

A solvent extractant agent must fulfil many requirements based on economic and safety factors. The ligand must selectively ligate the desired metals. The complexation and stripping reactions should be fast, and the complex formed must be stable in the extracting media. The complex must be soluble in an organic phase in order to be separated from the aqueous medium. The stability of the complex must be such that heteroatom concentration or protonation of the ligand or some other method yields the metal in high concentrations. In the oxime case this was by means of a "pH swing", and the complexed form of the ligand was protonated.

$$CuL_2 + 2H^+ \rightleftharpoons 2LH + Cu^{2+}$$

In the oxime extraction of copper the following equilibrium was created. A strong reagent helps to shift the equilibrium to the right.

$$[RH_2Cu]^{2+} \rightleftharpoons [R_2Cu] + 2H^+$$

1.3 Strength of the Extractant

The efficiency of the extractant is dependent upon the equilibria set up in the binary phase system. Equations for the extraction of copper from a sulphate solution by an oxime extractant are given below:

$$RH_{(org)} \rightleftharpoons RH_{(aq)}$$

$$RH_{(aq)} \rightleftharpoons H^+_{(aq)} + R^-_{(aq)}$$

$$R^-_{(aq)} + Cu^{2+}_{(aq)} \rightleftharpoons RCu^+_{(aq)}$$

$$RCu^+_{(aq)} + R^-_{(aq)} \rightleftharpoons R_2Cu_{(aq)}$$

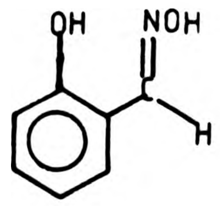
$$R_2Cu_{(aq)} \rightleftharpoons R_2Cu_{(org)}$$

The overall equation for the reaction in the aqueous phase may be written as:

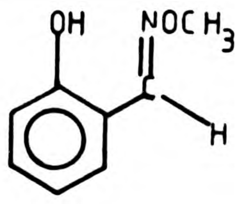
Salt of Strong Acid + Weak Acid → Salt of Weak Acid + Strong Acid

For ligand (1.1) the pK_a value was <u>ca</u> 9.2. For ligands 1.2 and 1.3 pK_a and $pH_{\frac{1}{2}}$ values are given below:

Ligand	1.2	1.3
pK_a	10.53	11.04
$pH_{\frac{1}{2}}$	0.2	>4.5

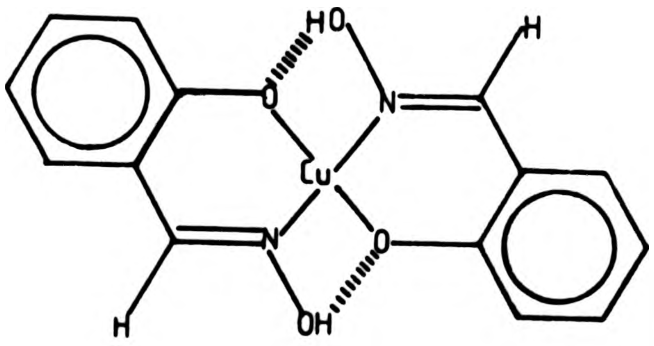


1.2



1.3

$pH_{\frac{1}{2}}$ is the pH at which 50 % of the copper is present in the complex form. From the figures above the ligand with R=OCH_3, was a weaker extractant than the one with R=OH. This was because the complex of ligand (1.3) R=OCH_3 was not stabilised by intramolecular hydrogen bonding when the chelate rings were formed with copper.



1.4 Selectivity of Complexation

Selectivity in extraction depends on several equilibria being set up simultaneously (see section 1.3). One of these is complex formation in the aqueous phase.

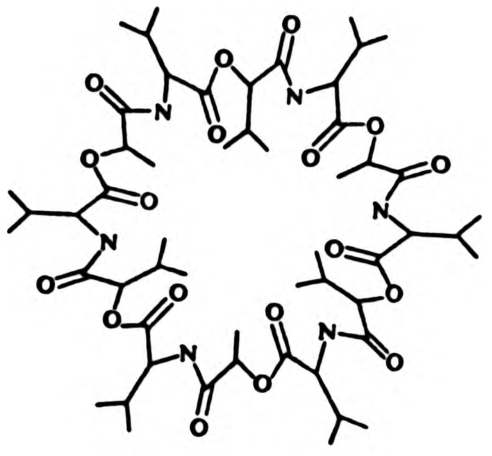
$$RCu^{+}_{(aq)} + R^{-}_{(aq)} \rightleftharpoons R_2Cu_{(aq)}$$

A useful way of considering selectivity of complexation of two metal ions was to compare overall stability constants. For two different divalent metal ions M_1^{2+} and M_2^{2+} the following equilibria may be set up on reacting with a given ligand.

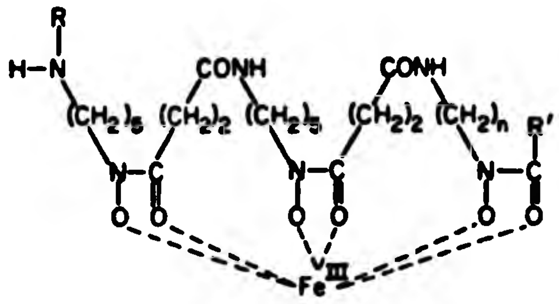
$$L + M_1^{2+} \rightleftharpoons LM_1^{2+}$$

$$L + M_2^{2+} \rightleftharpoons LM_2^{2+}$$

Selectivity was judged by the difference in $\log K_1$ values for the two metal ions, and $\Delta\log K_1$ was a measure of the discrimination shown by a particular ligand. Some naturally occurring systems have large $\log K_1$ values. These ligands tend to be cyclic and/or have rigid structures, e.g. the antibiotic valinomycin[2,3] binds to potassium much more readily than to sodium ions ($\Delta\log K_1$=3.0). Another example is the ferrioxamine group of ligands. These ligands complex in a highly selective manner to iron(III)[4]. Ferrioxamines have three hydroxamic acid groups per molecule so that a neutral complex is formed with iron(III). In ferrioxamines the three acid groups are part of a rigid ligand framework.



Valinomycin



Ferrioxamine

1.5 Ligand Systems Chosen for Study

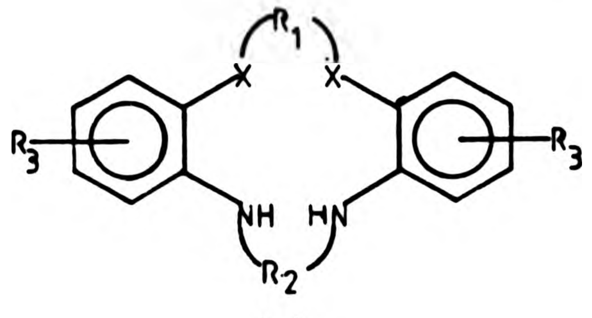
In this project ligands were designed to carry out a systematic investigation of the factors which influence selectivity of complexation. Macrocycles of the general type 1.4 had been chosen because these ligands offered the possibility of examining dependence of metal-ion discrimination ($\Delta\log K_1$ see above and section 1.4) on the following:

(i) Nature of the donor set. Synthetic routes could be envisaged for the compounds with X = NH, O and S (see below).

(ii) The ring-size of the macrocycle.

(iii) Variation of the nature and bulk of substituents on the inner-great-ring.

Initially the 14-membered rings 1.4 (with $R_1 = R_2 = -(CH_2)_3-)$ were studied and variation of the nature of X was investigated.

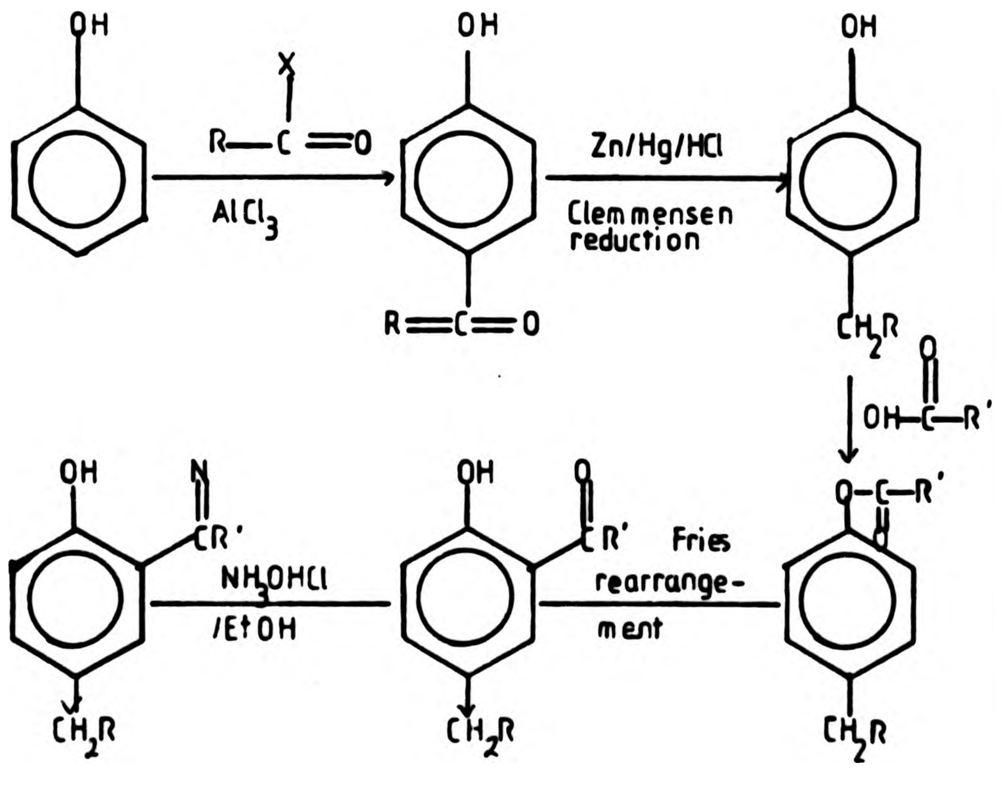


1.4

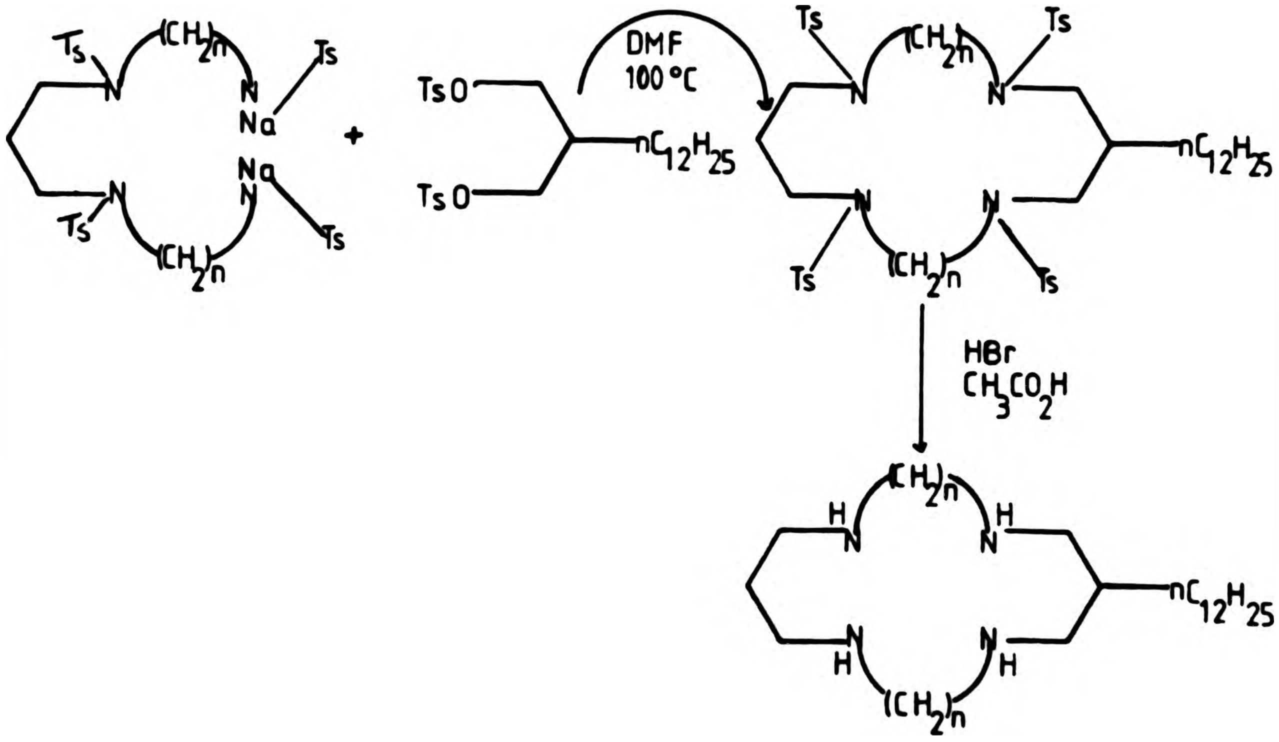
1.6 Functionalisation of Ligands to Incorporate Different Substituents

An obvious requirement for a good solvent extraction is solubility in an organic solvent (preferably kerosene) of both the reagent and its metal complex (see below). Normally this is imparted by introducing long-chain alkyl groups into the ligand (see section 1.2).

For the I.C.I. reagent (see section 1.1) the alkyl group was introduced very early in the synthetic scheme[5].

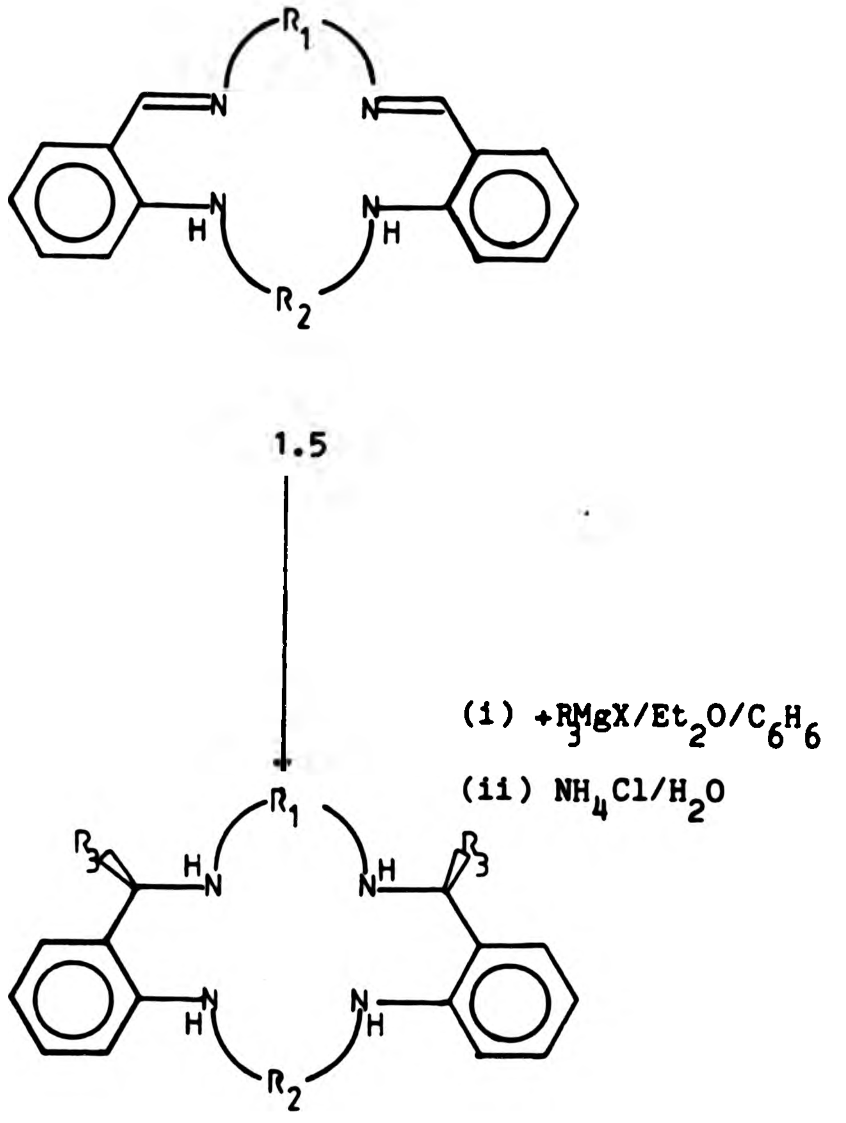


Similarly for macrocyclic ligands of the "cyclam" type introduction of lipophilic groups has also been achieved, by incorporating alkyl groups early in the synthetic scheme, e.g. into the ligand precursors for the cyclisation reaction[6].



In theory this approach could also be used to introduce long-chain substituents into the macrocycles 1.4 studied in this thesis. However, it may be necessary to develop different cyclisation conditions which are effective for precursors containing the large substituents.

An alternative strategy is to introduce a long-chain alkyl group into the preformed macrocycle. Recently alkyl groups have been introduced into certain types of N_4-macrocycles by reacting the appropriate di-imines with Grignard reagents[7] or alkyl lithium reagents (see below). These routes should offer a convenient method for introducing long-chain alkyl substituents.



1.5

(i) +$R_3MgX/Et_2O/C_6H_6$

(ii) NH_4Cl/H_2O

1.6

1.7 Macrocyclic Ligands

Synthesis of macrocyclic ligands has developed very rapidly over the last fifteen years. In general macrocyclic ligands contain rings with 12 or more atoms. The majority of synthetic ligands fall into two main chemical classes[8], based upon the donor atoms which are present in the inner-great-ring.

(i) "Crowns", cyclic polyethers. These have oxygen donors and show discrimination towards group IA and IIA metal ions.

(ii) Tetra-aza macrocycles. A large number of naturally-occurring and synthetic macrocycles contain four nitrogen donor atoms. These ligate well to most transition metal ions, but are weaker ligands towards many other ions such as those of group 1A and IIA metals.

Current interest[9] in metal complexes of tetra-aza macrocycles is partially due to these complexes being regarded as biological models for metalloporphyrins.

A much smaller number of synthetic macrocycles contain mixed donor atom sets for example O_2N_2 and S_2N_2 (see below). It may be possible to vary the metal-ion discrimination ($\Delta \log K_1$, see above) by varying the donor atom set.

1.7.1 Macrocyclic Effect

Usually both the kinetic[10] and thermodynamic stabilities[11] are higher for the cyclic ligands than for their linear analogues. Cabbiness and Margerum[12] first reported the "macrocyclic effect"[11] in 1969. This effect has been studied most thoroughly with aliphatic tetra-amines[9,13-18]. Cabbiness and Margerum ascribed the macrocyclic effect of tetra-amines in copper(II) complexes to a combination of restrained configuration (an entropic effect) and abated solvation effects (predominately an enthalpic effect) of the free macrocycles compared to their open-chain analogues.

Generally the thermodynamic effect[12] refers to the decrease of Gibbs free energy (ΔG^{o}) for the metathetic reaction[20]

$$ML^{n+}_{(noncyclic)} + L_{(cyclic)} \longrightarrow ML^{n+}_{(cyclic)} + L_{(noncyclic)}$$

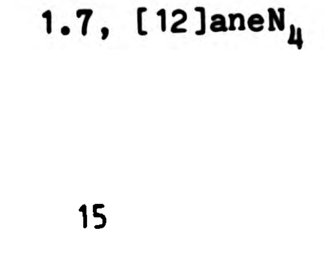
The Gibbs free energy for the macrocyclic effect can be split into its enthalpic and entropic components. Macrocyclic enthalpies are thought to arise from the following sources.

During complexation of the non-cyclic ligand to the metal ion enthalpy is expended in arranging the donor atoms around the metal. In the formation of the chelate rings from the linear ligands steric repulsions are experienced between components of the ligand. The macrocycle already has its donor atoms arranged in almost the correct position for co-ordination. When the metal ion is a good fit for the hole-size[21] of the macrocycle, strong bonding occurs and a large release of enthalpy results. The desolvation enthalpy of the macrocycle is more favourable than that for the linear ligand because extended configurations of the latter usually allow a greater degree of solvation (see also below).

The favourable entropy term results because there is only a small loss on complexation. The entropy loss for the linear ligand is much greater because the ligand has to be rearranged to the correct configuration prior to complexation. This results in considerable loss of flexibility in the chain linking the donor atoms. The relative importance of the entropy term in the origin of the thermodynamic macrocyclic effect is still debatable[20] and may vary from ligand to ligand.

The enhanced stability of cyclic tetra-amines over that for related linear tetra-amines was assigned to a more favourable enthalpy term by Hinz and Margerum[22]. In the case of the macrocycle fewer amine hydrogen bonded water molecules are displaced on metal co-ordination. Hence the favourable enthalpy term is assumed to be due to lower solvation of the ligand.

Kodama and Kimura[23] have reported thermodynamic enthalpy and entropic values for the copper(II) complex of 1,4,7,10-tetra-azacyclododecane, [12]aneN_4. They inferred that the greater stability was due to a favourable entropy term. Conversely Paoletti and co-workers[15] reported that for the same copper(II) complex of [12]aneN_4 a favourable enthalpic effect was observed on complexation. Recently, direct calorimetric determinations[9,15,22-25] have shown that a good fit of the hole-size of the macrocycle to the ionic radius of the metal results in a favourable enthalpy term. The macrocyclic entropy term was always found to be favourable. In conclusion both enthalpic and entropic factors play an equally substantial role in the macrocyclic effect shown by aliphatic tetra-aza ligands.

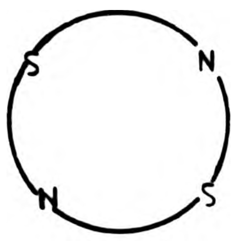


1.7, [12]aneN_4

1.8 Previous Work with Macrocycles of the Type Involved in this Project

1.8.1 S_2N_2 Macrocycles

Macrocycles with mixed nitrogen-sulphur donor sets have attracted considerable interest recently because they can be used as potential models for the co-ordination sites of certain copper proteins. Quadridentate S_2N_2-systems may potentially exist in the *cis*- and *trans*- forms[26] (1.9 and 1.8 respectively).



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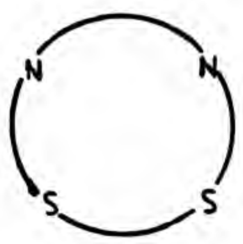
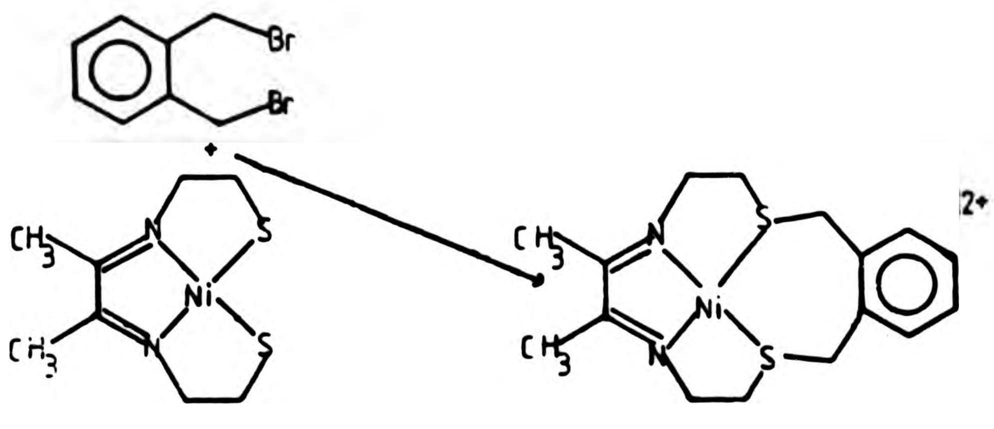


1.9

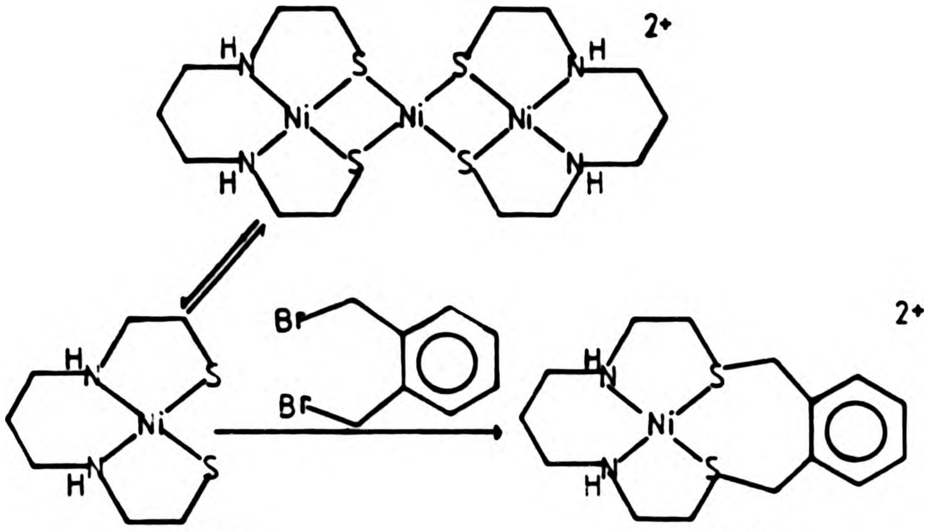
The preparation of the 14-membered ring system 1.11 in 1964 represented[27] one of the earliest examples of template synthesis, and made use of the nucleophilicity of co-ordinated thiolate groups[28,29].



1.10

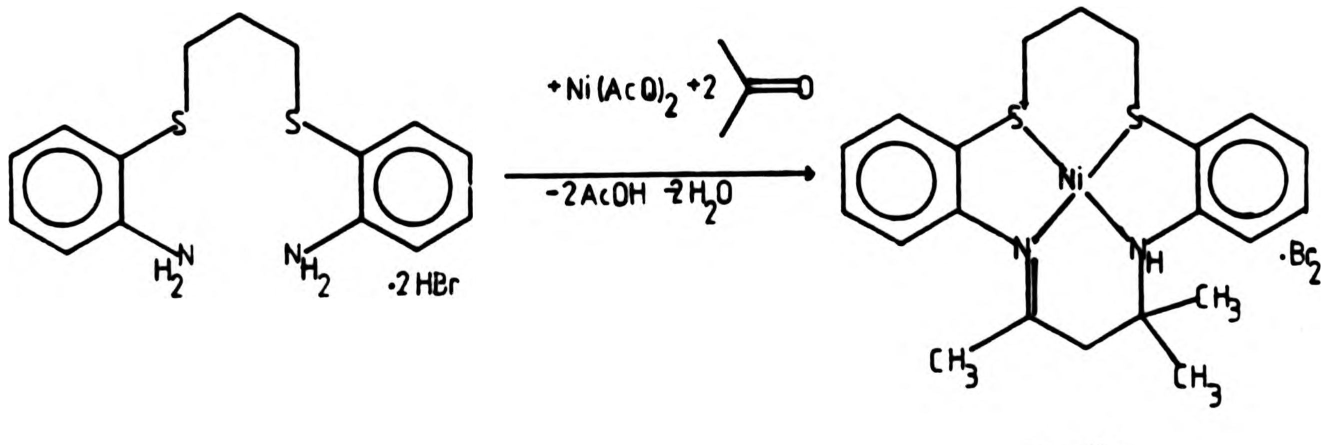
1.11

A very similar reaction was involved[30] in the preparation of 1.13.



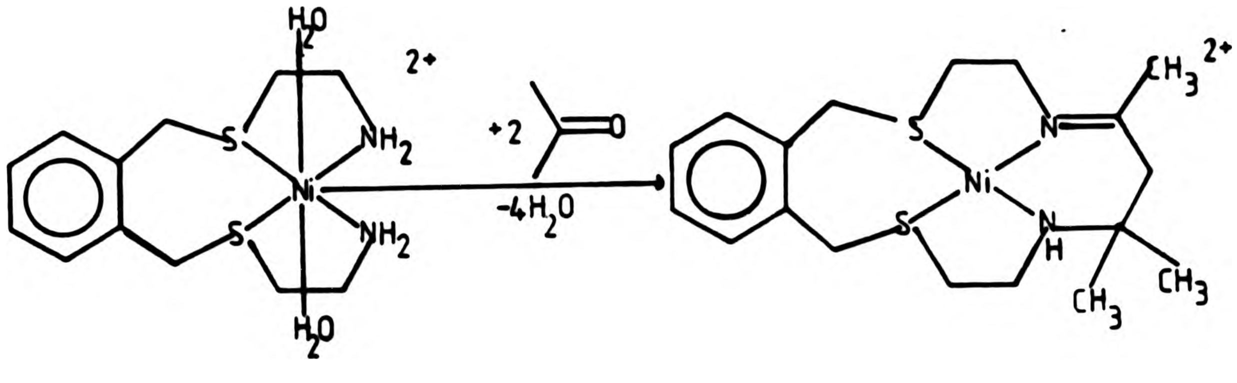
1.12 1.13

Another synthetic route to S_2N_2 macrocycles which depended on the "template-approach" involved the use of a condensation reaction of the type which was first studied by Curtis and co-workers[32,43-45]. The hydrobromide salt of 1,3-bis(o-thiophenylamino)propane gave[30] the high-spin dibromocomplex 1.14 when treated with nickel(II) acetate and acetone.



1.14

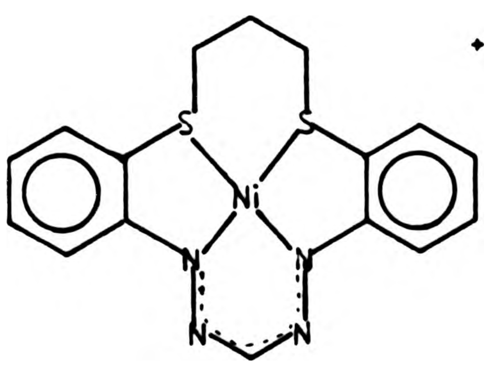
The conditions used were similar to those of Urbach and Busch[31], where the ring closure complex 1.16 was effected when the Ni(II) complex 1.15 was treated with refluxing acetone. 1.16 gave 4-, 5- or 6- coordinate complexes of nickel(II) with a variety of anions eg. ClO_4^-, NCS$^-$, Cl$^-$, Br$^-$, I$^-$.



1.15

1.16

Alcock and Tasker[33] obtained a nickel(II) complex of a novel monoanionic macrocyclic ligand 1.17 by reaction of 1,3-bis(o-hydrazinophenylthio)propane, HCHO and Ni(ClO$_4$)$_2$ in tetrahydrofuran. A similar reaction with cyclohexanone gave complex 1.18.



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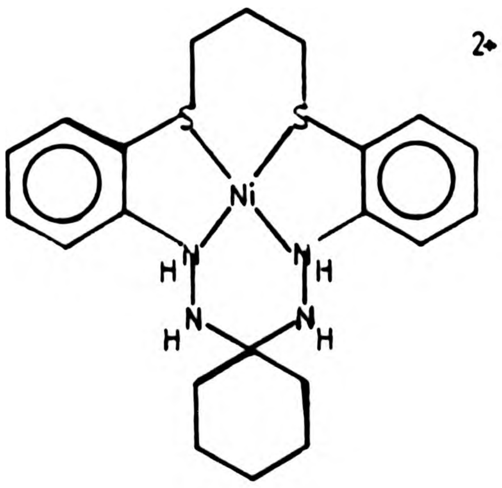
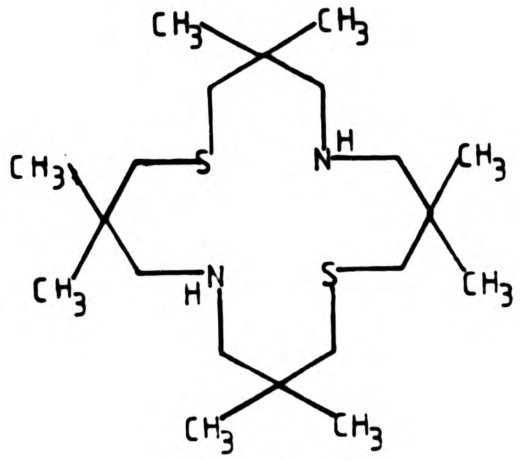


1.18

Recently the preparation of the free ligands 1.19 which has trans-arrangment of the S_2N_2 donors has been reported[34,35]. Macrocycle 1.20, 14-membered macrocycle with trans donors containing dibenzo-functionalities, has been synthesised by Wainwright and co-workers[55].



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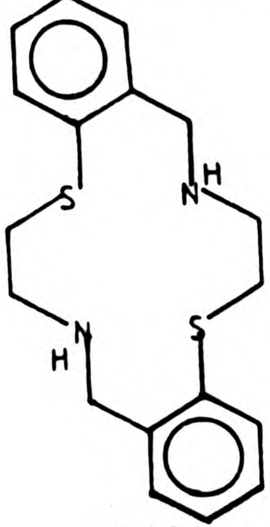
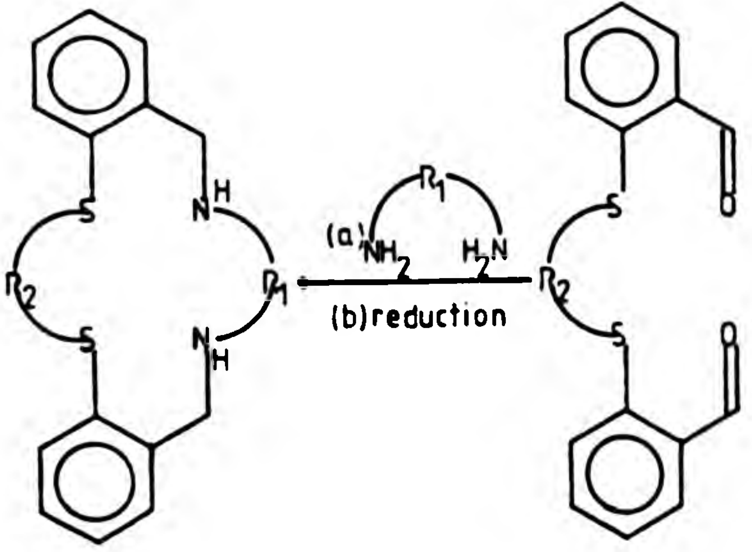


1.20

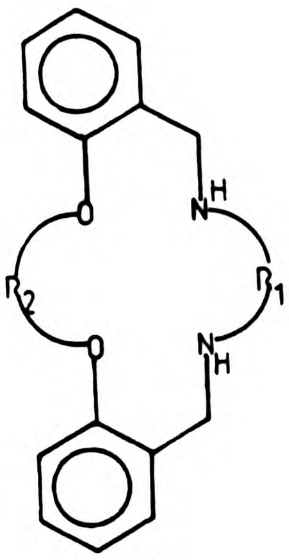
The metal-free 14-, 15- and 16-membered S_2N_2 macrocycles 1.21-1.23 have been prepared by Lindoy et al[36], by reaction of diaminoalkanes with the appropriate dialdehyde in methanol followed by in situ reduction of the imine groups.



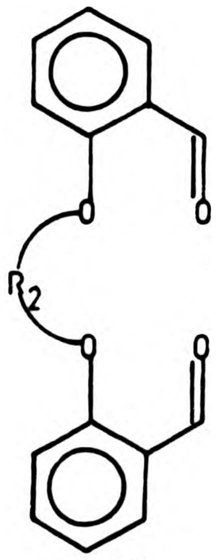
Macrocycle	R_1	R_2
1.21	$(CH_2)_2$	$(CH_2)_2$
1.22	$(CH_2)_3$	$(CH_2)_2$
1.23	$(CH_2)_3$	$(CH_2)_3$

1.8.2 O_2N_2 Macrocycles

Recently mixed donor macrocycles[37] with O_2N_2 donor sets have been considered as selective complexing agents. A considerable range of macrocycles of the general form 1.24 have been prepared by Lindoy and co-workers[8,37-41] by a synthetic scheme analogous to that for 1.21, but using the dialdehydes 1.25 which contain two ether donors.



1.24



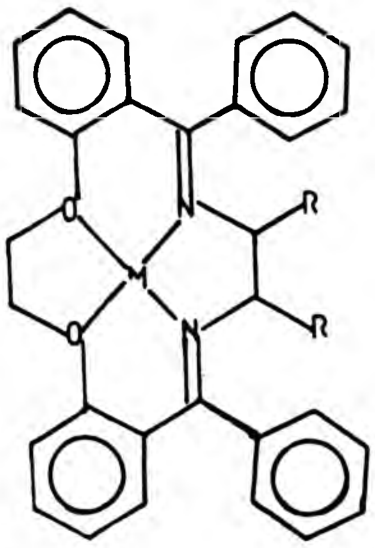
1.25

The ligands 1.24 have been used in systematic studies[39-41] of ring-size and substituent effects on kinetic and thermodynamic stabilities of transition metal complexes.

In particular, structural studies have been used to consider how kinetic and thermodynamic properties relate to the goodness-of-fit of the metal ion for the ligand donor set.

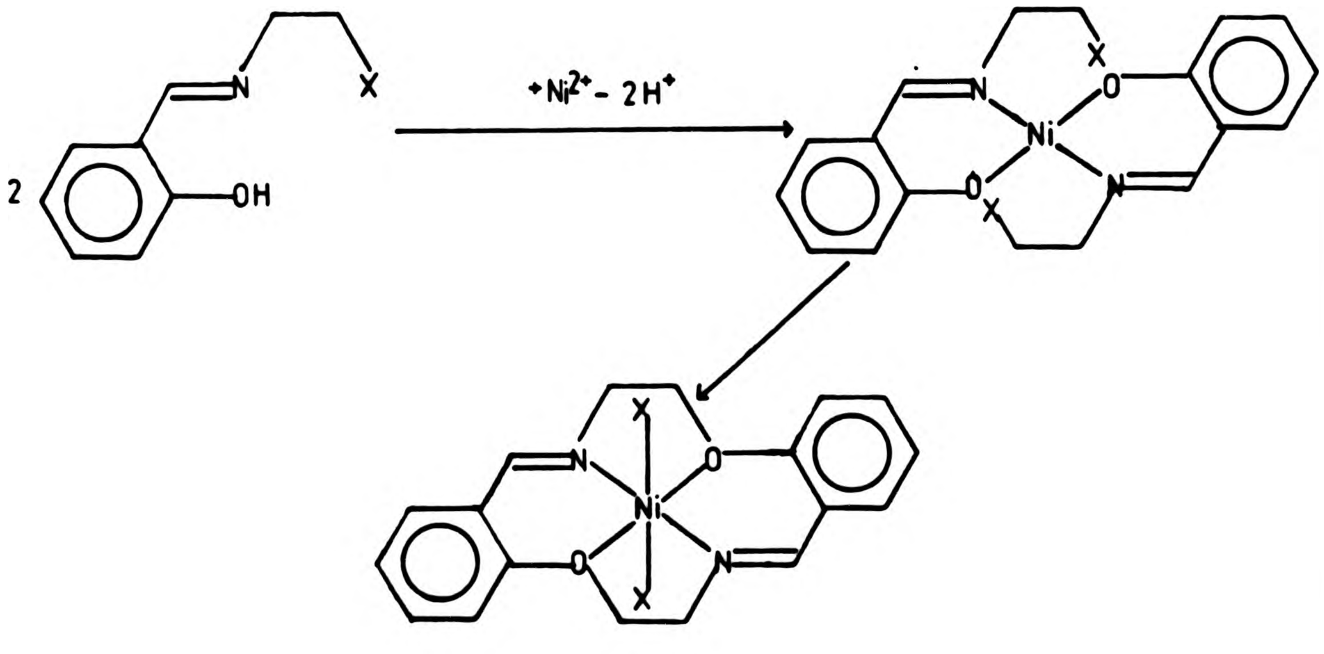
Some work has also been done on the metal complexes of the related di-imines (see below) but the solution studies have been limited by the hydrolytic instabilities of the imino groups.

Related ketimine complexes (e.g. 1.26) have been prepared from condensation reactions of the appropriate arylketones, under template conditions.



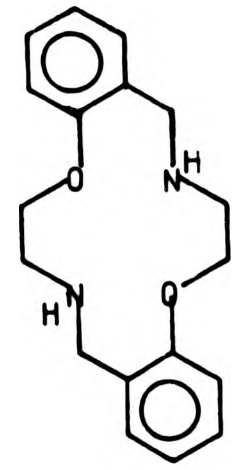
1.26

Analogous ligands to 1.24 and 1.26 with *trans*-O_2N_2 donor sets have only been prepared[42] for the nickel(II) complexes of the 14-membered ring.



X is a halide

A recent report has appeared[55] of non-template synthesis of chelating macrocycle 1.27 with trans-O_2N_2-donor atoms. There was no evidence of polymerisation taking place and the macrocycle was obtained in high yields under ambient conditions.



1.27

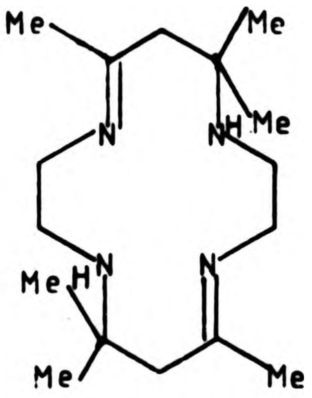
Aliphatic ligands[54] with mixed nitrogen-oxygen donor sets are known (i.e. Aza-crown ethers), but there are only a few examples of quadridentate O_2N_2- ligands with fused benzene rings which are closely related to the types studied in this project (see section 1.5).

1.8.3 N_4 Macrocycles

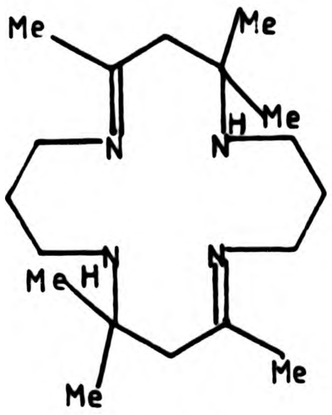
A very large amount of work has been done on tetra-aza ligands and their complexes. It is not practicable to review all the work in this area. Some of the significant developments of synthetic methods will be surveyed in a historical context and ligands will be described which are related to the systems in this work.

A convenient synthetic route to Ni(II) and Cu(II) complexes of aliphatic N_4 macrocycles was that by Curtis[32,43-45]. House and

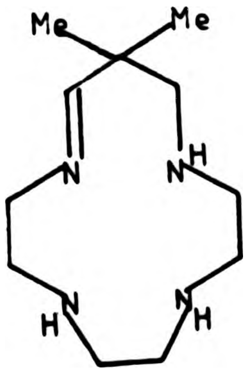
Curtis[32] discovered by accident that acetone and 1,2-diaminoethane in the presence of a metal salt such as nickel(II) perchlorate gave the macrocyclic complex 1.28. Many permutations of diamine and ketones could be used in such reactions, but in the majority of cases it has not been possible to isolate the metal-free di-imine ligands. However, if Ni(II) was replaced by Fe(II) in the reaction to form 1.28, the corresponding free ligand was formed. Complexes of macrocycles with different ring-sizes eg. 1.29 and 1.30 could be prepared by similar routes. Reduction of the imine groups, usually with sodium borohydride, yielded the related tetra-amine ligands, but often as complex mixtures of isomers, because reduction introduces an asymmetric centre at the imine carbon atom.



1.28

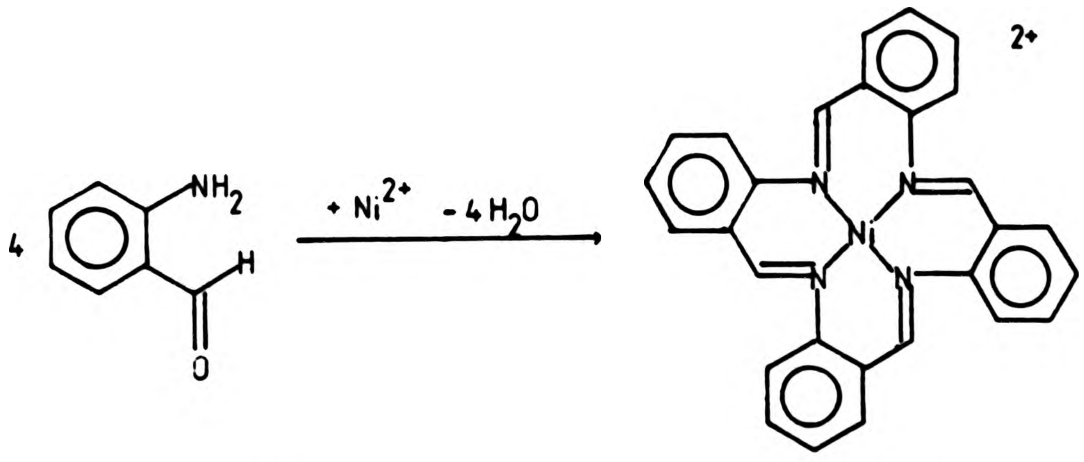


1.29



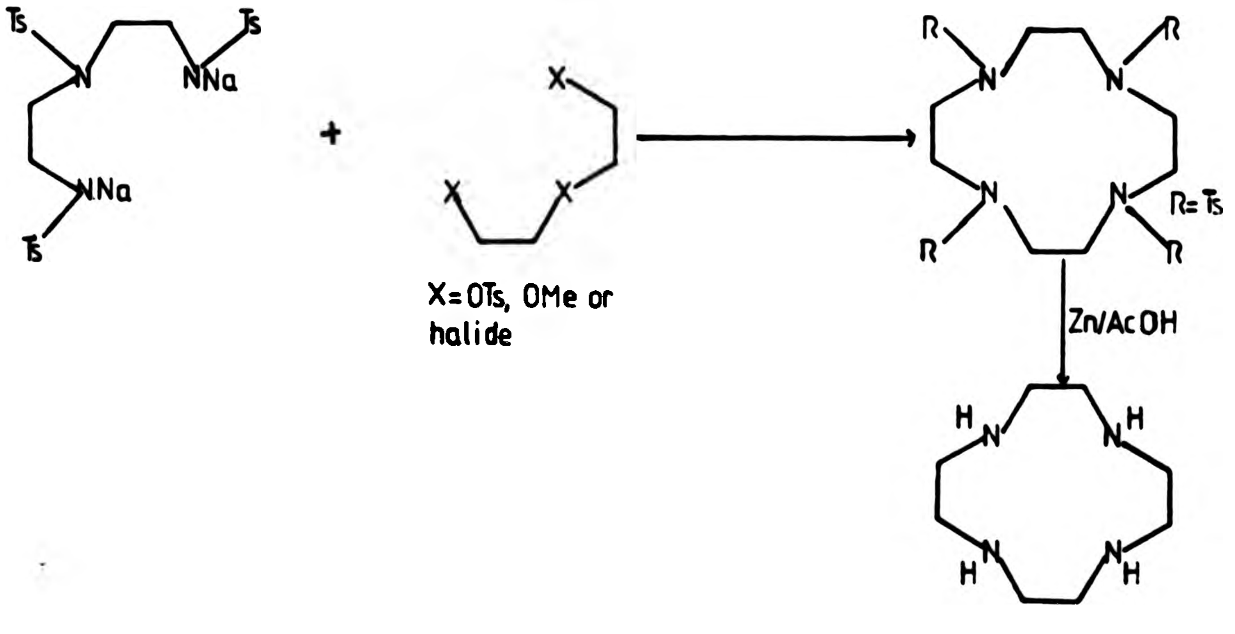
1.30

The preparation of 1.31 by Busch and Melson[46] was an important milestone in the development of the metal template approach to the synthesis of macrocyclic ligands. The metal complex of the ligand 1.31 was prepared by the self-condensation of o-aminobenzaldehyde 1.32 in the presence of Ni(II) ions.



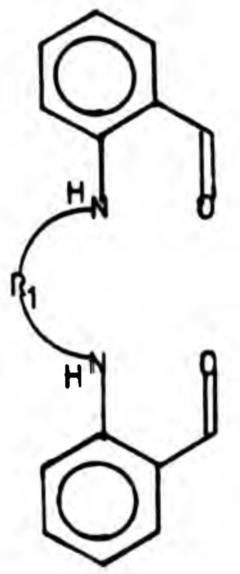
1.32 1.31

A wide range of simple aliphatic cyclic tetra-amines have been made available by the Atkins[47] procedure. This does not involve metal template conditions, and is illustrated below for the preparation of the 12-membered ligand "cyclen".

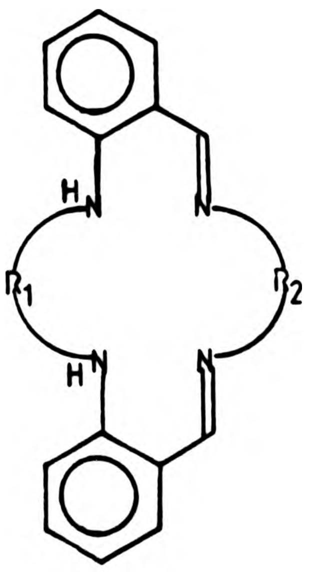


1.8.4 Macrocycles Containing Fused o-Benzene Rings

Several types of N_4 macrocycle have been prepared by the Schiff condensation reaction. The dialdehyde 1.33 reacted with diamines to yield[39,41,43,48,49] the macrocycle 1.34.

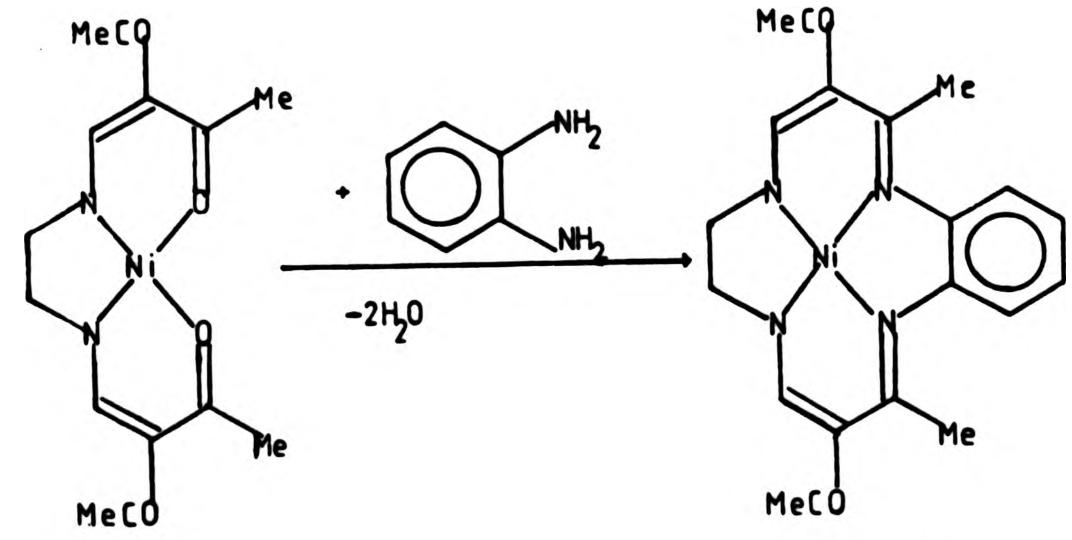


1.33



1.34

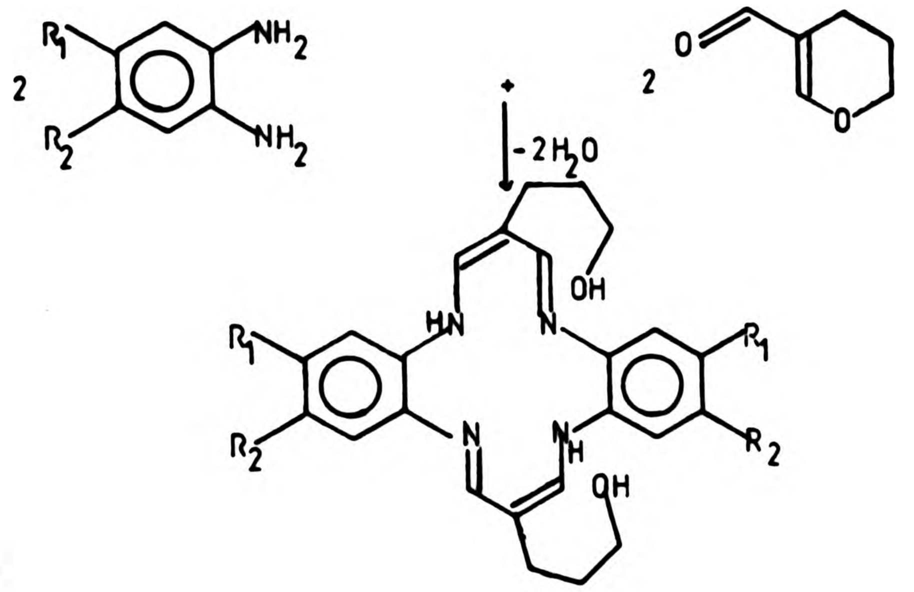
A similar reaction was observed by Jaeger[50], e.g. 1.35 reacted with 1,2-diaminobenzene to form the macrocyclic complex 1.36.



1.35

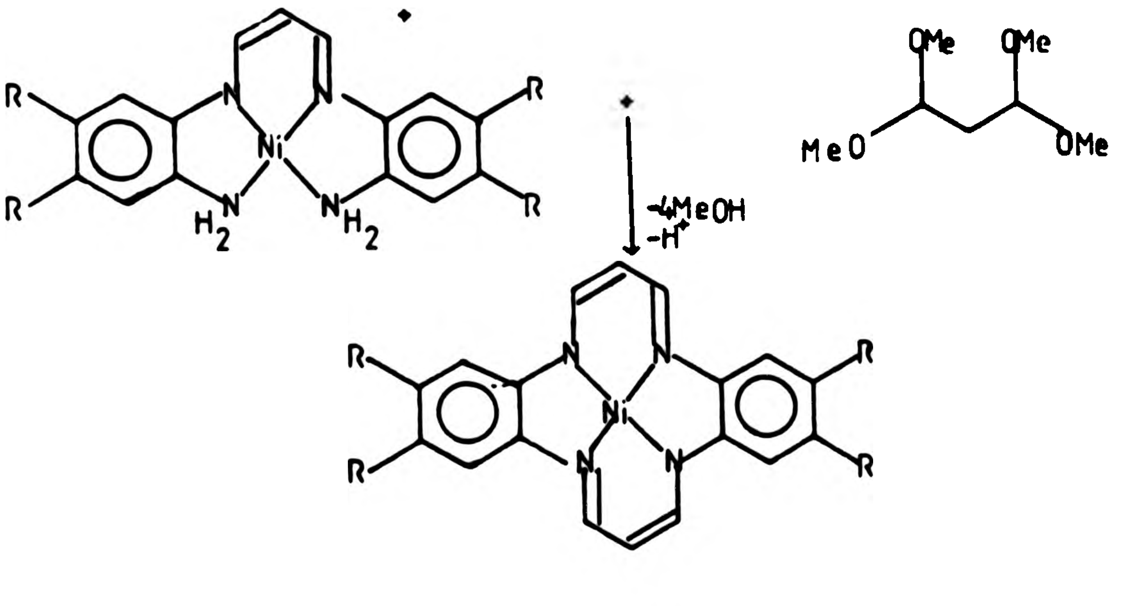
1.36

Harke and Brietmaier[51] have prepared the fully conjugated macrocyclic system 1.37 and its nickel(II) complex.



1.37, R_1,R_2 are alkyls

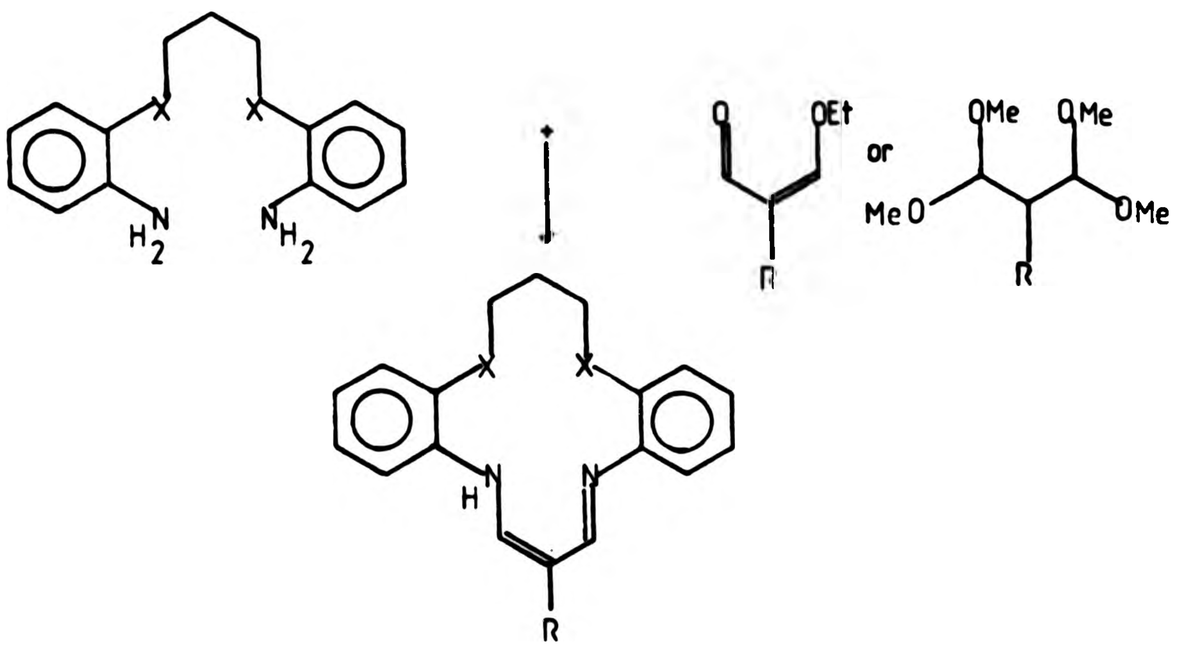
Cutler and Dolphin have prepared[52] the conjugated systems 1.38 using a nickel(II) metal template where 1,1,3,3-tetramethoxypropane was reacted with the diamine.



1.38

Recently Breitmaier and Behr[53] synthesised the metal free macrocycles 1.39a and 1.39b, by reaction of a linear diamine with 2-alkyl-3-

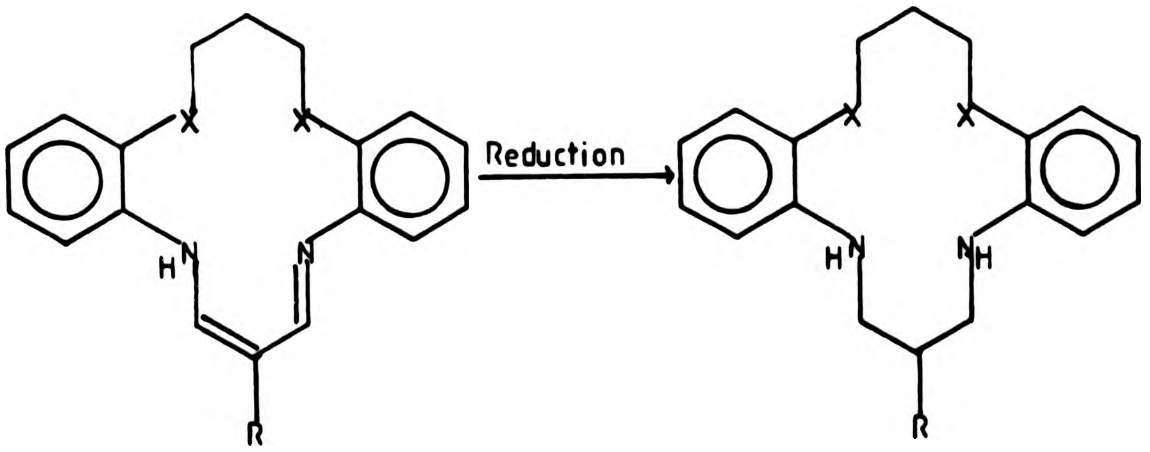
ethoxyacrolein or in some cases 2-alkyl-1,1,3,3-tetramethoxypropane.



1.39a, X=O , R=H or CH_3

1.39b X=S, R=H or CH_3

This method was adapted for the analogous N_4-macrocycle 1.40 by Ansell[37]. Hydrogenation of the bridge between the aniline nitrogen atoms in this class of macrocycles provided a route to the ligand 1.4 chosen for study in this project (see section 1.4).



X = S, O or NH

1.39 or 1.40

1.4

1.9 Layout of Material for Remainder of Report

Chapter 2 discusses the preparation of all the ligands and reaction pathways and some interesting features for characterisation of these ligands and their precursors. Some emphasis is placed on the difficulty of isolating the S_2N_2-macrocycle and new synthetic routes devised are reported.

Chapter 3 gives a description of detailed ligating properties of some of the ligands studied in this thesis. These are the protonation constants, rigidities of the ligands in solution, stability constants and X-ray crystallography of the N_4 macrocycle and its low- and high-spin nickel(II) complexes. A molecular mechanics study of this free ligand and its high-spin nickel(II) complex is reported.

Chapter 4 describes how the three structures in the thesis were solved (either by heavy atom solutions from the Patterson synthesis or direct methods).

Chapter 5 contains experimental details of all synthetic work relating to the preparation of the ligands mentioned above and their precursors. Metal complexes of these ligands are also included in this chapter. Metal template synthesis of two new nickel(II) complexes of the S_2N_2-ligands are also described.

References

1. Dennis, W.H., Extractive Metallurgy, Pitman (1964).
2. Pressman, B.C., Inorganic Biochemistry (Eichhorn, G.I., ed.)., vol 1 p203, Elsevier, Amsterdam (1973).
3. Williams, D.R., An Introduction to Bio-inorganic Chemistry, Thomas, C. C. (1976).
4. Hughes, M.N., The Inorganic Chemistry of Biological Processes, 2nd. ed., Wiley, J., and Sons (1972).
5. Preston, J.S., Luklinska, Z.B., J. Inorg. Nucl. Chem., 42, 431 (1980).
6. Muller, F.R., Handel, H., Tetr. Lett., 23, 2769 (1982).
7. Drummond, L.A., BSc. Thesis (PNL-1981).
8. Armstrong, L.G., Lindoy, L.F., McPartlin, M., Mockler, G.M., Tasker, P.A., Inorg. Chem. 16, 1665 (1977).
9. Anichini, A., Fabbrizzi, L., Paoletti, P., J. Chem. Soc. Dalton 577 (1978).
10. Lin, C.T., Rorabacher, D.B., Cailey, G.R., Margerum, D.W., Inorg. Chem., 14, 919 (1975).
11. Clay, R. M., Murray-Rust, J., Murray-Rust, P., J. Chem. Soc. Dalton 1135 (1979).
12. Cabbiness, S.K., Margerum, D.W., J. Amer. Chem. Soc., 91, 6540 (1969).
13. Sokol, L.S.W.L., Ochrymowyiz, L.A., Rorabacher, D.B., Inorg. Chem., 20, 3189 (1981).
14. Clay, R.M., Steele, W.V., Inorg. Chem., 19, 2414 (1980).
15. Anichini, A., Fabbrizzi, L., Paoletti, P., Clay, R.M., Inorg. Chim. Acta., 22, L25 (1977).

16. Clay, R.M., Micheloni, M., Paoletti, P., Steele, W.V., *J. Amer. Chem. Soc.*, *101*, 4119 (1979).

17. Clay, R.M., McCormac, H., Micheloni, M., Paoletti, P., *Inorg. Chem.*, *21*, 2494 (1982).

18. Anichini, A., Fabbrizzi, F., Paoletti, P., Clay, R.M., *Inorg. Chim. Acta.*, *24*, L21 (1977).

19. Fabbrizzi, F., Paoletti, P., Clay, R.M., *Inorg. Chem.*, *17*, 1042 (1978).

20. Micheloni, M., Paoletti, P., *J. Calorim. Anal. Therm. (Prepr.)*, *9-B*, 41 (1978).

21. Fabbrizzi, L., Micheloni, M., Paoletti, P., *J. Chem. Soc. Chem. Comm.*, 833 (1978).

22. Hinz, E.P., Margerum, D.W., *Inorg. Chem.*, *13*, 2941 (1974).

23. Kodama, M., Kimura, E., *J. Chem. Soc. Dalton*, *116*, 2341 (1976).

24. Anichini, A., Fabbrizzi, L., Paoletti, P., Clay, R.M., *J. Chem. Soc. Chem. Comm.*, 244 (1977).

25. Fabbrizzi, L., Paoletti, P., Clay, R.M., *Inorg. Chem.*, *17*, 1042 (1978)

26. Hay, R.W., Lawrence, G.A., Shone, U.R., *J. Chem. Soc. Dalton*, 942 (1976).

27. Bradshaw, J.S., Hui, J.Y.K., *J. Het. Chem.*, *11*, 649 (1974).

28. Thompson, M.C., Busch, D.H., *J. Amer. Chem. Soc.*, *84*, 1762 (1962).

29. Thompson, M.C., Busch, D.H., *J. Amer. Chem. Soc.*, *86*, 3651 (1964).

30. Hay, R.M., Galyer, A.L., Lawrence, G.A., *J. Chem. Soc. Dalton*, 939 (1976).

31. Urbach, F.L., Busch, D.H., Inorg. Chem., 12, 408 (1973).

32. Curtis, N.F., House, D.A., Chem. Ind. (London), 1708 (1961).

33. Alcock, N.W., Tasker, P.A., J. Chem. Soc. Chem. Comm., 1239 (1972).

34. McCridle, R., Ferguson, G., McAlees, A.J., Parvez, M., Stephenson, D.K., J. Chem. Soc. Dalton, 1291 (1982).

35. McCridle, R., McAlees, A.J., Stephenson, D.K., J. Chem. Soc. Perkin. Trans., I 320 (1981).

36. Lindoy, L.F., Smith, R.J., Inorg. Chem., 20, 1314 (1981).

37. Ansell, C.W.G., Chung, M.F.H.Y.J., McPartlin, M., Tasker, P.A., J. Chem. Soc. Dalton, 2113 (1982).

38. Goodwin, H.J., Henrick, K., Lindoy, L.F., McPartlin, M., Tasker, P.A., Inorg. Chem. ,21, 3261 (1982).

39. Ekstrom, A., Lindoy, L.F., Lip, H.C., Smith, R.J., Goodwin, H.J., McPartlin, M., Tasker, P.A., J. Chem. Soc. Dalton, 1027 (1979).

40. Tasker, P.A., Trotter, J., Lindoy, L.F., J. Chem. Res., 328 (1981).

41. Mangia, A., Tran. Met. Chem., 5 ,250 (1980).

42. Kluiber, R.W., Sasso, G., Inorg. Chim. Acta., 226 (1970).

43. Green, M., Smith, J., Tasker, P.A., Inorg. Chim. Acta., 17 (1971).

44. Curtis, N.F., Hay, R.W., J. Chem. Soc., 4409 (1960).

45. Curtis, N.F., Curtis, Y.M., Povell, H.K.J., J. Chem. Soc., A 1015 (1966).

46. Melson, G.A., Busch, D.H., J. Amer. Chem. Soc., 87, 1706 (1965).

47. Richman, J.E., Atkins, T.J., *J. Amer. Chem. Soc.*, *96*, 2268 (1974).

48. Melson, G.A., in *"Coordination Chemistry of Macrocyclic Compounds"*, Ed. Melson, G.A., Plenum Press, (1979) ch. 2.

49. Ansell, C.W.G., McPartlin, M., Tasker, P.A., Thambythuri, A., *Polyhedron*, *2*, 83 (1983).

50. Jaeger, E.G., *Z. Chemie.*, *4*, 437 (1964).

51. Hanke, R., Breitmaier, E., *Chem. Ber.*, *115*, 1657 (1982).

52. Cutler, A.R., Dolphin, D., *J. Coord. Chem.*, *6*, 59 (1976).

53. Breitmaier, E., Behr, H., *Chem. Ber.*, *111*, 913 (1978).

54. Luboch, E., Cygan, A., Biernat, J.F., *Inorg. Chim. Acta* *68*, 201 (1983).

55. Martin, J.W., Wainwright, K.P., Weerasuria, K.D.V., Wild, S.B., *Inorg. Chim. Acta.*, *99*, L5 (1985).

CHAPTER 2: Preparation of the Ligands

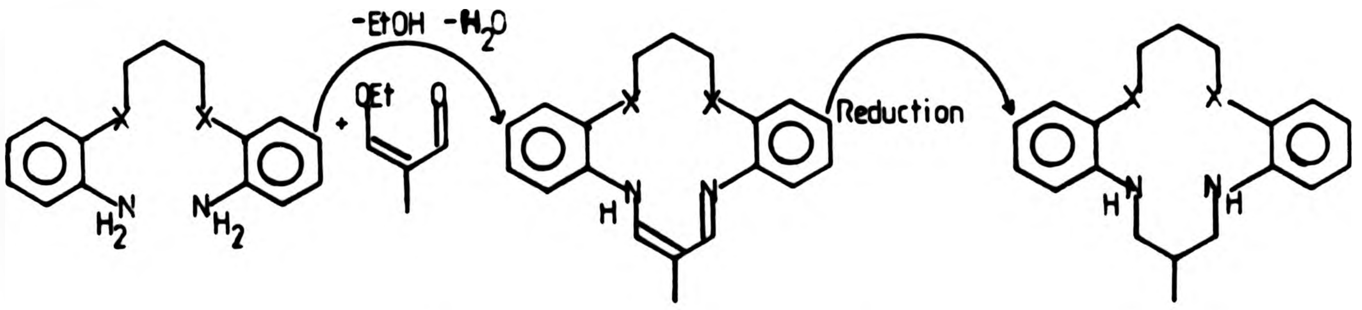
CHAPTER 2 Preparation of the Ligands

At the outset of the research programme it was intended to prepare the O_2N_2-, N_4- and S_2N_2-macrocyclic ligands of type 2.3 via hydrogenation of the related β-dialdimines 2.2.

2.1 Synthesis of the Precursor X_2N_2-β-Dialdimines

Recently Breitmaier and Behr[1] reported the syntheses of metal-free macrocyclic imines 2.2a and 2.2c containing O_2N_2 and S_2N_2 donor sets using the cyclocondensation of the appropriate diamine with 2-methyl-3-ethoxyacrolein in mesitylene (Scheme 2.1 step A).

Scheme 2.1



Step A Step B

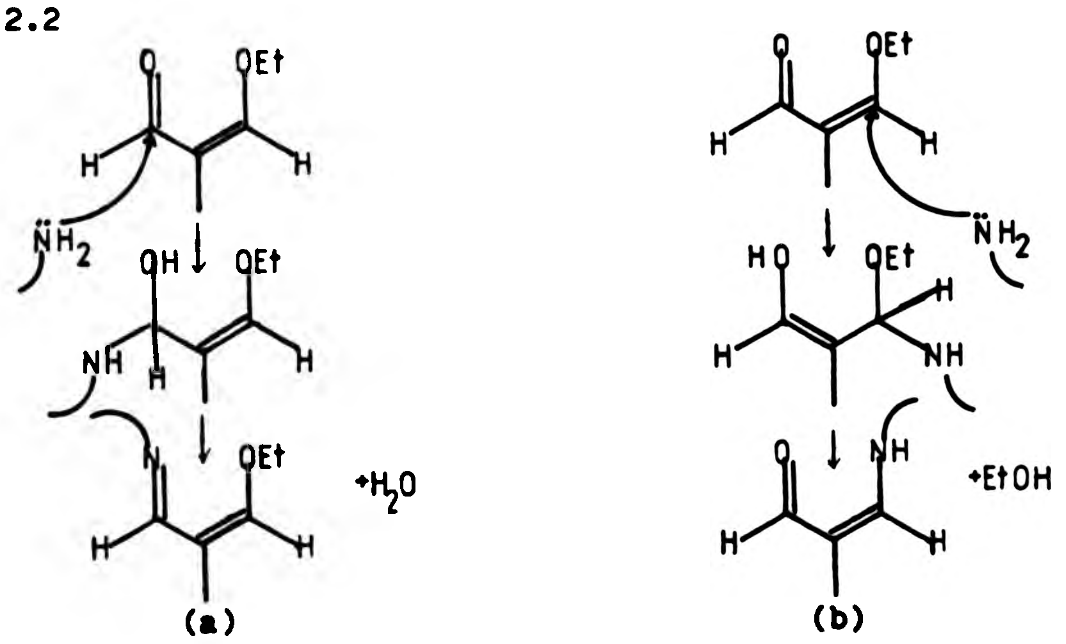
2.1a, X=O	2.2a, X=O	2.3a, X=O
2.1b, X=NH	2.2b, X=NH	2.3b, X=NH
2.1c, X=S	2.2c, X=S	2.3c, X=S

Ansell and co-workers[2] extended this synthetic procedure at the Polytechnic of North London to give, under slightly different conditions, the tetra-aza macrocycle 2.2b. In theory these macrocycles can be reduced (step B; see section 2.14) to yield the X_2N_2-systems 2.3 which contain only secondary-amine-type nitrogen donors.

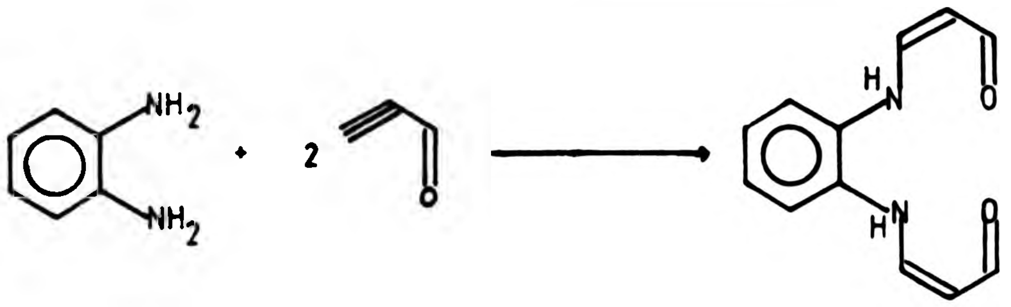
A combination of Breitmaier-Ansell procedures was used to prepare the imines 2.2a and 2.2b in reasonable yields (37-42 %). Both the imines thus obtained are very crystalline and are bright red (2.2b) or yellow (2.2a).

There are two possible mechanisms for the cyclocondensation to yield the β-dialdimines; either by initial nucleophilic attack of the amine at the carbonyl group of the acrolein or at the carbon atom bearing the ethoxy substituent (see Scheme 2.2).

Scheme 2.2

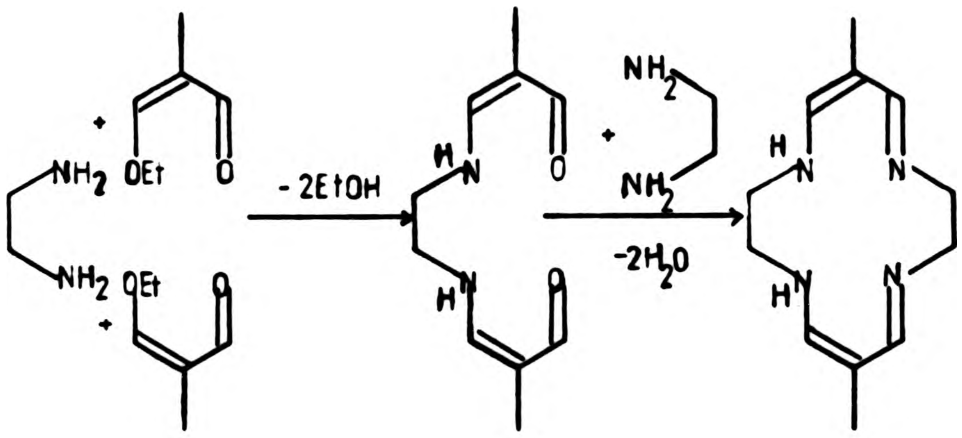


Muller and co-workers[3] and Hiller <u>et al</u>[4] have shown that with analogous precursors it is the non-carbonyl carbon atom which is preferentially attacked i.e. <u>o</u>-phenylenediamine reacts in a molar ratio of 1:2 with propynal to give the dialdehyde 2.3.



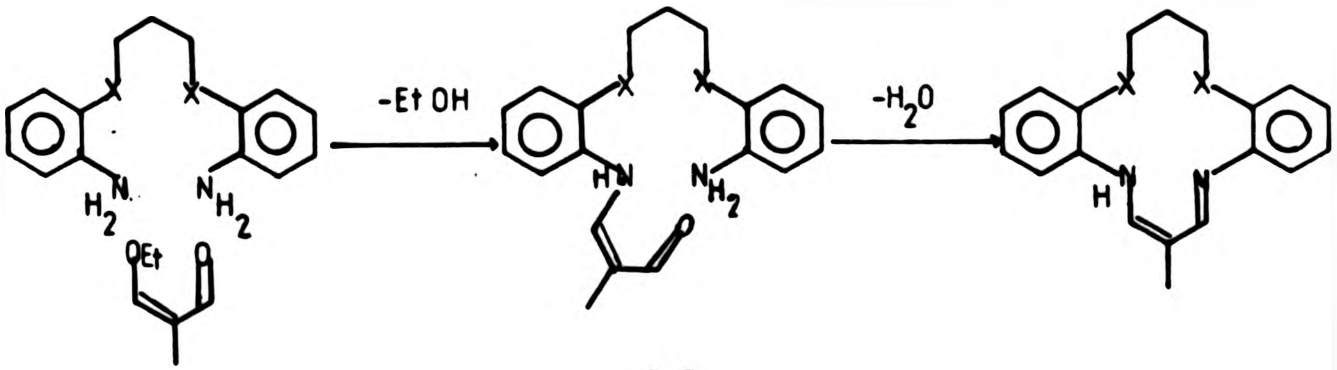
2.3

Breitmaier et al[5] has shown that ethylenediamine reacts with two moles of 2-methyl-3-ethoxyacrolein to give the intermediate 2.4, which reacts with a further mole of ethylenediamine to yield the tetra-azamacrocycle (Scheme 2.3).



2.4

It is therefore expected that the reaction for preparation of the β-dialdimines 2.2a and 2.2b will proceed in a similar manner, via the intermediates 2.5.



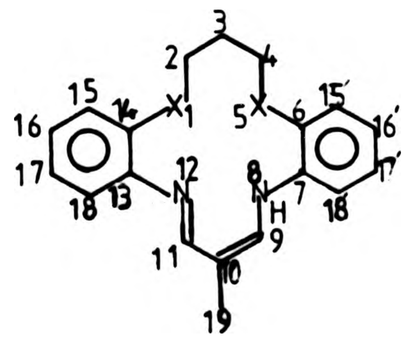
2.5

With the formation of the cycles, the double primary amine symmetric and asymmetric N-H stretches at 3353, 3348 (for 2.2a) and 3400 and 3380 cm^{-1} (for 2.2b) are lost in the infrared spectra. In the case of 2.2b there is a weak band at 3300 cm^{-1} due to the anilino NH. In both macrocycles the characteristic o-disubstituted benzene ring peaks occur close to 750 cm^{-1}. Mass spectra were also used to confirm the presence of the macrocycles. A much stronger parent ion peak was obtained for 2.2a at m/z 306 with a percentage of 35. The O_2N_2 macrocycle at m/z 308 had a parent ion of 5 % intensity. The next major fragment was due to loss of either an o-phenylenediamine (for 2.2b) or o-aminophenol group (for 2.2a).

The ^1H nmr spectra (220 MHz) of the two macrocycles 2.2a and 2.2b are very similar (Table 2.1). The methyl peaks in both compounds occur as singlets at 2.05 ppm. The methylene protons (2 and 4, see table 2.1) adjacent to the oxygen atoms in 2.2a are further downfield when compared with those for the N_4 macrocycle, in accordance with the relative electronegativities of the -O- and -NH- groups.

<u>TABLE 2.1</u> ^1H nmr (220 MHz, $CDCl_3$) Spectra of Macrocycles 2.2a and 2.2b

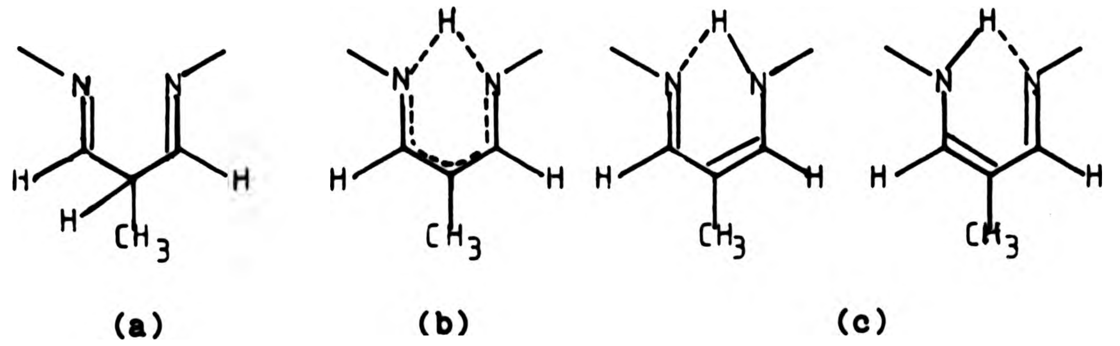
Site of Protons	2.2a	2.2b
2,4	4.23(t)	3.41(t)
3	2.33(p)	2.00(p)
9,11	7.85(d)	7.93(d)
15-18	6.70- 7.35(mc)	6.50- 7.40(mc)
19	2.05(s)	2.05(s)
NH(8)	6.70- 7.35(mc)	6.50- 7.40(mc)
NH(1,5)	-	4.72(s)



2.2a X=O
2.2b X=NH

X_2N_2 imine numbering system

The methine signals are observed as doublets as a result of coupling with the anilino protons at position 8. In the presence of D_2O a slow exchange is observed and the doublet collapses to give a singlet. The signal for the anilino proton associated with the unsaturated C_3-bridge occurs within the complex multiplet for the aromatic hydrogen atoms in both 2.2a and 2.2b. However in 2.2b the anilino protons at positions 1 and 5 give a broad peak further upfield at 4.72 ppm which is lost rapidly on D_2O exchange. These ^1H nmr data indicate that the methine protons at 9 and 11 are equivalent. The equivalence can be accounted for using one of the three models; a β-diimine system (a), a symmetrically hydrogen-bonded system involving delocalisation of π-electrons in the C_3 bridge (b) or rapid tautomerisation of the unsymmetrical hydrogen-bonded system (c).

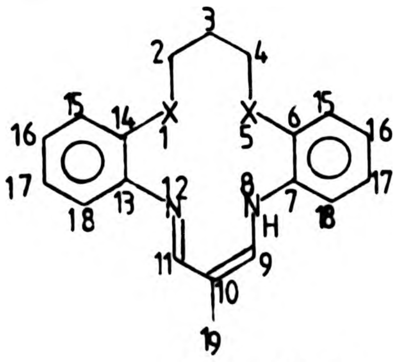


Formulation as (a) is incompatible with the observed singlet for the methyl groups. However, a distinction between models (b) and (c) cannot be made on the evidence available.

The ^{13}C nmr (20.12 MHz, $CDCl_3$) signals also show the presence of pseudo-mirror symmetry of the molecule. The chemical shifts of the two structures 2.2a and 2.2b are compared in table 2.2. The most significant differences in the spectra are for the methylene carbon atoms. Those for 2.2a are further downfield, again due to the greater deshielding of the carbon atom by the more electronegative oxygen atoms. Significantly weaker signals were obtained for the non-protonated benzene carbon atoms (6, 7, 13, 14) and for carbon atom 10 bearing the methyl substituent, due to the longer relaxation times on the nmr time scale.

TABLE 2.2 Broadband Decoupled ^{13}C nmr (20.12 MHz, $CDCl_3$) Signals for Macrocycles 2.2a and 2.2b

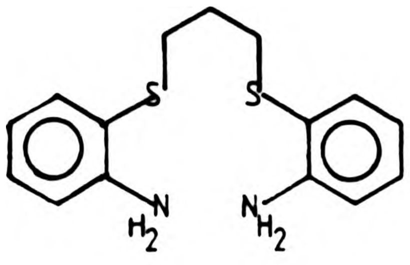
Site of Carbon atom	N_2O_2 (2.2a)	N_4 (2.2b)
19	18.1	18.3
3	29.8	28.7
2,4	67.8	45.4
10(w)	103.0	103.1
15	111.9	112.8
18	114.1	113.6
17	121.1	119.2
16	123.3	124.1
7,13(w)	136.0	134.9
6,14(w)	150.2	139.8
9,11	146.8	146.5



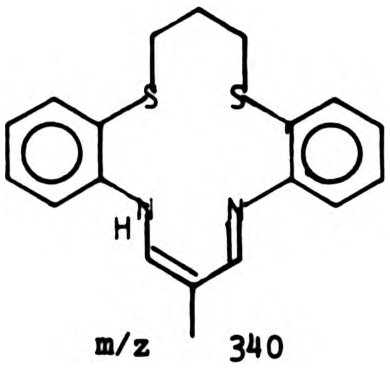
2.2a X=O
2.2b X=NH

When the preparation of the S_2N_2 imine 2.2c was attempted using the procedure which was successful for 2.2a and 2.2b a complex mixture was obtained. Only about 5 % of the macrocycle was obtained as judged from the ^1H nmr spectrum, with the major component of the resulting oil (90-95 %) being the linear precursor. Attempts to isolate the ligand via column chromatography using silica gel were unsuccessful.

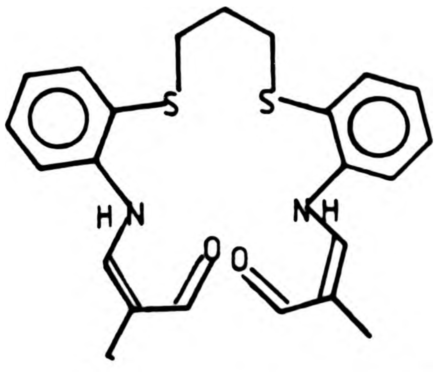
The cyclocondensation reaction was attempted in various solvent systems, monitoring by ^1H nmr spectroscopy so that the acrolein uptake could be followed. When no further acrolein was being consumed the reaction was stopped. The oils obtained were judged to contain four components by mass spectroscopy and thin layer chromatography. The probable structures are shown below.



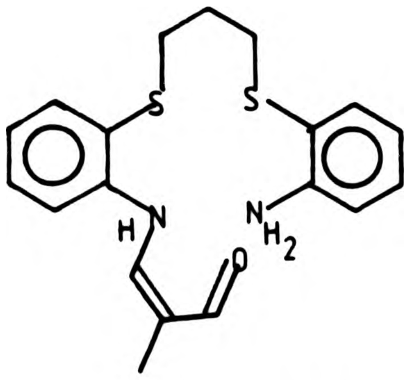
m/z 290



m/z 340



m/z 426

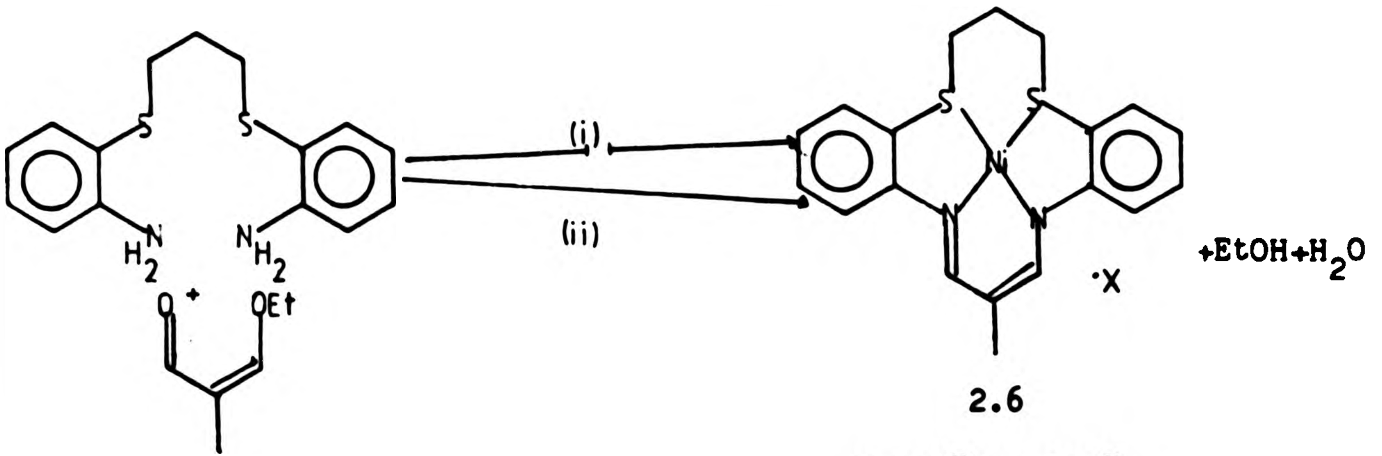


m/z 360

The maximum yield of 2.2c was found to be about 5 %. Attempts to isolate 2.2c from these reaction conditions failed despite numerous attempts, via chromatography or crystallisation under conditions which had been reported by Breitmaier[1]. Therefore, many variations of conditions had to be considered including metal template syntheses.

2.2 Attempted Template Syntheses of Nickel(II) Complexes of 8,12-Diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradeca-9,11-diene

Scheme 2.4 Attempted Template Syntheses of the Monocationic Macrocyclic Nickel(II) Complex



2.6

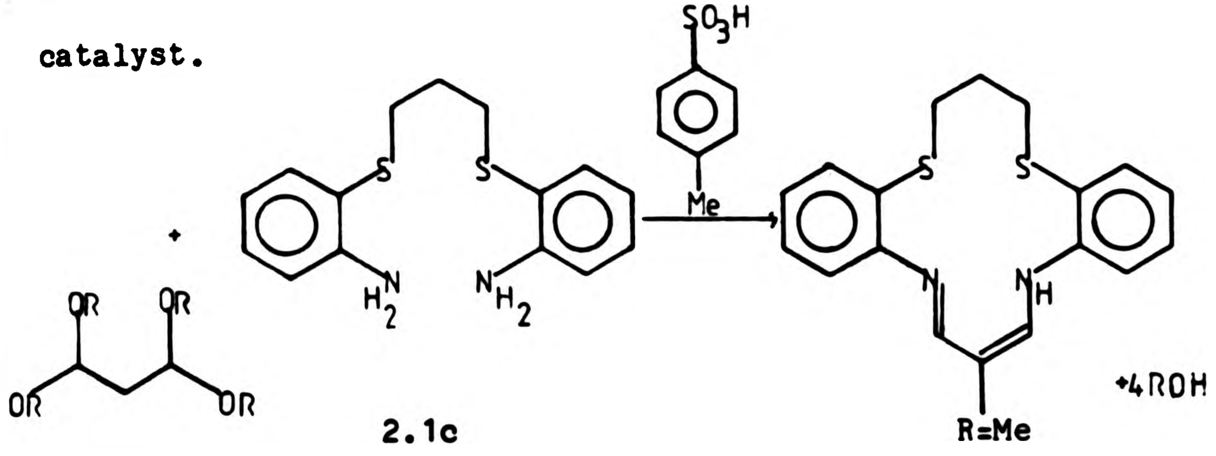
X=AcO$^-$ or BF$_4^-$

(i) Ni(ac)$_2$.4H$_2$O/EtOH (or DMA) -unsuccessful

(ii) 0.5 Ni(ac)$_2$.4H$_2$O and 0.5 Ni(BF$_4$)$_2$/DMA -successful

Under the reaction condition (i), the precursors were recovered unchanged. It was then decided to attempt the reaction in the presence of a monoanionic counterion which would facilitate precipitation of the monocationic complex as in the reaction (ii). In this case the acetic acid and ethanol generated in the reaction were removed by fractional distillation. A green precipitate of the nickel(II) tetrafluoroborate salt 2.6 was obtained in 50-53 % yield. The structure was confirmed by microanalysis, and mass and infrared spectra. A very broad band was observed in the infrared spectrum at 1170 cm^{-1}, characteristic of non-coordinated BF$_4^-$. The mass spectrum contained peaks with m/z values corresponding to monocationic nickel(II) complex 2.6 at m/z 398 (4 %), and fragments resulting from the loss of nickel(II), m/z 341 (5 %), and of a C_3 chain, m/z 290(4 %) to give the linear diamine 2.1c.

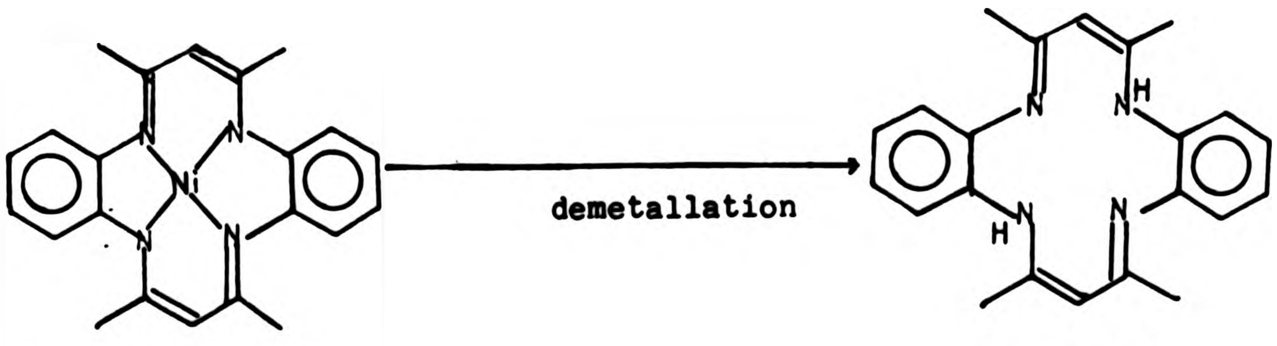
Breitmaier has reported[1] an alternative cyclocondensation procedure using 1,1,3,3-tetramethoxypropane and p-toluenesulfonic acid as catalyst.



2.1c

Attempts to reproduce these reactions, and to prepare the nickel(II) complexes by in situ "template" reactions were unsuccessful in our hands.

Since the only successful cyclocondensation reaction to form a S_2N_2-macrocycle involved its isolation as the monocationic nickel(II) complex 2.6, attempts were made to isolate the free ligand by displacement of the nickel ion. Demetallation was tried by following a procedure reported[6] for displacement of nickel(II) from a related unsaturated N_4-system.



$Ni(C_{22}H_{22}N_4)$

$C_{22}H_{24}N_4$

Scheme 2.5

1. $$[Ni(C_{22}H_{22}N_4)] \quad + \quad 4HCl \xrightarrow[/EtOH]{} [C_{22}H_{26}N_4][NiCl_4]$$

2.7

2. $$[C_{22}H_{26}N_4][NiCl_4] \quad + \quad 2NH_4[PF_6] \xrightarrow[/H_2O]{} [C_{22}H_{26}N_4][PF_6]_2$$

$$+ \; 2NH_4Cl \; + \; NiCl_2$$

3. $$[C_{22}H_{26}N_4][PF_6]_2 \quad + \quad 2N(Et)_3 \xrightarrow[/EtOH]{} C_{22}H_{24}N_4$$

$$+ \; [2NH(Et)_3][PF_6]$$

This involves 3-steps. In the first a salt of the protonated ligand is isolated as the tetrachloronickelate(II) from a reaction with a saturated hydrogen chloride in ethanol solution. This compound 2.7 is then converted to a different salt using ammonium hexafluorophosphate not containing nickel. This step has to be undertaken because simple neutralisation of the terachloronickelate(II) salt 2.7 results in the Ni(II) ion being reinserted into the macrocycle. The haxafluorophosphate salt of the ligand is then treated with triethylamine in ethanol to give the free neutral ligand.

In the case of the 14-membered S_2N_2-nickel(II) tetrafluoroborate salt 2.6, demetallation, under the conditions involved in step 1 of Scheme 2.5 caused the ligand to decompose. The ligand is apparently unstable in saturated ethanolic hydrogen chloride.

When reductive demetallation was attempted with lithium aluminium hydride, a "thiol" smell was obtained suggesting that the ligand had broken down. Displacement of the metal using dilute hydrochloric acid, or sodium cyanide[7,8] or disodium ethylenediaminetetraacetate[9] was attempted, but the free S_2N_2-macrocycle 2.2c was not obtained. It is possible that the C-S bond may not be able to withstand reductive conditions, and that the ligand is susceptible to hydrolysis in the absence of the metal ion. The C-S bond is relatively weak when compared with C-N and C-O bonds and is cleaved[10] more readily.

In contrast to the O_2N_2 and N_4 macrocycles (2.2a and 2.2b respectively) it seems that the S_2N_2 macrocycle (2.2c) is hydrolytically unstable. This may be due to increased ring strain in the 14-membered ring which is created by the longer carbon-sulphur bonds. In this connection it is possibly significant that very few S_2N_2-14-membered macrocyclic ligands with imine nitrogens have been reported (see section 1.8.1 in chapter 1), whereas considerably more 15- and 16-membered ring systems have been successfully prepared via Schiff base condensations.

Bond Length[a] in Å	C-N	C-O	C-S
	sp^3-N 1.47	sp^3-O 1.40	sp^3-S 1.81
	sp^2-N 1.36	sp^2-O 1.34	sp^2-S 1.75
Bond Enthalpy[a] kcal/mol	69-75	85-91	66

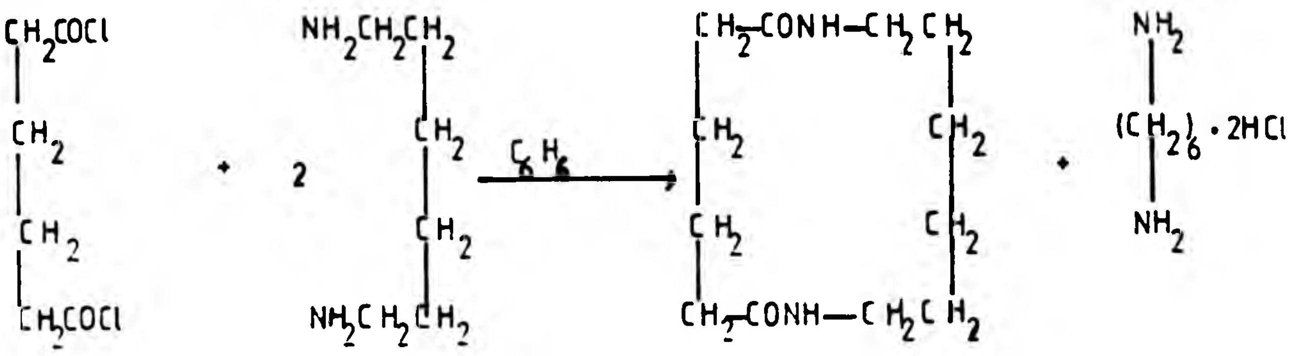
a- Ref 10

In view of the lower bond enthalpy of C-S bonds in the thioethers and their susceptibility to reductive cleavage it is therefore very likely that even if the free imine 2.2c had been isolated it would not have withstood the reduction step required to isolate the fully saturated "target" macrocycle 2.3c.

Alternative precursors to generate the three-carbon linkage between the anilino nitrogen atoms were considered.

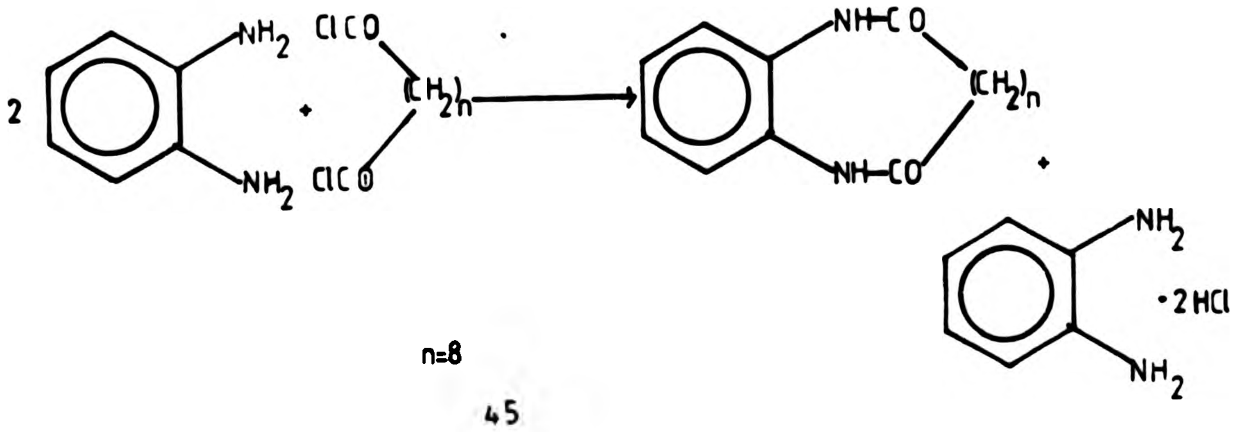
2.3 Attempted Cyclisation Using Malonyl Dichloride

Stetter[11,12] has reported routes to macrocyclic aliphatic amides;



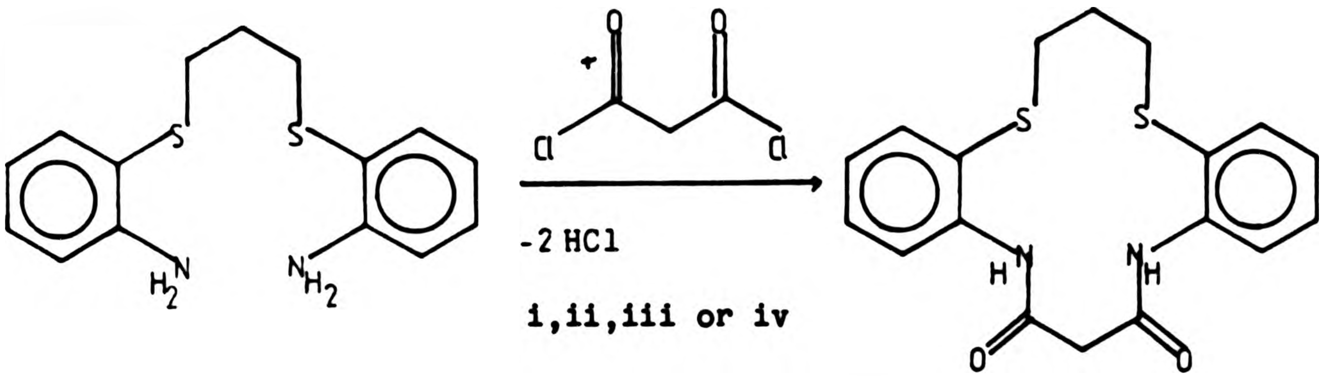
high-dilution

This was then used to prepare anilides[11] with o-phenylenediamine. Two moles of o-phenylenediamine were used for one mole of the dichloride.



Attempts were made to prepare the cyclic diamide from malonyl dichloride and the S_2N_2-diamine 2.1c as in scheme 2.6.

Scheme 2.6



2.1c

2.8

(i) High dilution techniques in diethyl ether, with 2.1c and malonyl dichloride.

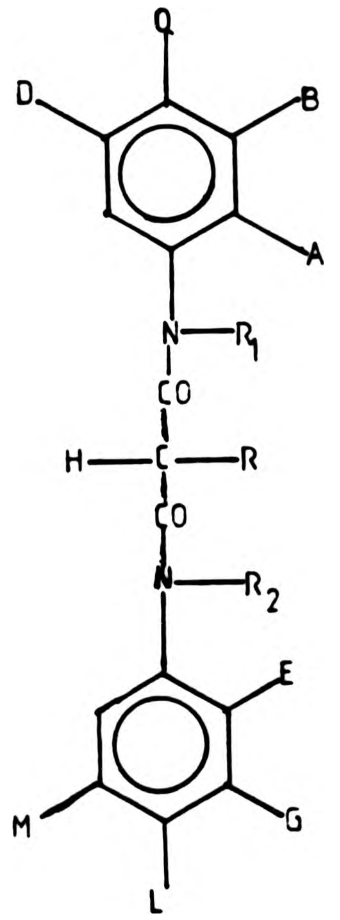
(ii) As above but dichloromethane or benzene used instead of diethyl ether.

(iii) 2.1c, malonyl dichloride, and sodium carbonate in dichloromethane or benzene.

(iv) 2.1c, malonyl dichloride and proton sponge (1,8-bis(dimethylaminonaphthalene) in benzene.

Very little of the desired macrocyle 2.8 was obtained in all preparations. When no base was used (i and ii) and high dilution condition were used the major product (>90 %) was the dihydrochloride salt of the diamine 2.1c. Any traces of the macrocycle were identified from the mass spectra which showed weak molecular ion peaks at m/z 358. The reason why so little macrocycle was obtained may be due to the fact that no base had been used to react with the liberated hydrogen chloride. A base is required which will react with the hydrogen chloride but which will not compete with the diamine 2.1c in reacting with malonyl dichloride. Using sodium carbonate or proton sponge did not improve the yields, but in these cases the major product was the unreacted diamine 2.1c.

Gold[13] has prepared several malonylanilides (see below) without using a base.



(a) A, B, Q, D, E, G, L and M are selected groups consisting of H, NO_2, CF_3, Cl and Br, with the proviso that 3 to 5 are H and that A and E cannot be NO_2

(b) R_1 and R_2 are H or C_1-C_4 alkyl groups

(c) R = C_1-C_6 alkyl group

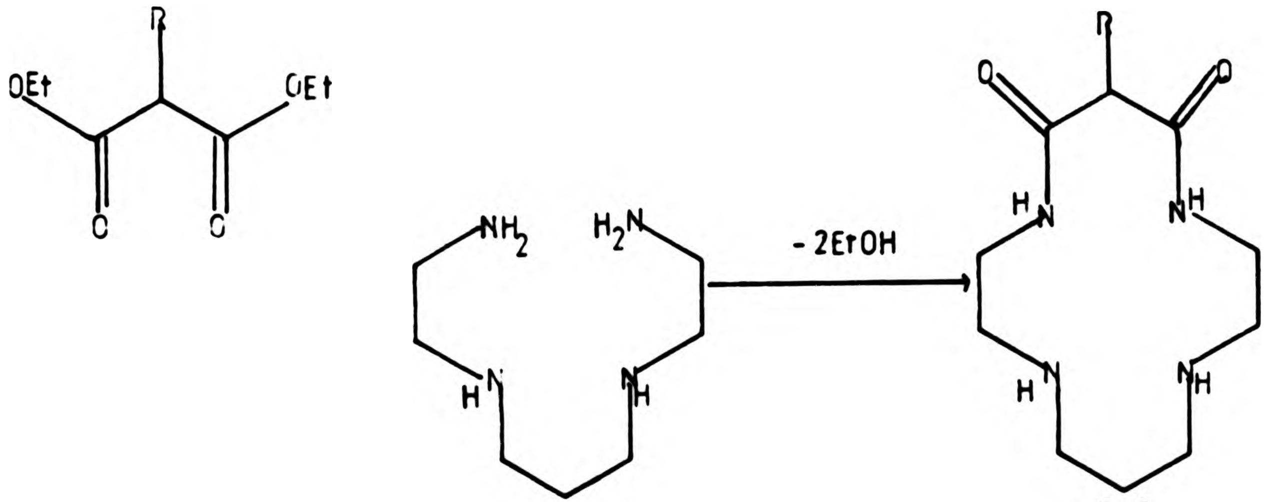
No malonanilide was prepared with R=H i.e. in every successful preparation the malonyl dichloride was alkyl-substituted on the central methylene group. The other requirement for this type of reaction is the presence of electron-withdrawing aromatic substituents.

Since neither of the conditions in the successful synthesis are ensured in the preparation of the S_2N_2 macrocycle via the malonyl dichloride route (scheme 2.6), it is probable that the reaction will not go to completion.

2.4 Attempted Cyclisation with Dialkyl Malonate

Aliphatic primary diamines have been shown[14] to react with malonate diesters to give cyclic 14-membered diamide ligands.

Scheme 2.7

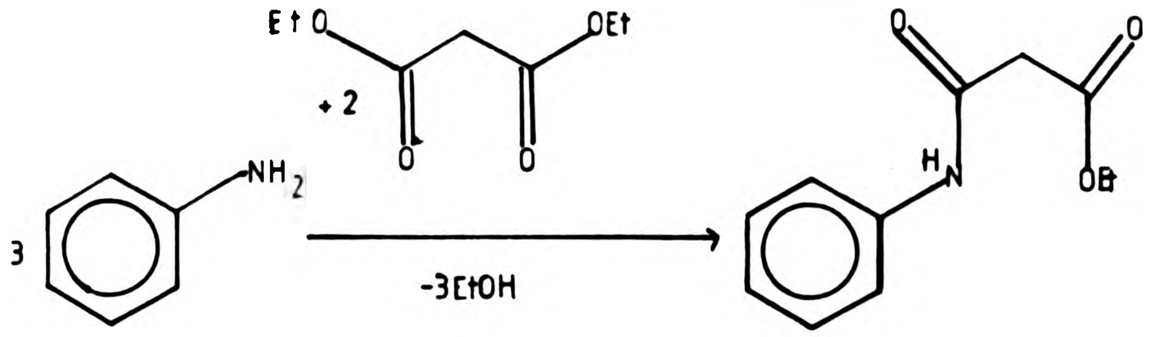


2.9

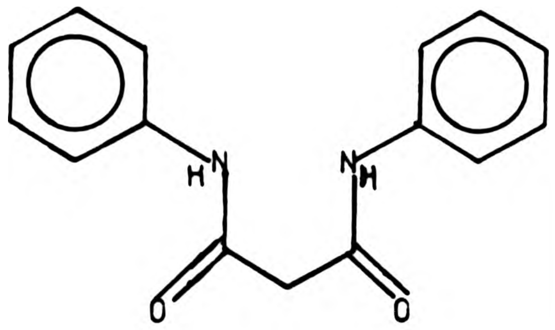
R=alkyl group or H

The possibility that aromatic diamines precursors such as 2.1c could be used in such reactions is supported by the report[15] that diethyl malonate reacts with aniline to give a mixture of mono- and di-anilides 2.10 and 2.11 (see scheme 2.8).

Scheme 2.8



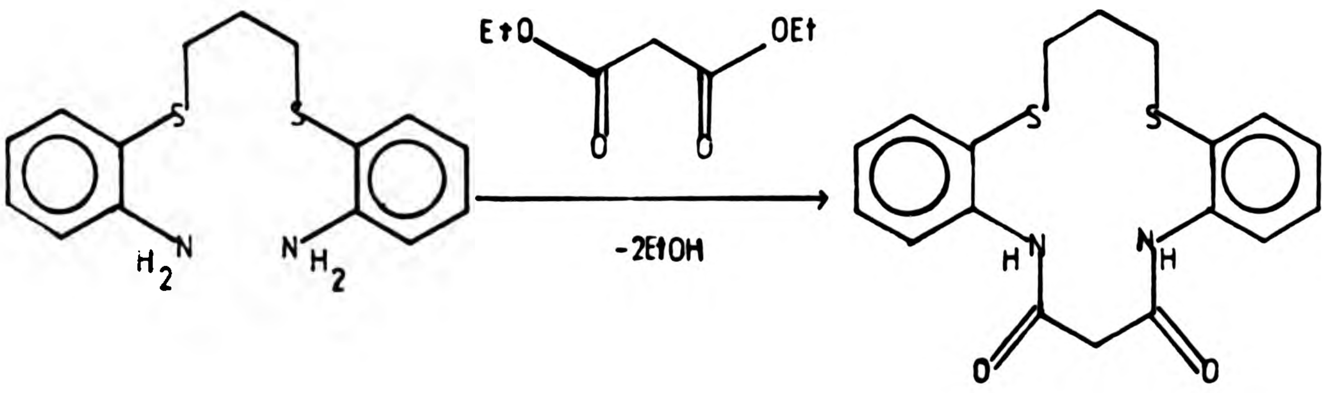
2.10



2.11

The ratio of products is dependent upon the quantities of precursors used.

Scheme 2.9



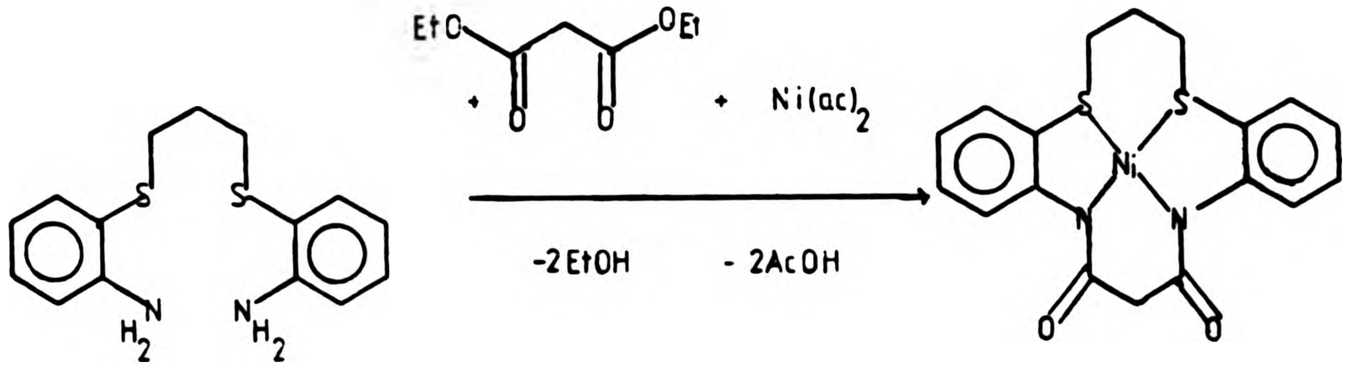
2.1c

2.8

Using solvent systems and conditions reported by Tabushi[14] the reaction shown in scheme 2.9 failed to give significant quantities of the macrocyclic diamide 2.8. Even under the most forcing conditions, after work up, the resulting material was found to be mainly (>90 %) unchanged 2.1c. The presence of a small quantity of the desired macrocycle 2.8 was suggested by weak molecular ion peaks in the mass spectra at m/z 358 (0.2 %).

Since non-template syntheses involving dialkyl malonates were unsuccessful, template syntheses were tried using nickel(II) salts.

Scheme 2.10



2.12

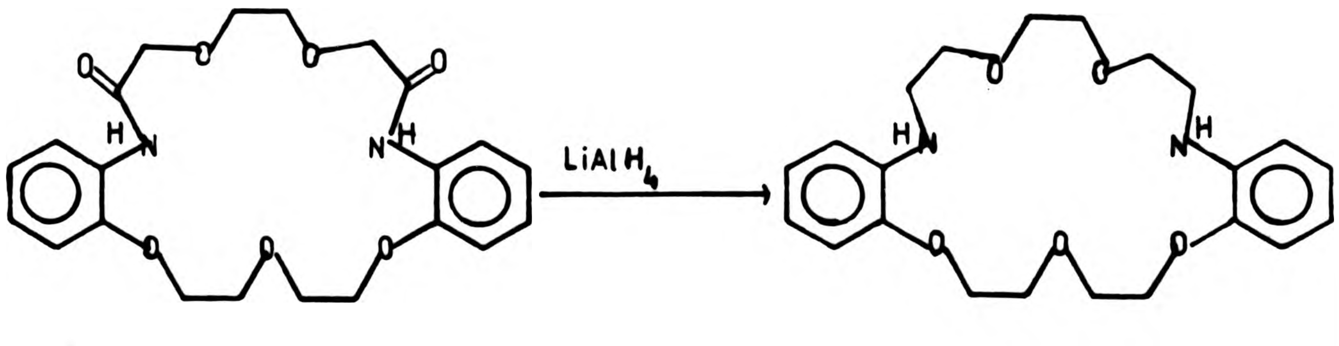
Xylene was used as a solvent and ethanol and acetic acid liberated in the reaction were removed by fractional distillation. Water from the hydrated Nickel(II) acetate was removed using a Dean-Stark trap. The nickel(II) complex 2.12 of the macrocycle was obtained in very high yields (87 %). The infrared spectrum of the resulting brown solid was consistent with the presence of the neutral nickel complex having a strong band at 1675 cm^{-1} associated with amide carbonyl groups.

The solid once obtained was very insoluble and could not be purified by recrystallisation, but microanalysis data and the mass spectrum were consistent with the structure 2.12 [highest m/z at 414(15 %) being the macrocyclic complex and loss of nickel giving the metal-free ligand at m/z 358(15 %)].

Attempts were made to prepare the analogous zinc(II) complex which could in theory be characterised by nuclear magnetic resonance spectroscopy, but unfortunately template syntheses using zinc(II) acetate were unsuccessful and the linear precursor was recovered unchanged.

Cyclic diamides have been reduced successfully in a number of different cases to yield macrocyclic ligands, some examples are given below (schemes 2.11-2.14). Lockhart[16] <u>et al</u> have used lithium aluminium hydride to reduce diamides to give the related secondary amines, e.g. the O_5N_2-ligand in scheme 2.11.

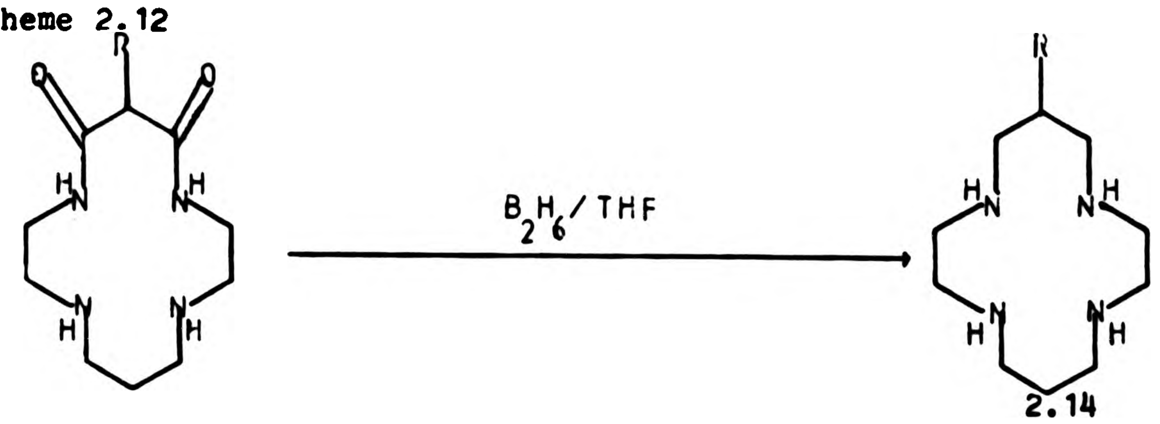
Scheme 2.11



2.13

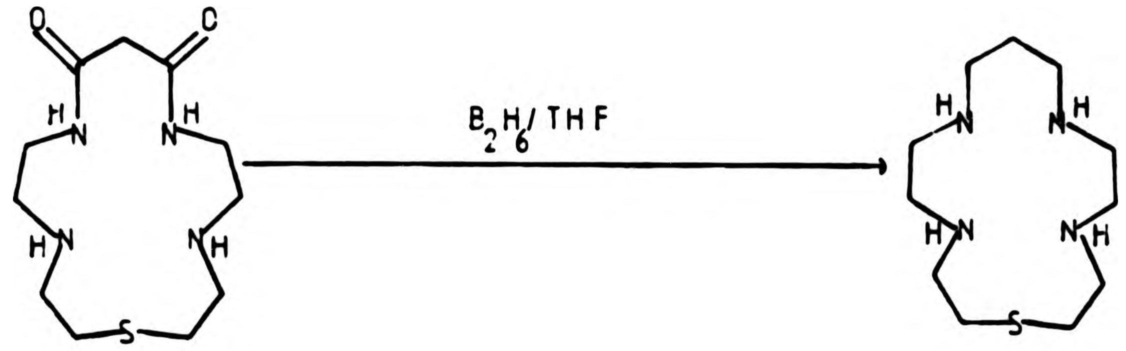
Borane in THF has been used as a reducing agent for diamides, for example to yield[14,17,18] the N_4-ligand 2.14, the N_4S-ligand 2.15 and the N_2S_3 and ON_2S_2-ligands 2.16.

Scheme 2.12



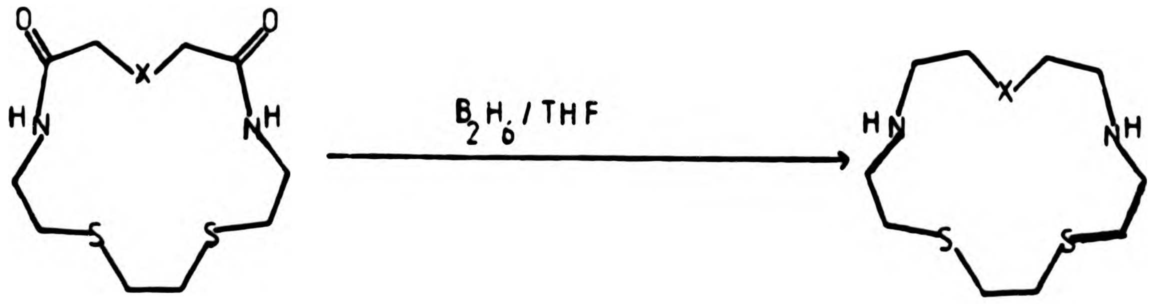
2.14

Scheme 2.13



2.15

Scheme 2.14



2.16

X=O

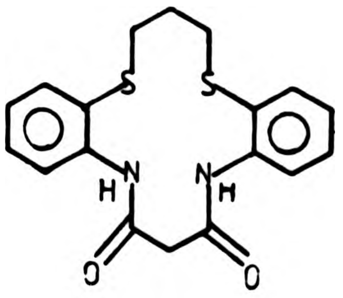
X=S

X=O

X=S

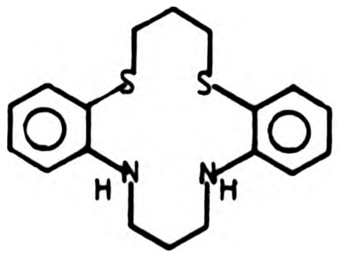
Attempts to reduce the Ni(II) complex 2.12 with lithium aluminium hydride in THF were accompanied by a strong "thiol" smell and a complex mixture was obtained which showed very few high molecular peaks in the mass spectrum. It is probable that the S_2N_2-ligand breaks down readily in the presence of strong reducing agents (see section 2.2).

One advantage of using the BH$_3$thf is that selective reduction of amide linkages in aliphatic sulphur-containing macrocycles is successful[14,17,18] without cleavage of C-S bonds. Treating the complex 2.12 with borane in THF yields a black solid and a brown oil. The solid is a combination of unreacted starting material (ca. 90 %) and some nickel(0). The mass spectrum of the oil showed peaks at m/z 358(3 %), 330(18 %) and 290(62 %) consistent with the structures below.



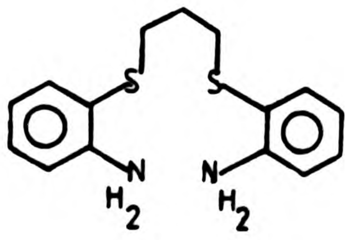
m/z 358

2.8



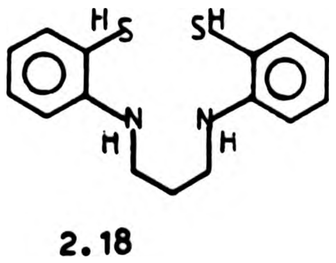
m/z 330

2.17



m/z 290

2.1c or



2.18

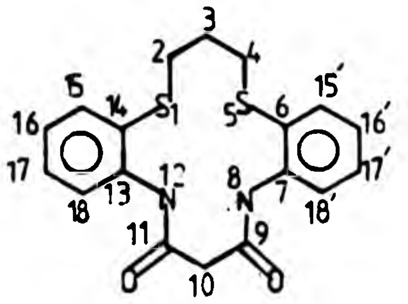
The ^{1}H nmr (60 MHz, CDCl$_3$) is consistent with the major component being 2.1c and indicates that the yield of the free ligand is approximately 5 %.

Simultaneous reduction and demetallation of the nickel(II) complex 2.12 is not successful under "standard" conditions (see section 2.2). Additionally there is also some evidence for ligand decomposition.

Borax and sodium borohydride was used in an attempt to demetallate the complex 2.12. Very little of the diamide 2.8 was obtained as judged by proton nmr of the resulting mixture (see Table 2.3) but a strong molecular parent ion peak was observed in the mass spectrum at m/z 358 (81 %).

TABLE 2.3 Chemical Shifts in the ^{1}H nmr (60 MHz, $CDCl_3$) of the Diamide 2.8

Chemical Shift /ppm	Site of Proton
6.80-8.00(mc)	15-18
3.69(s)	10 and 8,12
2.70(t)	2,4
1.35-2.00(mc)	3
9.18(s)	8,12



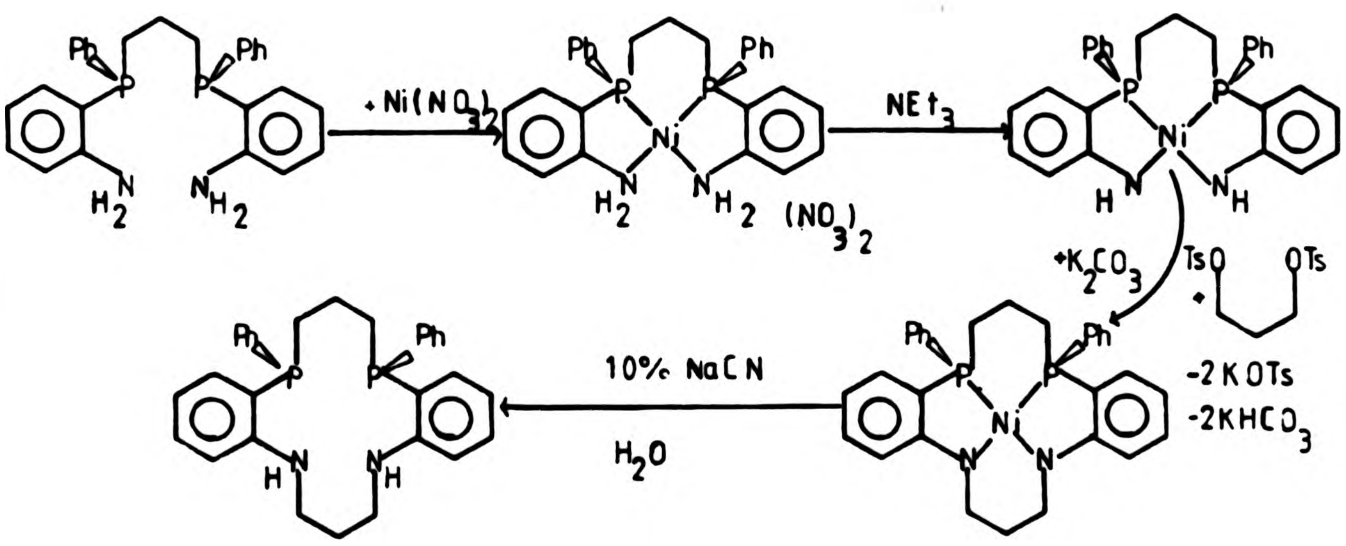
Numbering system for 2.8

A small quantity of the free diamide ligand was also obtained when demetallation was performed using potassium cyanide and dimethylsulphoxide or with a mixture of 10 % aqueous sodium cyanide[7,8] and benzene.

2.5 Attempted S_2N_2-Cyclisation Via Co-ordinated Anilido Groups

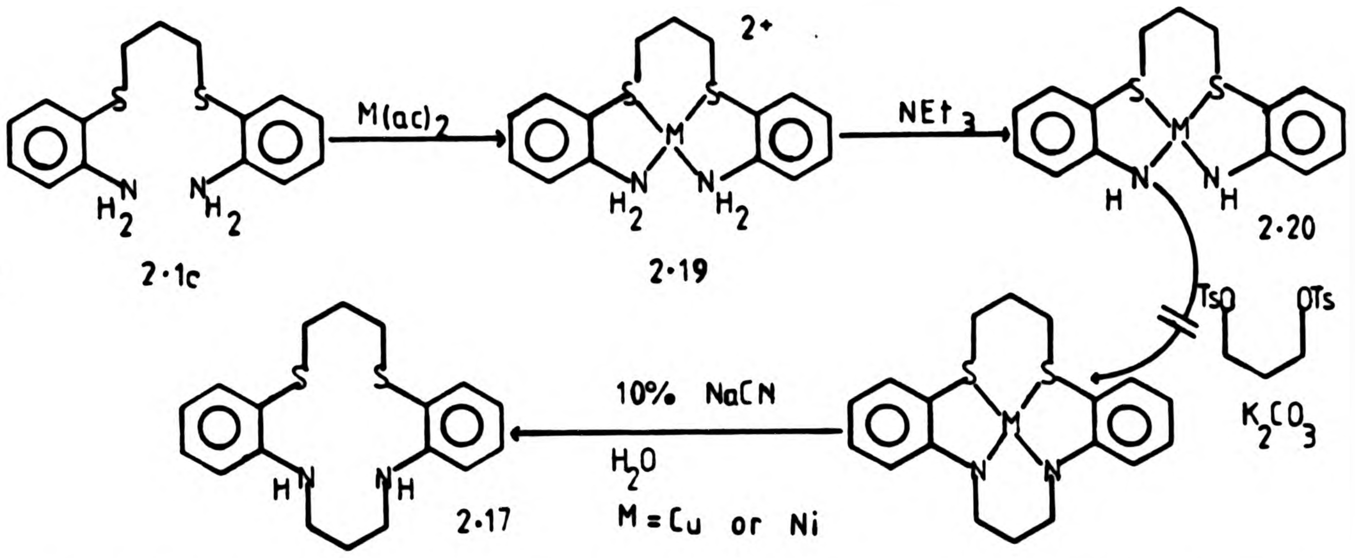
The lack of success of the standard reagents in achieving selective reduction of the anilide group in the presence of thioether moiety required us to consider alternative strategies for synthesis of the S_2N_2-macrocycles of the type 2.3c. Direct alkylation of the anilino nitrogen atom is possible in theory, although the problem of achieving cyclisation rather than linear polymerisation must be considered. Promotion of the cyclisation reaction involving direct alkylation of amine groups using template methods is rare because the co-ordinated nitrogen atoms have no nucleophilic activity unless the amine can be deprotonated. A closely related P_2N_2-macrocyclic system[19,20] has been prepared using this strategy (scheme 2.15).

Scheme 2.15



This synthesis was attempted on the S_2N_2-diamine 2.1c, with nickel(II) and copper(II) ions. In the presence of nickel(II) ions no solid complex could be isolated. With copper(II) the complex 2.19 and its deprotonated form 2.20 were obtained. However, cyclisation was not successful, and the unreacted starting materials were reobtained.

Scheme 2.16

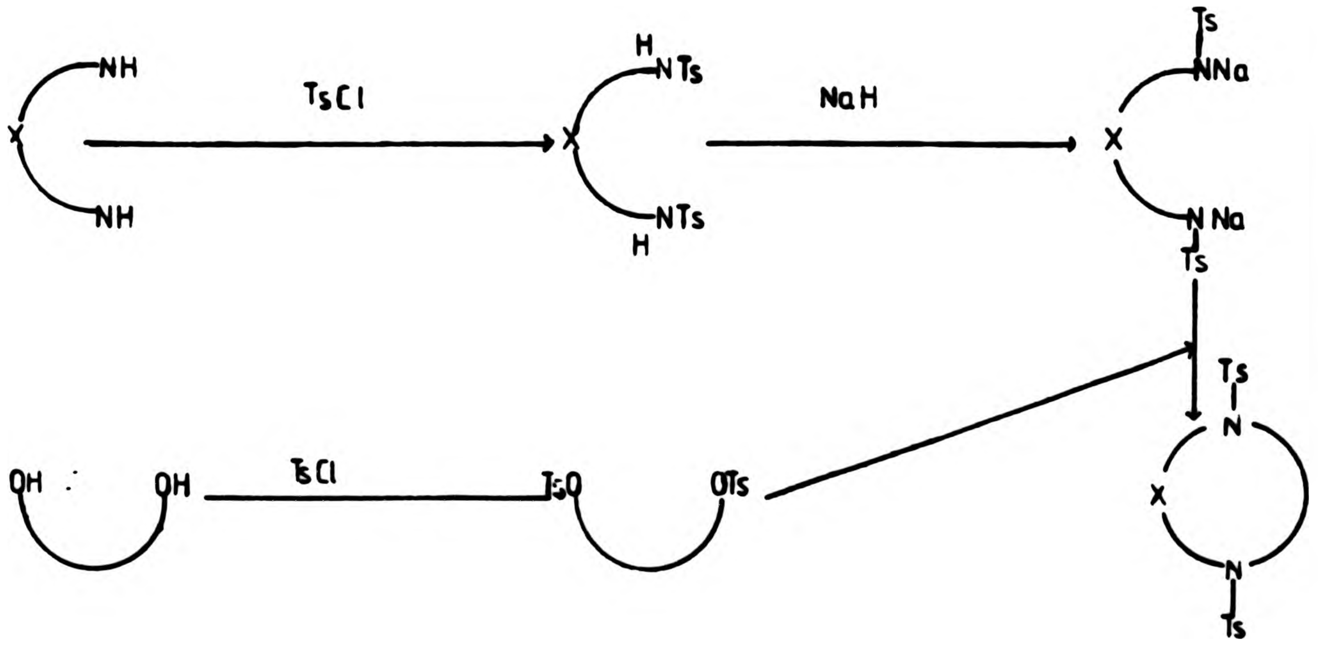


An alternative synthetic procedure based on enhancing the nucleophilic activity of the aniline nitrogens in 2.1c is described in the next section.

2.6 New S_2N_2-Macrocyclic Syntheses Via Tosylation Reactions

Recently a lot of use has been made of cyclisations following the Richman-Atkins[21] procedures.

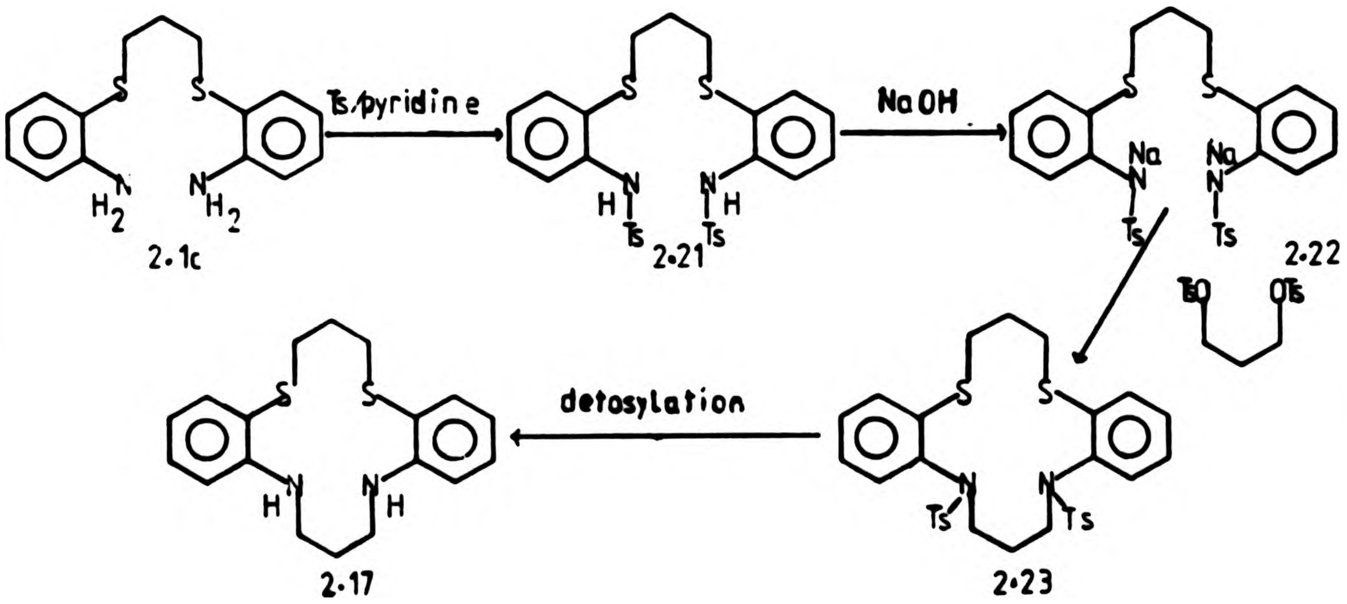
Scheme 2.17



The majority of work on these types of systems has been done on aliphatic polyamines[21-31]. Since the reactions do not involve high dilution techniques large scale preparations are practicable. The deprotonation of the sulfonamide group increases the nucleophilicity of the amine component and the sulfonate esters are better leaving groups than halides which had been used to a large extent previously.

The syntheses of the S_2N_2-macrocycles were attempted using the tosyl derivatives shown in scheme 2.18.

Scheme 2.18



This scheme was tested first for preparation of the 14-membered ring compound 2.17.

The tosylation of 2.1c was achieved in high yields from a reaction in pyridine. Reaction involving mixed solvent systems e.g. ether/sodium hydroxide[26] or tetrahydrofuran/sodium hydroxide solution were much less successful. The disodium salt 2.22 of the deprotonated disulfonamide can be isolated readily as a solid, although this is very hygroscopic.

In the cyclisation reactions to give 2.23 the deprotonation of 2.21 was carried out in situ by addition of potassium carbonate. The ditosylated macrocycle was obtained in high yields (>80 %) using such conditions.

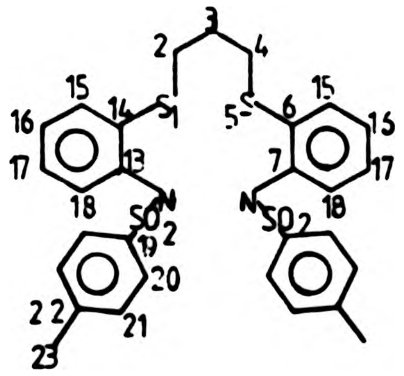
Complete conversion of precursor 2.21 was indicated by absence of bands attributable to N-H stretching modes at 3260 cm^{-1} in the infrared spectrum of the product 2.23. Attempts to use 1,3-dibromopropane as an alternative to 1,3-propaneditosylate were not successful.

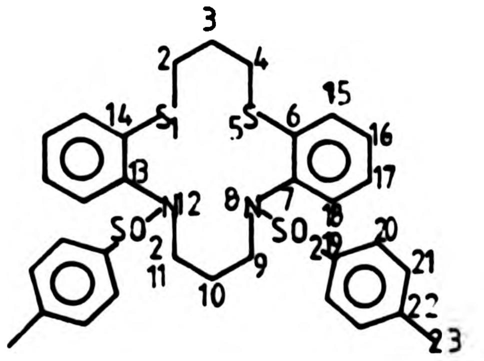
The ^1H nmr spectra of compounds 2.21 and 2.23 can be compared. A relatively simple spectrum is obtained for 2.21 but for 2.23 it is more complex. This is due to the greater rigidity of the molecule upon cyclisation.

TABLE 2.4 Comparative ^{1}H nmr (80 MHz, $CDCl_3$) Chemical Shifts of Molecules 2.21 and 2.23

2.21		2.23	
Site of* proton	δ/ppm	Site of proton	δ/ppm
3	1.49(p)	3,10	1.63-2.13(mc)
2,4	2.47(t)	2,4,9,11	2.60-3.33(mc)-6H 3.50-4.00(mc)-2H
Aromatic	6.60-7.90(mc)	Aromatic	6.37-7.75(d)
23	2.27(s)	23	2.38(s)
-NH-	6.60-7.90(mc)		

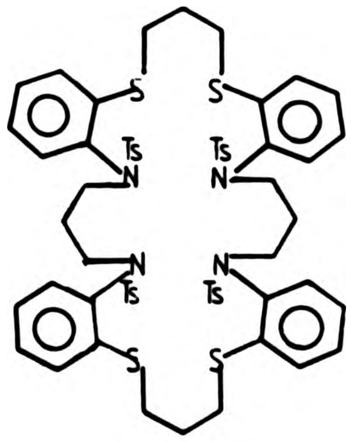
* Numbering systems used for 2.21 and 2.23 are:





On the whole the chemical shifts in the proton nmr of 2.23 are downfield compared to 2.21. The methyl protons of the macrocycle 2.23 are slightly downfield at 2.38 ppm. The central methylene protons between the sulfur atoms in 2.23 no longer appear as a simple pentet but occur in a complex multiplet centred at 1.91 ppm due to the overlap with the signals for protons at position 10. The simple triplet at 2.47 ppm is replaced by very complex and broad signals centred at 3.04 and 3.80 ppm. These are due to protons 2,4,9,11. Six of these protons appear in the region 2.60-3.33 ppm and the other two are in the range 3.50-4.00. The two different environments for -NH$\underline{CH_2}$ protons with two protons being further downfield is a consequence of non-equivalence of methylene protons.

The aromatic region for 2.23 now appear as two multiplets comprising a doublet at 6.50 ppm and a complex multiplet centred at 7.18 ppm. There is less free rotation in the macrocycle. The ^{1}H nmr does not help to distinguish between formation of cyclic monomer, oligomers (such as 2.24) or a mixture of components.



2.24

The ^{13}C nmr spectra provides evidence for the product of the cyclisation reaction being a single component. Assignments for the carbon resonances are based on similar arguments to those used for the precursors and related O_2N_2- and N_4-molecules (see section 2.1).

TABLE 2.5 ^{13}C nmr (20.12 MHz, CDCl$_3$) Signals for Compounds 2.21 and 2.23

Carbon Atom no^a	2.21	2.23
23	21.5	21.6
3	28.5	25.9
10	-	28.8
2,4	34.6	33.7
9,11	-	50.4
18	119.6	127.0
21	127.3	127.9
16	124.8	128.6
15	130.0	129.1
20	129.8	129.6
17	135.6	131.5
22(w)	123.7	136.0
6,14(w)	136.4	140.0
7,13(w)	138.8	140.6
19(w)	144.2	143.6

a-same numbering system used as in table 2.4

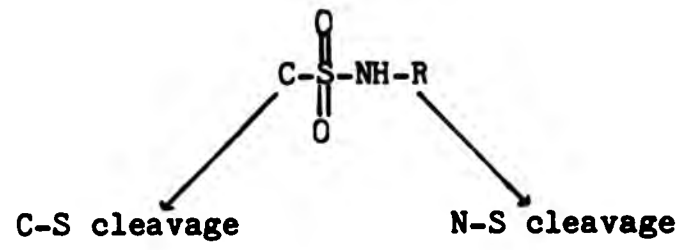
The signals for carbon atoms 20 and 21 were assigned on the basis of their approximately double intensity relative to other C-H benzene carbon atoms (15-18). The lowest field signal was that of carbon 19, adjacent to the very electron-withdrawing -SO$_2$- group. There is pseudomirror symmetry of both 2.21 and 2.23 as shown by ^{13}C nmr spectroscopy. From the spectrum, 2.23 seems to be a single component. The methyl carbon atoms, 23 are at similar chemical shifts for both structures. Carbon atoms 2, 3 and 4 are further upfield for 2.23. The carbon atoms between nitrogen atoms appear further downfield than those between the sulfur atoms. Considering the aromatic region, atoms 18 and 16 in molecule 2.23 are further downfield than those for 15 and 17. Similarly for the tosyl aromatic rings 21 is downfield, Carbon atoms 6, 7, 13, 14 and 22 shift downfield upon cyclisation whereas 19 shifts upfield.

The mass spectrum helps to confirm the presence of a monomer with a molecular parent ion peak at m/z 638 (22 %), with loss of tosyl groups at m/z 483 (93 %) and m/z 328 (5 %) respectively. Additionally the macrocycle is extremely soluble in most organic solvents. This also implies that 2.23 is most likely to be a monomer.

To obtain the target molecule 2.17 from macrocycle 2.23, detosylation is required.

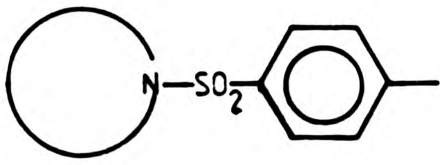
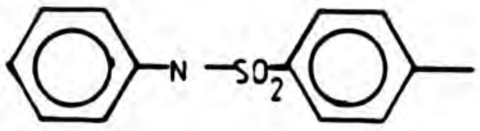
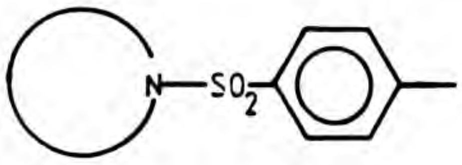
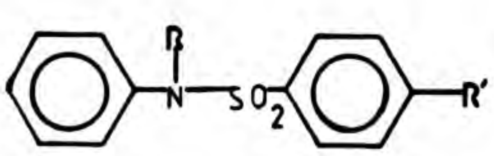
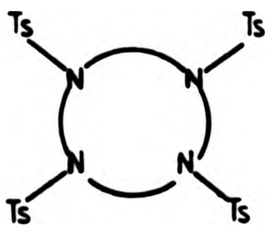
2.7 Detosylations

Sulfonamides in general are very stable and cleavage of the N-S or C-S bonds requires forcing conditions[32].



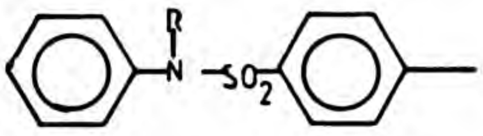
Detosylation of 2.23 requires N-S cleavage for which two approaches have been described. The more common involves use of hydrolytic procedures and reagents which promote hydrolysis of arylsulfonamides are listed in table 2.6. An alternative procedure relies on reductive cleavage and a number of reagents have been reported to be successful in such reactions (see also table 2.6).

TABLE 2.6 Some Procedures for Detosylations by Hydrolysis and Reductions

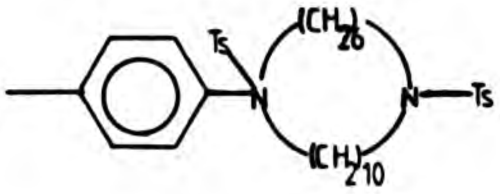
Reagent	Arylsulfonamide	References
Hydrolysis		
(a) HBr/AcOH		24-27
(b) HBr/AcOH/phenol		22
		33,34
(c) 25 % HCl	 R'=H or Me R=H or Me	35
(d) H_2SO_4		5,21,22,28,32

Reductions

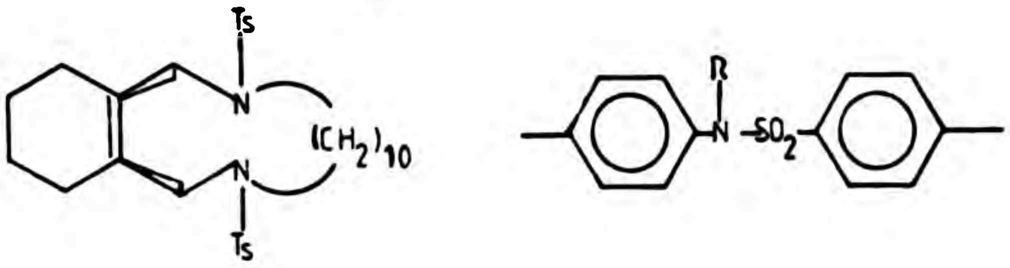
(a) Zn/HCl (R = Et etc.) 32,36



(b) Na/Hg/NaHPO$_4$ 30



(c) Na/naphthalene R = Me etc. 37,38



At the onset it was clear that care would have to be taken in chosing reductive reagents for detosylations because the sensitivity of the thioether linkage to reduction has already been demonstrated (see sections 2.3 and 2.4). As a consequence initially hydrolytic cleavage was studied. In each case the reactions were monitored by ^1H nmr spectroscopy, after washing aliquots with base to remove sulfonate derivatives such as p-toluenesulfonate. The depletion of the tosyl methyl peak at 2.38 ppm and the deviations of the ratio of aromatic to aliphatic protons from 16:18 were used to assess the extent of detosylation.

TABLE 2.7 Results of Attempted Detosylations

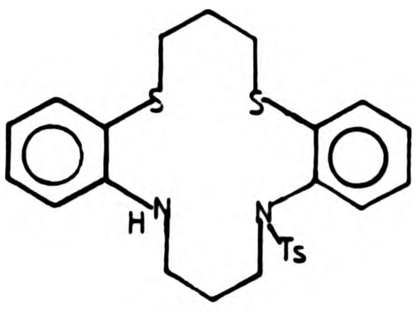
	Reagents	References	Result
(i)	25 % HCl	32,35	no detosylation
(ii)	48 % HBr/AcOH	26,32	partial detosylation
(iii)	AcOH/HCl/Zn	36	no detosylation
(iv)	Na/Hg/$NaHPO_4$	30	no detosylation
(v)	Na/naphthalene/THF	37,38	detosylation

The macrocycle 2.23 seems to be quite stable to detosylation by hydrolysis. No detosylation was detected when the reagents were used under literature conditions for attempts (i), (iii) and (iv). When 48 % HBr/acetic acid was used and refluxing maintained for 65 hours, some of the macrocycle 2.23 went into solution and after neutralisation an oil was obtained which apparently contained a little of the singly or doubly detosylated macrocycle, as judged by ^1H nmr spectroscopy and the presence of an N-H band at 3360 cm^{-1} in the infrared spectrum.

TABLE 2.8 ^1H nmr (60 MHz, $CDCl_3$) Spectrum of Oil From HBr/AcOH Detosylation of 2.23

Chemical Shift /ppm	Relative nos. of Protons	Possible Assignment
6.30-8.00(mc)	12	Aromatic
3.80(b)	1	-NH-
2.95-3.40(mc)	4	$-NH\underline{CH_2}-$
2.60-2.95(mc)	4	$-S\underline{CH_2}-$
2.22(s)	3	$-\underline{CH_3}$
1.55-2.15(mc)	4	$-SCH_2\underline{CH_2}-$ and $-NHCH_2\underline{CH_2}$

The appearance of a new tosyl methyl signal at 2.22 ppm and the observed aromatic:aliphatic proton ratio of 12:16 suggests that a major component of the mixture is the mono-tosylated macrocycle 2.25, rather than a mixture of 2.23 and 2.17.



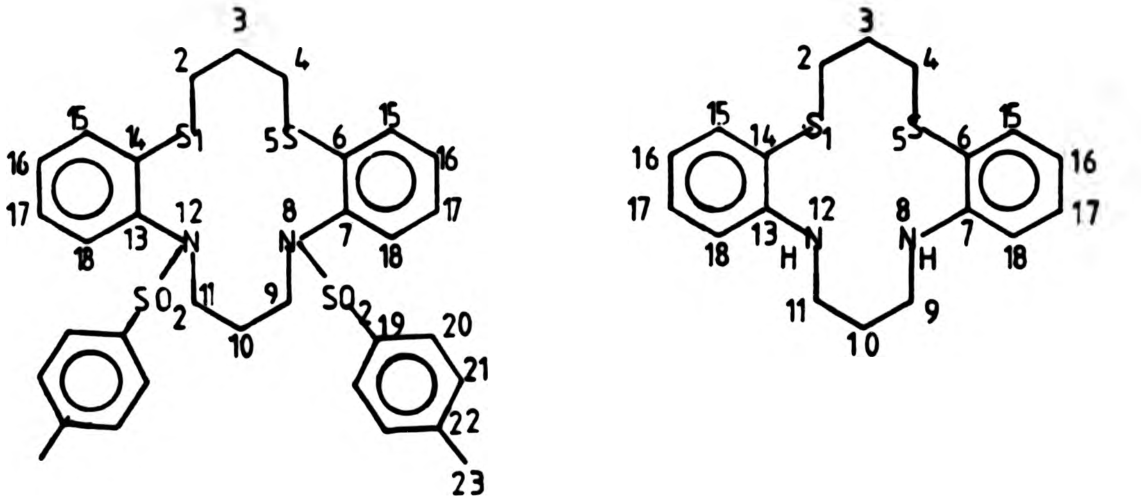
2.25

Complete detosylation was successfully achieved using sodium/naphthalenide[37,38] in tetrahydrofuran. The mass spectrum of the resulting oil (70 %) had a parent ion peak at 330 (49 %) with the next fragment being at 290 (3.5 %) with the loss of a C_3 bridge. The infrared spectrum of the oil had a strong band at 3390 cm^{-1} characteristic of a secondary amine. The ^1H nmr spectrum (table 2.9) suggested that the major product is 2.17 with only slight traces of tosylated compounds being present.

TABLE 2.9 Comparison of ^{1}H nmr (80 MHz, $CDCl_3$) Spectra of 2.23 and 2.17

Macrocycle	2.23	2.17	
Site of protons[a]	δ/ppm	Site of protons	δ/ppm
3,10	1.63-2.13(mc)	3,10	1.35-2.00(mc)
23	2.38(s)		-
2,4,9,11	2.60-3.33(mc)-6H	2,4	2.65(t)
	3.50-4.00(mc)-2H	9,11	3.15(t)
5-18, 20,21	6.37-7.75(mc)	15-20	6.30-7.50(mc)
		-NH-(8,12)	5.12(b)

a- The numbering systems for 2.23 and 2.17 are:



The ^{13}C nmr (20.12 MHz) spectrum of the oil had a lot more peaks than the 10 signals which are expected for the symmetrical molecule. The signals for the free macrocycle 2.17 can be predicted with confidence from comparative assignments of precursors and from calculated values. The chemical shifts for benzene carbons can be calculated from tables[39] of values of substituted benzene carbon atoms and deviations from the theoretical value of 128.5 ppm for unsubstituted benzene.

TABLE 2.10 Comparison of the ^{13}C nmr (20.12 MHz, $CDCl_3$) Chemical Shifts for 2.23 and Peaks Assigned to 2.17 in the Impure Materials from Detosylation Reactions

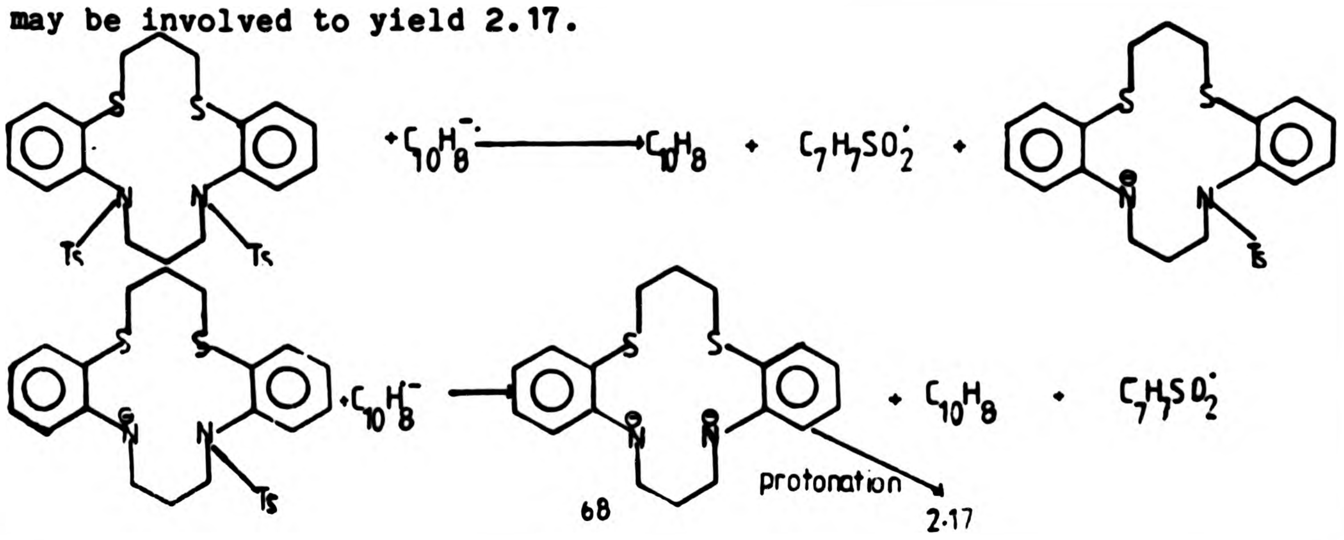
Carbon Atom[a]	2.23	2.17
23	21.6	-
3	25.8	29.1
10	28.8	29.1
2,4	33.7	33.4
9,11	50.4	41.5
18	127.0	110.2
21	127.9	-
16	128.6	116.9
15	129.1	130.2
20	129.6	-
17	131.5	136.4
22(w)	136.0	-
6,14(w)	140.0	117.5
7,13(w)	140.6	149.3
19(w)	143.6	-

a- Carbon atoms labelling system as in table 2.9

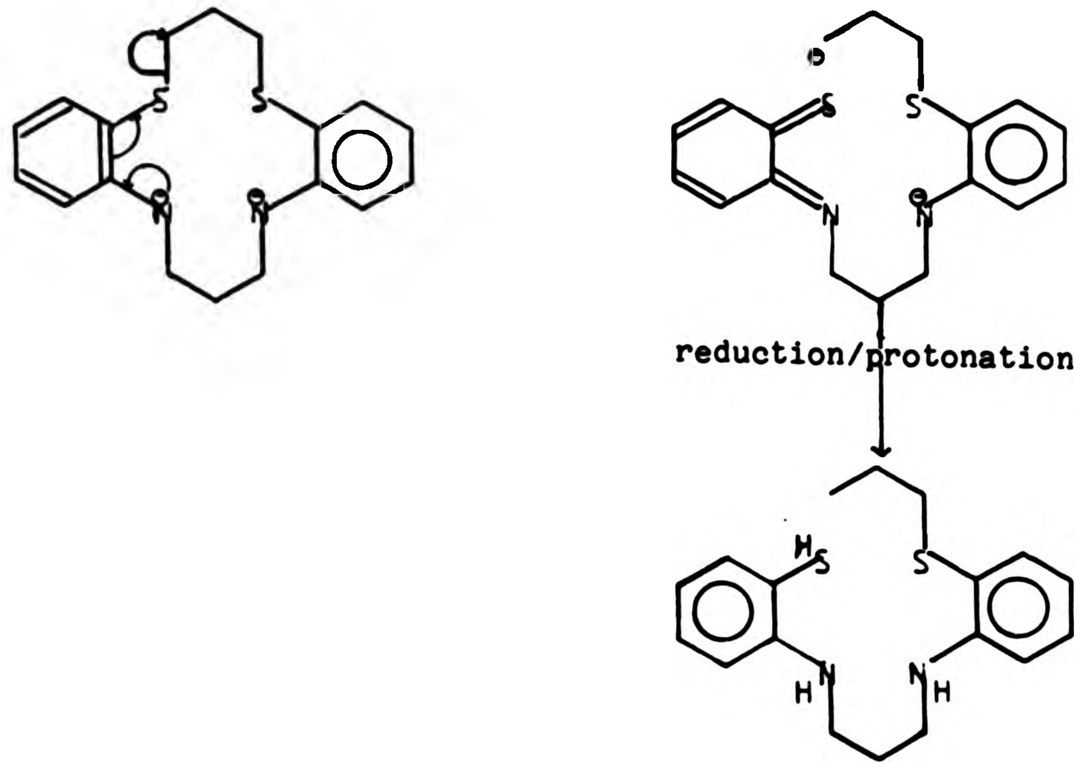
The ^{13}C nmr spectra of the oil suggests that the major component is the desired macrocycle 2.17 but there is approximately 15 % of impurities present. These could be naphthelene, residual tosylated derivatives or some decomposition product of the macrocycle.

2.8 Possible Mechanism of Detosylation

The mechanism of detosylation involves the naphthanelide[38] radical species. In the detosylation of sulfonamide 2.23 the following steps may be involved to yield 2.17.



The cleavage of C-S bonds which appears to accompany this detosylation may arise from the following type of pathway.



Several strategies were used in attempts to isolate the pure ligand.

2.9 Purification of Products From Detosylations Using Sodium Naphthalenide

The composition of the oil was assessed by ^{13}C nmr spectroscopy and the following methods of obtaining the pure ligand were considered.

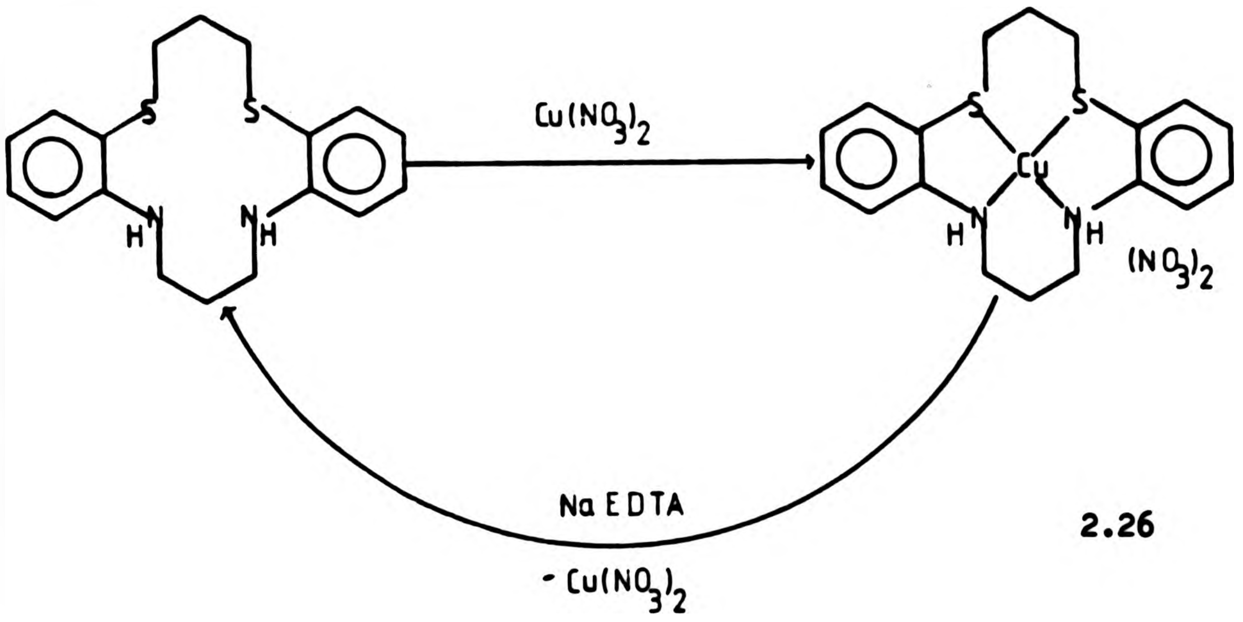
(i) Via preparation of metal complexes

(ii) Via protonation of the ligand

(iii) By repeating the detosylation under varying conditions

(iv) By using column chromatography

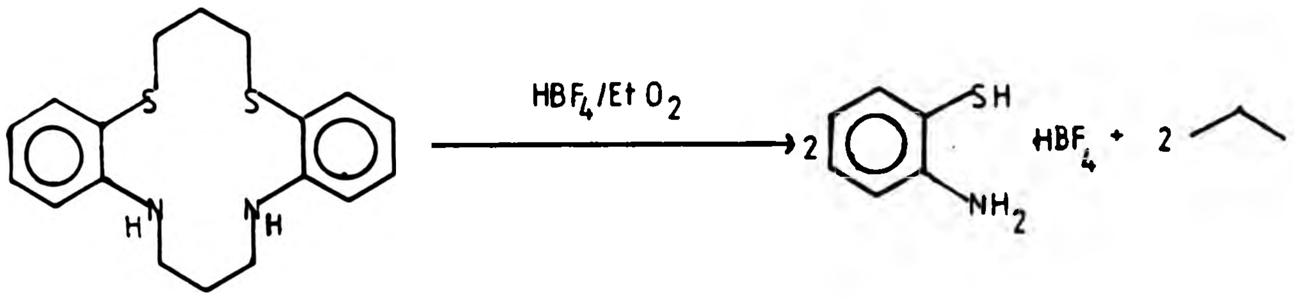
An attempt was made to isolate the macrocyclic ligand via its copper(II) nitrate complex 2.26 according to the scheme:



2.26

The copper complex(es) generated in this reaction sequence was extremely highly coloured. The sequence was very effective in separating the ligands from residual naphthalene but the regenerated ligand was still a mixture as judged by the number of ^{13}C signals in the methylene region. It is assumed that decomposition of 2.17, e.g. by reductive cleavage of C-S bonds also generates strong complexing agents which are recovered unchanged for the "purification" sequence.

Attempts to protonate and isolate insoluble salts of the ligand were unsuccessful with various acids, e.g. fluoroboric, perchloric, trifluoromethanesulphonic, nitric and sulfuric. In every case, and using a wide variety of solvent mixtures no solid material could be isolated. It appeared that prolonged contact of the ligand with acidic solutions pomotes decomposition of the ligand which is accompanied by a darkening of the solution. Treating the oil containing 2.17 with fluoroboric acid in ether results in a white solid separating from a red solution. The white solid showed only aromatic signals in the ^{1}H nmr spectra in D$_2$O and has broad infrared stretching bands at 3400 and 1050 cm^{-1} which are due to R-NH$_3^+$ and BF$_4^-$ respectively. Decomposition to give *o*-aminobenzenethiol is assumed to occur under these conditions.



2.27

Attempts were made to optimise the reductive detosylation method to minimise the decomposition of 2.17, and secondly various types of chromatography were investigated to separate the complex mixture of products.

Attempts to reduce side reactions were made by changing the detosylation solvent to dimethoxyethane, and reducing the contact time. The reaction were also undertaken at low temperatures, again to reduce formation of side products. The ditosylated ligand was added in some cases in the solid form and in others as a solution in the reaction solvent.

Attempts at purification by column chromatography using silica or alumina gave no effective separation of the individual components in the mixture, but residual naphthalene was removed in this way. Analyses of the product indicated the presence of four components.

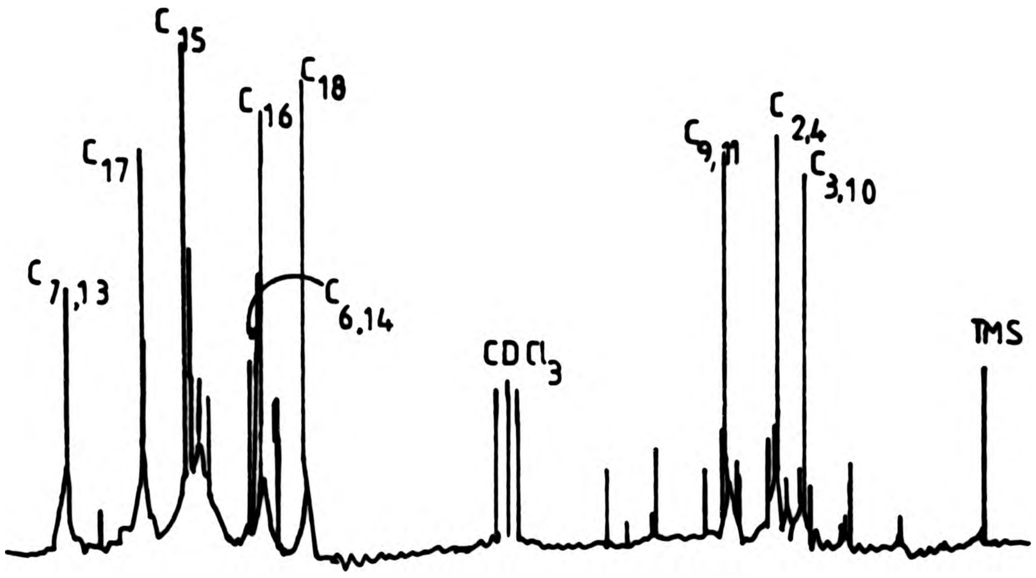
Preparative glc was attempted on the mixture using 10 % SE 30 [this is 10 g of methyl silicone (stationary liquid phase) and 90 g of Chromosorb W/HP (similar to fire brick as the inert support), the moving phase was nitrogen gas, with dichloromethane as elutant, the glass column had dimensions 12 ft by 0.25 inch diamater. Samples were manually injected 20-50 μl each time and the instrument used was a Pye Unicam 105 preparative gas chromatogram and the sample was collected on a turntable trap, at 200-220 °C]. Some separation was obtained but the process was very tedious and the major component was unpurified 2.17.

Gel filtration techniques proved to be the most effective method of purification, using a Sephadex LH-20 column and dichloromethane as elutant and swelling agent. In this technique the larger particles pass down quicker and the smaller particles are preferentially retained. Only about 20 % of the sample is obtained in the "pure" form in the first fraction of elutant. The remaining fractions contain the impurities noted previously . The ^{13}C nmr spectrum of the "pure" sample (spectrum 2.2) has three aliphatic signals only. The central methylenes carbons (C_3 and C_{10}) have identical shifts. The aromatic region has major signals due to 2.17, with weak signals for any remaining impurity. Repeating gel filtration with THF gave similar results. The first fraction gave about 20 % "pure" macrocycle but with later fractions the impurities came down simultaneously with the macrocycle.

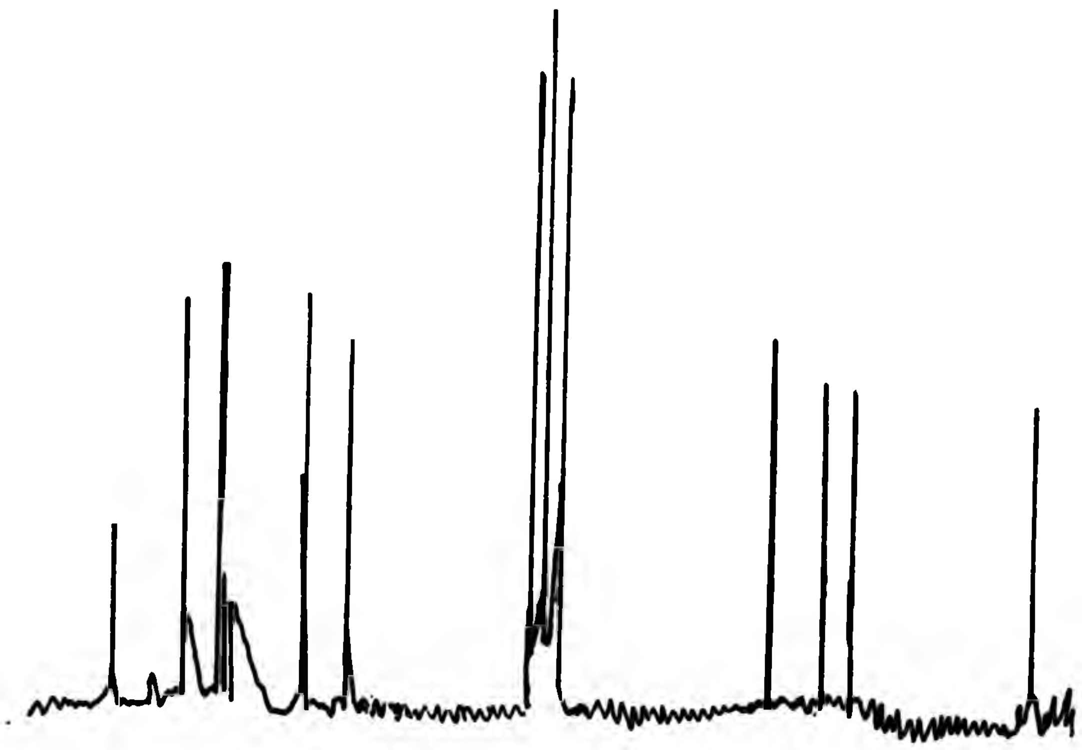
Purification using Sephadex LH-20 has a number of problems, the most significant being that Sephadex LH-20 is very light and when chloroform is used as the swelling and eluting agent the

Sephadex LH-20 floats. When low boiling elutants are used the column cracks easily. Also, Sephadex LH-20 is expensive, consequently column chromatography is only possible on a small scale and had to be repeated many times before appreciable quantities of the macrocycle 2.17 were obtained. This proved to be a very tedious process. The synthetic route to 2.17 outlined in scheme 2.18 is unfortunately severely restricted by the final (deprotection step). The earlier steps, including the cyclisation, proceed in greater than 87 % yield, but detosylation which under optimum conditions gives approximately 70 % of detosylated material is accompanied by ligand fragmentation reactions and the subsequent recovery of pure 2.17 is never greater than 20 %. The limitation in the detosylation step is particularly frustrating in the light of the generality of application of the cyclisation procedures which allow easy preparation of the ditosylated forms of a wide range of S_2N_2-macrocycles (see below).

Spectrum 2.1 ^{13}C nmr Spectrum of the Impure Oil from the Detosylation Reaction



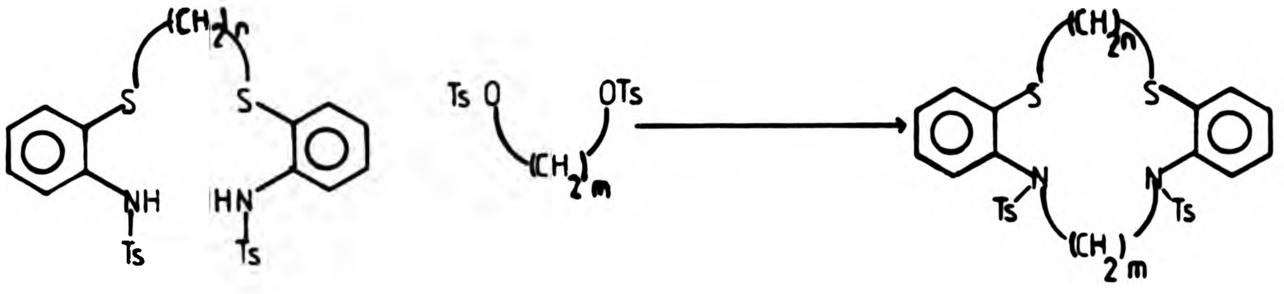
Spectrum 2.2 ^{13}C nmr Spectrum of Pure 2.17 After Purification of the Impure Oil from the Detosylation Reactions



2.10 Preparations of S_2N_2-Macrocycles with Variable Ring Sizes

In theory the synthetic procedure for preparation of macrocycles containing anilino nitrogen atoms seems to be versatile and may be adapted for preparation of S_2N_2-macrocycles with variable ring-sizes.

Scheme 2.22



2.28, n=2
2.21, n=3
2.19, n=4

2.30, m=2
2.31, m=3
2.32, m=4

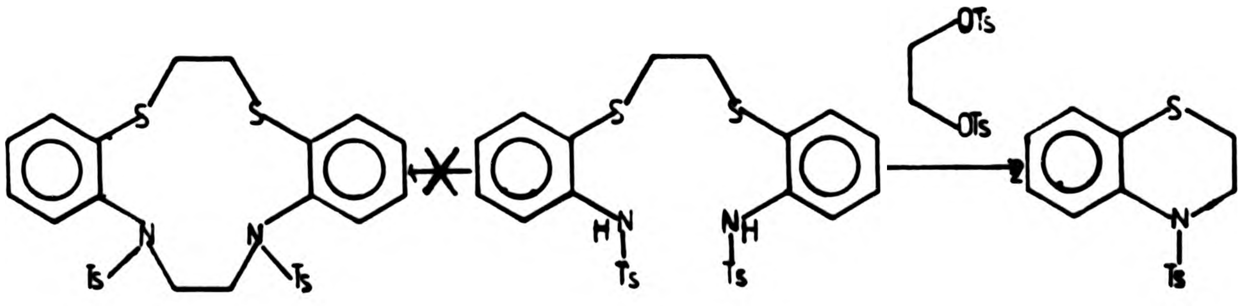
2.33, n=2, m=2
2.34, n=2, m=3
2.35, n=2, m=4
2.36, n=3, m=2
2.37, n=3, m=4
2.38, n=4, m=2
2.39, n=4, m=3
2.40, n=4, m=4

This synthetic route was attempted for macrocycles 2.33-2.40. The macrocycles were identified by conventional means, which rely heavily on mass spectral data (table 2.10). The possibility of oligomeric products being present cannot definitely be excluded (see section 2.6).

TABLE 2.10: Yields and Mass Spectral Results for Macrocyles 2.33 to 2.40

Macrocycle no	2.33	2.34	2.35	2.36	2.37	2.38	2.39	2.40
Ring Size	12	13	14	13	15	14	15	16
n	2	2	2	3	3	4	4	4
m	2	3	4	2	4	2	3	4
Macrocycle Obtained	No	Yes	Yes	No	Yes	Yes	Yes	Yes
% yield	-	70	69	-	71	91	82	86
Molecular peak, m/z	305	624	638	598	652	638	652	666
%	100	8	1	5	5	3	1	20
Loss of Ts m/z	150	469	483	-	497	483	497	612
%	100	40	40	-	2	5	3	15
Loss of 2Ts m/z	-	314	328	-	342	328	343	511
%	-	10	6	-	1	2	6	56

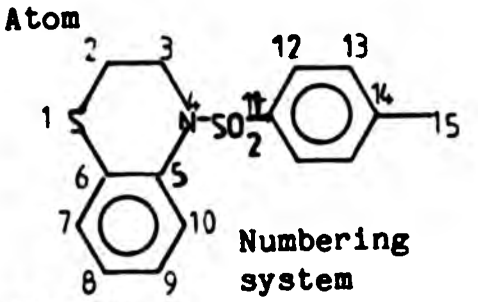
With the exception of macrocycles 2.33 and 2.36 with ethane bridges between the aniline nitrogen atoms, all the macrocycles were obtained in very high yields (69-91 %). The attempted preparation of 2.33 yielded the six-membered SN-heterocycle 2.41 (parent ion peak at m/z 305(100 %).



2·33 2·28 2·41

TABLE 2.11 ^{1}H nmr (80 MHz, $CDCl_3$) Spectrum of 2.41

δ/ppm	Assignment	Site of Hydrogen Atom
2.40(mc)	$-CH_3$	15
2.88(t)	$-SCH_2-$	2
3.97(t)	$-NCH_2-$	3
6.75-7.75(mc)	Aromatic	7-10, 12, 13



Numbering system for 2.41

Macrocycle 2.36 was not obtained, and the starting materials were recovered. Of all the permutations of the alkane linkages considered in scheme 2.22 it is only those leading to the smallest ring-macrocycles (the 12-membered ring and one of the 13-membered rings) which fail to give a high yield of ditosylated S_2N_2-macrocycles. This suggests that some ring strain (or steric interaction involving the bulky tosyl groups) is present in these smaller rings.

TABLE 2.12 ^{1}H nmr (80 MHz, $CDCl_3$) Spectra of S_2N_2-Macrocycles

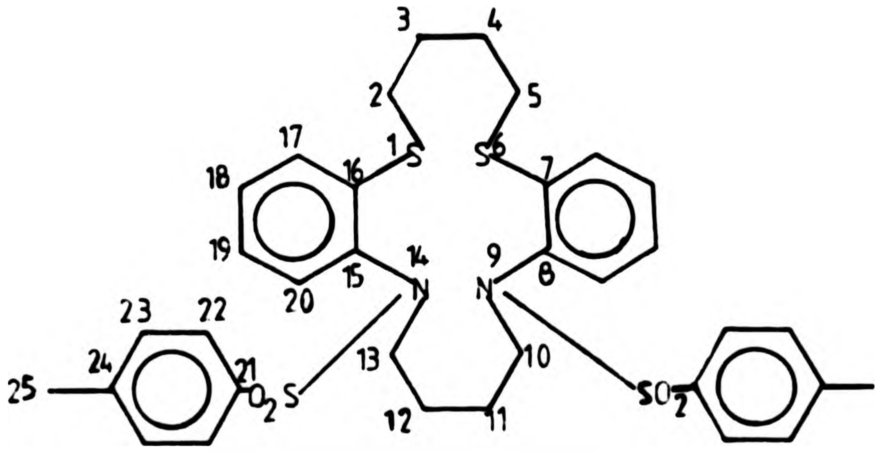
Macrocycle	2.34	2.35	2.37	2.38	2.39	2.40
n	2	2	3	4	4	4
m	3	4	4	2	3	4
Assignments						
$-\underline{CH}_3$	2.46(s)	2.40(s)	2.40(s)	2.40(s)	2.40(s)	2.40(s)
$-SCH_2\underline{CH_2}-$	-	-	1.12- 1.68(mc)	1.30- 2.00(mc)	1.25 1.85(mc)	1.25- 2.00(mc)
$-S\underline{CH_2}-$	2.25- 2.50(mc)	2.25- 2.63(mc)	2.63- 3.25(mc)	2.25- 2.63(mc)	2.60- 3.00(mc)	2.63- 3.10(mc)
$-NCH_2\underline{CH_2}-$	1.38- 1.88(mc)	1.25 1.83(mc)	1.68 2.19(mc)	-	1.25- 1.85(mc)	1.25- 2.00(mc)
$-N\underline{CH_2}-$	3.00- 4.00(mc)	3.00- 3.50(mc)	2.63- 3.90(mc)	2.87- 3.00(mc)	3.00- 4.00(mc)	3.13- 3.88(mc)
Aromatic	6.50- 7.75(mc)	6.00- 7.75(mc)	6.37- 7.75(mc)	6.75- 7.00(mc)	6.25- 7.87(mc)	6.50- 8.00(mc)

Generally the signals for the methylene protons between the sulfur atoms are further upfield compared with the corresponding methylenes between the nitrogen atoms. Most of the signals occur as complex multiplets.

TABLE 2.13 ^{13}C nmr (20.12 MHz, $CDCl_3$) Signals[a] for the *cis*-S_2N_2-Macrocycles

Macrocycle	2.34	2.35	2.37	2.38	2.39	2.40
n	2	2	3	4	4	4
m	3	4	4	2	3	4
Carbon Atom						
25	21.6	21.6	21.5	21.6	21.6	21.6
3,4	-	-	25.6	25.8	28.2	25.9
11,12	31.9	26.8	25.1	-	30.7	28.4
2,5	35.2	30.0	32.3	31.5	31.6	32.6
10,13	48.5	53.1	50.7	44.6	50.0	50.9
20	126.2	128.3	127.3	136.9	125.3	125.6
23	127.3	128.6	128.2	127.2	127.3	127.3
18	128.0	129.5	128.7	128.1	128.2	128.0
17	128.6	129.9	129.4	128.2	129.1	128.2
22	129.6	135.5	129.8	129.5	129.6	129.0
19	129.9	136.3	136.4	131.0	129.8	129.5
24(w)	136.1	137.6	137.3	136.4	135.5	129.8
7,16(w)	138.4	139.5	140.5	138.7	137.4	129.9
8,15(w)	143.6	140.3	140.9	143.6	141.2	136.4
21(w)	143.7	143.6	143.6	144.2	143.8	143.5

a- The numbering system is based on the 16-membered macrocycle below:

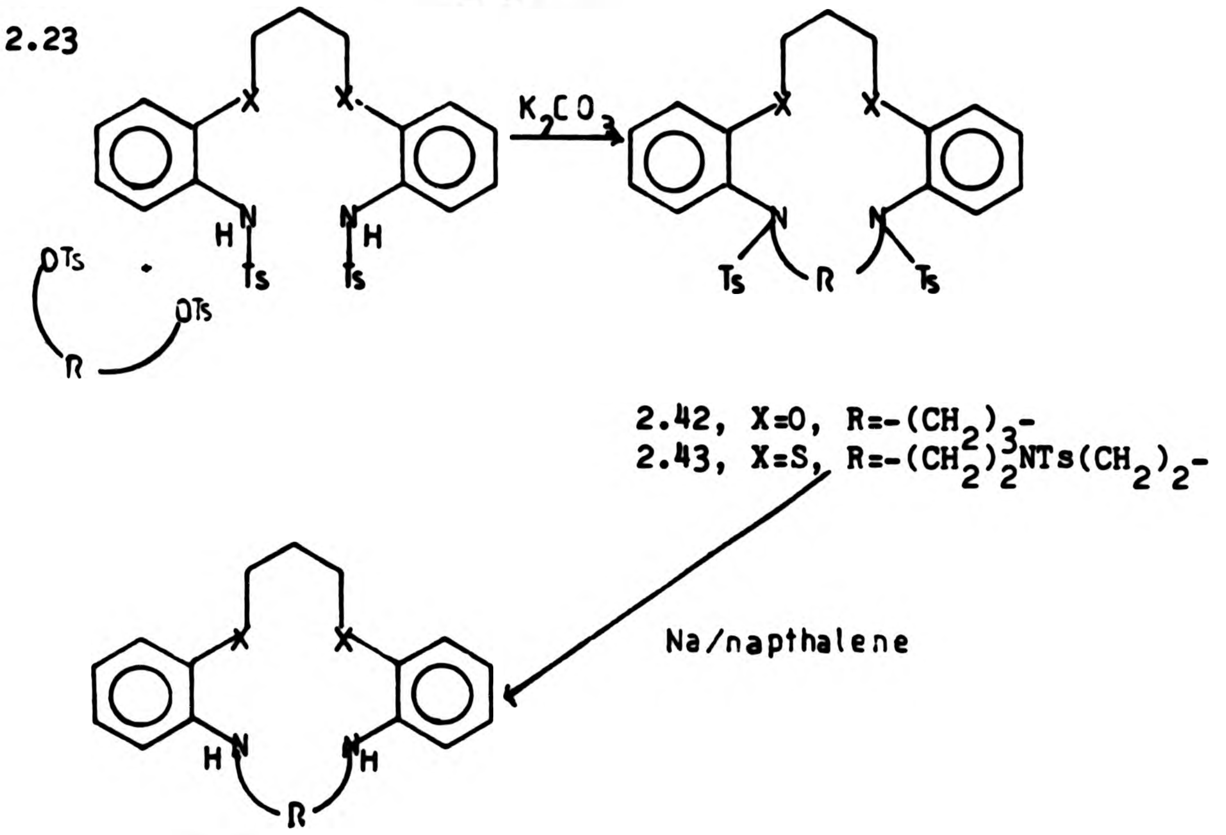


The chemical shifts in the ^{13}C nmr spectra were assigned on the basis of relative intensities and by comparison with the precursors' spectra. Many of the spectra of the macrocycles are very similar. In each case the molecules show pseudomirror symmetry. Carbon atoms at positions 2 and 5 are more upfield than carbons 10 and 13 and all the tosyl-methyl signals are found at 21.6 ∓ 0.1 ppm. All the macrocycles show bands characteristic of $-SO_2R-$ and p-disubstituted benzene groups in their infrared specta. The tosylated macrocycles are all very soluble in organic solvents. In the mass spectrum the intensities of the molecular parent ion peak are variable. Although the possibility of polymeric species may not be completely ruled out, the combined analytical data seems to suggest monomers being produced upon cyclisation. Detosylations on these macrocycles were not attempted in the light of the problems encountered with purification of the 14-membered S_2N_2 macrocycle (see section 2.9).

The general applicability of the synthetic procedure was also investigated for macrocycles with other donor sets.

2.11 Attempted Preparation of O_2N_2- and S_2N_3-Macrocycles

Scheme 2.23



2.42, X=O, R=-$(CH_2)_3$-
2.43, X=S, R=-$(CH_2)_2NTs(CH_2)_2$-

2.44, X=O, R=-$(CH_2)_3$-
2.45, X=S, R=-$(CH_2)_2NH(CH_2)_2$-

Both the macrocycles 2.42 and 2.43 were obtained in reasonable yields; 46 and 57 % respectively (Previous preparations of 2.44 reported by Biernat[40] had yields of 3.5 %, and were prepared via alkylation of ditosyl derivatives followed by reduction with sodium naphthalenide). Both were obtained as solids but 2.42 was significantly less soluble in organic solvents than the analogous S_2N_2-macrocycle 2.23. Upon cyclisation the -HN- bands in the infrared spectra were lost. Detosylation was successful and macrocycles 2.44 and 2.45 were obtained in reasonable yields, and the N-H stretching band reappeared in the infrared spectra. The -NH- protons were readily exchanged in the ^1H nmr on treatment with D_2O. The ^1H nmr of compounds 2.42 and 2.43 were quite complex when compared with the detosylated macrocycles 2.44 and 2.45 and multiplets were obtained for protons with similar chemical shifts. For macrocycle 2.42 the $-NCH_2\underline{CH}_2-$ and $-N\underline{CH}_2$-signals overlap with those of the methylene groups between the oxygen atoms. Similarly for 2.43 the methylene signals $-S\underline{CH}_2$ overlap with those of the $-N\underline{CH}_2$ group. No attempt was made to purifiy the detosylated macrocycles 2.44 and 2.45 via gel filtration because of the difficulties encountered in the purification of the 14-membered detosylated macrocycle 2.17 (see sections 2.7 and 2.9).

TABLE 2.14 Comparison of ^1H nmr Chemical Shifts of S_2N_2- O_2N_2, and S_2N_3-Macrocycles

Macrocycle	2.42		2.23		2.43
$-\underline{CH}_3$	2.40(s)	$-\underline{CH}_3$	2.38(s)	$-\underline{CH}_3$	2.41(s) 2.48(s)
$-NCH_2\underline{CH}_2$	1.15-1.95(mc)	$-NCH_2\underline{CH}_2$	1.63-2.13(mc)	$-SCH_2\underline{CH}_2$	1.38-2.00(mc)
$-OCH_2\underline{CH}_2$		$-SCH_2\underline{CH}_2$			
$-N\underline{CH}_2$	3.35-3.95(mc)	$-N\underline{CH}_2$	2.60-4.00(mc)	$-HN\underline{CH}_2$	2.55-4.00(mc)
$-O\underline{CH}_2$		$-S\underline{CH}_2$	2.60-3.33(mc)	$-S\underline{CH}_2$	
Aromatic	6.65-7.75(mc)	Aromatic	6.37-7.75(mc)	Aromatic	6.50-7.88(mc)

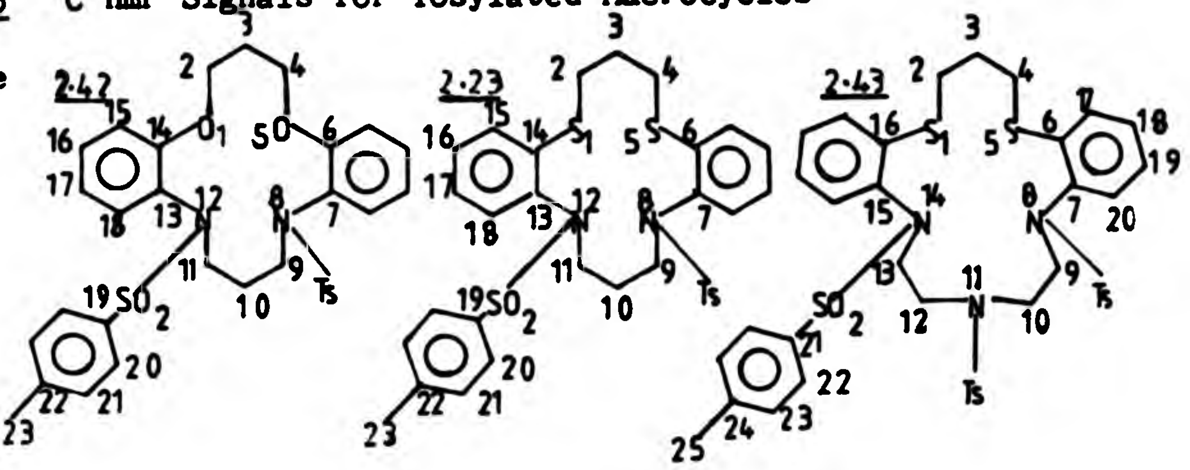
The protons for the central methylene of the propane bridges of S_2N_2-macrocycle 2.23 are the most downfield when compared with the other two macrocycles. Upon detosylation the ^1H nmr spectra are better resolved for compounds 2.17, 2.44 and 2.45 due to the relative increase in flexibility of the ligands when the bulky tosyl groups are removed.

TABLE 2.15 Chemical Shifts for Detosylated Macrocycles

Macrocycle	2.44		2.17		2.45
$-NCH_2\underline{CH_2}$ $-OCH_2\underline{CH_2}$	1.80- 2.50(mc)	$-NCH_2\underline{CH_2}$ $-SCH_2\underline{CH_2}$	1.35- 2.00(mc)	$-SCH_2\underline{CH_2}$	1.20- 1.85(mc)
$-N\underline{CH_2}$	3.00- 3.50(mc)	$-N\underline{CH_2}$	3.15(t)	$-N\underline{CH_2}$ $-S\underline{CH_2}$	2.10- 4.00(mc)
$-O\underline{CH_2}$	3.90 4.40(mc)	$-S\underline{CH_2}$	2.65(t)		
-NH-	4.75(b)	-NH-	5.12(b)	-NH-	5.35(b)
Aromatic	6.50- 7.10(mc)	Aromatic	6.30- 7.50(mc)	Aromatic	6.40- 7.70(mc)

In the detosylated macrocycles the central methylene protons are most upfield in macrocycle 2.45. In 2.44 the greater electronegativity of the oxygen atoms causes the signal for $-XCH_2$ methylenes to be further downfield than in the other macrocycles. $-XCH_2$ signals overlap only in macrocycle 2.45. The ^1H nmr spectra for 2.17 shows that this structure is the most flexible of the three since the $-XCH_2$ methylenes are obtained as triplets rather than complex multiplets which are obtained in 2.44 and 2.45. Thus the protons of the methylene groups are equivalent in the former macrocycle. The ^{13}C nmr signal were assigned for the tosylated and detosylated macrocycles.

TABLE 2.16 ^{13}C nmr Signals for Tosylated Macrocycles



Macrocycle	2.42		2.23		2.43	
	23	21.5	23	21.6	25	21.7
	3	28.5	3	25.9	3	33.2
	2,4	66.7	2,4	33.7	2,4	48.7
	9,11	48.5	9,11	50.4	9,13	50.7
	10	28.8	10	28.8	10,12	49.8
	18	120.8	18	127.0	20	127.1
	21	128.0	21	127.9	18	127.4
	16	129.2	16	128.6	23	128.0
	15	113.1	15	129.1	22	129.7
	20	129.5	20	129.6	17	131.1
	17	127.7	17	131.5	19	136.1
	22(w)	136.8	22(w)	136.0	24(w)	137.4
	6,14(w)	156.4	6,14(w)	139.9	6,16(w)	139.0
	7,13(w)	137.7	7,13(w)	140.0	7,15(w)	140.0
	19(w)	142.9	19(w)	143.6	21(w)	143.8

TABLE 2.17 ^{13}C nmr Chemical Shifts[a] for Detosylated Macrocycles

Macrocycle		2.44		2.17		2.45
Atom δ/ppm	3	28.7	3	29.1	3	29.1
	2,4	67.9	2,4	33.4	2,4	36.9
	9,11	44.6	9,11	41.5	9,13	40.0
	10	26.8	10	29.1	10,12	47.0
	18	111.6	18	110.2	20	116.8
	16	116.6	16	116.8	18	118.8
	15	110.1	15	130.2	17	131.6
	17	121.8	17	136.4	19	136.2
	6,14(w)	146.7	6,14(w)	117.5	6,16(w)	114.8
	7,13(w)	138.8	7,13(w)	149.3	7,15(w)	148.8

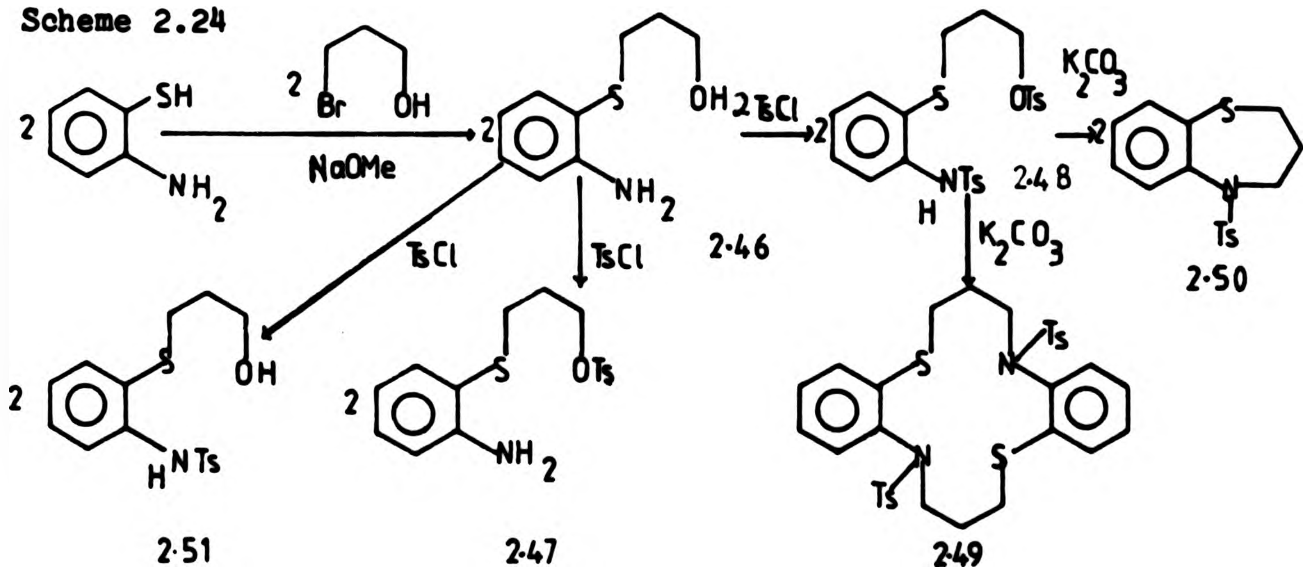
[a] Same numbering system as in table 2.16

From the ^{13}C nmr spectra it can be seen that the position of XCH_2 is dependent on the electronegativity of X, thus the signal for carbon atoms 2 and 4 is most downfield for the O_2N_2-macrocycle, and is most upfield for the S_2N_2-macrocycle. Overall, on detosylation the ^{13}C nmr signals for the ligands are generally further upield than those in the tosylated structures (2.23, 2.42 and 2.43).

2.12 Preparation of trans-S_2N_2-14-Membered Macrocycles

The preparations of the tosylated forms of the S_2N_2-macrocycles of variable ring-size proved to be very successful and it is possible in theory to adapt the cyclisation route to the preparation of macrocycles with trans-S_2N_2 donor-sets (type 2.49) as in scheme 2.24:

Scheme 2.24



The preparation of macrocycles with such trans-S_2N_2 donor sets was first attempted on the 14-membered macrocycle. Alkylation of the thiol group of o-aminothiophenol yielded 2.46 in 78 % yield. Tosylation of 2.46 gave an oil consisting of two components (tlc chromatography and ^1H nmr spectra), which were separated easily using a silica column. The two components are the mono and ditosylated species (2.47 or 2.51 and 2.48). The monotosylated derivative was removed by using neat toluene as the elutant and the remaining major component was eluted with 1:1 toluene/dichloromethane. When 2.48 was treated with base in dimethylformamide alkylation of the aniline nitrogen atoms was indicated by the loss of secondary amine stretches in the infrared spectrum of the product, but the 7-membered ring 2.50 (m/z, 319 (100 %)) was obtained instead of the desired macrocycle 2.49.

In this case the <u>intra</u>molecular reaction is presumably favoured because the tosylated alcohol is a good leaving group, and once the tosylated aniline has been deprotonated it is favourably aligned to attack the carbon bearing the tosylated alcohol group.

TABLE 2.18 ^{1}H nmr (60 MHz) Data for Compounds 2.46, 2.48, 2.50 and 2.51

	2.46	2.48	2.50	2.51
$-SCH_2\underline{CH}_2$	1.70(p)	1.76(p)	1.75- 2.25(mc)	1.75(p)
$-S\underline{CH}_2$	2.78(t)	2.55(t)	2.73(t)	2.60(t)
$-O\underline{CH}_2$ or $-N\underline{CH}_2$	3.60(t)	4.00(t)	3.75(t)	3.43(t)
-NH- and -OH-	3.83(s)	6.90- 7.90(mc)	7.05- 7.80(mc)	6.80- 7.90(mc)
Aromatic	6.50- 7.50(mc)	6.90- 7.90(mc)	7.05- 7.80(mc)	6.80- 7.90(mc)
$-\underline{CH}_3$	-	2.36(s) 2.25(s)	2.38(s)	2.23(s)

In all cases the ^{1}H nmr spectra are well resolved. The -NH- signal appears under the complex aromatic multiplet. Ditosylation of the alcohol/amine functionalities gives two chemical shifts in the ^{13}C nmr spectrum for the tosyl methyl protons. The $-O\underline{CH}_2$ signal is shifted further downfield as a consequence of the adjacent electron withdrawing tosyl group. Upon cyclisation to give 2.50 all the proton signals move further downfield except for the signal for $-OCH_2$ which is replaced by $-NCH_2$ and hence occurs further upfield. The two signals for the methyl protons are replaced by a single chemical signal in the ^1H nmr spectrum.

When tosylation was carried out for 2.46 a monotosylated species was also produced in about 20 % yield (see page 84). The proton nmr of this indicates that tosylation has taken place of the amine nitrogen atom as opposed to the alcohol group. This is based on the fact that the $-OCH_2$ signal is obtained as a triplet at 3.43 ppm. If tosylation had taken place on the alcohol functionality then the signal would be expected closer to 4.0 ppm as in compound 2.48.

The proton nmr spectrum of 2.50 may be compared to the analogous 6-membered heterocycle 2.41 (see section 2.10).

<u>TABLE 2.19</u> Comparative ^1H nmr (80 MHz, $CDCl_3$) Chemical Shifts for Heterocycles 2.41 and 2.50

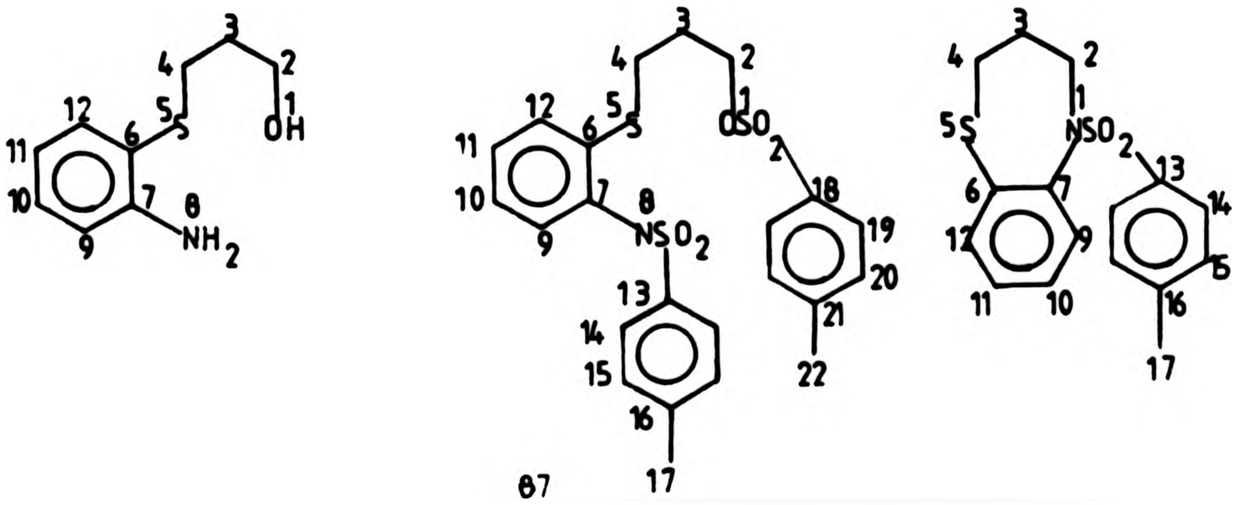
	2.41	2.50
$-\underline{CH}_3$	2.40(s)	2.38(s)
$-SCH_2\underline{CH}_2$	-	1.75-2.25(mc)
$-S\underline{CH}_2$	2.88(t)	2.73(t)
$-N\underline{CH}_2$	3.97(t)	3.75(t)
Aromatic	6.75-7.75(mc)	7.05-7.80(mc)

Spectra for both heterocycles are well resolved and are similar except that 2.50 has an additional methylene present since this ring is seven membered. This extra methylene cause the signals for $-SCH_2$ to appear further upield in 2.50 when compared with 2.41. The ^{13}C nmr signals for the molecules prepared in scheme 2.24 for the trans-S_2N_2 macrocylic preparation are given below.

TABLE 2.20 ^{13}C nmr Signals[a] for 2.46, 2.48 and 2.50

Carbon Atom	2.46 δ/ppm	2.48 δ/ppm	2.50 δ/ppm
17	-	21.5	21.5
22	-	21.7	-
3	31.3	28.6	30.9
4	32.3	32.0	31.4
2	61.2	68.3	49.8
9	115.2	119.7	128.2
16	-	123.5	136.4
11	118.8	124.8	128.5
20	-	127.3	-
15	-	128.0	127.7
19	-	129.8	-
14	-	130.1	129.4
12	129.7	133.0	130.6
21	-	135.4	-
10	135.8	135.6	133.7
6	118.0	136.6	138.3
7	148.2	138.8	143.1
13	-	144.3	143.3
18	-	145.2	-

a- The numbering system for the molecules are:

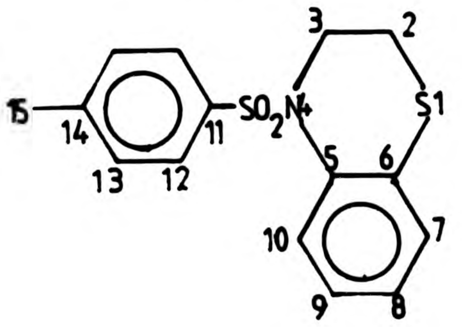


From the carbon nmr spectrum it can be seen that on tosylation to give 2.48 carbon atoms 3 and 4 move upfield but 2 occurs 7.1 ppm further downfield due to the adjacent tosyl group. The general trend is that tosylation of both the alcohol and amine groups tends to shift the signals downfield, i.e. 6 changes from 118.0 ppm to 136.6 ppm, the exception is benzene carbon atom 7 which moves further upfield.

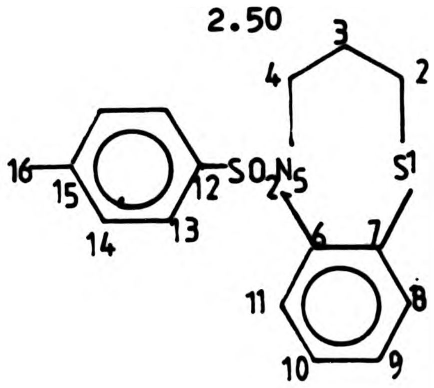
For the heterocycles 2.41 and 2.50 it can be seen that the aliphatic carbon signals in the ^{13}C nmr spectra are further downfield in 2.50 than those of the analogous carbon atoms in 2.41. This is also the situation for most of the aromatic signals.

TABLE 2.21 Comparative ^{13} C nmr Signals of Heterocycles 2.41 and 2.50

2.41



2.50



Carbon Atom δ/ppm

15	21.5	16	21.5
2	25.7	2	31.4
	-	4	49.9
3	44.7	3	30.9
10	124.6	11	128.2
8	126.5	9	128.5
7	126.9	8	130.6
13	128.0	14	127.7
9	128.4	10	133.7
12	129.8	13	129.4
14(w)	119.9	15(w)	136.4
6(w)	130.0	7(w)	138.3
5(w)	135.4	6(w)	143.1
11(w)	144.0	12(w)	143.4

Overall the tosylation route is not successful for preparation of trans-S_2N_2 macrocycles because intramolecular cyclisation takes place in preference to intermolecular cyclisation to give the SN-heterocycles which are obtained in high yields.

2.13 Alternative Method for Preparation of the 14-Membered S_2N_2-Macrocycle

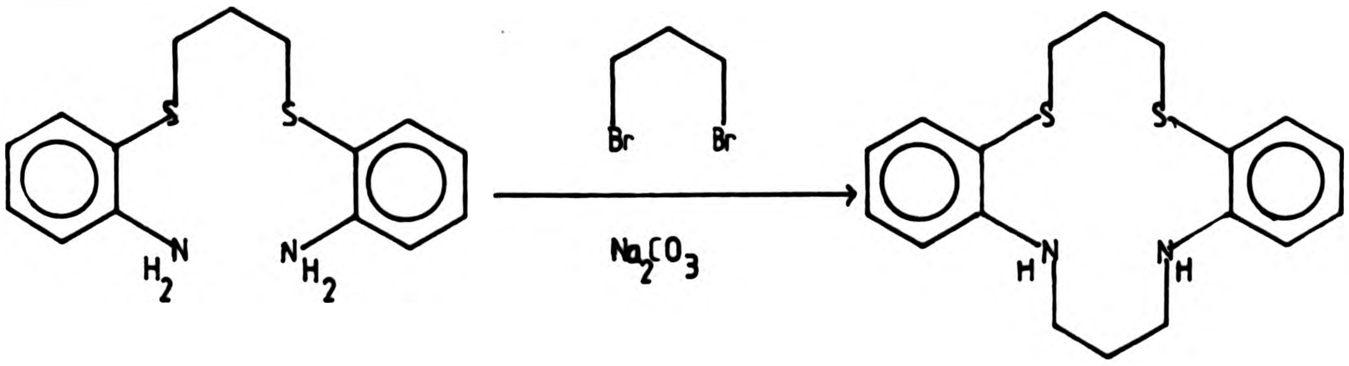
Although cyclisation is very effective for N-tosyl derivatives (sections 2.6, 2.10 and 2.11), the major limitation is that detosylation produces a mixture of components which are difficult to separate in large quantities therefore, direct alkylation of the free anilino nitrogen may be considered, although

(i) there is reduced nucleophilicity when compared with the deprotonated tosylates and

(ii) additionally difficulties may be experienced in cyclisations.

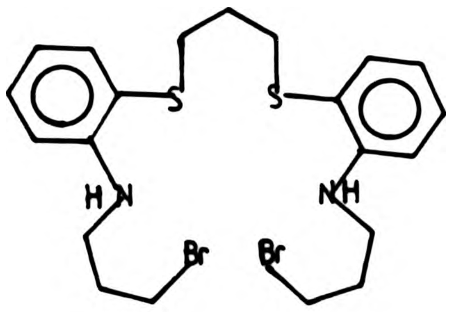
Preparation of 2.17 was attempted using direct alkylation with 1,3-dibromopropane as in scheme 2.25.

Scheme 2.25



2.17

Alkylation of the nitrogen atoms was suggested by changes in the regions 3200-3400 cm^{-1} of the infrared spectrum. A tlc of the oil produced showed that it contains at least 3 components. The ^{1}H nmr (spectrum number 2.3) of the sample is very similar to that for the material obtained from the detosylation reaction (spectrum number 2.1) in section 2.8. The slight excess of protons in the $-N\underline{CH}_2$ region when compared with $-S\underline{CH}_2$ could be accounted for if some of the impurity 2.52 is present.

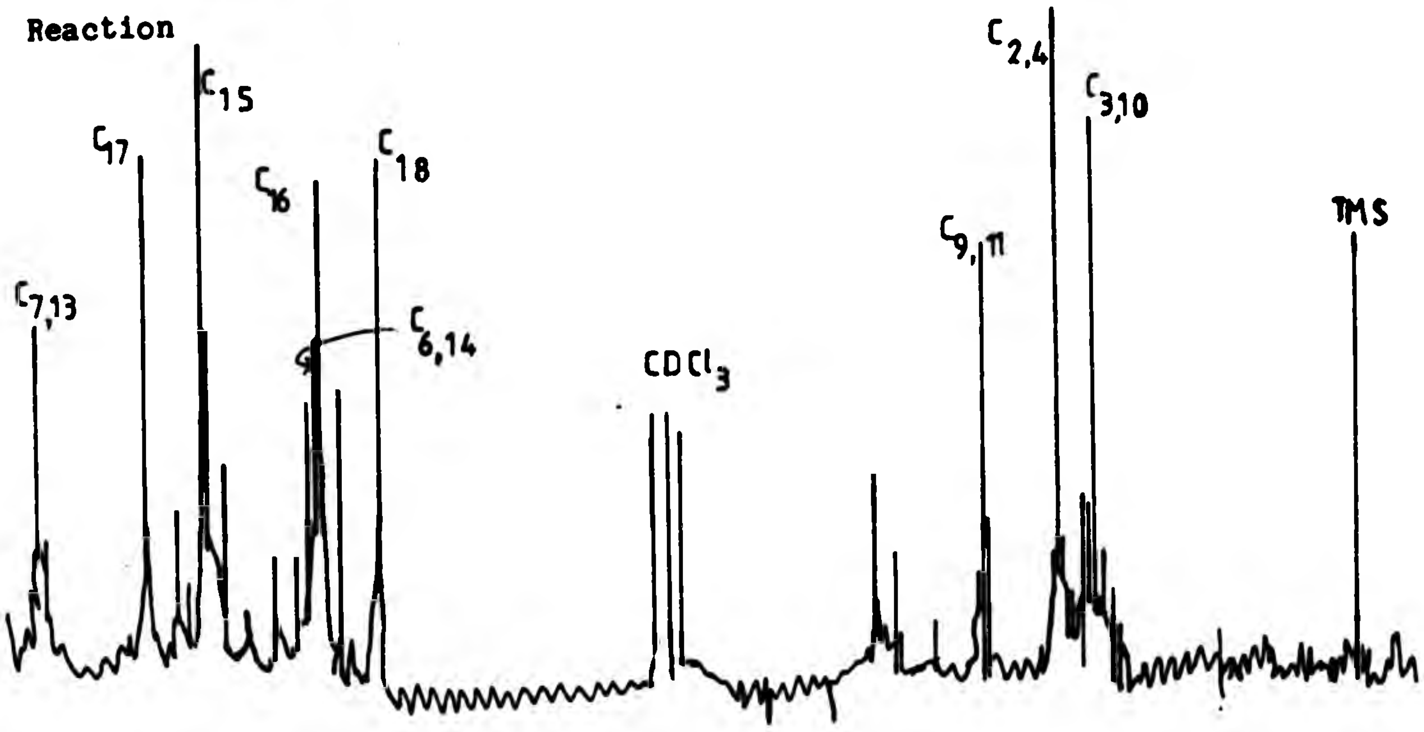


2.52

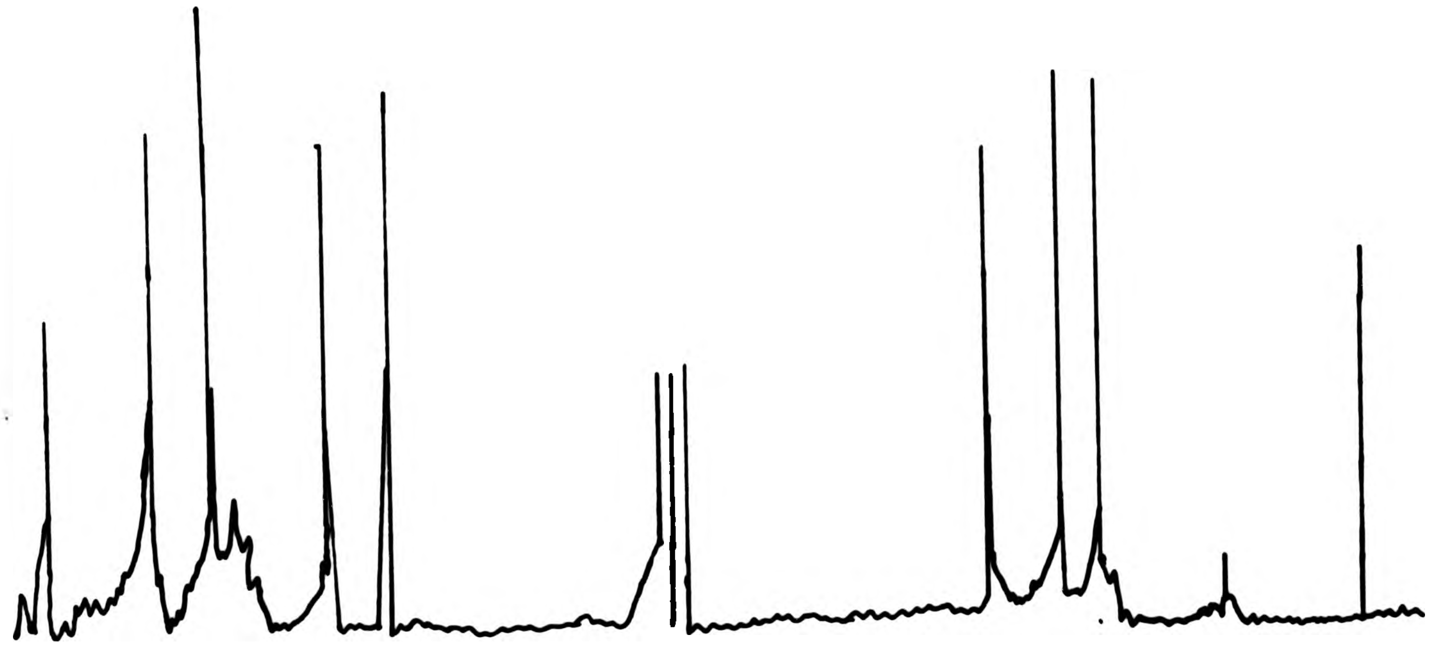
A ^{13}C nmr spectrum of the oil (spectrum 2.3) is also similar to that of pure 2.17 as obtained from the detosylation reaction (see section 2.7and 2.9). The only difference is that there are fewer impurities present in the aliphatic region. The oil was purified by column chromatography, removing some impurities by using a silica column. Further purification was achieved by gel filtration using Sephadex LH-20 and chloroform as elutant. By these techniques the "pure" macrocycle 2.17 was obtained as judged by carbon nmr (spectrum 2.4) in 20-37 % yields.

Thus the direct alkylation with 1,3-dibromopropane proves to be a more effective route to the 14-membered S_2N_2-macrocycle 2.17. This route may be applicable to other S_2N_2-macrocycles but the drawback to this

Spectrum 2.3 ^{13}C nmr Spectrum of the Impure Oil from Direct Alkylation Reaction



Spectrum 2.4 ^{13}C nmr Spectrum of Pure 2.17 After Purification of the Impure Oil from Direct Alkylation Reactions

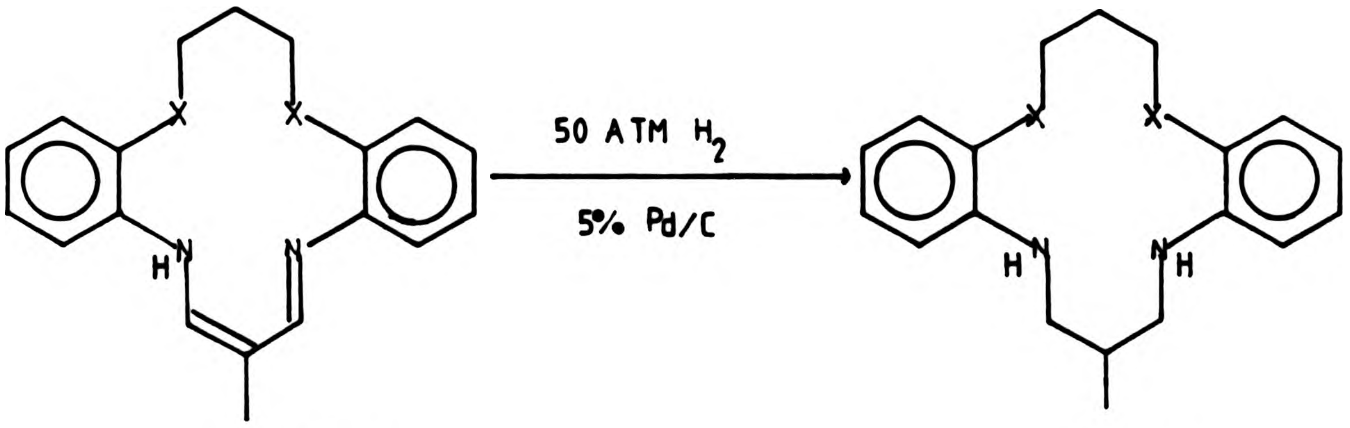


route is that the reaction conditions will have to be adapted for each individual ring size, thus it is unlikely to be as versatile as cyclisations involving the tosyl derivatives.

2.14 Reduction of β-Dialdimines to Obtain the Saturated Dibenzo Macrocycles 2.3

The β-dialdimines have been obtained in good yields (section 2.1) and the target molecules 2.3 can be obtained by high pressure hydrogenation. These reductions were performed in the collaborating institution's laboratories (ICI Organics Division), giving the macrocycles 2.3a and 2.3b in high yields (> 57 %).

Scheme 2.26



2·2a X = O
2·2b X = NH

2·3a X = O
2·3b X = NH

Strong parent ion peaks of intensity 96 % were obtained at m/z 312 (2.3a) and 310 (2.3b). Reduction of the cycles was indicated by loss of C=C and C=N stretches in the infrared spectrum. In addition the ^1H nmr spectra have doublets for the methyl protons in both macrocycles.

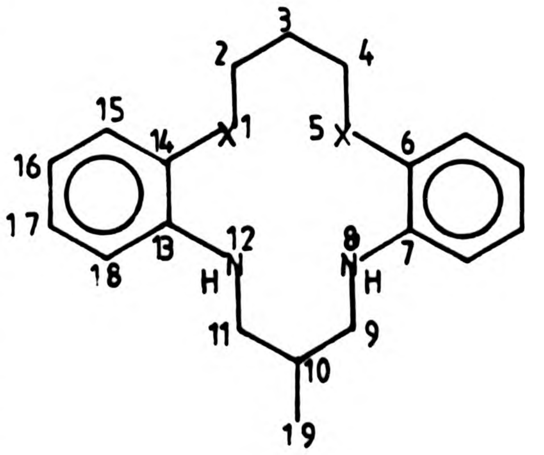
TABLE **2.22** ^{1}H nmr (220 MHz, $CDCl_3$) Spectra of Macrocycles 2.3a and 2.3b

	2.3a		**2.3b**
$-\underline{CH_3}$	1.05(d)	$-\underline{CH_3}$	1.05(d)
$-OCH_2\underline{CH_2}$ and $-CH_3\underline{CH}$	2.00-2.50(mc)	$-NHCH_2\underline{CH_2}$ and $-CH_3\underline{CH}$	1.95-2.45(mc)
$-NH\underline{CH_2}$	3.03(t)	$-N\underline{CH_2}$	2.94(t) 3.10-3.26(mc) 3.36-3.60(mc)
$-O\underline{CH_2}$	3.35-3.54(mc)		-
-NH-	5.05(s)	-NH-	4.35(s)
Aromatic	6.60-7.00(mc)	Aromatic	6.60-7.00(mc)

The ^{1}H nmr spectra of 2.3a and 2.3b are discussed in more detail in chapter 3, section 3.2.2. The ^{13}C nmr signals for the two molecules are given below.

TABLE **2.23** ^{13}C (20.12 MHz, $CDCl_3$) nmr Spectra of 2.3a and 2.3b

Macrocycle Carbon Atom[a] /ppm	2.3a	2.3b
3	31.4	31.6
10	28.6	26.7
2,4	67.8	52.7
9,11	51.5	45.7
18	109.7	111.1
16	116.4	119.3
15	111.1	111.2
17	121.3	119.4
6,14	146.5	137.7
7,13	138.1	
19	17.8	17.9



Numbering System for 2.3a, (X=O) and 2.3b, (X=NH)

The ^{13}C nmr spectra of the two macrocycles are quite similar and any differences are a consequence of the greater electronegativity of the oxygen atoms in macrocycle 2.3a compared to nitrogen atoms in 2.3b. The macrocycles 2.3a, 2.3b, 2.17 were characterised by the "sporting methods" outlined above. Detailed discussion of comparative structural features of 2.3a, 2.3b and 2.17 is contained in chapter 3.

References

1. Behr, H, Breitmaier, E, Chem. Ber., 111, 913 (1978).
2. Ansell, C.W.G., Chung, M.F.H.Y.J., McPartlin, M., Tasker, P.A., J. Chem. Soc. Dalton 2113 (1982).
3. Muller, R., Wohrle, D., Makromol. Chem., 176, 2775 (1975).
4. Hiller, H., Dimroth, P., Pfitzner, H., Ann. Chem., 717, 137 (1968).
5. Lorch, V.E., Breitmaier, E., Chem. Z., 99, 87 (1975)
6. Goedken, V.L., Weiss, M.C., Inorg. Synth. 115 (1980).
7. Wainwright, K.P., J. Chem. Soc. Dalton, 2117 (1980).
8. Fabbrizzi, L., Paoletti, P., Clay, R.M., Inorg. Chem., 17, 1042 (1978).
9. Kluiber, R.W., Sasso, G., Inorg. Chim. Acta., 4, 226 (1970).
10. March, J., Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 2nd ed. McGraw-Hill, International Book Company (1984).
11. Stetter, H., Marx-Moll, L., Chem. Ber. 1, 677 (1958).
12. Stetter, H., Marx, J., Ann. Chem. 606, 59 (1957).
13. Gold, E.H., U. S. Patent, 3,965,175, June 22nd, (1976).
14. Tabushi, I., Taniguchi, Y., Kato, H., Tetr. Lett., 12, 1049 (1977).
15. Chattaway, F.R., Olmsted, J.M.D., J. Chem. Soc., 97, 938 (1910).
16. Lockhart, J.C. Thompson, M.E., J. Chem. Soc. Perkin I, 202 (1977).
17. Kimura, E., Machida, R., Kodama, M., J. Amer. Chem. Soc., 106, 5497 (1984).

18. Pelissard, D., Louis, R., Tetr. Lett. 45, 4589 (1972).

19. Duckworth, P.A., PhD Thesis, University of Sydney, (1984).

20. Ansell, C.W.G., Cooper, M.K., Dancey, K.P., Duckworth, P.A., Henrick, K., McPartlin, M., Tasker, P.A., J. Chem. Soc. Chem. Comm., 439 (1985).

21. Richman, J.E., Atkins, T.J., J. Amer. Chem. Soc., 96, 2268 (1974).

22. Searle, G.H., Geue, R.J., Aust. J. Chem., 37, 959, (1984).

23. Clay, R.M., McCormac, H., Micheloni, M, Paoletti, P., Inorg. Chem., 21, 2494 (1984).

24. Fabbrizzi, L., J. Chem. Soc. Dalton, 1857 (1979).

25. Fabbrizzi, L., Sabatini, L., Inorg. Chem., 18, 438 (1979).

26. Sugimoto, M., Nonoyana, M., Ito, T., Fujita, J., Inorg. Chem., 22, 950 (1983).

27. Muller, F.R., Handel, H., Tetr. Lett., 23, 2769 (1982).

28. Atkins, T.J., Richman, J.E., Oettle, W.F., Org. Synth., 58, 86 (1978).

29. Bencini, A., Fabbrizzi, L., Poggi, A., Inorg. Chem., 20, 2544, (1981).

30. Vriesema, B.K., Buter, J., Kellogg, R.M., J. Org. Chem., 49, 110 (1984).

31. Laakso, T.M., Reynolds, D.D., J. Amer. Chem. Soc., 73, 3518 (1951).

32. Searles, S., Nukina, S., Chem. Rev., 59, 1077 (1959).

33. Snyder, H.R., Heckert, R.E., J. Amer. Chem. Soc., 74, 2006 (1952).

34. Snyder, H.R., Geller, H.C., J. Amer. Chem. Soc. , 74, 4864 (1952).

35. Schreiber, R.S., Shriner, R.L., J. Amer. Chem. Soc. 56, 1618 (1934).

36. Klamann, D., Hofbauer, G., Chem. Ber., 86, 1246 (1953).

37. Closson, W.D., Ji, S., Schulenberg, S., J. Amer. Chem. Soc, 92, 650 (1970).

38. Ji, S., Gortler, L.B., Waring, A., Battisti, A., Bank, S., Closson, W.D., Wriede, P., J. Amer. Chem. Soc., 89, 5311 (1967).

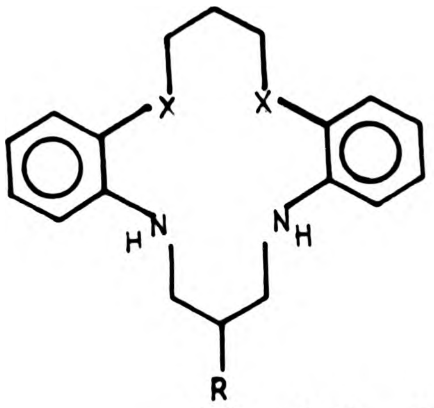
39. Levy, G.C., Lichter, R.L., Nelson, G.L., Carbon-13 Nuclear Magnetic Resonance Spectroscopy, 2nd ed., John Wiley & Sons, pages 110-112 (1980).

40. Biernat, J.F., Luborch, E., Tetr. , 40, 1927 (1984).

CHAPTER 3: PROPERTIES OF X_2N_2-MACROCYCLES

3.1 Ligating Properties of the X_2N_2-Macrocycles

The macrocycles of type 3.1 have been prepared successfully as reported earlier in chapter 2, sections 2.7, 2.13 and 2.14.



3.1a, X=O, R=Me
3.1b, X=NH, R=Me
3.1c, X=S, R=H

The ligating properties of these macrocycles will be considered under two main headings:

(i) solution chemistry of the ligands and

(ii) solid-state structures of the ligands and their metal complexes.

3.2 SOLUTION CHEMISTRY OF THE X_2N_2-MACROCYCLES

3.2.1 Basicities of the Ligands

In general, the co-ordination chemistry of the three X_2N_2-macrocycles chosen for study is very different. The protonation constants for the O_2N_2- and N_4-ligands, 3.1a and 3.1b respectively, have been obtained in 95 % methanol by Lindoy and co-workers at James Cook University.

Protonation constants ($\log K_i$, for the ith protonation) were obtained for equilibria of the type given below where L is the ligand.

$$H_{(i-1)}L^{(i-1)+} + H^+ \overset{K_i}{\rightleftharpoons} H_iL^{(i)+} \qquad K_i = \frac{[H_iL^{(i)+}]}{[H_{(i-1)}L^{(i-1)+}][H^+]}$$

The protonation constant listed below are quoted as values of $\log_{10}K_i$. The overall protonation constant $\log\beta_i$ is the sum of the stepwise constants $\log K_i$.

$$\text{i.e. } \mathrm{Log}\beta_i = \log K_i + \log K_{i-1} + \log K_{i-2} \ldots\text{etc to } \log K_1$$

Because the ligands 3.1 contain four donor atoms, there is the possibility of tetra-protonation of the ligands and thus four equilibria are possible:

$$3.1 + H^+ \overset{K_1}{\rightleftharpoons} [3.1)H]^+ \quad ; \quad K_1 = \frac{[(3.1)H]^+}{[3.1][H^+]}$$

$$[(3.1)H]^+ + H^+ \overset{K_2}{\rightleftharpoons} [(3.1H_2]^{2+} \quad ; \quad K_2 = \frac{[(3.1)H_2]^{2+}}{[(3.1)H]^+[H^+]}$$

$$[(3.1)H_2]^{2+} + H^+ \overset{K_3}{\rightleftharpoons} [(3.1)H_3]^{3+} \quad ; \quad K_3 = \frac{[(3.1)H_3]^{3+}}{[(3.1)H_2]^{2+}[H^+]}$$

$$[(3.1)H_3]^{3+} + H^+ \overset{K_4}{\rightleftharpoons} [(3.1)H_4]^{4+} \quad ; \quad K_4 = \frac{[(3.1)H_4]^{4+}}{[(3.1)H_3]^{3+}[H^+]}$$

The protonation constants for 3.1a and 3.1b are given in table 3.1 and allow comparison with related linear ligands and other macrocycles.

TABLE 3.1 LogK and Logβ Values for Protonation of Macrocycles and Their Precursors in 95 % Methanol (I=0.1 M; Et_4NClO_4)

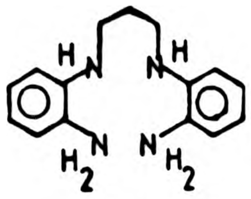
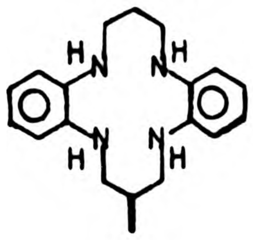
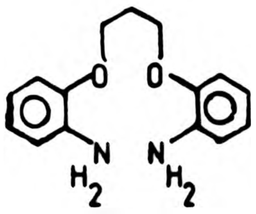
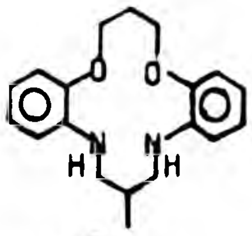
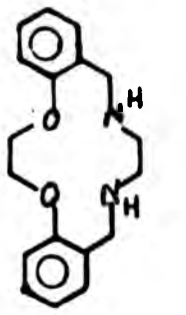
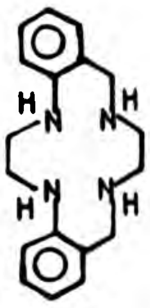
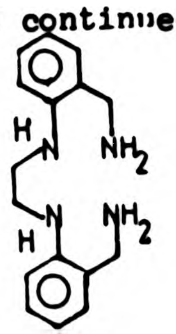
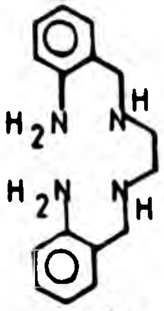
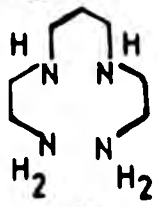
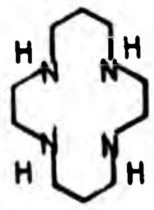
Ligand Number	Ligand Structure	LogK$_1$ (logβ_1)	LogK$_2$ (logβ_2)	LogK$_3$ (logβ_3)	LogK$_4$ (logβ_4)
3.3[a]		5.37 (5.37)	4.30 (9.67)	-	-
3.1b[a]		4.18 (4.18)	3.10 (7.28)	-	-
3.2[a]		4.98 (4.98)	4.07 (9.05)	-	-
3.1a[a]		4.28 (4.28)	1.83 (6.11)	-	-
3.8[b]		9.19 (9.19)	5.40 (14.59)	-	-
3.7[c]		9.45 (9.45)	3.68 (13.13)	1.36 (14.49)	1.10 (15.59)

TABLE 3.1 continued

3.6[c]		9.75 (9.75)	8.80 (18.55)	-	-
3.9[c]		9.05 (9.05)* 9.00* (9.00)	5.31 (14.36)* 5.90* (14.50)	2.60 (16.96)* 2.32* (17.22)	1.28 (18.24)* 2.00* (19.22)
3.4[d]		10.24 (10.24)	9.50 (19.74)	7.26 (27.00)	6.01 (33.01)
3.5[e,f]		11.59 (11.59)	10.63 (22.22)	1.61 (23.83)	2.42 (26.26)

a- This work

b- Anderegg, A., Ekstrom, A., Lindoy, L.F., Smith, R.J., <u>J. Amer. Chem. Soc.</u>, <u>102</u>, 2670 (1980)

c- Private communications with L.F. Lindoy

d- Calculated from ΔG values in water reported by Fabbrizzi, L., Barbucci, R., Paoletti, P., <u>J. Chem. Soc. Dalton</u>, 1527, (1972)

e- Micheloni, M., Sabatini, A., Paoletti, P., <u>J. Chem. Soc. Perkin</u> II, 828, (1978)- measured in water

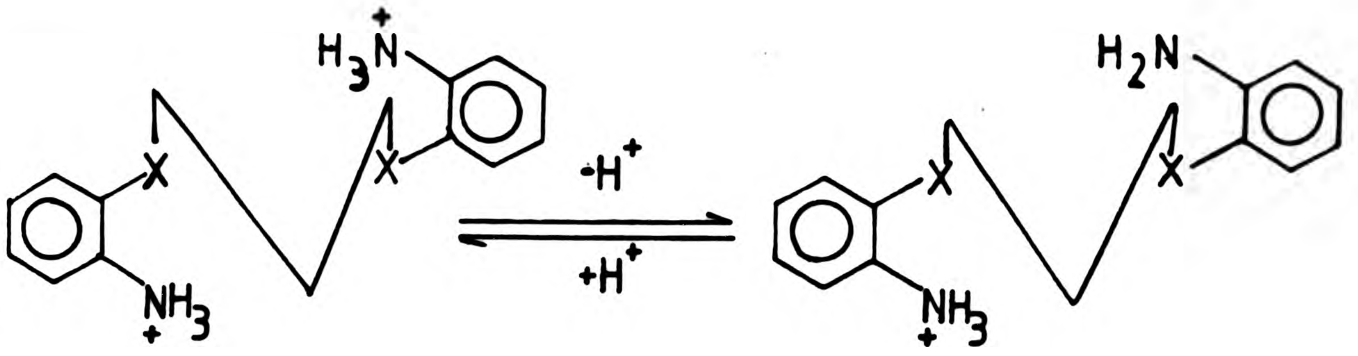
f- Also $\log K_1$, $\log K_2$, $\log K_3$, $\log K_4$ reported 11.5, 10.2, 1.6, 0.9 respectively measured in water by Kimura, E., Kodama, M., <u>J. Chem. Soc. Dalton</u>, 116 (1976) and references therein

*- These values have been reported by Smith, R.M., Martell, A.E., <u>Critical Stability Constants, Vol 2 : Amines</u>, Plenum, New York, (1975).

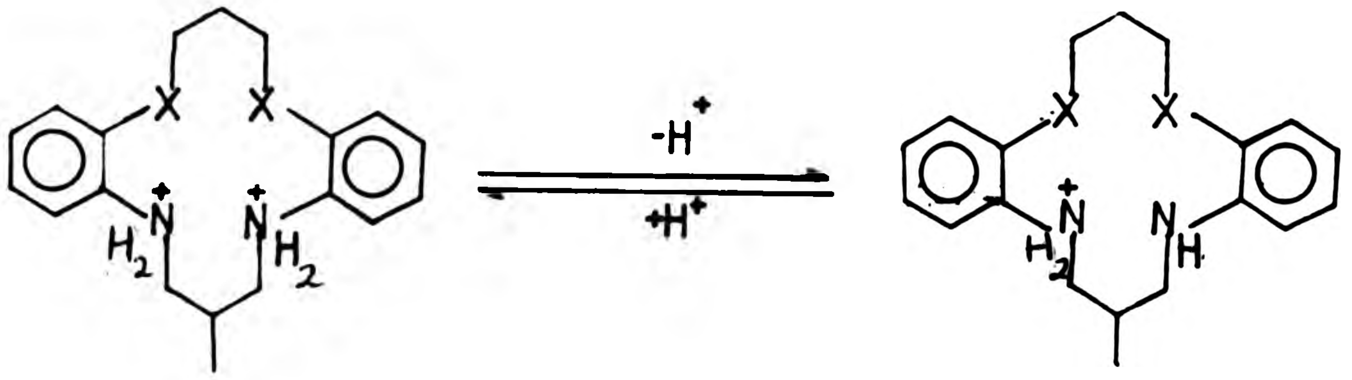
The O_2N_2- and N_4-macrocycles 3.1a and 3.1b, respectively, are both relatively poor bases and therefore are not expected to form very stable metal complexes. Unfortunately the protonation constants for the S_2N_2-macrocycle 3.1c could not be determined due to the very low solubility of the ligand and its protonated form in 95 % methanol. This solvent mixture was used for the potentiometric titrations to determine the logK values of the other ligands. (However, recently a paper has been published[1] on protonation constants of the aliphatic S_2N_2 analogue of cyclam, and the first and second constants are 9.77 and 5.72 respectively). The proton basicities of macrocycles 3.1a and 3.1b and their linear analogues 3.2 and 3.3 may be compared with the values obtained for related dibenzo and aliphatic quadridentate ligands (table 3.1).

It can be seen that 3.1a, 3.1b and their linear precursors are the weakest bases. This is presumably because they only contain anilino nitrogen atoms; it has been well documented[2-6] that anilines are weak bases because of delocalisation of nitrogen lone-pair electron density into the aromatic rings.

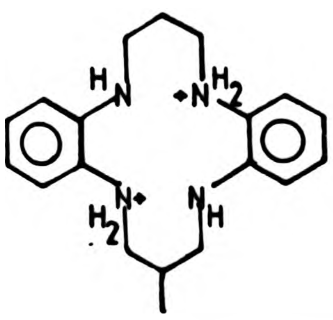
The $\log K_1$ values for 3.1a and 3.1b and their linear analogues (3.2 and 3.3, respectively) are of the same order of magnitude and fall in the range typical for <u>o</u>-disubstituted anilines[2-6]. It is noticeably easier to add a second proton to the linear ligands 3.2 and 3.3. This is presumably because electrostatic repulsions between protonated nitrogen atoms will be significantly reduced in the extended conformations (3.10) which are possible for the linear ligands but are not available to the macrocycles.



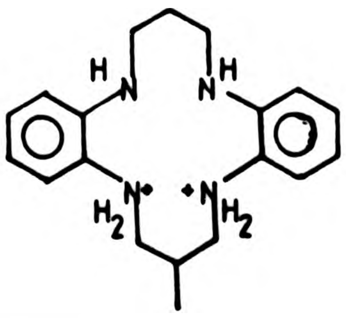
3.10
X=O or NH



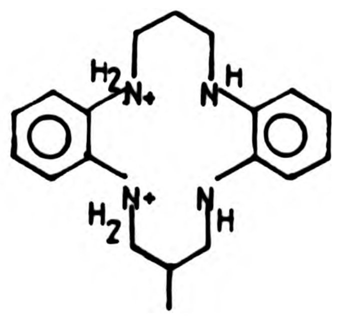
A similar explanation may be given for the greater ease with which the protonation of 3.1b occurs relative to 3.1a. A trans arrangement of the two C-NH_2^+-C groups (3.11) is possible in the diprotonated N_4-macrocycle and this is presumably more favourable than the alternate cis arrangements (3.12 or 3.13) which would experience a more serious intramolecular repulsion between the charged centres. Such a cis-arrangement of quaternary atoms (3.14) is inevitable for the diprotonated form of the O_2N_2-macrocycle 3.1a.



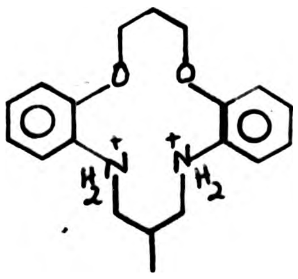
3.11



3.12



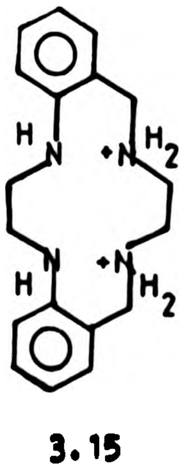
3.13



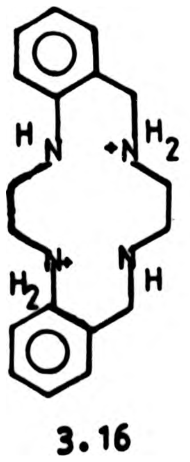
3.14

The effect of changing from aniline to benzyl amine-type nitrogen atom can be considered by comparing 3.1a with 3.8. The value of $\log K_1$ is significantly higher for 3.8 because the first protonation can occur at an aliphatic nitrogen atom. In theory, the second protonation of the related N_4-system 3.7 could occur either at the aliphatic or anilino nitrogen atom. The observed value of $\log K_2$ (3.68) suggests that the second protonation in fact occurs at the anilino nitrogen atom because its value is similar to the second protonation constant in the all-anilino system 3.1b.

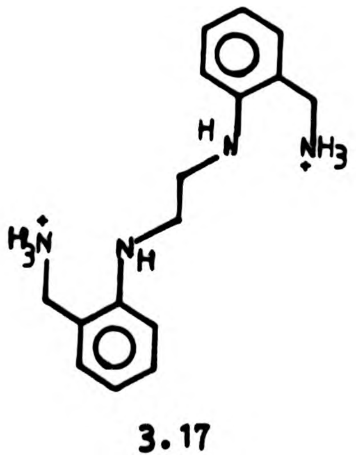
The benzylamino-macrocycle 3.7 can be compared with the linear analogues 3.9 and 3.6. The first protonation constants, presumably involving a benzylamino nitrogen atom in each case, are similar. However, diprotonation of 3.6 is greatly favoured over that for 3.7 and 3.9. The least favourable second protonation occurs for the macrocycle 3.7, where the sites of protonation either involve the second benzylamino nitrogen (with the significant electrostatic repulsion, as in 3.15) or the "<u>trans</u>"-anilino nitrogen which will be associated with a smaller electrostatic repulsion, but involves protonation of a less basic nitrogen atom (3.16).



3.15



3.16



3.17

3.18

As 3.6 contains two terminal aliphatic nitrogens, diprotonation can be achieved using the more basic nitrogen atoms and having these well separated as in the extended form represented by 3.17. For 3.9 the second protonation will occur either at the anilino or at the more remote benzylamino nitrogen; however, in both cases the protonated nitrogen atom sites can never be as far apart as in the diprotonated form of 3.6.

Both the 14-membered N_4-macrocycles bearing fused o-benzene substituents, 3.1b and 3.7, are significantly less basic than their completely aliphatic analogue cyclam 3.5. This is to be expected in terms of the nature of the donor atoms in 3.5 which are all aliphatic secondary amines.

The first protonation of 3.5 is slightly more favourable than for its linear analogue 3.4. This is possibly because the nitrogen lone-pair electrons in 3.5 are directed towards the centre of the N_4-donor set (see 3.18) and intramolecular hydrogen bonding involving the added protons may be more favourable.

For the linear ligand 3.4, the third protonation constant is higher than for the macrocycle 3.5. Once again, this is presumably because 3.4 can adopt an extended conformation which allows the three positively charged centres to become relatively well-separated as described above for the anilino-containing systems.

In conclusion, it can be said that the most basic ligands are those containing all aliphatic nitrogen atoms i.e. of cyclam type. These are also expected to be the most flexible systems. The mixed benzylamino/anilino ligands (i.e. 3.6, 3.7 and 3.9) have intermediate

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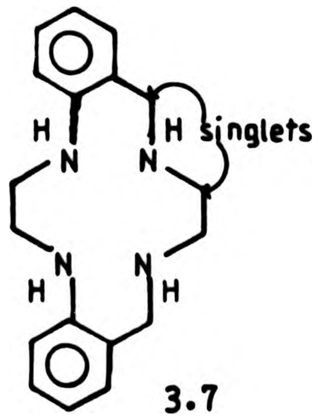
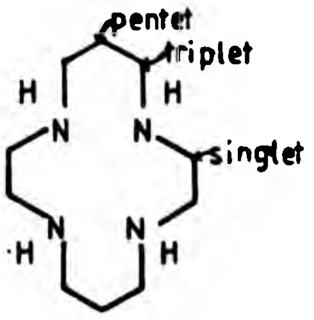
In conclusion, it can be said that the most basic ligands are those containing all aliphatic nitrogen atoms i.e. of cyclam type. These are also expected to be the most flexible systems. The mixed benzylamino/anilino ligands (i.e. 3.6, 3.7 and 3.9) have intermediate basicity. The most weakly basic ligands are those possessing only anilino donors (i.e. 3.1a and 3.1b) and these systems are also likely to have the most rigid structures. The combination of the poor basicity of the N_4-macrocycle 3.1b and its rigidity is likely to make it a significantly worse ligand than its o-aminobenzylamino and aliphatic (cyclam) analogues for metal ions other than those for which it has ideal geometry (see also below). Similarly, the O_2N_2-ligand 3.1a is likely to be a much less effective complexing agent than its benzylamino analogue 3.8 (see table 3.1).

3.2.2 Rigidities of the Ligands in Solution

Detailed high-resolution ^1H nmr (220 MHz) spectral studies on ligands 3.1a and 3.1b suggest that these have greater rigidities than the analogous 14-membered macrocycles 3.7 and 3.5. Simple multiplets are obtained for the methylene protons in these two compounds, indicating that the two hydrogen atoms are equivalent or that their environments interconvert rapidly on the nmr scale.



3.7

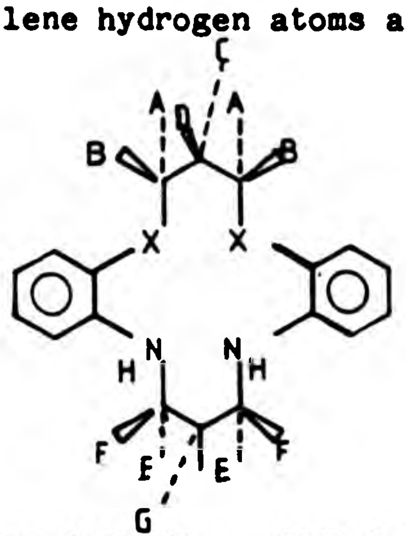


3.5

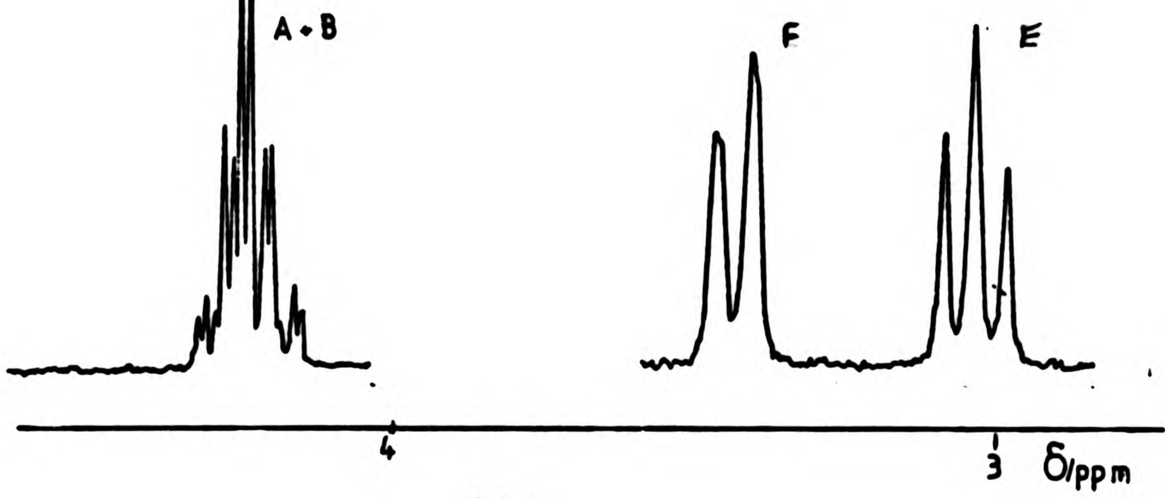
The rigidity in 3.1a and 3.1b leads to the non-equivalence of methylene protons. Very complex spin multiplets for the central methylenes of the propane bridges are observed.

The spectra in the regions associated with the methylene groups adjacent to the heteroatoms in 3.1a and 3.1b are given below.

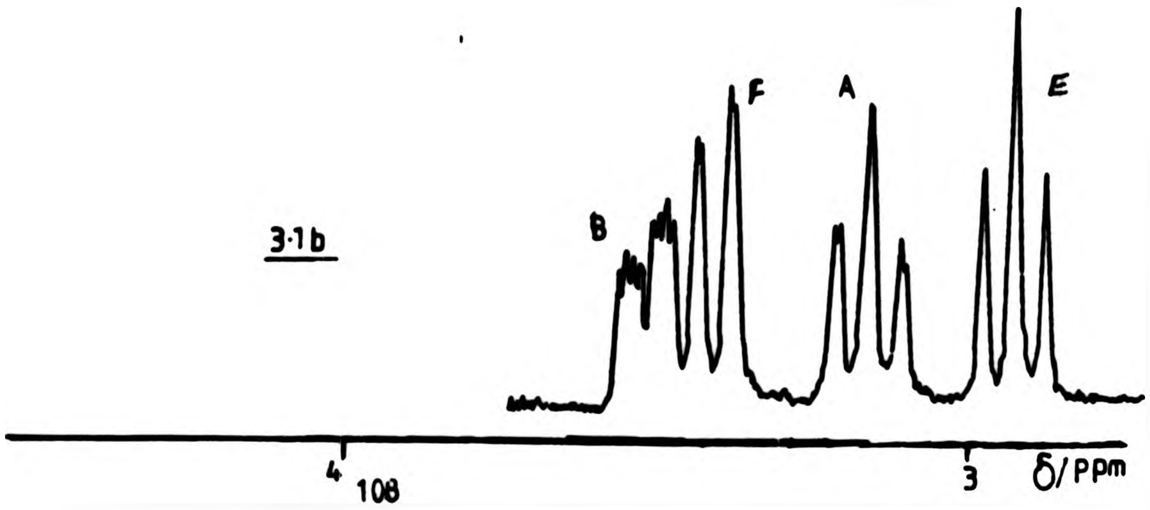
For the macrocycles the methylene hydrogen atoms are identified using the lettering system below.



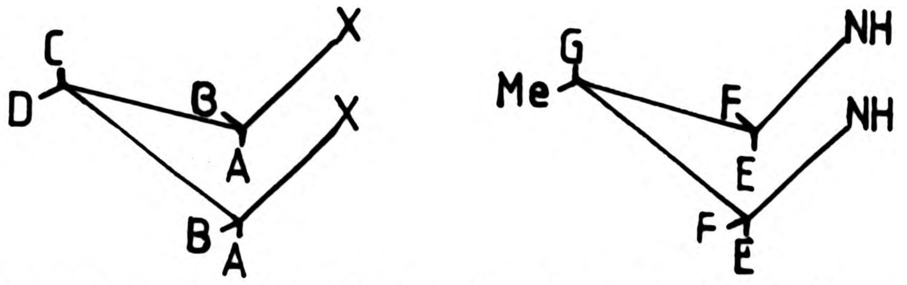
Methylene Signals in the ^{1}H nmr (220 MHz, $CDCl_3$) Spectra of 3.1a and 3.1b



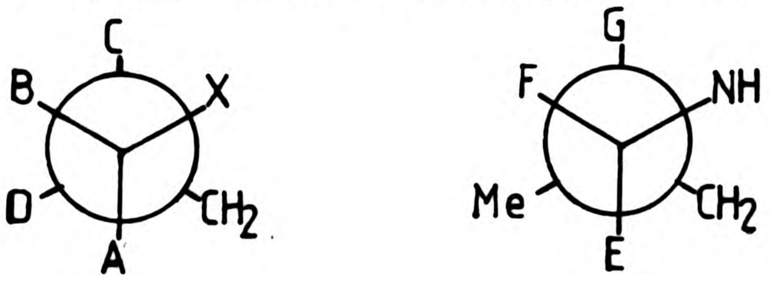
3.1a



The two propane bridges may adopt a cyclohexane-like ring configuration (see X-ray determination of 3.1b), and thus the protons may be located in axial or equatorial sites. Newman projections may also be used to assist in interpreting the spectra and are presented below.



Axial/Equatorial Configurations for the Propane Bridges



Newman Projections Corresponding to the Above Configurations

Geminal coupling across two bonds is usually stonger than vicinal coupling through three bonds. Innumerable results from spectra of compounds containing 6-membered rings[7] in the chair form, have been obtained and vicinal coupling constants have been reported; J(axial,axial) in the range 8-13 Hz, and J(axial,equatorial) in the range 2-6 Hz, and J(equatorial,equatorial) significantly smaller, about 1 Hz.

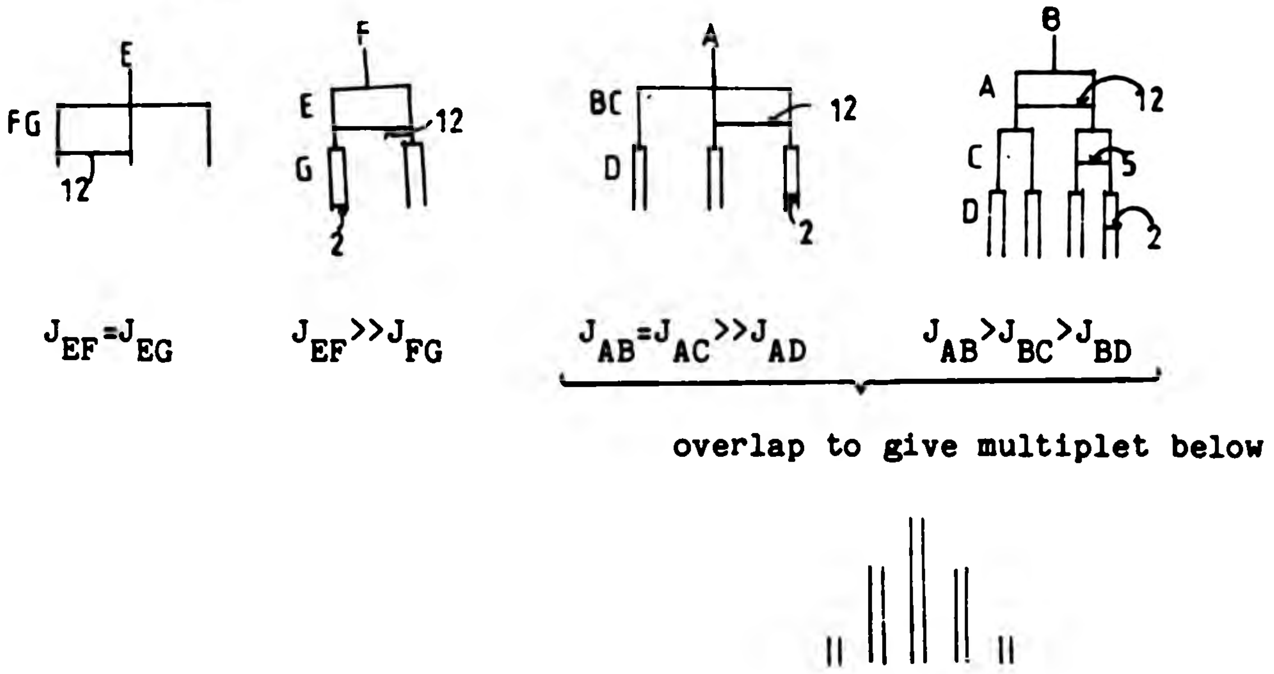
The ^{1}H nmr spectrum of the O_2N_2 macrocycle can be interpreted if it is assumed that geminal coupling of proton E to F and vicinal coupling to G are equivalent. Similarly for proton A, geminal coupling to B is apparantly identical to cis (axial,axial) vicinal coupling to C, and a weak coupling (2 Hz) to D completes the splitting into six lines (see figure 3.1).

F is strongly coupled to the geminal proton E and shows a weak (axial,equatorial) coupling to the vicinal proton G giving four lines (see figure 3.1).

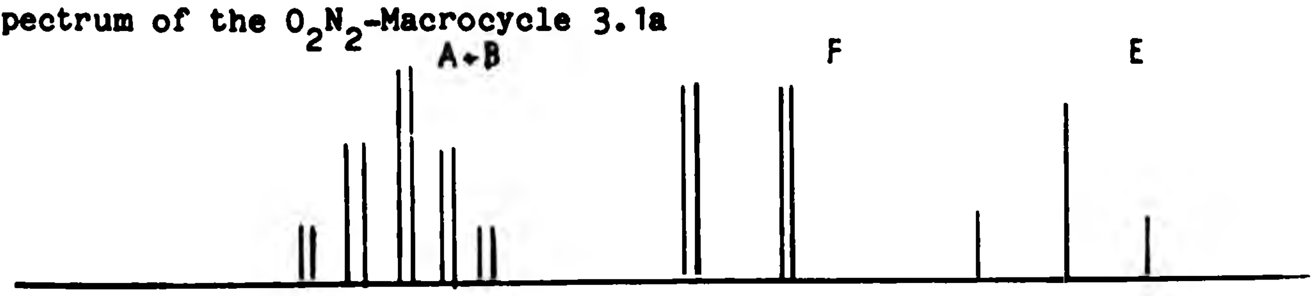
Proton B gives rise to a more complex signal; a stong coupling (12 Hz) to proton A, a weaker vicinal coupling (5 Hz) to C, and a still weaker coupling (2 Hz) to vicinal proton D.

A further complication is that signals for A and B overlap and give rise to a total of ten lines as shown in figure 3.1.

FIGURE 3.1 Multiplet Systems for Protons A, B, E and F in 3.1a

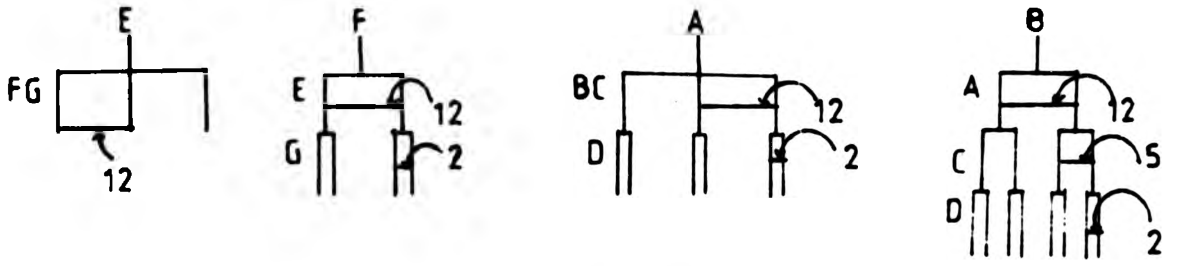


Coupling Between Protons in the Methylene Groups in the ^1H nmr Spectrum of the O_2N_2-Macrocycle 3.1a



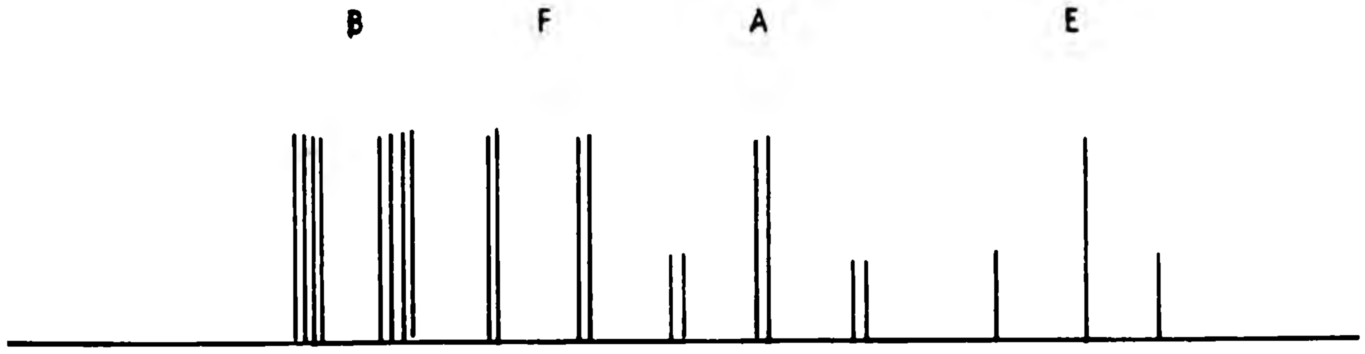
The spectrum of the N_4-macrocycle can be interpreted in an analogous manner, see figure 3.2. In this compound the spectrum is easier to interpret because the methylene hydrogens do not overlap.

FIGURE 3.2 Multiplet Systems for Protons A, B, E and F of 3.1b



$J_{EF}=J_{EG}$ $J_{EF}>>J_{FG}$ $J_{AB}=J_{AC}>>J_{AD}$ $J_{AB}>J_{BC}>J_{BD}$

Coupling Between Protons in the Methylene Groups in the ^1H nmr Spectrum of the N_4-Macrocycle 3.1b



The interpretation of the ^1H nmr spectra assumes that the methyl substituent is in the equatorial position because axial-axial vicinal coupling of E with G is obtained (J_{EG} = 12 Hz), if G had been equatorial the coupling to either E or F would be significantly small (< 6 Hz). The location of the methyl at an equatorial site is supported by molecular mechanics calculations (see section 3.3.5).

Macrocycles 3.1a and 3.1b are marginally more rigid than their linear analogues 3.7 and 3.5, as seen from the ^1H nmr spectra. Thus the methylene proton signals are obtained as complex multiplets due to the non-equivalence of methylene protons in the nmr time scale.

3.2.3 Formation Constants of Metal Complexes

Potentiometric titrations measurements have been used to assess the thermodynamic stabilities of the metal complexes in solution.

The stability constants correspond to logK values for formation of the respective 1:1 complexes. The equilibrium constants (really concentration constants) are defined by:

$$M^{2+} + L \xrightleftharpoons{K_1} [ML]^{2+}$$

$$\text{where } K_1 = \frac{[ML]^{2+}}{[M^{2+}][L]}$$

The stability constants for the systems chosen for study were determined by Lindoy and co-workers at James Cook University. The pH titration method was used to obtain values (see section 3.2.1 above) for dicationic metal complexes of the ligands 3.1a, 3.1b and their linear analogues in 95 % methanol (I = 0.1 M $[(CH_3)_4N]ClO_4$, with $[(CH_3)_4N]OH$ (0.096 M) used as titrant). Values are included in table 3.2. Unfortunately stability constants could not be obtained for complexes of 3.1c under comparable conditions due to the insolubility of the ligand in 95 % methanol. However, values for stability constants of the copper(II) and nickel(II) complexes of the S_2N_2 cyclam analogue have been reported[1] to be 15.96 and 8.91 respectively. The values for particular complexes of 3.1b, 3.2, and 3.7 could not be accurately determined because the strong complexation involved resulted in the complexes being virtually totally formed over the pH region used for the measurements. In particular, this applied to the copper(II) complexes of 3.1b and 3.7 and the nickel(II) complexes of 3.7. Alternatively, for the cobalt(II) complex of 3.1b, precipitation occurred early in the titration. An additional problem arose for the nickel(II) complex of 3.1b since very highly coloured materials, assumed to be the result of ligand oxidation, separated out during titration.

TABLE 3.2 Stability Constants ($\log K_1$) for Metal Complexes of Macrocycles and Their Linear Analogues

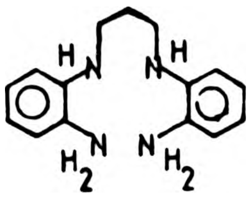
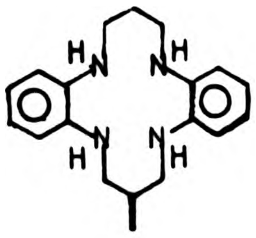
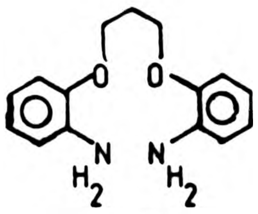
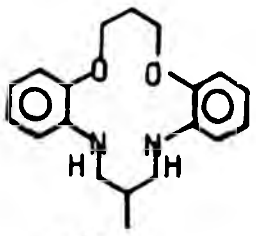
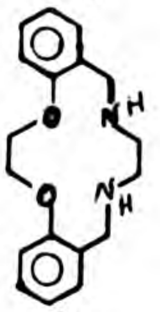
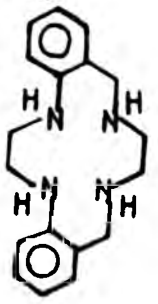
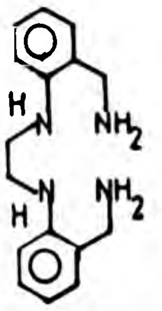
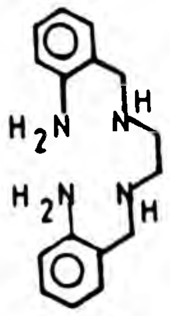
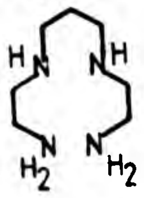
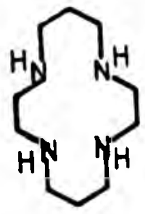
Ligand number	Structure	$\log K_1$ for Metal Complexes				
		Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
3.3[d]		~3.5	6.29	>13	3.13	<3
3.1b[d]		a	b	c	3.81	-
3.2[d]		<2.5	<2.5	a	<2.5	<2.5
3.1a[d]		<3	<3	3.5+.1	<3	<3
3.8		-	3.7[e]	8.2[f]	~3.0[g]	-
3.7		-	c	c	8.57[h]	7.75[h]

Table 3.2 cont

3.6		-	-	-	8.57[h]	8.12[h]
3.9		7.00[l]	10.00[l]	-	7.92[h] 7.17[l]	7.66[h]
3.4*		-	15.8[i]	23.9[j]	12.83[k]	-
3.5*		-	22.2[l]	27.2[m] 26.5[n]	15.5[o] 15.34[p]	11.23[q]

*- Measurements were obtained in aqueous medium

a- Precipitation early in titration, therefore value unobtainable

b- Very highly coloured materials separate during titration, assumed to be result of ligand oxidation.

c- Measurement too high to be determined accurately under analogous conditions to those used for other entries in the table

l- Reported in Smith, R.M., Martell, R.E., Critical Stability Constants Vol 2 : Amines, Plenum, New York, (1975)

d- This work

e- Refs 8-11

f- Refs 9, 11,12

g- Ref 12

h- Ref 13

Table 3.2 cont

i- Refs 14-16,23

j- Refs 17-23

k- Refs 17,22

l- Refs 14-16, 24-27

m- Refs 21,28,32

n- Refs 29-31

o- Ref 18

p- Ref 33

q- Ref 29

The systems chosen for study (3.1a, 3.1b, 3.2, 3.3) gave relatively weak complexes with the Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}. The highest values observed were for the nickel(II) and copper(II) complexes of the N_4-linear ligand 3.3. The stability constants for this ligand follow the Irving Williams Rule with Ni(II) < Cu(II) > Zn(II). Very low stability constants were observed for the O_2N_2 ligand 3.2 because the incorporation of phenoxy ether groups lowers the π-donor capabilities of the quadridentate ligand. Ligand 3.1a is also a poor ligand and the only stability constant which can be recorded with any precision is that for the copper(II) complex.

The metal ion which allows most favourable comparison of the stability constants for the various 14-membered macrocycles and related linear analogues is Zn(II). Comparing 3.1a and 3.1b with their linear analogues suggests that a slight macrocyclic effect operates ($\Delta \log K_1$ value of ca. 0.5 and 0.68, respectively). The N_4-macrocycle 3.1b gives a slightly more stable complex with Zn(II) than the O_2N_2-macrocycle 3.1a.

When the O_2N_2-macrocycles 3.1a and 3.8 are compared, it can be seen as expected (see section 3.2.1) that the benzylamino ligand 3.8 gives stronger complexes with Ni(II) and Cu(II) than does the anilino system 3.1a. Analogously the N_4 system 3.7 gives a more stable Zn(II) complex than 3.1b presumably for similar reasons.

No major macrocyclic effect is observed when 3.7 is compared with its linear analogues 3.6 and 3.9. More stable Zn(II) and Cd(II) complexes are observed for 3.6. Additionaly, for these ligand systems, the cadmium(II) complexes are less stable than the zinc(II) complexes, possibly because the cadmium ion is larger in size (i.e. the cavity of the macrocycle 3.7 is too small to accommadate the Cd(II) ion).

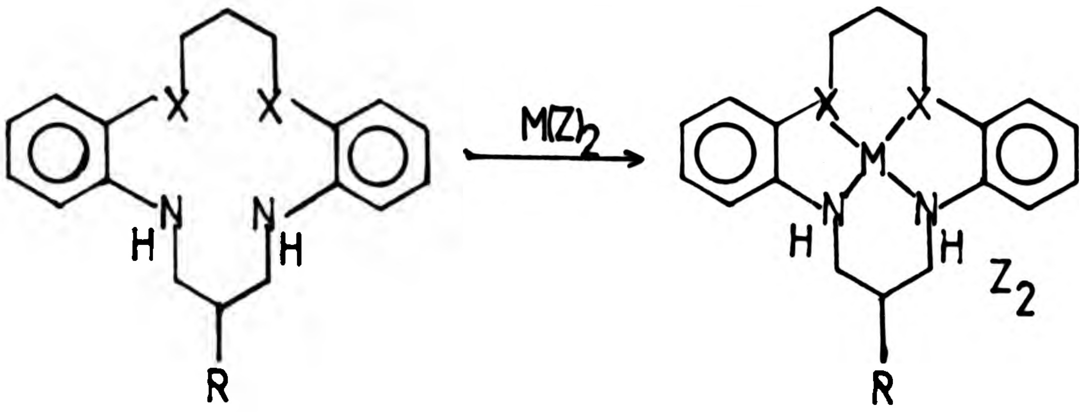
The stability constants for the aliphatic ligands 3.4 and 3.5 cannot be strictly compared with the others in table 3.2 because the measurements were carried out in aqueous media. However, it is clear that the stabilities of these metal complexes are much higher than those of both ligand types 3.1b and 3.7. Also, there appears to be a much larger macrocyclic effect operating for the aliphatic N_4-system (i.e. the nickel(II) complex of 3.5 is approximately 10^3 times more stable than for 3.4).

In conclusion, it can be said that the most favourable and thermodynamically stable complexes obtained are for the most flexible systems containing all aliphatic amines nitrogens (3.4 and 3.5). The most weak complexes were obtained for the all anilino nitrogen donor systems (3.1a, 3.1b, 3.2 and 3.3). The mixed anilino/benzylamino ligands with fused benzene rings have intermediate stability constants. Thus the poor donor ability of ligands 3.1a and 3.1b together with their inherent rigidity (which makes these systems less able to accommodate to the steric requirements of different metals) might both be expected to make these poorer ligands than other systems contained in table 3.2. This conclusion is borne out by attempts to prepare the metal complexes (see below).

3.2.4 Preparations of Metal Complexes

Two strategies were considered for the preparation of the divalent metal ion complexes of the macrocyclic ligands. The first is the precipitation of a salt of the dicationic complex $[Ni(macrocycle)]^{2+}$ from solution using large counter-ions (e.g. ClO_4^-, BF_4^-, PF_6^-, NO_3^- etc.). Bosolo concludes[34] that "solid salts separate from aqueous solution easiest for combinations of either small cation-small anion or large cation-large anion preferably with systems having the same but opposite charges on the counterions". If this "rule of thumb" is applied to preparations of $[M(macrocycle)]X_2$ complexes, particularly large anions X^- will be needed. The alternative approach is to use strongly co-ordinating anions, (such as NCS^-, Cl^-, Br^-, CN^- etc.) to isolate the neutral metal complexes of the type $[Ni(macrocycle)X_2]$.

Preliminary attempts were made to prepare the metal complexes of the three macrocycles 3.1 using large counter-anions, via the following reaction scheme:



3.1a, X=O, R=CH_3

3.1b, X=NH, R= CH_3

3.1c, X=S, R=H

M=Ni(II), Cu(II), Co(II)

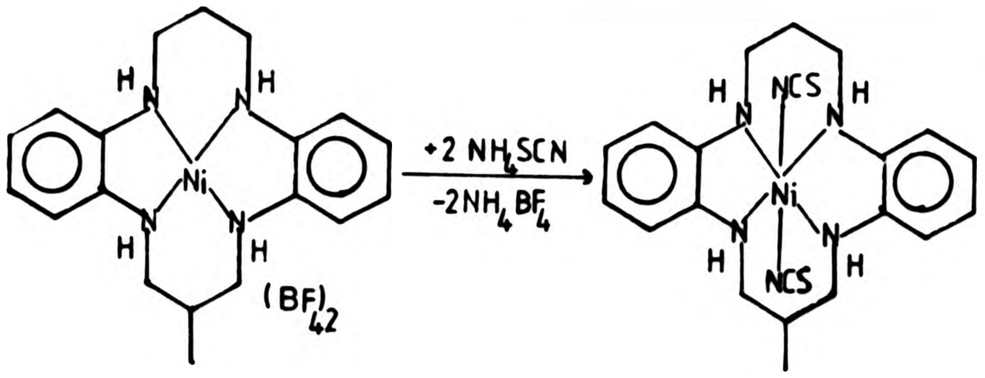
Z=BF_4^-, NO_3^-

Using the O_2N_2-macrocycle 3.1a only the copper(II) dinitrate complex [Cu(3.1a)]$(NO_3)_2$ could be isolated. Attempts to prepare complexes of cobalt(II) and nickel(II) using the three counterions and a variety of solvents failed to give solid complexes and no evidence for complex formation was detected by colour change in solution.

Analogously, for the S_2N_2-macrocycle 3.1c, the only solid isolated was the copper complex [Cu(3.1c)]$(BF_4)_2$, and the related cobalt(II) and nickel(II) complexes were not obtained.

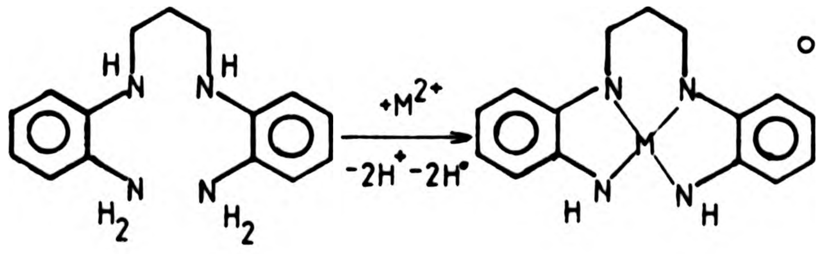
The N_4-macrocycle was comparatively better at complexing with cobalt(II), nickel(II) and copper(II) giving the ditetrafluoroborate complexes, which were isolated with relative ease.

The low-spin nickel(II) complex [Ni(3.1b)]$(BF_4)_2$ was obtained from the reaction mixture, and on addition of ammonium thiocyanate the high-spin nickel(II) complex [Ni(3.1b)$(NCS)_2$] was obtained (X-ray work has been done on both these complexes see section 3.3.1). In every case all the anilino protons were retained on complexation.



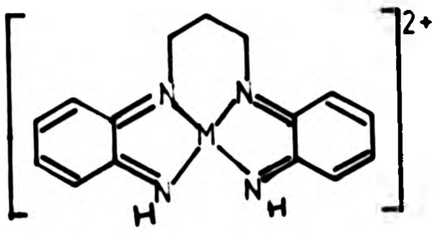
All the isolated complexes were analysed by standard techniques. Colour, yields and characteristic infrared bands are given in table 3.3.

One major problem encountered in the preparation of the complexes of the N_4-macrocycle 3.1b was the sensitivity of the ligand and/or metal complexes to oxidation, resulting in intense colouration of the solutions (see also section 3.2.3). Such side reactions were significantly reduced when the complexation reactions were undertaken under a nitrogen atmosphere. The development of intense colouration in the presence of metal ions (particularly copper(II) and nickel(II)) may be associated with "electron-transfer-series-complex" formation which arise from ligand dehydrogenation and deprotonation. Similar behaviour for analogous linear N_4-quadridentate ligands in the presence of nickel(II) and palladium(II) have been reported by Fleischer *et al*[35]. When 3.3 is treated with these metals in air, an extremely highly coloured neutral product 3.19 is obtained, in which the ligand has lost two protons and two hydrogen atoms upon complexation.

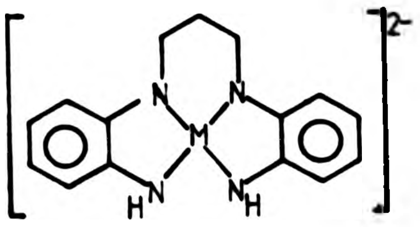


3.3 **3.19**

Pol~~a~~ographic measurements demonstrate[35] that up to two electrons can be readily removed or added to the neutral complex 3.19. Species 3.20 and 3.21 are examples of the two extreme forms from a series of five electron-transfer-series-complexes which includes 3.19 as its central member.

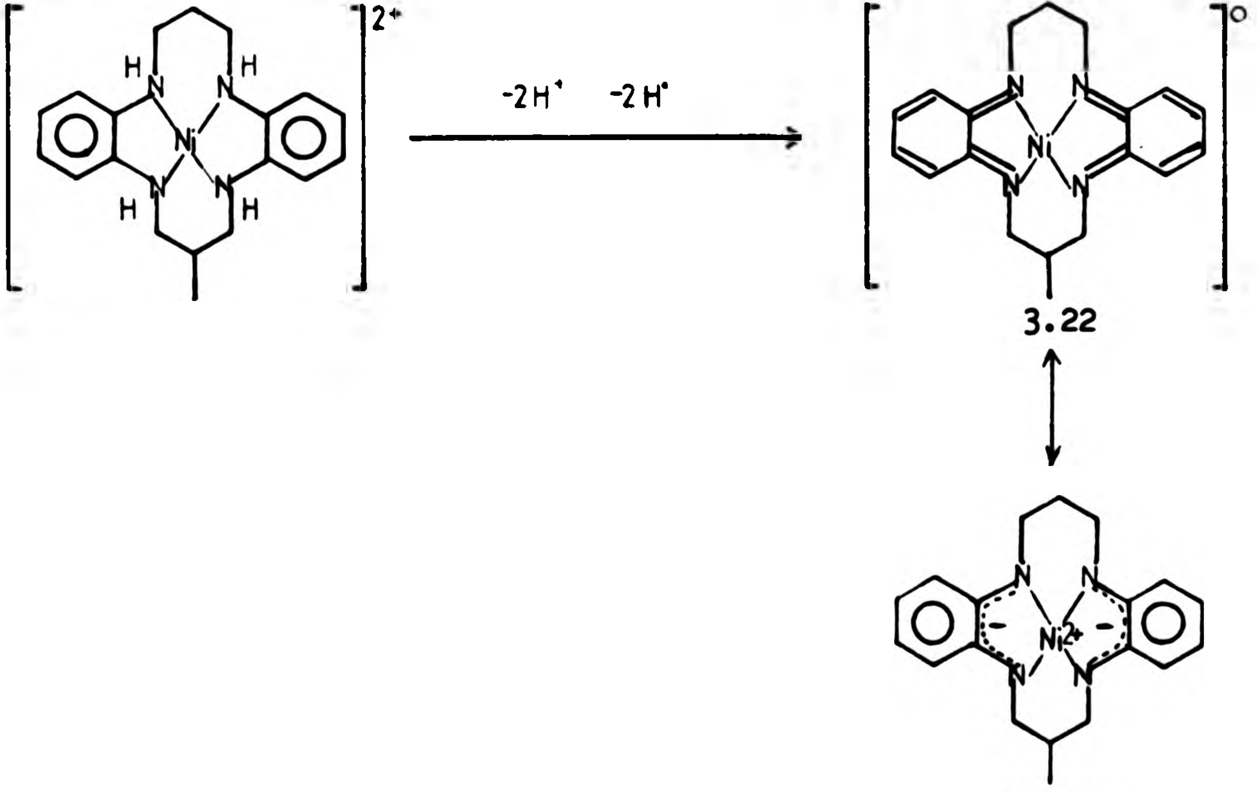


3.20



3.21

A similar situation appears to be possible for the nickel(II) complexes of ligand 3.1b in solution where highly coloured (intense red) species of the type 3.22 with extensively delocalised electronic ground states, best represented by 3.23 would be analogous to the linear complex 3.19.



3.23

The side reactions described above are the most probable origin of the highly coloured byproducts. However, other side reactions may be possible for nickel complexes in the light of recent discoveries of extremely facile redox catalysis promoted by macrocyclic nickel complexes. Some examples of this are given below.

(i) Deprotonation and dehydrogenation reactions in macrocycles[36].

(ii) Macrocyclic dioxopentamines as nickel(II) dioxygen adducts[37].

(iii) Monovalent nickel complexes with tetra-aza macrocyclic ligands[38],

(iv) Studies on nickel(III)/nickel(II) redox couple potentials with 13 and 14-membered macrocycles[39],

(v) Kinetic aspects of redox reactions of nickel(III) complexes[40].

(vi) Trivalent and tetravalent nickel complexes in co-ordination chemistry[41].

(vii) Nickel(I) complexes in enzymic systems[42,43].

(viii) Nickel(II) cyclam as a selective electrocatalyst[44] for reduction of carbon dioxide in water.

The observations in the case of preparation of metal complexes noted above are compatible with log K data obtained in section 3.2.3. These ligands give weak metal complexes and thus may be used in solvent extraction systems since metal complexes are required of intermediate strength in this technique, see chapter 1.

TABLE 3.3 Metal Complexes of Quadridentate Macrocycle 3.1

Complex	Solvent	Colour	Yield	Infrared	Bands
$[Cu(3.1a)](NO_3)_2$	Acetone	Green	57 %	3440	-NH
				1390' 840	$-NO_3^-$
$[Cu(3.1b)](BF_4)_2$	MeOH/	Brown	51 %	3240	-NH
	CH_2Cl_2			1120- 955	$-BF_4^-$
$[Co(3.1b)](BF_4)_2$	MeOH/	Blue/	40 %	3400	-NH
	CH_2Cl_2	Purple		1150- 1040	$-BF_4^-$
$[Ni(3.1b)](BF_4)_2$	MeOH	Orange	57 %	3400	-NH
				1150- 1040	$-BF_4^-$
$[Ni(3.1b)(NCS)_2]$	MeOH	Pink	51 %	3240	-NH
				2085	-C=N
$[Cu(3.1c)](BF_4)_2$	MeOH/	Green	42 %	3400	-NH
	MeCN/ CH_2Cl_2			1150- 1030	$-BF_4^-$

3.3 STRUCTURES OF THE MACROCYCLES AND THEIR METAL COMPLEXES

The N_4-macrocyle 3.1b and its low- and high-spin nickel(II) complexes (see section 3.2.3) are a suitable series for investigating the changes of macrocyclic geometry accompanying complex formation.

3.3.1 X-Ray Structures of the N_4-Ligand and its Low and High Spin Nickel(II) Complexes

Crystalline samples of low- and high-spin complexes of nickel(II) containing the N_4-ligand (3.1b) were obtained.

The X-ray crystal data for the three compounds 3.1b, [Ni(3.1b)]$(BF_4)_2$ and [Ni(3.1b)$(NCS)_2$] are summarised in table 3.4.

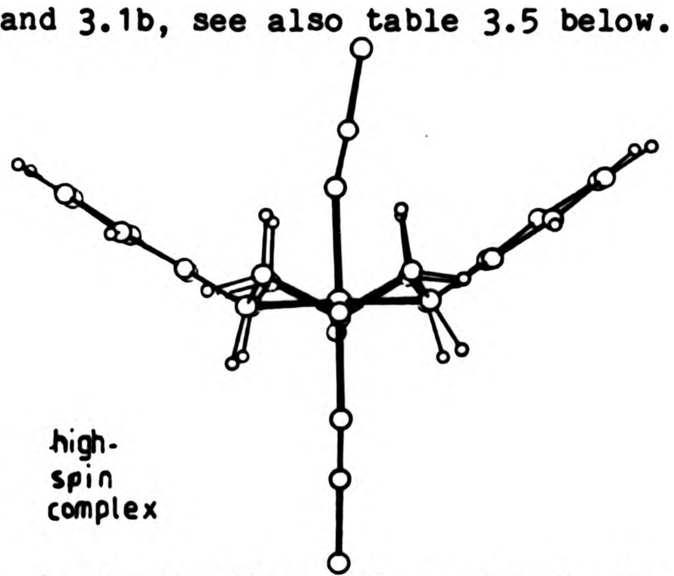
__TABLE__ __3.4__ **Crystal Data and Selected Details[a] of the Structure Determinations of 3.1b, [Ni(3.1b)]$(BF_4)_2$ and [Ni(3.1b)$(NCS)_2$]**

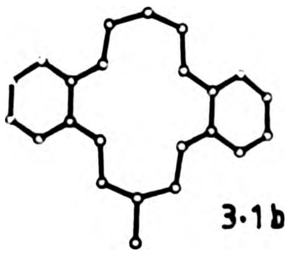
	[Ni(3.1b)]$(BF_4)_2$	3.1b	[Ni(3.1b)$(NCS)_2$]
Mol. formula	$C_{19}H_{26}N_4B_2F_8Ni$	$C_{19}H_{26}N_4$	$C_{21}H_{26}N_6NiS_2$
M_r	542.76	310.44	485.32
a/ Å	9.200(2)	12.843(2)	13.210(2)
b/ Å	8.549(2)	5.449(1)	15.926(3)
c/ Å	7.994(2)	23.839(4)	11.184(2)
α/ deg.	109.10(2)	(90)	(90)
β/ deg.	112.91(2)	101.52(2)	103.05(3)
γ/ deg.	74.17(2)	(90)	(90)
V/ $Å^3$	538.22	1634.51	2292.15
Z	1	4	4
d_{calc}/ g cm^{-3}	1.674	1.261	1.406
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Unique data[b]	1108	2870	1250
R	0.0732	0.1093	0.0849
R_w	0.0723	0.1051	0.0812
colour	orange	pale yellow	pink
crystal size/mm	0.18 x0.19 x 0.21	0.32 x 0.39 x 0.29	0.06 x 0.78 x 0.07

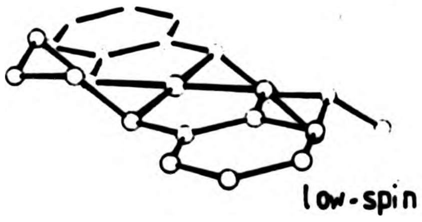
a- Further details are given in appendix 1

b- Unique data with $|F_o| > 3\sigma(|F_o|)$

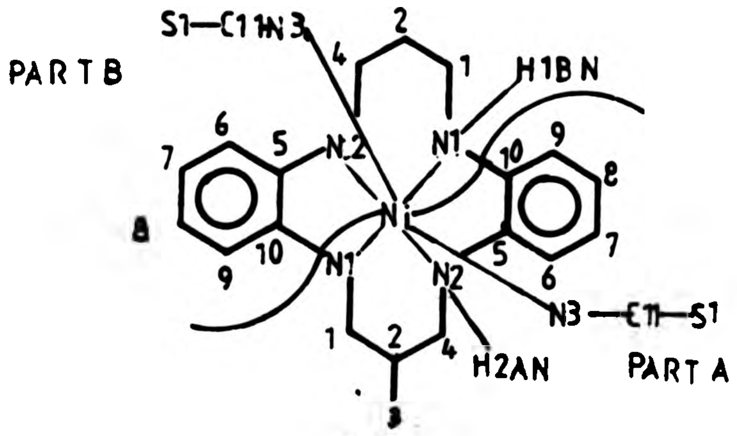
The low-spin complex $[Ni(3.1b)](BF_4)_2$ has a square planar co-ordination geometry with the nickel atom residing at a crystallographic centre of symmetry. The metal complex in $[Ni(3.1b)](BF_4)_2$ is a dication, confirming that there is no deprotonation of the anilino groups accompanying complex formation. The tetrafluoroborate anions are not within co-ordinating distances of the nickel atom (Ni...B =3.643 Å and shortest Ni...F distances fall in the range 2.848-3.749 Å). In contrast, the high-spin nickel(II) complex $[Ni(3.1b)(NCS)_2]$ has a trans-pseudo-octahedral geometry. The complex is neutral with the two thiocyanate groups co-ordinated to the nickel atom through their nitrogen atoms. The N_4-donor set provided by the macrocycle is very nearly planar (with nitrogen atoms deviating by ∓ 0.008 Å from the N_4 least-square-plane) as is that for the free ligand 3.1b, see also table 3.5 below.


high-spin complex


3·1b


low-spin cation

The bond lengths and angles in the co-ordination spheres of 3.1b, $[Ni(3.1b)](BF_4)_2$ and $[Ni(3.1b)(NCS)_2]$ are given in table 3.5. The atom labelling used for $[Ni(3.1b)(NCS)_2]$ is



Compound [Ni(3.1b)](BF$_4$)$_2$ is centrosymmetric and therefore the atoms in part B are symmetry related to the equivalently numbered atoms in part A. To allow comparisons within the N$_4$-donor cavities, data for the free ligand are included in the tables (based on the centroid of the N$_4$-donor set rather than the position of the nickel(II) atom). Otherwise the atom labelling in 3.1b is identical to that of [Ni(3.1b)(NCS)$_2$].

TABLE 3.5 Molecular Dimensions in the N$_4$-Donor Cavities in [Ni(3.1b)](BF$_4$)$_2$, 3.1b and [Ni(3.1b)(NCS)$_2$]

(a) Bond Lengths/ Å

	[Ni(3.1b)](BF$_4$)$_2$^{a}	3.1b^b		[Ni(3.1b)(NCS)$_2$]	
	M=Ni	M=CE		M=Ni	
	Part A	Part A	Part B	Part A	Part B
M-N1	1.931(7)	1.928(15)	1.891(15)	2.104(18)	2.082(15)
M-N2	1.920(6)	1.961(15)	1.999(15)	2.122(16)	2.114(13)
M-N3	-	-	-	2.041(14)	2.114(14)

(b) Bond Angles/ deg.

	[Ni(3.1b)](BF$_4$)$_2$^{a}	3.1b^b	[Ni(3.1b)(NCS)$_2$]
	M=Ni	M=CE	M=Ni
N1A-M-N2A	92.0(3)	94.6(8)	98.1(7)
N1B-M-N2B	-	94.4(8)	100.4(6)
N2A-M-N1B	88.0(3)	85.8(8)	80.6(6)
N1A-M-N2B	-	85.3(8)	80.8(6)
N1A-M-N1B	(180.0)	178.0(6)	177.8(6)
N2A-M-N2B	(180.0)	177.9(6)	178.6(7)
N3A-M-N1B	-	-	91.3(6)
N3A-M-N2B	-	-	91.1(6)
N1A-M-N3B	-	-	87.8(6)
N2A-M-N3B	-	-	89.7(6)
N3A-M-N3B	-	-	178.1(7)
N1A-M-N3B	-	-	87.8(6)
N2B-M-N3B	-	-	89.4(6)

TABLE 3.5 continued

(c) Bond Angles Involving the Donor Atoms/ Deg

	$[Ni(3.1b)](BF_4)_2$[a]	3.1b[b]	$[Ni(3.1b)(NCS)_2]$
	M=Ni	M=CE	M=Ni
M-N1A-C1A	112.3(9)	127.2(7)	117(1)
M-N2A-C4A	113.6(5)	127.0(7)	116(1)
M-N1A-C10B	108.9(7)	106.4(6)	106(1)
M-N2A-C5A	109.9(5)	105.8(6)	103(1)
M-N2B-C5B	-	105.1(5)	104(1)
M-N1B-C10A	-	106.3(8)	106(1)
M-N2B-C4B	-	126.3(1)	114(1)
M-N1B-C1B	-	127.8(1)	114(1)
M-N3A-C11A	-	-	156(2)
M-N3B-C11B	-	-	163(1)

(d) Geometry of the Thiocyanate Groups in $[Ni(3.1b(NCS)_2]$

	Part A	Part B
C-N	1.137(21)	1.153(23)
C-S	1.606(18)	1.621(18)
C11-N3-Ni	156(2)	163(1)
S1-C11-N3	176(2)	180(2)

a- Since the molecule $[Ni(3.1b)](BF_4)_2$ lies on a crystallographic inversion centre atoms in part B are symmetry-related to the equivalently numbered atoms in part A

b- For the free ligand the centroid of the N_4-donor set (CE) is used instead of the nickel atom.

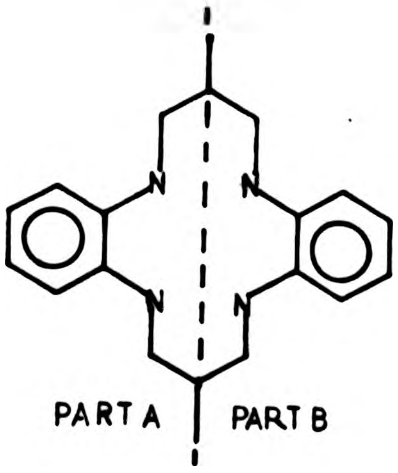
The N_4-donor set is planar in $[Ni(3.1b)](BF_4)_2$ as a consequence of the crystallographic inversion centre, and very close to planar in the other two structures, 3.1b and $[Ni(3.1b)(NCS)_2]$, which have slight "tetrahedral" displacements of the donors from the respective least squares planes (see table 3.6). The nickel atom deviation from the N_4-plane is -0.025 Å for $[Ni(3.1b)(NCS)_2]$. This deviation is associated with a slight distortion from the pseudo-octahedral geometry towards a square pyramid, giving significantly different nickel to thiocyanate bond lengths (see table 3.5).

TABLE 3.6 Deviations of Atoms from the Least Sqares Plane Through the N_4-Donor Set

Atom	$[Ni(3.1b)](BF_4)_2$	3.1b	$[Ni(3.1b)(NCS)_2]$
N1A	0	-0.035	+0.008
N2A	0	+0.035	-0.008
N1B[a]	0	-0.035	+0.008
N2B[a]	0	+0.035	-0.008
Ni	0	-	-0.025

a- For $[Ni(3.1b)](BF_4)_2$, these atoms are generated using the crystallographic inversion centre from N1A and N2A, respectively.

All three molecules have a pseudo-mirror plane perpendicular to the mean plane of the molecule and passing through the central atoms of the propane bridges and the nickel ion or centroid of the N_4-donor set.



There are only small differences between bond lengths and angles in the two chemically equivalent halves (A and B) of the co-ordination sphere (see Table 3.5). Similarly, chemically related bond lengths and angles in the ligands have values which agree within the limits of error of the structure determination in almost every case (see appendix 1).

The conformation of the six-membered chelate rings involving the propane bridges, nickel (or centroid) and two nitrogen donors may be examined by considering the displacements of the C_3 bridges from the N_2M plane.

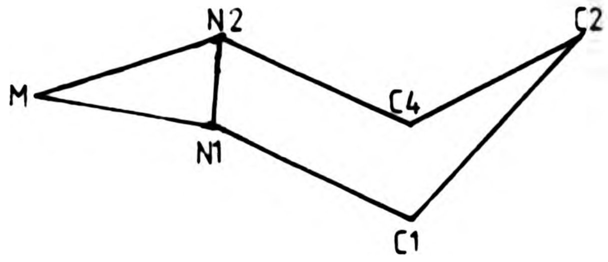


TABLE 3.7 Puckering of the C_3 Bridges from N_2M Plane

	[Ni(3.1b)]$(BF_4)_2$		3.1b		[Ni(3.1b)$(NCS)_2$]	
	Part A	Part B	Part A	Part B	Part A	Part B
	M=Ni		M=centroid		M=Ni	
C1	-1.14	1.14	-0.03	-0.13	-0.50	-0.54
C2	-0.97	0.97	0.53	0.53	0.24	0.14
C4	-1.11	1.11	-0.09	-0.10	-0.47	-0.55

For all three structures the six-membered rings have chair conformations, consistent with the pseudo-mirror molecular symmetry. For [Ni(3.1b)]$(BF_4)_2$ there is one chair above and the other below the N_4 plane giving a "step" arrangement (see figure 3.3). This is analogous to the arrangement for the free ligand 3.1b and [Ni(3.1b)(NCS)$_2$]. For 3.1b and [Ni(3.1b)(NCS)$_2$] the two chairs for the chelate rings are on the same side of the N_4-plane thus giving both the molecules a "saddle-shaped" arrangment (figures 3.4 and 3.5 respectively). In such an arrangement the aniline hydrogen atoms are displaced to the same side of the N_4-plane (see table 3.7), whereas the "step" arrangement of [Ni(3.1b)](BF$_4$)$_2$ has two hydrogens "up" and two hydrogens "down" relative to the N_4 plane.

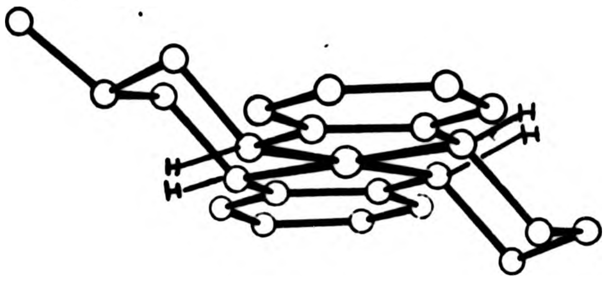


Figure 3.3

The data in table 3.7 reveal that the propane bridges in [Ni(3.1b)](BF$_4$)$_2$ are bent away from the co-ordination N_4-plane to a greater extent than those in the free ligand or the complex [Ni(3.1b)(NCS)$_2$]. Presumably this conformational difference arises from the ligand adjusting its geometry to provide the smaller N_4-cavity size required for the smaller low-spin Ni^{2+} ion (see also 3.3.4).

TABLE 3.8 Deviations of the Anilino Protons

Atom	$[Ni(3.1b)](BF_4)_2$	3.1b	$[Ni(3.1b)(NCS)_2]$
H1AN	1.09	0.80	0.93
H2AN	0.95	0.96[a]	1.00
H1BN	-1.09	0.80	0.90
H2BN	-0.95	0.73	1.02

a- There is some uncertainty associated with the location of this hydrogen atom (see below).

For the free ligand all the N-H are displaced to the same side of the N_4 plane. There was some slight ambiguity in assigning the position of the amine proton (H2AN) from difference Fourier maps. Three positions of the electron density were detected around N2A.

Fractional Coordinates		x	y	z
H atom	(i)	0.6159	0.2669	0.1393
	(ii)	0.6917	0.0550	0.1310
	(iii)	0.2893	0.2422	0.2426

Position (i) has all the anilino hydrogen atoms displaced to the same side of the N_4 plane. The most favourable position to permit intramolecular hydrogen bonding corresponds to the hydrogen atom being located at position (ii), whereas the atom at position (iii) gave the highest electron density in the map. Position (ii) was found to be associated with the minimum strain energy in the molecule using the molecular mechanics calculations described in section 3.3.5 and involves a slight degree of hydrogen-bonding interaction between H2AN and the lone pair electrons of N1A.

TABLE 3.9 Inclination of Benzene Rings

(a) Inclination Relative to the N_4 Plane

$[Ni(3.1b)](BF_4)_2$		3.1b		$[Ni(3.1b)(NCS)_2]$	
Part A	Part B	Part A	Part B	Part A	Part B
0.70	0.70	32.35	31.51	34.67	34.18

(b) Inclination Relative to the N_2M Plane

$[Ni(3.1b)](BF_4)_2$		3.1b		$[Ni(3.1b)(NCS)_2]$	
M=Ni		M=CE		M=Ni	
Part A	Part B	Part A	Part B	Part A	Part B
0.70	0.70	33.70	32.89	34.44	33.88

For the low-spin complex $[Ni(3.1b)](BF_4)_2$ the N_4-plane and the benzene rings are almost coplanar. In contrast, for the high-spin complex $[Ni(3.1b)(NCS)_2]$ and the free ligand 3.1b, there is considerable deviation from planarity and the benzene rings are each inclined at $33 \mp 2^\circ$ to the same side of the respective N_4-planes, resulting in a "saddle-shaped" arrangements.

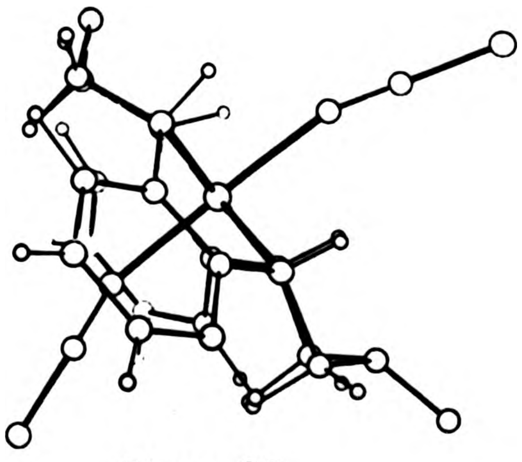


Figure 3·5

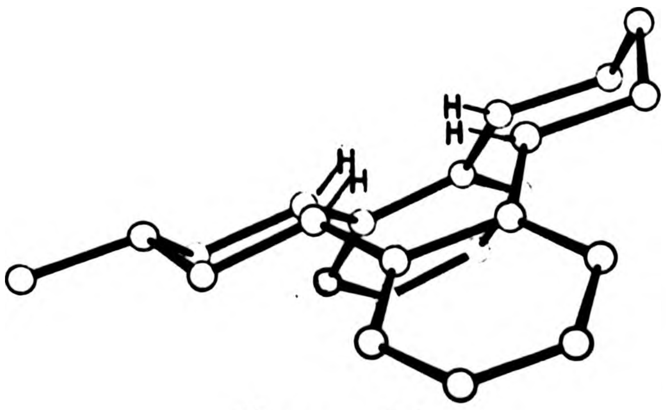
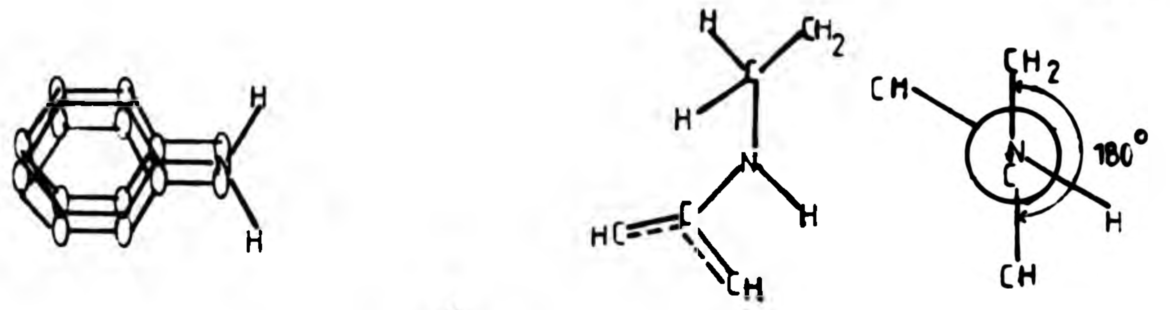


Figure 3·4

A comparison of corresponding torsion angles in the three structures may be used to investigate strain about particular bonds due to geometry variation in the three structures.

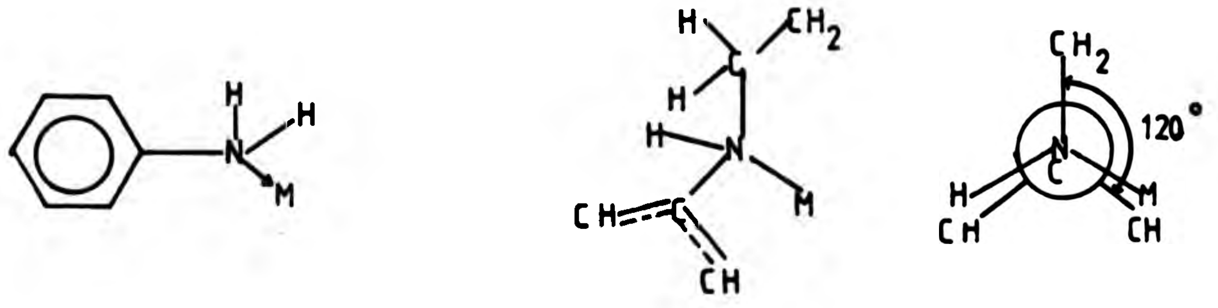
For a simple aniline, the lone pair electrons of the nitrogen atoms are withdrawn into the benzene ring and thus the nitrogen atom is in effect sp^2 hybridised; for unstrained alkylated anilines the torsion angle is expected to be 180 °. In the case of the complexed anilines the lone pair electrons of the nitrogen atoms are directed towards the metal ion and thus the nitrogen atom is sp^3 hybridised. This results in the angles about the nitrogen atom being near tetrahedral and thus the torsion angles involving sp^3 nitrogen atoms are in fact 120 °.



pi-pi overlap of orbitals of sp^2 anilines with the phenyl ring

torsion angle for alkylated aniline

Figure 3.6 Illustration of Torsion Angles for Uncomplexed Aniline



donation of electrons to the metal

Torsion angles

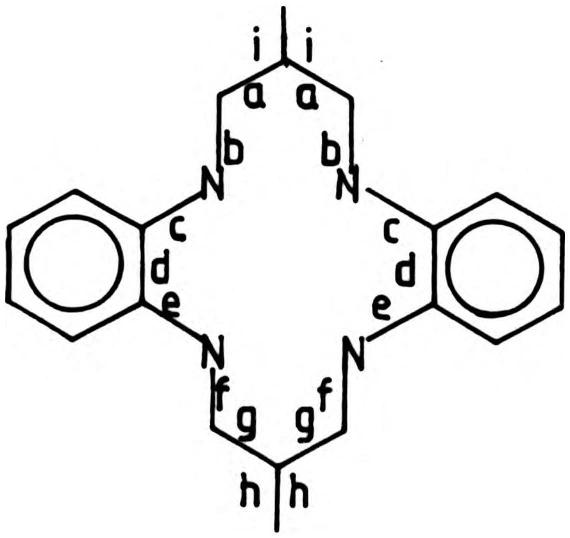
Figure 3.7 Illustration of Torsion Angles for Alkylated Complexes

The torsion angles for all the three structures chosen for study are given in table 3.10.

TABLE 3.10: Torsion Angles^a for the Three Structures

Bond^a	$[Ni(3.1b)](BF_4)_2$		3.1b		$[Ni(3.1b)(NCS)_2]$	
	Part A	Part B	Part A	Part B	Part A	Part B
a	-66.4	67.6	68.8	-69.4	81.3	-80.5
b	-170.2	170.7	-173.6	178.4	-173.2	174.3
c	-125.2	124.0	168.4	-174.0	152.3	-151.2
d	-1.4	1.4	1.2	1.0	-1.6	-2.4
e	-124.0	125.2	-178.2	170.4	-154.5	156.5
f	-170.7	170.2	176.2	-172.7	176.0	-173.7
g	-67.6	66.4	-62.0	63.8	-79.6	81.1
h	166.2	-167.9	173.9	-171.5	157.6	-156.6
i	-	-	-	-	-163.3	167.7

a- The torsion angles quoted involve atoms in the inner-great-ring and the methyl substituents, for the bonds a-h is



From the table of torsion angles (table 3.10) it can be seen that for all three structures there is pseudo-mirror symmetry in the molecule. For the free ligand 3.1b, only minor deviations from strain-free angles (0, 60 or 180 °) are observed and thus it can be assumed that the molecule is relatively unstrained overall. In particular, it can be seen that the torsion angles involving the sp^2 anilino nitrogens in 3.1b (about bonds c and e) approach 180 °. The low-spin nickel(II) complex $[Ni(3.1b)](BF_4)_2$ shows relatively little strain about bonds c and e since the strain-free torsion angles are expected to be about 120 ° where the o-phenylenediamine unit is forced to be planar. On the other hand the high-spin complex [Ni(3.1b)(NCS)$_2$] shows angles of -151.2 and 156.5 ° for bonds c and e, which implies that the nitrogen atom hybridization is half way between sp^2 (as in the free ligand) and sp^3 (as in the low-spin nickel(II) complex). This possibly indicates that some ligand strain is induced allowing the nitrogens to approach the nickel at distances suitable for high-spin complexation formation (see section 3.3.4).

Another feature of interest concerning these three structures is the positioning of the methyl substituents on the propane bridges. These may occupy either axial or equatorial positions. Further there is the possibility that disorder of the methyl positions occurs in the solid complexes. This may be expected since it is only the methyl substituent which destroys perfect inversion symmetry in each of these molecules. Consequently, two sites may occur for each methyl group, such that the difference Fourier maps gives two electron density positions for the methyl carbons near both propane linkages, each having an electron density approximately half that expected for a carbon atom.

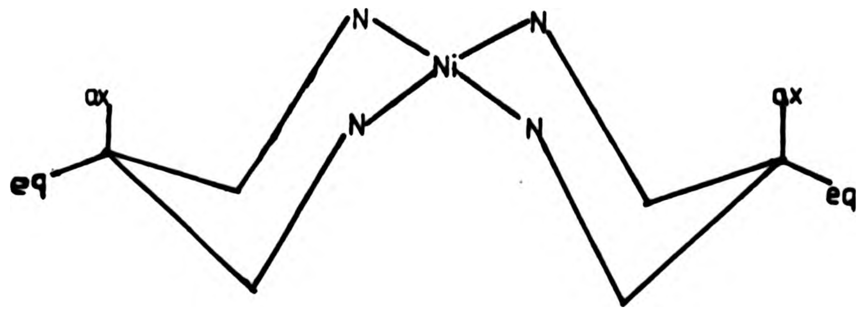


Figure 3.8 Representation of Axial (ax) and Equatorial (eq) Methyl Groups on C_3 Bridges

For the free ligand 3.1b, no disorder was observed in the structure and the methyl substituent was found near one propane bridge only. The methyl group is solely equatorial. The torsional angles (table 3.10) involving the methyl substituent (along bond h) are 173.9 and -171.5 ° as expected for an equatorial configuration.

In the low-spin complex [Ni(3.1b)]$(BF_4)_2$ some disorder is expected as a result of having a crystallographic inversion centre coincident with the nickel atom. Electron density in the structure determination was found to correspond to "half" a "full" equatorial methyl near both the propane bridges. The geometry observed for the propane bridge is thus that for the average of C-substituted and unsubstituted bridges.

In the X-ray structure of the high-spin nickel(II) complex, [Ni(3.1b)$(NCS)_2$], the methyl substituent was found on both sides of the molecule. The greatest electron density was found for the two equatorial sites and the final model for refinement included 0.5 carbon in equatorial positions. There was also some indication of much lower population (<1/8 carbon i.e. less electron density than for a hydrogen atom) at the axial sites. In the high-spin nickel(II) complex [Ni(3.1b)$(NCS)_2$] high thermal parameters were also obtained for C2A and, to a lesser extent, C1A and C4A. This is due to disorder[45] in the structure. Molecular mechanics calculations for the high-spin complex [Ni(3.1b)$(NCS)_2$] (section 3.3.5) in which the methyl group was (i) axial and (ii) equatorial yielded strain energies of 150·7 and 141·1 kJ mol^{-1}, respectively. The calculations thus confirm that the equatorial position is prefered for the methyl substituent. Further, the torsion angles about bonds h and i are in the range 156.6-167.7 ° implying that the methyl substituents are equatorially positioned as opposed to axial (this is also confirmed by detailed ^{1}H nmr (220 MHz) coupling constants for 3.1b, in section 3.2.2).

For $[Ni(3.1b)(NCS)_2]$, the angle generated by the *trans* donors at Ni (N3-Ni-N3) shows a slight deviation from linearity. The inclinations of the two thiocyanates to the co-ordination sphere are different (C-N3-Ni angles being 156(2) ° and 163(1) ° for the A and B parts of the molecule). This difference may be a consequence of *inter*molecular interactions in the solid state. Thus, the two thiocyanate sulphur atoms are involved in weak hydrogen bonds to neighbouring anilino groups (see table 3.11). The different inclinations of thiocyanates A and B appear to relate to the different *inter*molecular NCS...HN interactions. This hydrogen bonding scheme is represented schematically in figure 3.9. Thiocyanate B has a stronger hydrogen bond to an adjacent anilino group resulting in less deviation from linearity of the C11-N3-Ni angle (see table 3.5). To some extent *inter*molecular packing forces and hydrogen bonding can account for the irregular co-ordination geometry in this complex.

TABLE 3.11 Closest Intermolecular Contact Distances for $[Ni(3.1b)(NCS)_2]$ Involving Hydrogen Bonding of the Anilino Protons to Sulphur Atoms

	Distance	Symmetry Operation		
HIBN...S(1A)	2.97	1-x	-y	1-z
H2BN...S(1B)	2.54	0.5+x	0.5-y	0.5+z

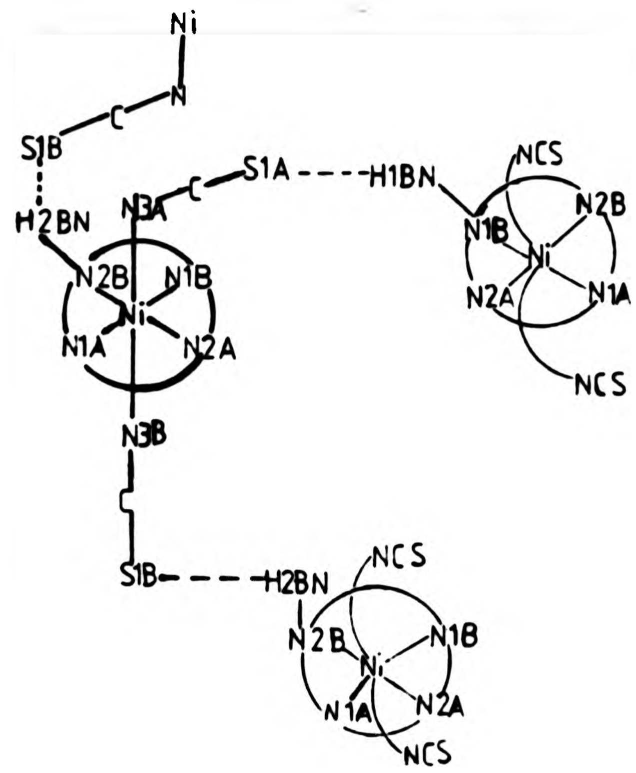


Figure 3.9 Intermolecular Hydrogen Bonding in [Ni(3.1b)(NCS)$_2$]

There is also some intramolecular hydrogen bonding present in the low-spin Ni(II) complex, [Ni(3.1b)](BF$_4$)$_2$, chosen for study. This occurs between anilino protons and the very electronegative fluorines on the tetrafluoroborate groups. The shortest distances available for intramolecular interactions are given below.

	Distance	Symmetry Operation		
H2AN...F(1)	1.89	x	y	z
H1AN...F(1)	2.26	x	y	z
H2AN...F(3)	2.48	x	y	z
H1AN...F(3)	2.86	x	y	z
H1AN...F(2)	2.06	x	-y	z

The most favourable intramolecular hydrogen bonding is for H2AN with F1. The other contact distances are slightly longer and there is only weak hydrogen bonding interaction between H1AN and F3. There is also a small degree of intermolecular hydrogen bonding between the anilino proton on N1A and a fluorine atom (F2).

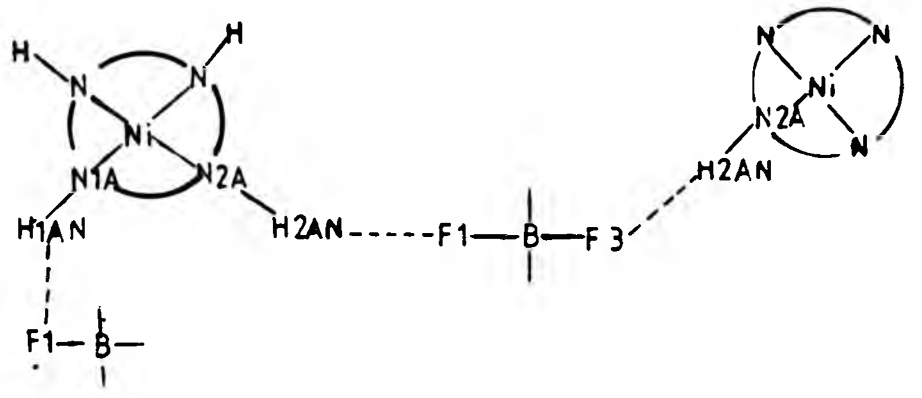
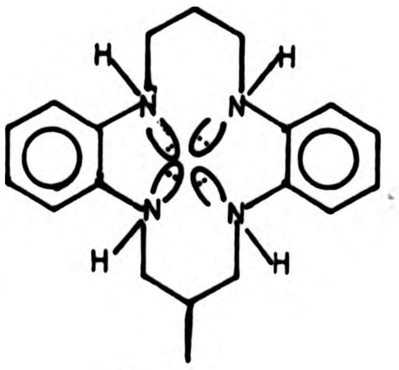


Figure 3.10 Intramolecular Hydrogen Bonding in [Ni(3.1b)]$(BF_4)_2$

In the case of the free ligand 3.1b some intramolecular hydrogen bonding may be expected. This would alleviate lone pair-lone pair repulsion terms associated with the four nitrogen atoms which are necessarily in close proximity. The extent to which 3.1b will adopt such a hydrogen bonding scheme will depend upon the cavity size and ligand rigidity.

The X-ray structure determination of this ligand suggests that only weak intramolecular NH...N hydrogen bonds exist since the closest contacts are rather long. A possible exception involves the hydrogen H2AN. The location of this atom in the difference Fourier maps presented some problems (see table 3.8 and page.132). Of the three possible sites located, the one giving the lowest strain energy in molecular mechanics calculations (see page..155) places the hydrogen relatively close to the neighbouring atom N1A. In this position, presumably a favourable hydrogen bonding interaction would occur (see section 3.3.5).



lone pair-lone pair
repulsion in 3·1b

TABLE 3.12 HYDROGEN BOND DISTANCES FOR 3.1b

	Distance	Symmetry	Operation	
H2AN...N1A	1.73	x	y	z
H2BN...N1A	2.30	x	y	z
H1BN...N2A	2.45	x	y	z
H2AN...N1B	2.66	x	y	z
H1AN...N2B	2.78	x	y	z
H1AN...N2A	2.88	x	y	z
H1BN...N3B	3.00	x	y	z

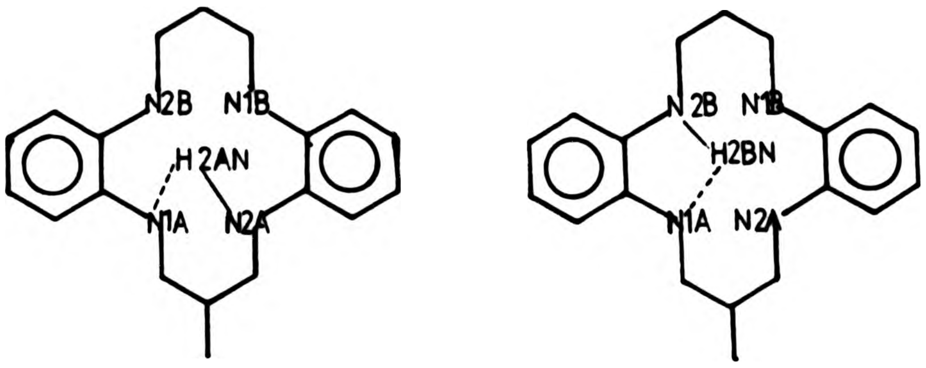
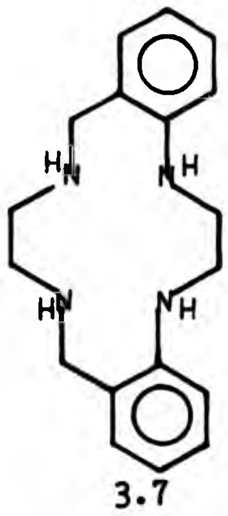
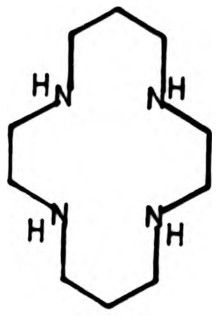


Figure 3.11 Intramolecular Hyrogen bonding in the Free Ligand 3.1b

X-ray structural data have also been obtained recently[46,47] for nickel complexes of other 14-membered N_4-macrocycles of types 3.7 and 3.5. A comparison of the geometries of $[Ni(3.1b)](BF_4)_2$ and $[Ni(3.1b)(NCS)_2]$ with the low- and high-spin complexes of the above ligands will be presented in sections 3.3.2 and 3.3.3 below. In addition, the structure of the free ligand 3.21 has been determined and this allows a comparison with 3.1b and also provides the basis for assessing the goodness-of-fit of ligands of these types for low- and high-spin nickel(II). These aspects are considered in some detail in section 3.3.4.

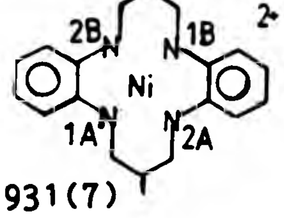
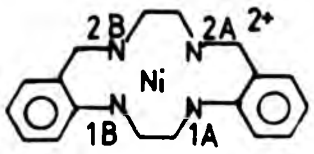
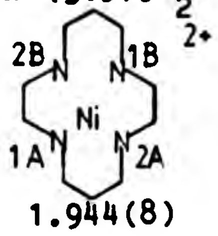

3.7


3.5

3.3.2 Comparison of Co-ordination Geometries of Low-spin 14-Membered N_4-Macrocycles

The two crystallographically independent Ni-N bonds in $[Ni(3.1b)](BF_4)_2$ and $[Ni(3.5)]I_2$ have very similar lengths whereas in $[Ni(3.7)](BF_4)_2$ they differ considerably (see table 3.13). This is to be expected because there are two types of nitrogen donors, and the benzylamino nitrogen (N2A) is expected to be the better donor and to result in a stronger (shorter) bond to nickel.

TABLE 3.13 Bond Lengths in Low-Spin Nickel(II) Complexes of 14-Membered N_4-Macrocycles

	$[Ni(3.1b)](BF_4)_2$[a]	$[Ni(3.7)](BF_4)_2$[b]	$[Ni(3.5)]I_2$[c]
			
Ni-N1	1.931(7)	1.949(8)	1.944(8)
Ni-N2	1.920(6)	1.908(4)	1.935(9)

a- This work

b- B. Shah, BSc. Project Dissertation; Polytechnic of North London, 1985; the complex has mirror-plane symmetry relating N1A to N2B and N2A to N1B.

c- D. Proserpio, Unpublished Results, Polytechnic of North London, 1984.

In complexes $[Ni(3.1b)](BF_4)_2$ and $[Ni(3.5)]I_2$, similar orientations of nitrogen protons occur: two adjacent protons lie on the one side of the donor plane while the remaining two are on the opposite side giving the ligand an overall "step" configuration (see also section 3.2.1). In $[Ni(3.7)](BF_4)_2$, the alternating orientations of the N-H groups leads to a "saddle-shaped" configuration.

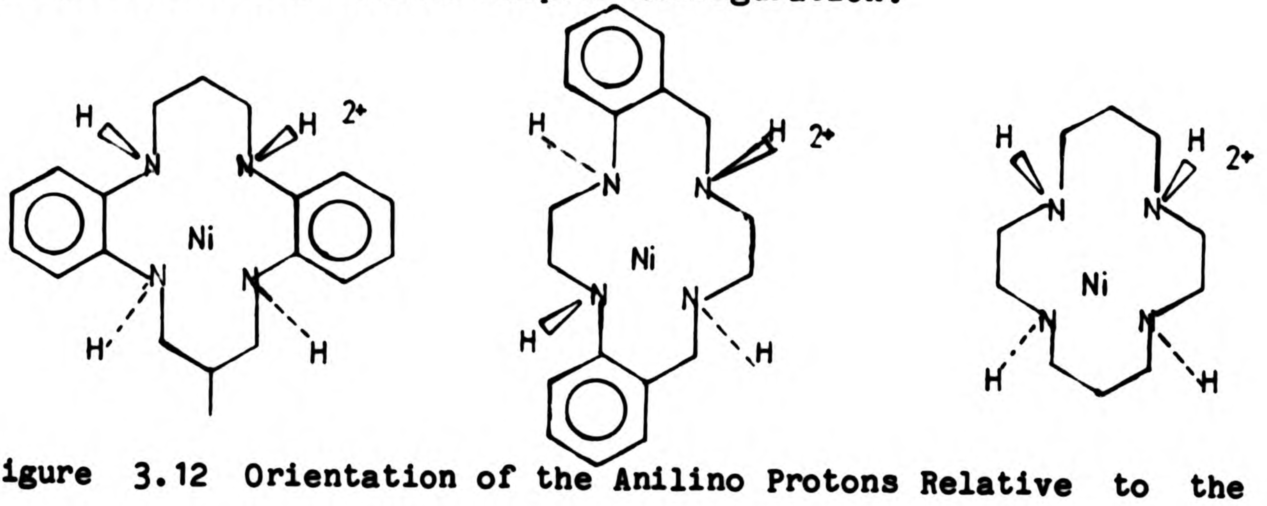
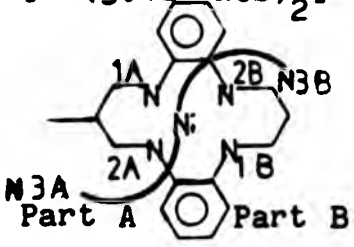
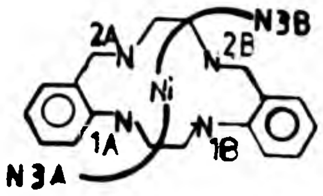
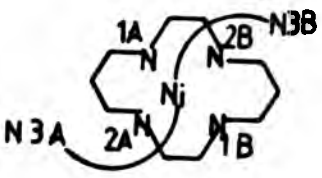


Figure 3.12 Orientation of the Anilino Protons Relative to the N_4 Plane

3.3.3 Comparison of Co-ordination Geometries of the High-spin 14-Membered N_4-Macrocycles

In the case of the high-spin nickel(II) complexes, $[Ni(3.7)(NCS)_2]$ and $[Ni(3.5)(NCS)_2]$, there are only two crystallographically independent Ni-secondary amine bonds. Complex $[Ni(3.7)(NCS)_2]$ has one in-plane Ni-N bond slightly shorter (2.046(2) Å) than the other (2.091(2) Å). For the high-spin cyclam complex, $[Ni(3.5)(NCS)_2]$, the lengths of the equatorial Ni-N bonds are almost identical as is expected. There is no inversion centre in $[Ni(3.1b)(NCS)_2]$ and one equatorial Ni-N bond is slightly shorter (2.082(15) Å) than the others (range (2.104(18)-2.122(16) Å). This short bond is compensated by a slightly longer Ni-N2A bond with the remaining two equatorial Ni-N bonds being quite similar to each other. A CSSR search from the Cambridge Database on nickel(II) octahedral complexes containing thiocyanate groups was carried out and the average Ni-N thiocyanate distance was found to be 2.06 Å (for nine complexes). In both [Ni(3.5)(NCS)$_2$] and [Ni(3.7)(NCS)$_2$], the Ni-N thiocyanate bond lengths are much longer than this (see table 3.14). However, in [Ni(3.1b)(NCS)$_2$] one Ni-N thiocyanate bond length is longer and the other shorter than 2.06 Å. This difference in axial Ni-N bond lengths reflects some tendency for deviation from a regular octahedron towards a "distorted pyramidal" geometry in this complex.

TABLE 3.14 Bond Lengths in High-Spin Nickel(II) Complexes of 14-Membered Macrocycles

	[Ni(3.1b)(NCS)$_2$]^a		[Ni(3.7)(NCS)$_2$]^d	[Ni(3.5)(NCS)$_2$]^e
				
	Part A	Part B		
Ni-N1	2.104(18)	2.082(15)	2.091(2)	2.074(2)*
Ni-N2	2.122(16)	2.114(13)	2.046(2)	2.074(2)
Ni-N3	2.041(14)	2.114(14)	2.108(2)	2.121(3)

a- This work

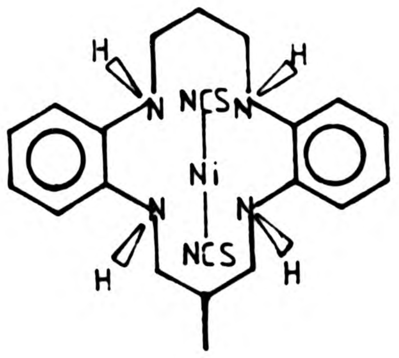
d- ref 46

e- ref 47

*- Average bond lengths for four half molecules in the asymetric unit.

The respective axial Ni-N bond lengths in [Ni(3.7)$(NCS)_2$] and [Ni(3.5)$(NCS)_2$] are longer than those for the in-plane (equatorial) Ni-N distances and thus the structures are pseudo-octahedral.

In [Ni(3.1b)$(NCS)_2$], all the anilino protons are displaced to the same side of the N_4-plane whereas in [Ni(3.7)$(NCS)_2$] the nitrogen protons are alternatively orientated "up" and "down" with respect to the N_4-plane.



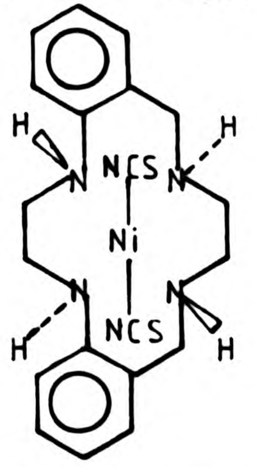


TABLE 3.15 Bond Angles for Thiocyanate Groups for the High-spin Complexes

	[Ni(3.1b)$(NCS)_2$]		[Ni(3.7)$(NCS)_2$]	[Ni(3.5)$(NCS)_2$]^a
	Part A	Part B		
C-N-Ni	156(2)	163(1)	156(2)	156.2(2)-168.2(2)
S-C-N	176(2)	180(2)	178.4(3)	177.8(5)-179.2(2)

a- A range is given for this complex because the asymetric unit contains four independent half molecules.

Hydrogen bonding in [Ni(3.5)$(NCS)_2$] results in deviation of the thiocyanate groups from linearity. The four independent half molecules observed in the structure determination are all involved in weak <u>inter</u>molecular hydrogen-bonding between the secondary amine groups and thiocyanate sulfur atoms in adjacent molecules. The situation is similar to that which occurs in $[Ni(3.1b)(NCS)_2]$ (see section 3.2.1).

3.3.4 Goodness-of fit of the 14-Membered Macrocycles for Low- and High-Spin Nickel(II)

Hole size calculations[48] may be used to estimate the goodness-of-fit of a metal ion for a particular ligand cavity. The radius of the macrocyclic hole (R_H) may be defined by the positions of the donor atoms. R_H is the mean distance of the donor atoms from their centroid. The hole-size radius R_H has to be corrected, (since the donor atoms have a finite radius) before the bonding cavity available (of radius R_A) to the metal ion may be determined. A set of covalent radii for various donor atoms (R_D) have been determined from the Cambridge data base using CSSR searches. In the case of nickel(II), the Pauling covalent radius for low-spin (1.39 Å) or high-spin (1.20 Å) nickel is then subtracted from the mean of the corresponding Ni-donor distances obtained from the data base to give the covalent radius of the donor atoms. The apparent radius (R_A), of the void available for the nickel(II) ion is then given by R_A:

$$R_A = R_H - R_D$$

The ratio $R_A : R_P$ may then be used to assess the goodness-of-fit of the metal ion; an R_A/R_P value of one implies a perfect fit.

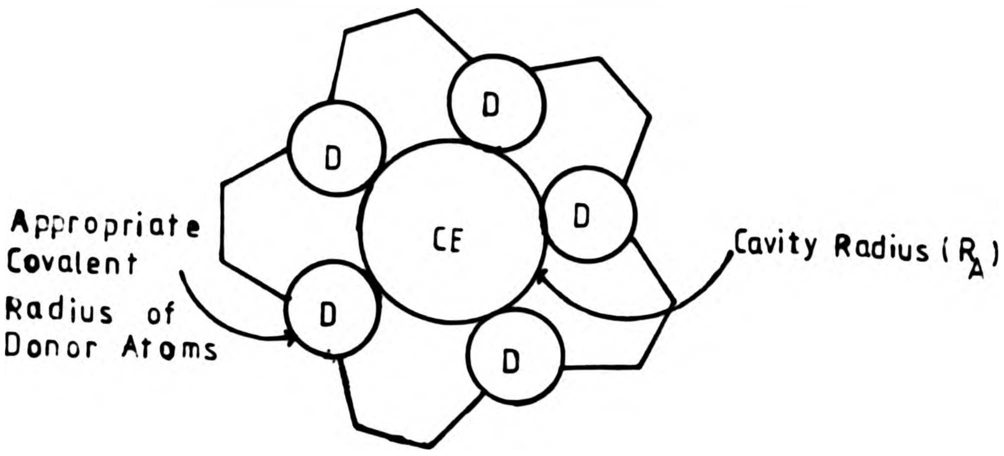


Figure 3.13 Bonding Cavity Radius Available to the Metal Ion

The "hole-size" in the macrocycle 3.1b and its nickel complexes has been calculated in this manner using the X-ray structural data, (table 3.16-see also table 3.17).

TABLE 3.16 Hole-Sizes for the Three Structures

	$[Ni(3.1b)](BF_4)_2$	3.1b		$[Ni(3.1b)(NCS)_2]$
R_H^a/ Å	1.93	1.95		2.11
R_A^b/ Å	1.21	1.23		1.39
R_A/R_P^c	1.01	1.03	0.88	1.00
R_P/ Å	1.20	1.20	1.39	1.39
		for low- nickel(II)	high-spin	

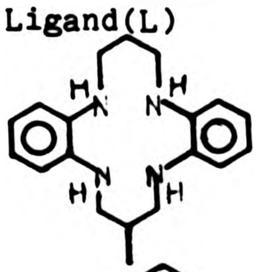
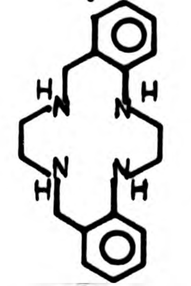
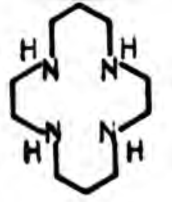
a- Radius of the macrocyclic hole (uncorrected) is defined as the mean distance of the donor atom positions from the centroid.

b- "Apparant" radius of the metal cavity (see text)

c- R_P the Pauling covalent radiusis 1.39 Å for high-spin nickel(II) and 1.20 Å for low-spin nickel(II).

The hole-size in the free ligand 3.1b was found to be 1.95 Å and is intermediate between the values observed for the low- and high-spin nickel(II) complexes but lies slightly closer to that for the $[Ni(3.1b)](BF_4)_2$. This ligand thus appears to provide a relatively good fit for both low-spin and high-spin nickel(II) complexes with the R_A/R_P values being 1.01 and 1.00, respectively. In this regard, the dibenzo-ligand 3.1b appears to be more readily adaptable to the requirements of the high-spin nickel(II) than are the analogues 3.7 and 3.5 (See table 3.17). These ligands each contain a hole-size which is somewhat too small for this high-spin ion. For the low-spin complexes, the hole sizes obtained for all three ligand types on co-ordination appear satisfactory (or perhaps slightly too large) for low-spin nickel(II).

TABLE 3.17 : **Comparison of Hole-sizes of 14-Membered Macrocycles**

Ligand(L)	R_H for $[Ni(L)]^{2+}$	R_H for Ligand	R_H for $[NiL(NCS)_2]$
	1.93^c (R_A/R_P =1.01)	1.95^c	2.11^c (R_A/R_P =1.00)
	1.93^* (R_A/R_P =1.01)	2.02^a	2.07^a (R_A/R_P =0.97)
	1.94^* (R_A/R_P =1.02)	-	2.07^b (R_A/R_P =0.97)

*- Unpublished results Polytechnic of North London, 1985
a- Reference 46
b- Reference 47
c- This work

The hole-size data suggest that ligand 3.1b should fit both low- and high-spin nickel(II) quite well whereas both the aliphatic 3.5 and dibenzo 3.7 ligands appear to match low-spin nickel(II) well but have a smaller hole-size than is ideal for the high-spin nickel(II) ions. The hole-size of the most rigid ligand 3.1b is 1.95 Å and much smaller than that for 3.7 (2.02 Å). However, even though 3.1b is rigid compared to the other two ligands, it is still able to expand or contract its hole-size to accept nickel(II) ions of both spin-states. Although 3.5 is a flexible ligand it still does not appear to present as ideal a cavity to high-spin nickel(II) ions as occurs with 3.1b.

Analysis of the strain energy required to change the ligand geometry to give a better fit for low-spin or high-spin nickel(II) is considered in some detail below.

3.3.5 Molecular Mechanics

"Molecular Mechanics" is an expression used[49] to describe a method to calculate structures and energies for molecules. The method has been applied successfully to organic molecules for many years, and is based on the fact that bonds have "natural" lengths and angles, and simple molecules try to adjust their geometries to attain these values. In addition to to the terms involving deformation of "natural" bond lengths and angles Van der Waals potential functions are included in the calculations to take acount of <u>intra</u>molecular repulsions between atoms.

Molecular mechanic calculations currently involve an empirical approach and the potential functions used are called force fields and contain parameters that are adjusted to give the best fit between calculated and experimental properties of the molecule, such as geometries, conformational energies, heats of formation etc. In the calculations an assumption is made in that[49] simple molecular mechanic force fields interactions such as Van der Waals (VDW) are included and that the sum of all these terms is the steric energy (V) of the molecule.

$$V = \sum V_{stretch} + \sum V_{bend} + \sum V_{torsion} + \sum V_{VDW}$$

The summations are extended over all bonds, bond angles, torsion angles and non-bonded interactions between all atoms not bonded to each other or to a common atom.

Molecular mechanics is thus a complementary technique to experimental methods for structure determinations.

It is only very recently [50-57] that force fields methods have been applied to calculate strain energies in metal complexes. Unlike the organic systems on which a lot of work has been done and for which parameters associated with most common bond types have been optimised, for metal complexes it is more difficult to estimate force field parameters associated with the co-ordination sphere. This is because transition metal ions show a wide range of different co-ordination sphere geometries and metal-ligand bonding is intricate and complex.

Force fields may be used for obtaining various conformations of the free ligand and complexed forms and for calculating hole-sizes for macrocycles[57]. A minimum energy conformation for macrocyclic systems can be calculated as a starting point for hole-size calculations. The match of a particular metal ion for the hole-size of a macrocycle may then be estimated. Results can be compared with the observed hole-sizes in cyclic complexes and goodness-of-fit[48] as estimated from covalent radii of donors (see also section 3.3.4).

Molecular mechanics is thus also a useful tool for the solution in X-ray crystallography problems where the structure is disordered. It is also used in improving the geometry of the molecule from the X-ray crystallography data input. The hole-size can now be predicted from these calculations too.

Molecular mechanic calculations for the free ligand 3.1b and its low-spin $[Ni(3.1b)](BF_4)_2$ and high-spin complex $[Ni(3.1b)(NCS)_2]$ are currently being carried out at James Cook University by Mr Larry Brigden. Preliminary work has involved Allinger's MM1 program[58] but recent work using the MM2 program[59] on $[Ni(3.5)]I_2$ (see below) has shown that this gives better results and eventually all the above three structures will be treated using the MM2 system. Preliminary results for 3.1b and $[Ni(3.1b)(NCS)_2]$ are reported here. Results are still awaited for $[Ni(3.1b)](BF_4)_2$.

3.3.5.1 Free Ligand 3.1b

The starting set of atomic positional co-ordinates for the molecular mechanics calculations were those obtained from the X-ray structure determination. The force field parameters were those from the MM1 system[60].

The angles and bond lengths for the calculated structure are compared with those of the X-ray solution in table 3.18. The mumbering system used for the free ligand is:

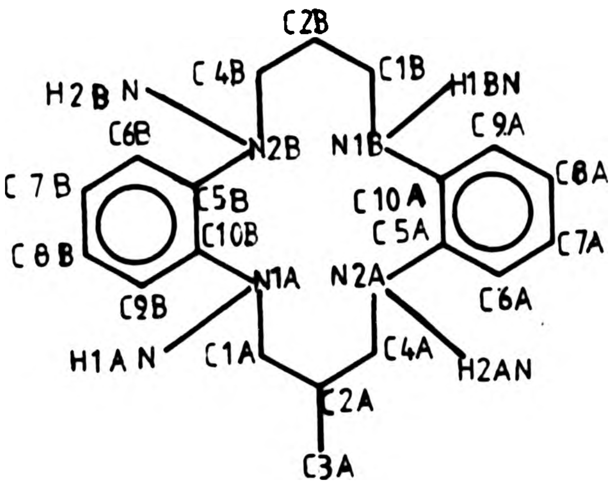


TABLE 3.18 Table of Bond Lengths and Angles of the Calculated Structure from Molecular Mechanics Compared with those from the X-ray Structure Solution of 3.1b

(a) Bond Lengths

Bond	Calculated Structure from Molecular Mechanics	From X-Ray Solution
N1A-C1A	1.46	1.47(2)
N1B-C1B	1.46	1.49(2)
N2A-C4A	1.46	1.46(2)
N2B-C4B	1.46	1.44(2)
N1A-C10B	1.44	1.40(2)
N1B-C10A	1.44	1.43(2)
N2A-C5A	1.44	1.39(2)
N2B-C5B	1.44	1.41(2)
C1A-C2A	1.54	1.49(2)
C1B-C2B	1.54	1.51(2)
C2A-C4A	1.54	1.50(2)
C2B-C4B	1.54	1.52(2)
C2A-C3A	1.54	1.53(2)
C5A-C6A	1.40	1.39(2)
C5B-C6B	1.40	1.36(2)
C6A-C7A	1.40	1.37(2)
C6B-C7B	1.40	1.39(2)
C7A-C8A	1.40	1.35(2)
C7B-C8B	1.40	1.36(2)
C8A-C9A	1.40	1.39(2)
C8B-C9B	1.40	1.36(2)
C9A-C10A	1.40	1.39(2)
C9B-C10B	1.40	1.38(2)
C5A-C10A	1.40	1.41(2)
C5B-C10B	1.40	1.41(2)

Table 3.18 cont

(b) Bond Angles /°

Angle	Calculated by Molecular Mechanics	From the X-ray Solution
C1A-N1A-C10B	120	120(1)
C4A-N2A-C5A	120	118(1)
C10A-N1B-C1B	120	117(1)
C4B-N2B-C5B	120	119(1)
N1A-C1A-C2A	111	112(1)
C1A-C2A-C3A	111	109(1)
C1A-C2A-C4A	112	119(1)
C3A-C2A-C4A	111	108(1)
N2A-C4A-C2A	111	111(1)
N2A-C5A-C10A	116	115(1)
N1B-C10A-C5A	116	115(1)
N1B-C1B-C2B	111	108(1)
C1B-C2B-C4B	113	116(1)
N2B-C4B-C2B	111	109(1)
N2B-C5B-C10B	116	116(1)
N1A-C10B-C5B	116	117(1)

From Table 3.18 it can be seen that in general the calculated geometry of the minimum energy form of the molecule agrees well with the X-ray structure. The maximum differences between calculated and observed bond lengths is 0.05 Å. These differences could in theory be "real", reflecting differences which result from the molecular mechanics calculations being performed on an isolated molecule, while the observed structure is in the solid state and must therefore take into account *inter*molecular interactions, "packing forces". In practice it is more likely that the differences arise because the force field parameters used in the calculations are not the appropriate values for some or all of the components of the molecule. Such an interpretation is supported by the observation (table 3.18) that all the calculated C-C lengths in the benzene ring are 1.40 Å while the observed lengths in the benzene rings vary considerably (admittedly with the relatively high esd's in the determined structure of 3.1b, but often significantly in the X-ray structure determinations of related compounds containing o-substituted benzene rings). Such variations are unlikely to result from packing forces. The lack of variation of C-C lengths in the benzene rings of the calculated structure implies that too large values of the force field stretching C-C parameters have been used for these atoms.

The MM1 parameters which were used initially in the MOLMIN systems developed at James Cook University were established mainly for aliphatic compounds. It is hoped that the agreement for the ligands involved in this thesis and in related projects at James Cook University and ICI Organics Division will be improved when MM2 parameters are used and optimised for o-substituted aromatic systems.

For the initial calculations (using MM1 parameters) sp^2 hybridisation of the anilino nitrogen atoms was assumed. This has resulted in reasonable agreement for bond angles about the nitrogen atoms (see table 3.18). However, calculated lengths of phenylcarbon to nitrogen bonds are significantly greater than observed values and therefore shorter "ideal lengths" for these bonds will be considered in future calculations.

An interesting potential application of the molecular mechanics method is in resolving ambiguities which arise from X-ray structure determinations, for example in predicting relative populations of disordered structures resulting from different conformations of molecules by predicting the relative energies of these conformations, or in predicting the positions of very light atoms which have very low

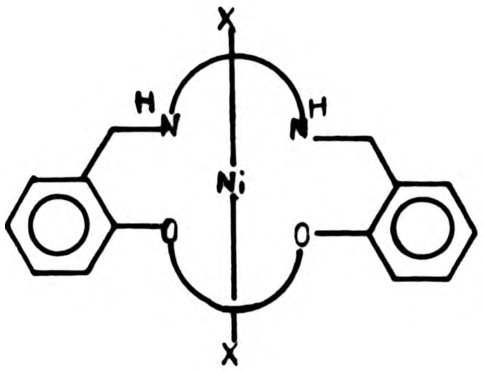
X-ray scattering power and therefore are difficult to "find" in electron density Fourier maps. The latter problem arises with the X-ray determination of 3.1b (see also page 176). Three sites for the hydrogen atom attached to nitrogen N2A were located within a bonding distance of N2A.

	Positional Parameters for H2AN			Energy/kJ mol^{-1}
	x	y	z	
(i)	0.6159	0.2669	0.1393	138.6
(ii)	0.6917	0.0550	0.1310	122.2
(iii)	0.2893	0.2422	0.2426	139.5

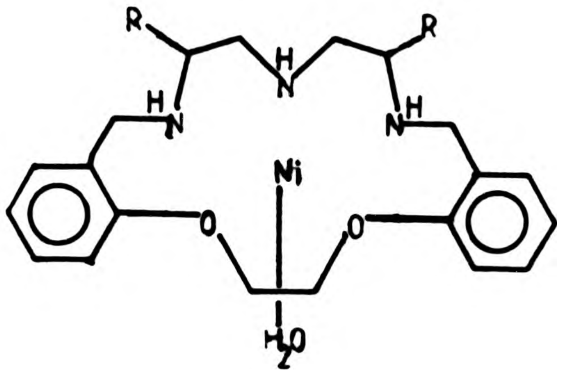
The MOLMIN energy minimisation procedure was applied to three different starting structures containing three different sites of the anilino proton by Mr Brigden at James Cook university. The structure corresponding to the position (ii) gave a significantly lower molecular energy (see table above) and therefore used in the last stages of the X-ray structure refinement (see chapter 4, section 4.7).

3.3.5.2 High-Spin Complex [Ni(3.1b)$(NCS)_2$]

A similar approach was used in the calculations performed on the high-spin complex [Ni(3.1b)$(NCS)_2$]. In this case in addition to the difficulties associated with selection of appropriate parameters for the aromatic components of the ligands (see above), force field parameters have to be established for all the bonds in the co-ordination sphere of the metal atom. The starting set for the calculations on [Ni(3.1b)(NCS)$_2$] was based on values used at James Cook University for calculations[61,62] on nickel(II) complexes of macrocycles with mixed oxygen/nitrogen (phenoxyether:benzylamino) donor sets, e.g. compounds 3.24 and 3.25.



3.24 X=Cl or NCS



3.25 R=H or CH$_3$

Given the uncertainity of the starting set of parameters, the initial agreement between calculated and observed geometry was encouraging. The results shown in table 3.19 have been obtained by Mr Brigden using MM1 parameters for most of the ligand with the exception of the anilino nitrogen atoms. After a series of runs the best agreement between calculated and observed molecular geometry has been obtained by assuming a hybridisation at these nitrogen atoms which is intermediate between sp^2 and sp^3, and setting the Ni-N(anilino) force constant parameters to be significantly smaller than values for benzylamino or aliphatic amine donors. The current agreement between calculated and observed geometry in the co-ordination sphere (see figures 3.15 below) is very encouraging, particularly for the chelate "bite" angles which follow a pattern which would be expected for alternating 5 and 6 membered chelate rings within the structure.

TABLE 3.19 Comparison of Bond Lengths of the Calculated and X-ray Structures of [Ni(3.1b)(NCS)$_2$]

Bond	Calculated from Molecular Mechanics	From the X-ray Solution
Ni-N1A	2.09	2.11(2)
Ni-N2A	2.09	2.12(2)
Ni-N3A	2.06	2.04(1)
Ni-N1B	2.10	2.08(2)
Ni-N2B	2.10	2.11(1)
Ni-N3B	2.09	2.11(1)
N1A-C1A	1.46	1.48(3)
N2A-C4A	1.42	1.42(3)
N1B-C1B	1.45	1.48(3)
N2B-C4B	1.47	1.43(3)
N2A-C5A	1.45	1.46(3)
N1A-C10B	1.45	1.44(2)
N2B-C5B	1.45	1.49(2)
N1B-C10A	1.45	1.49(2)
N3A-C11A	1.16	1.14(2)
C11A-S1A	1.62	1.61(2)
N3B-C11B	1.16	1.15(2)
C11B-S1B	1.62	1.62(2)

The numbering system for the high-spin complex is:

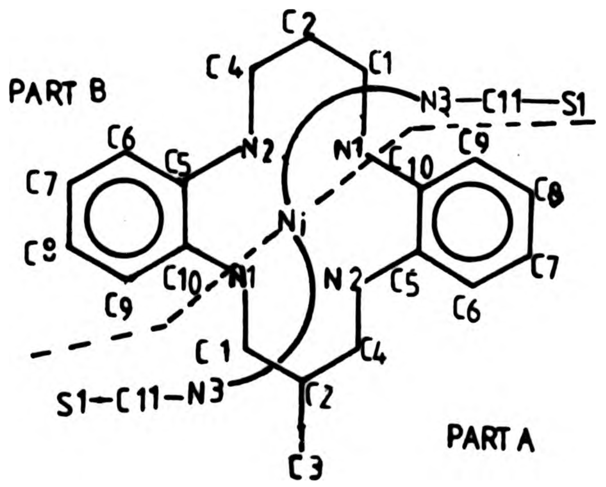
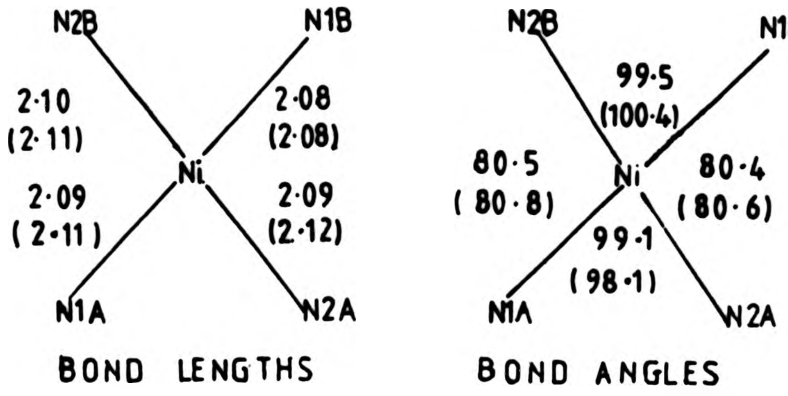
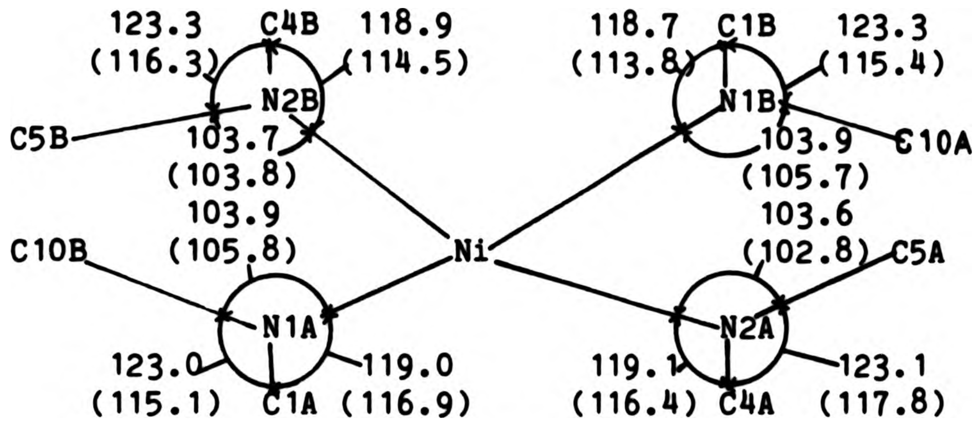


Figure 3.15 Comparisons between MOLMIN calculated minimium energy bond lengths and angles and those observed in the X-ray structure determination (the latter values are in parentheses) of [Ni(3.1b)(NCS)$_2$]





BOND ANGLES INVOLVING NITROGEN DONORS

The bond angles and lengths are similar for the calculated and observed structures. The Ni-N distances for the N_4 donor set were calculated to be approximately 2.09 ∓ 0.01 Å whereas those in the X-ray structure were 2.08 ∓ 0.04 Å. The hole-size of the calculated structure is 2.09_5 Å and is a little smaller than from the X-ray data (2.10_5 Å).

These differences are consistent with the current MOLMIN parameters not yet fully taking into account the weakness of the anilino nitrogen to nickel bond. The starting set parameters have all been based on structures containing more basic nitrogen donors with shorter "ideal" N-Ni lengths and longer force-field stretching parameters.

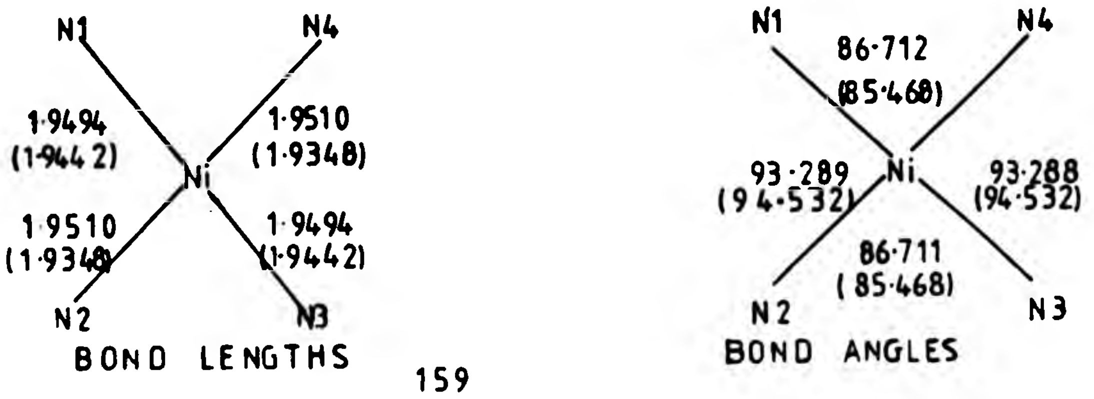
During the solution of the X-ray structure some ambiguity arose in locating the methyl substituents on the propane linkages. Low electron density in the Fourier maps resulted from disorder of the methyl as a consequence of pseudo symmetry with a mirror plane passing through the benzene rings. The alleviations of "axial" or "equatorial" sites could not clearly be resolved, although relative electron densities indicated a higher population of the equatorial site.

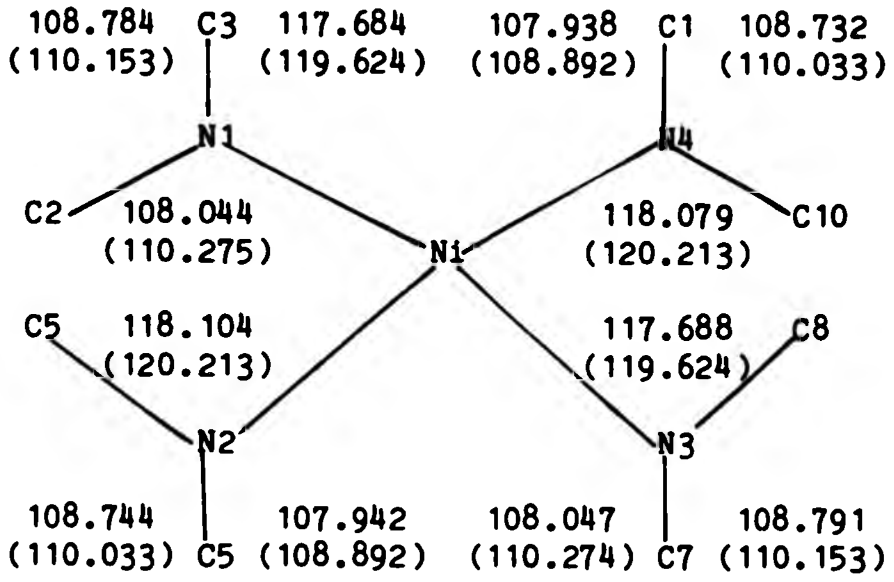
The MOLMIN energy minimisation procedure was applied to two starting structures with methyl substituents in the equatorial and axial positions and the energies of the two forms were found to be 141.1 and 150.7 kJ mol^{-1} respectively. Thus, as expected the equatorial isomer is favoured. Final refinement of the X-ray structure, allowing site occupation factors for the methyl carbon atoms to vary, was in agreement with these calculations, giving an almost negligable occupancy of the axial site.

3.3.5.3 Low-Spin Complex $[Ni(3.1b)](BF_4)_2$

Calculations on the low-spin nickel(II) complex of the ligand 3.1b will be undertaken at James Cook University. For the low-spin nickel(II) complexes force field parameters for the co-ordination sphere had not been devised previously. Such parameters were optimised by Mr L Brigden for the cyclam complex $[Ni(cyclam)]I_2$, using structural data obtained at the Polytechnic by Mr Davide Proserpio. For this structure the MM2 organic parameters were used for the first time. Excellent agreement has been obtained between the calculated and observed geometries (see figure 3.16).

Figure 3.16 Comparison between MOLMIN calculated minimum energy bond lengths and angles and those observed in the X-ray structure determination of $[Ni(cyclam)]I_2$ (the latter values are in parentheses).



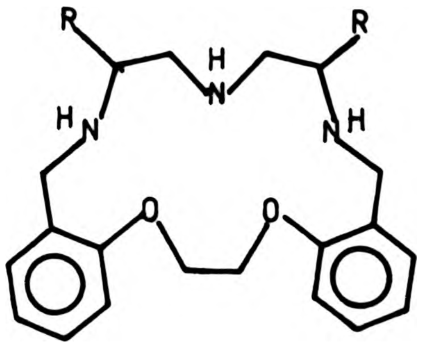


Such agreement is easier to achieve for highly symmetrical structures, but also indicates that the MM2 parameters for aliphatic amines can be used without modification in metal complexes. Work on $[Ni(3.1b)](BF_4)_2$ will require use of some additional parameters for 1,2-diaminobenzene components and will presumably only lead to good agreement between calculated and observed structures if allowance is made for the much poorer donor characteristics for the nitrogen donor atoms in 3.1b when compared with cyclam (3.5).

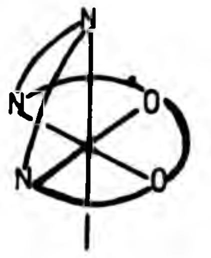
3.3.5.4 Future Applications of Molecular Mechanics Calculations

The results obtained to date from the MOLMIN system are encouraging. Once parameters have been empirically devised for a particular donor set about a metal ion it should prove possible to predict which is the lowest energy of several isomers or configurations and thus to predict the goodness-of-fit of a particular metal ion.

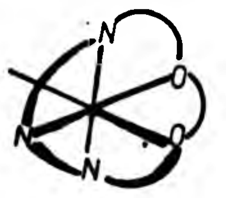
MOLMIN calculations have been able[62] to model a structural dislocation which has been observed for high-spin nickel(II) complexes of quinquedentate O_2N_3-ligands 3.26. For the unsubstituted ligand 3.26a (R=H) it has been shown that the mode of co-ordination with a facial arrangement of the three nitrogen donors (3.27) has significantly lower energy than meridional geometry (3.28). In contrast, the dimethyl substituented ligand 3.26b (R=Me) gives a more stable complex with the mer-geometry (3.27), because severe steric repulsion is found in the fac-arrangement. Consequently the dislocation from one geometry to another which was proposed to account for the significant drop in $\log K_1$ on dimethyl substitution of the ligand is predicted by the MOLMIN calculations.



3.26a R=H
3.26b R=Me



3.27 fac-arrangement
of three N donors



3.28 mer-arrangement
of three N donors

3.4 Conclusions

The systems chosen for study 3.1 were found to be weak bases and very rigid in structure resulting in non-equivalence of methylene protons. Stability constant data have shown that these ligands complex only weakly with transition metal ions. Such weak complexes could be advantageous in solvent extraction systems where the metal needs to be stripped easily after the solvent extractant has picked up the metal. The weak complexation was examplified when metal complexation was attempted in solution. Selectivity was obvious, the O_2N_2 macrocycle 3.1a gave only a copper(II) complex. This was also the case for the S_2N_2 system 3.1c. The N_4 system on the other hand was less selective, complexing with Co(II), Ni(II), Cu(II) and Zn(II). It was the most air-sensitive ligand in solution because of the presence of four anilino groups. However, the N_4-macrocycle gave a very good fit for the nickel(II) ion in both low- and high-spin states. This was also confirmed to some extent by molecular mechanics calculations.

References

1. Micheloni, M., Paoletti, P., Siegfried-Hertlin, L., Kaden, T.A., J. Chem. Soc. Dalton, 1169 (1985).
2. Stability Constants Supplement No 1, Special Publications No 25, The Chemical Society.
3. Armeanu, V., Luca, C., Z. Phys. Chem. (Leipzig), 214, 81 (1960).
4. Nazorova, N.L., Ablov, A.V., Dagaev, V.A., Russ. J. Inorg. Chem., 9, 1150 (1964).
5. Nazarova, N.L., Ablov, A.V., Dagaev, V.A., Russ. J. Inorg. Chem., 9 2129 (1964)
6. Smith in Patai, The Chemistry of the Amino Group, 161-204, Interscience Publishers, New York, (1968).
7. Huitric, A.C.; Carr, J.B., Trager, W.T., Nist, B.J., Tetr. 19, 2145 (1963).
8. Anderegg, G., Ekstrom, A., Lindoy, L.F., Smith, R., J. Amer. Chem. Soc., 102, 2670 (1980).
9. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., Christensen, J.J., Chem. Rev., 85, 271 (1985).
10. Adam, E.K., Lindoy, L.F., Smith, R.J., Anderegg, G., Henrick, K., McPartlin, M., J. Chem. Soc. Chem. Comm., 812 (1979).
11. Adam, K.R., Anderegg, G., Lindoy, L.F., Lip, H.C., McPartlin, M., Rea, J.H., Smith, R.J., Tasker, P.A., Inorg. Chem., 19, 2956 (1980).
12. Lindoy, L.F., Lip, H.C., Rea, J.H., Smith, R.J., Henrick, K., McPartlin, M., Tasker, P.A., Inorg. Chem., 19, 3360 (1980).

13. Unpublished Results, L.F. Lindoy, James Cook University, 1985.

14. Fabbrizzi, L., Paoletti, P., Clay, R.M., Inorg. Chem., 17, 1042 (1978).

15. Hinz, F.P., Margerum, D.W., Inorg. Chem., 13, 2941 (1974).

16. Hinz, F.P., Margerum, D.W., J. Amer. Chem. Soc., 96, 4993 (1974).

17. Barbucci, R., Fabbrizzi, L., Paoletti, P., Vacca, A., J. Chem. Soc. Dalton, 1762, (1973) and references therin.

18. Paoletti, P., Fabbrizzi, L., Barbucci, R., Inorg. Chim. Acta. Rev., 7, 43 (1973).

19. Anichini, A., Fabbrizzi, L., Paoletti, P., Clay, R.M., Inorg. Chim. Acta., 22, L25 (1977).

20. Barbucci, R., Fabbrizzi, L., Paoletti, P., Coord. Chem. Rev., 8 (1972).

21. Clay, R.M., Corr, S., Micheloni, M., Paoletti, P., Inorg. Chem., 24, 3330 (1985).

22. Kodama, M., Kimura, E., J. Chem. Soc. Dalton, 2296 (1977).

23. Weatherburn, D.C., Billo, E.J., Jones, J.P., Margernum, D.W., Inorg. Chem., 9, 1557 (1970).

24. Kodama, M. Kimura, E., J. Chem. Soc. Chem. Comm., 326 (1975).

25. Kodama, M., Kimura, E., J. Chem. Soc. Chem. Comm., 891 (1975).

26. Kodama, M., Kimura, E., J. Chem. Soc. Dalton, 2235 (1976).

27. Diaddario, L.L., Zimmer, L.L., Jones, T.E., Sokol, L.S.W.L., Cruz, R.B., Yee, E.L., Ochrymowycz, L.A., Rorobacher, D.B., J. Amer. Chem. Soc., 97, 7485 (1975).

28. Kodama, M., Kimura, E., J. Chem. Soc. Dalton, 1473 (1977).

29. Thom, V.J., Hosken, G.D., Hancock, R.D., Inorg. Chem., 24, 3378 (1985).

30. Leugger, A.P., Hertlin, L., Kaden, T.A., Helv. Chim. Acta., 61, 2298 (1978).

31. Micheloni, M., Sabatini, A., Paoletti, P., J. Chem. Soc. Perkin II, 828 (1978).

32. Kodama, M., Kimura, E., J. Chem. Soc. Dalton, 116, 1720 (1976).

33. Micheloni, M., Paoletti, P., Inorg. Chim. Acta., 43, 109 (1980).

34. Basolo, F., Coord. Chem. Rev., 3, 213 (1968).

35. Fleischer, E.B., Gebala, A.E., Tasker, P.A., Inorg. Chim. Acta., 6, 72 (1972).

36. Peng, S., Goedken, V.L., J. Amer. Chem. Soc., 98, 8500 (1976).

37. Kimura, E., Machida, R., Kodama, M., J. Amer. Chem. Soc., 106, 5497 (1984).

38. Jubran, N., Cohen, H., Meyerstein, D., Isreal J. Chem., 25, 118 (1985).

39. Fabbrizzi, L., Licchellic, M., Perotti, A., Poggi, A., Soresi, S., Isreal J. Chem., 25, 112 (1985).

40. McAuley, A., Norman, P.R., Isreal J. Chem., 25, 106 (1985).

41. Chakravorty, A., Isreal J. Chem., 25, 99 (1985).

42. Leumann, C., Eschenmoser, A., J. Chem. Soc. Chem. Comm., 20, 1365 (1984).

43. Leumann, C., Eschenmoser, A., J. Chem. Soc. Chem. Comm., 20, 1368 (1984).

44. Beley, M., Collin, J., Ruppert, R., Sauvage, J., J. Chem. Soc. Chem. Comm., 1315 (1984).

45. Griggs, C., Hason, M., Henrick, K.F., Matthews, R.W., Tasker, P.A., Inorg. Chim. Acta., 25, L29 (1977).

46. Henrick, K.F., Lindoy, L.F., McPartlin, M., Tasker, P.A., Wood, M.P., J. Amer. Chem. Soc., 106, 1641 (1984).

47. Ito, T., Kato, M., Ito, H., Bull. Chem. Soc. Jpn., 57, 2641 (1984).

48. Henrick, K.F., Tasker, P.A., Lindoy, L.F., Prog. Inorg. Chem., 33, 1 (1985).

49. Burbert, U., Allinger, N.L., Molecular Mechanics, A.C.S. Monograph 177, American Chemical Society, Washington D.C., (1982).

50. Endicott, J.F., Brubaker, G.R., Ramasami, T., Bumar, K., Dwarakanath, K., Cassel, J., Johnson, D., Inorg. Chem., 22, 3754 (1983).

51. Thom, V.J., Boeyens, J.C.A., McDougall, G.J., Hancock, R.D., J. Amer. Chem. Soc., 106, 3198 (984).

52. Thom, V.J., Fox, C.C., Boeyens, J.C.A., Hancock, R.D., J. Amer. Chem. Soc., 106, 5947 (1984).

53. Hung, Y., Martin, L.Y., Jackels, S.C., Taik, A.M., Busch, D.H., J. Amer. Chem. Soc., 99, 4029 (1977).

54. DeHayes, L.J., Busch, D.H., Inorg. Chem., 12, 1505 (1973).

55. Brubaker, G.R., Johnson, D.W., Coord. Chem. Rev., 53, 1 (1984).

56. Hambley, T.W., J. Chem. Soc. Chem. Comm., 1228 (1984).

57. Drew, M.G.B., Hollis, S., Yates, P.C., J. Chem. Soc. Dalton, 1829 (1985).

58. Allinger, N.L., Yuh, Y.H, MM1 Q.C.P.E. no 318, Quantum Chemistry Program Exchange, Indiana University Chemistry Department, Indiana, U.S.A., modified version.

59. Allinger, N.L., Yuh, Y.H., MM2 Q.C.P.E. no 395, Quantum Chemistry Program Exchange, Indiana University Chemistry Department, Indiana, U.S.A., modified version.

60. Wertz, D.H., Allinger, N.L., Tetr., 30, 1579 (1974).

61. Adam, K.R., Bridgen, L.G., Lindoy, L.F., Unpublished results, 1985.

62. Adam, K.R., Brigden, L.G., Lindoy, L.F., McPartlin, M.R., Mimnagh, B., Tasker, P.A., J. Chem. Soc. Chem. Comm., 710 (1985).

CHAPTER 4: X-RAY STRUCTURE DETERMINATION

CHAPTER 4: X-Ray Structure Determination

4.1 Single Crystal X-ray Diffraction

Single crystals were selected using a binocular microscope and were mounted in a random orientation at the end of a quartz fibre and centred upon the goniometer head of a four circle computer controlled Philips PW 1100 X-ray diffractometer using translational arcs. X-Rays from a molybdenum target (λ= 0.71069 Å) were used with a graphite crystal monochromator. Initially the computer moved the four circles systematically in small increments until diffraction was detected and the setting angle of the reflection were measured. The angular ranges scanned in every case were θ = 4 to 15 °, χ = -80 to 80 ° and ϕ = 0 to 360 °. The procedure was continued until the setting angles of 25 reflections had been found. The angles from the reflections were used by the computer to calculate the primitive unit cell, and to get the orientation matrix relative to the diffractometer axes. The original unit cell found by the diffractometer was examined as well as the the M-matrix which is related to the unit cell dimensions. The crystal cell type (e.g. triclinc etc.) was determined from the unit cell shape and the intensity relationships, i.e. for triclinic $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$ (where I is the intensity for an hkl reflection).

The original 25 reflections were replaced by 25 high angle reflections θ= 10 °) to get a more accurate unit cell.

4.2 Data Collection

All the unique reflections within a range of 3 to 25 ° were scanned at a constant speed of $0.05^\circ\ s^{-1}$ and a scan width of 1.00 ° using a $\theta/2\theta$ scan mode. Data recorded at this stage were hkl values, total scan counts and background measurements which were recorded on magnetic tape.

Reflections with total number of counts in the first scan <500 were scanned again to increase their accuracy. All "unique" data were collected for the cell type e.g. for triclinc hkl, $\bar{h}kl$, $\bar{h}\bar{k}l$, $h\bar{k}l$. Background measurements were made at both ends of the scan. The computer was then used to calculate a preliminary value of the intensity (I_{hkl})prel. by subtracting the two background counts from the total counts.

$$(I_{hkl})\text{prel.} = \text{Total counts} - \text{Total background counts}$$

Each (I_{hkl})prel. value was then corrected by the computer for Lorentz and polarization factors (which are geometric factors). This was done using

$$I_{hkl} = (I_{hkl})\text{prel.} \times 1/L_p$$

where L_p is the Lorentz polarization factor, which varies from instrument to instrument, by a program written for the Philips diffractometer.

Reflections with $I_{hkl} < 3\sigma$ were rejected (σ is the standard deviation). Equivalent reflections were averaged to give the total number of reflections.

4.3 Determination of the Space Group

From the corrected data the amplitude of the structure factors ($|F_{hkl}|$) were determined from

$$I_{hkl} \propto |F_{hkl}|^2$$

and systematic absences in the intensity data were considered to help determine the space group.

4.4 Solution of the Structure

This was done by using "direct methods" for the free ligand (see section 4.7) and by the "heavy atom method" for the metal complexes using Patterson vector maps for the position of heavy atoms and also for the confirmation of the space group (see section 4.9).

4.5 Patterson Vector Map Solution

The Patterson map is a map which relates peak height (of the heavy atoms) with the vectors between respective atoms.

The Patterson vector map may be used to locate the position of the heavy atoms.

From the intensity data a Patterson vector map is then obtained using the Fourier summation

$$P_{(u,v,w)} = \frac{1}{V}\sum_{hkl} I_{hkl} e^{-2\pi i(hu + kv + lw)}$$

where $P_{(u,v,w)}$ corresponds to a vector or Patterson density at point (u,v,w) and V is the volume of the unit cell. A Patterson map is a three dimensional map where there is a peak for every pair of atoms inside the unit cell.

One peak is obtained from the map for two atoms in the unit cell, situated at a distance and a direction from the origin equivalent to vector between the pair of atoms, so that for any atoms at (x_1,y_1,z_1) and (x_2,y_2,z_2) a peak occurs in the map at

$$u = x_1 - x_2$$
$$v = y_1 - y_2$$
$$w = z_1 - z_2$$

The height of every peak in the Patterson map is proportional to the products of the atomic numbers of the two atoms Z_1 and Z_2 respectively. This implies that the peaks due to the heavy atom are readily distinguishable as they have large peak heights.

4.6 Structure Solutions and Refinements

Calculated structure factor values are obtained using the co-ordinates x_n,y_n,z_n of the atoms

$$(F_{hkl})_c = \sum_{n=1}^{n=N} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

where n corresponds to the heavy atom and f_n is the scattering factor for the n^{th} heavy atom, and N is the total number of atoms, hence initially

$$F_c = f_{HA}e^{2\pi i(hx_{HA} + ky_{HA} + lz_{HA})}$$

gives an approximate value for F_c based on one heavy atom (HA).

The observed structure factors and the calculated signs from the calculated structure factors were used to calculate the electron density map given by

$$\rho_{xyz} = \frac{1}{V} \sum_{hkl} S_c \, |F_o| e^{-2\pi i(hx + ky + lz)}$$

where S_c is the calculated sign, F_o is the modulus of the observed structure factor.

It was then possible to assign peaks from the map and thus positions of further atoms were obtained and used to calculate better values of F_c, and thus more correct signs and hence a better map. This iterative process was continued until all the atoms had been located.

The atomic co-ordinates and thermal parameters together with the overall scale factor (K) were varied in a 3-dimensional least square refinement.

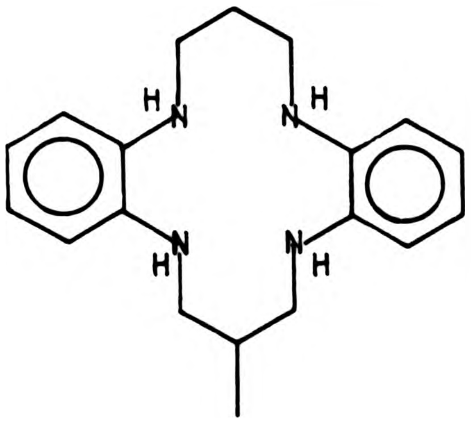
The matrix which relates all components in the least squares procedures was then inverted to give the standard errors on all the refined parameters. From all the values of the atomic positional parameters x, y and z and their standard deviations the complete geometry of the molecule was obtained (i.e. all the bond lengths and interbond angles together with their estimated standard deviations).

In the final stages selected non-hydrogen atoms were assigned anisotropic thermal parameters whereas the remaining atoms and all the hydrogen atoms had isotropic thermal parameters. A final R-factor was thus obtained from:

$$R = \frac{\sum (K|F_o| - |F_c|)}{\sum K|F_o|}$$

4.7 X-Ray Structure Determination of the Free Ligand $C_{19}H_{26}N_4$

Crystal data: $C_{19}H_{26}N_4$, M_r = 310.4, monoclinic space group $P2_1/c$, a = 12.843(2), b = 5.449(1), c = 23.839(4) Å beta = 101.52(2) °, V = 1634.51 Å^3, Z = 4, $d_{(calc)}$ = 1.261 g cm^{-3}. Crystal size = 0.32 x 0.39 x 0.29 mm, Mo-K_α radiation, λ = 0.71069 Å, number of reflection data = 2870, $[I > 3\sigma(I)]$.



Pale yellow crystals of $C_{19}H_{26}N_4$ separated from a toluene solution upon prolonged standing. A scan width of θ = 1.0 ° was used with a background measuring time of 10 seconds, to collect data of type hkl etc. Three standard reflections were measured every 3 hours during data collection and showed no significant variations in intensity.

From the relationship of the parameters of the unit cell and intensity relationships $(I_{hkl} = I_{\bar{h}\bar{k}\bar{l}} = I_{h\bar{k}l} = I_{\bar{h}kl})$ a monoclinic space group was assumed. Systematic absences in data for 0k0 (where k was odd) and h0l (where l was odd) were observed and indicated that the space group is $P2_1/c$. Since no heavy metals were present in the molecule a "direct methods" solution was used to determine the structure. This was solved using the SHELX program by TANGENT multisolution refinement with values of E > 1.2. The starting origin and multisolution phases were selected as in table 4.1.

TABLE 4.1 Origin and Multisolution Phases

Origin h	k	l	E	Multisolutions h	k	l	E
6	3	8	3.340	-13	0	6	4.248
-11	0	6	4.240	-13	2	14	2.705
-1	1	5	1.539	-4	3	14	3.358
				-3	1	1	1.461

From the E map with the highest figure of merit of 0.144 the non-hydrogen atoms were found from the highest 23 peaks. All the N-H and C-H hydrogen atoms were located from a Fourier difference map except one hydrogen of the methyl substituent (H3A2) and an aromatic hydrogen atom (H7A). Hydrogen atoms H3A2 and H7A were thus placed in calculated positions "riding" on the atoms to which they were bonded at a fixed distance of 1.08 Å. All the hydrogen atoms were unrefined. Anistropic thermal parameters were assigned to all non-hydrogen atoms and the hydrogen atoms were given a common thermal parameter of 0.08 $Å^2$. There was some uncertainity in the assignment of the position of one anilino hydrogen atom (H2AN). Three sites of electron density were detected near the nitrogen atom N2A.

Fractional Coordinates

	x	y	z
(i)	0.6159	0.2269	0.1393
(ii)	0.6917	0.0550	0.1310
(iii)	0.2893	0.2422	0.2426

Position (ii) was selected for H2AN on the basis of strain energy calculated as described in section 3.3.5. A final R-factor of 0.1093 and R_w of 0.1051 were obtained.

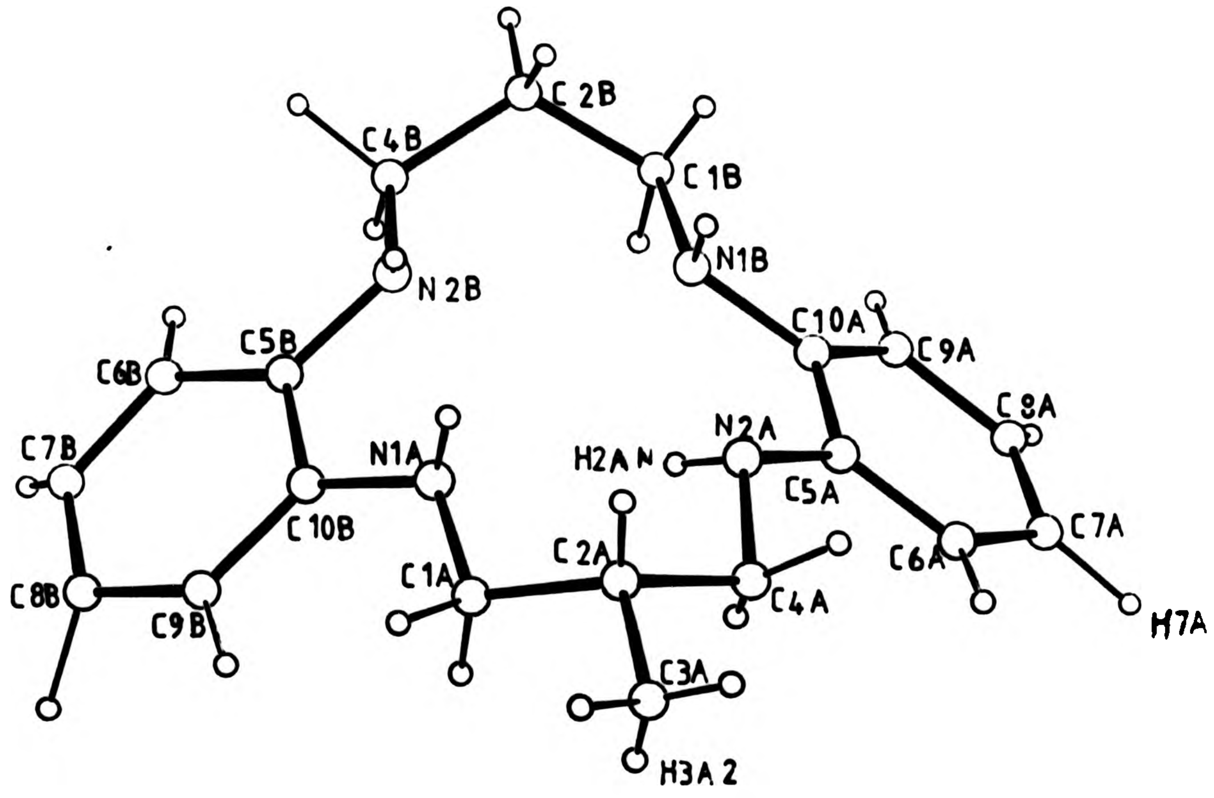
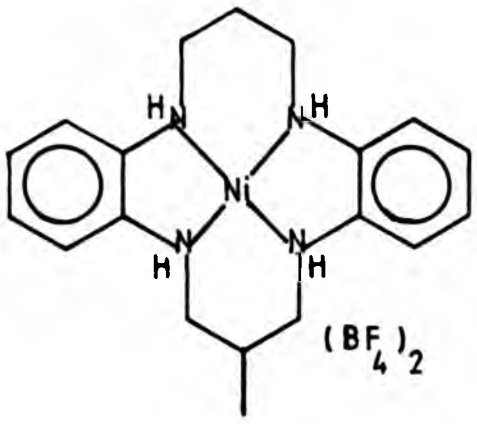


Figure 4·1 Ortep diagram of ($C_{19}H_{26}N_4$).

4.8 X-ray Structure Determination of $[Ni(C_{19}H_{26}N_4)](BF_4)_2$



Crystal Data: $C_{19}H_{26}N_4B_2F_8Ni$ M_r = 542.8, triclinic space group $P\bar{1}$, a = 9.200(2), b = 8.549(2), c = 7.994(2) Å, alpha = 109.10(2), beta = 112.91(2), gamma = 74.17(2) °, V = 938.22 Å^3, Z = 1, d_{calc} = 1.674 g cm^{-3}. Crystal size = 0.18 x 0.19 x 0.21 mm, Mo-K_α radiation, λ= 0.71069 Å, number of reflection data = 1108 [$I \geq 3\sigma(I)$].

An orange single crystal obtained from a methanolic reaction solution was used for data collection and structure determination. The orientation matrix and crystal system (triclinic) were determined by the same procedures as outlined above (section 4.7). The calculated density implied that there is one molecule in the unit cell, Z = 1. There are two space groups available for a triclinic unit cell, P1 or $P\bar{1}$, which have one and two equivalent positions respectively.

Initially the $P\bar{1}$ space group was assumed which required the nickel atom to be located at the centre of symmetry (e.g. at the origin of the unit cell 0,0,0) because Z = 1. A Fourier map phased with this assignment for the nickel atom revealed the sites of all the other non-hydrogen atoms. The electron density for the methyl group was half that of a "full" methyl group thus C3A was assigned half occupancy. This disorder is an inevitable consequence of the molecule being sited on a crystallographic inversion centre, because only the methyl substituent prevents the molecule from having a centre of symmetry. Refinement in the centrosymmetric space group yielded normal thermal parameters for all atoms and difference Fourier electron density maps revealed only maxima which could be ascribed to hydrogen atoms. Consequently no attempt was made to refine the structure in the P1 space group since sufficent data was not available for this solution. All the hydrogen atoms were found from the difference Fourier maps except for H1A2, H4A2, H9A and the methine protons (H2B1), which were included in calculated positions, "riding" at a fixed distance of 1.08 Å. H2A2 was also given half occupancy. The methyl hydrogens were not located or calculated. In the final cycles of refinement, anisotropic thermal parameters were assigned to all non-hydrogen atoms and all the hydrogen atoms were given a common thermal parameter of 0.05 Å^2. This resulted in R = 0.0732 and R_w of 0.0723.

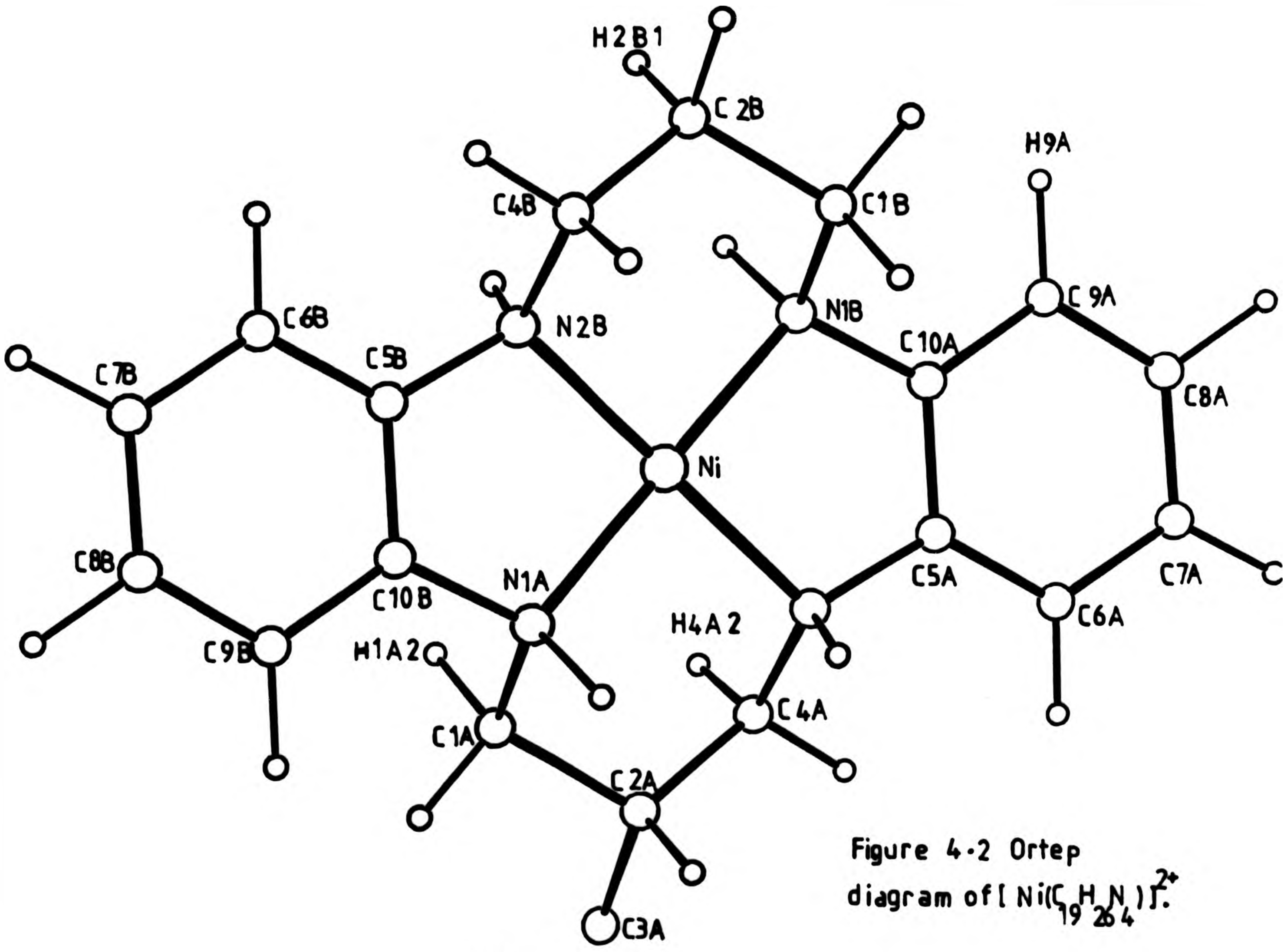
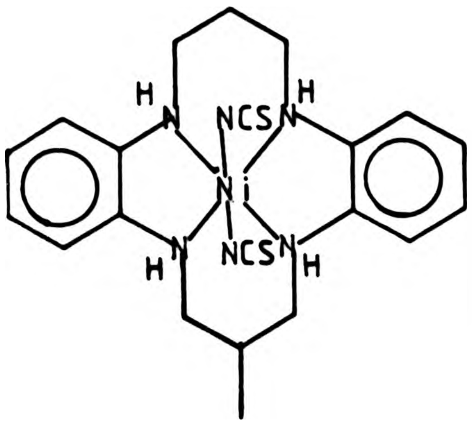


Figure 4·2 Ortep diagram of [Ni($C_{19}H_{26}N_4$)]$^{2+}$.

4.9 X-Ray Structure Determination of $[Ni(C_{19}H_{26}N_4)(NCS)_2]$



Crystal Data: $C_{21}H_{26}N_6S_2Ni$, M_r = 485.32, monoclinic space group $P2_1/n$, a = 13.210(2), b= 15.926(3), c = 11.184(2) Å, beta = 103.05(2), V = 2292.15 $Å^3$, Z = 4, $d_{(calc)}$ = 1.406 g cm^{-3}. Crystal size = 0.06 x 0.78 x 0.07 mm, Mo-K_α radiation, λ = 0.71069 Å, number of reflection data = 1250 [$I \geqslant 3\sigma(I)$].

A pink needle-like crystal obtained from the methanolic reaction mixture was used for data collection. The orientation matrix and crystal system (monoclinic) were determined by the same procedure as outlined above (section 4.7). Systematic absences in hkl data (when h0l, h+l=2n+1 and 0k0, when k=2n+1) indicated that the space group is $P2_1/n$, a non-standard solution of $P2_1/c$.

A Patterson map was used to solve the structure.

TABLE 4.2 Equivalent positions for the space group $P2_1/n$

(i)	x, y, z
(ii)	-x, -y, -z
(iii)	0.5 - x, 0.5 + y, 0.5 - z
(iv)	0.5 + x, 0.5 - y, 0.5 + z

TABLE 4.3 Unique vectors between the four symmetry related nickel atoms

(a) (i)-(ii) = 2x, 2y, 2z

(b) (iii)-(i) = 0.5 - 2x, 0.5, 0.5 - 2z

(c) (iv)-(i) = 0.5, 0.5 - 2y, 0.5

TABLE 4.4 Patterson Synthesis from the Diffraction Data of the Complex $[Ni(C_{19}H_{26}N_4)(NCS)_2]$

	Height (arbitrary units)	u	v	w
Q1	999.	0.000	-0.000	0.000
Q2	999.	0.000	-0.000	1.000
Q3	447.	0.500	0.278	0.500
Q4	318.	0.072	0.500	0.806
Q5	270.	0.298	0.500	0.208
Q6	269.	0.367	-0.000	0.009
Q7	269.	0.367	-0.000	1.009
Q8	177.	0.434	0.221	0.705
Q9	156.	0.160	0.000	0.036
Q10	155.	0.130	0.279	0.498
Q11	144.	0.197	0.225	0.291
Q12	140.	0.327	-0.000	0.483
Q13	138.	-0.003	0.094	0.867
Q14	138.	0.003	0.094	0.133
Q15	117.	0.241	0.500	0.847
Q16	107.	-0.003	0.037	0.713
Q17	107.	0.003	0.037	0.287
Q18	105.	0.314	0.500	0.902
Q19	104.	0.011	-0.000	0.429
Q20	100.	0.195	0.243	0.636

The position of the nickel atom was deduced using the two highest vector peaks from the Patterson map. These were assigned to vectors of the type (c) and (b) above respectively.

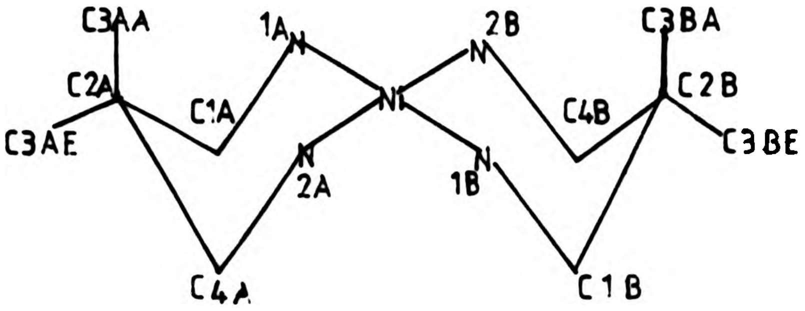
TABLE 4.5 Vectors Between the Nickel Atoms

Vector				Patterson Peak				
(c)	0.5,	0.5 - 2y,	0.5	Q3	447	0.500	0.278	0.500
(b)	0.5 - 2x,	0.5,	0.5 - 2z	Q4	318	0.072	0.500	0.806
(b)-(c)	-2x,	2y	-2z			-0.428	0.222	0.306

Therefore -2x, 2y, -2z is equivalent to (-0.428), 0.222, (0.306) i.e. 2x, 2y, 2z would be at 0.428, 0.222, -0.306. A vector which corresponds to this in the Patterson map is

Q8 177 0.434 0.221 0.705

Thus the vector between the two nickel atoms is Q8 and so 2x, 2y, 2z is 0.434, 0.221, 0.705. The co-ordinates of the nickel atom at x, y, z would have half of these values. The co-ordinates of the nickel atom are therefore 0.217, 0.110, 0.352. The co-ordinates of the nickel atom were used to phase a Fourier map used to determine the complete structure. The hydrogen atoms were included in calculated positions, "riding" on the carbon atoms to which they were bonded at a fixed distance of 1.08 Å, and were assigned a common thermal parameter of 0.08 Å^2. The anilino hydrogen atoms were found from a difference Fourier map. The position of the methyl substituents on the propane bridge could not be readily determined from the Fourier maps. Low poorly resolved, peaks were found at bonding distances from the central carbon at both propane bridges. This was interpreted as due to disorder of the molecule since the observed structure (minus the methyl group) was very close to having pseudo mirror symmetry. There were two positions available for each methyl because of the possibility of axial and equatorial positioning.



Each methyl was given half occupancy but the thermal paramaters obtained in the refinement of the structure were too high and thus the occupancy of the methyl carbons was varied until reasonable thermal parameters were obtained. The axial position of the methyl was found to be less favourable than the equatorial position because the axial carbons had higher thermal parameters when compared with the equatorial. The best solution was when both the equatorial methyl carbons were given an occupancy of 0.4 and those in axial position an occupancy of 0.1 (an occupancy of 0.1 is even less than that of a hydrogen atom). In the final run equatorial methyl carbon atoms (C3AE and C3BE) with half occupancy were assigned to both sites at idealised positions since the equatorial positioning is predominant. The hydrogens on the carbon with the methyl substituents were calculated and also given half occupancy. Anisotropic thermal parameters were assigned to all the heteroatoms, nickel and carbon atoms C1A, C2A and C4A. Thermal parameters for carbon atoms of the propane bridge of part A were relatively high when compared to those of the other propane bridge (C1B, C2B and C4B). All the atoms were refined in the structure except hydrogen atoms and the two methyl carbons to give an R of 0.0849 and R_w of 0.0812.

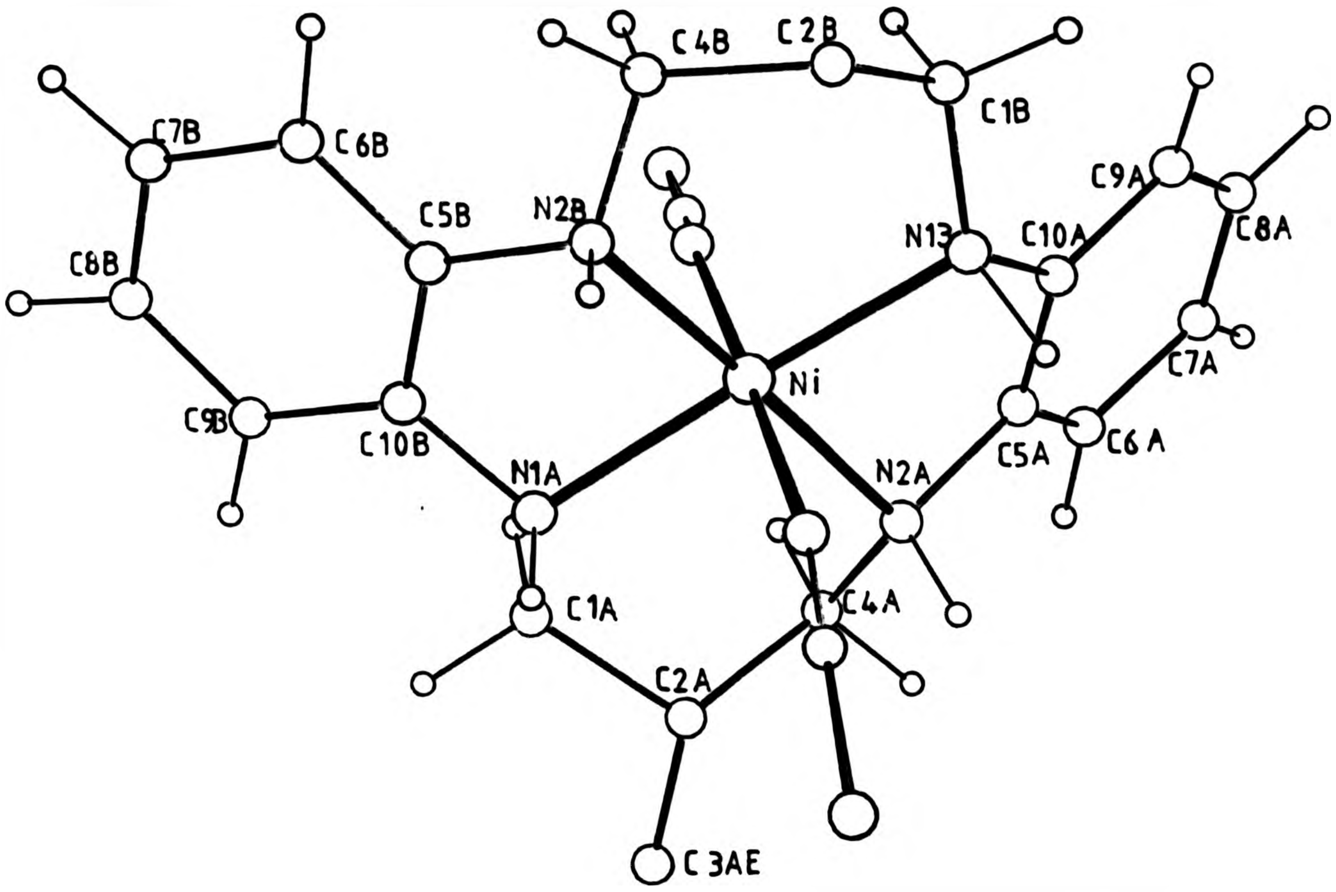


Figure 4·3 Ortep diagram of $[(C_{19}H_{26}N_4)(NCS)_2]$.

4.10 References

General reference : Sheldrick, G.M., SHELEX Program. The University of Cambridge, (1976).

CHAPTER 5-EXPERIMENTAL SECTION

CHAPTER 5 Experimental Section

General Experimental

All infrared spectra were obtained either as nujol and hexachlorobut-1,3-diene mulls of the samples between KBr discs or as KBr discs of the solids. The spectra were run on Pye Unicam SP3 200, SP 2000 or Perkin-Elmer 781 spectrometers. Mass spectra and microanalyses were done at ICI Organics Division and the analytical department, Polytechnic of North London. ^{1}H nmr spectra (60 MHz) were obtained on a Perkin-Elmer R12B. ^{1}H nmr spectra (220 MHz) were obtained from P.C.M.U., and ^{13}C nmr spectra and ^{1}H nmr (80 MHz) were run on a Bruker WP 80. X-ray crystallographic data were obtained on a Philips PW 1100 diffractometer with Mo-K_{α} radiation.

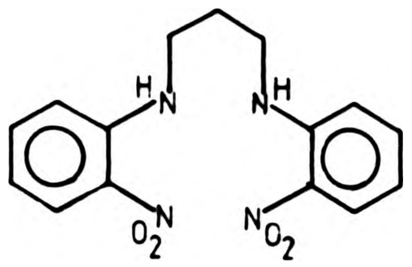
All chemical and solvents were used as obtained from the manufacturers except the following which were treated before use:

(i) THF was dried by distilling over sodium/benzophenone

(ii) Pyridine was dried over potassium hydroxide

(iii) Tosyl chloride was recrystalliseed from dichloromethane-cyclohexane.

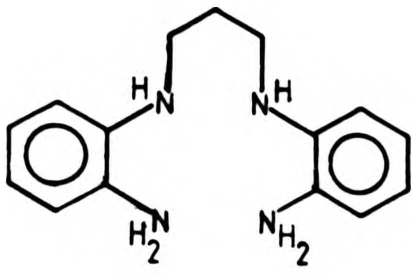
1,3-Bis(*o*-nitrophenylamino)propane 5.1



5.1

Yellow crystals of 1-chloro-2-nitrobenzene (599.15 g, 3.80 mol) were heated with 1,3-diaminopropane (105.8 cm^3, 1.26 mol). When all the 1,3-diaminopropane had reacted the orange solution practically solidified and HCl was no longer evolved. The solution was kept from solidifying by heating and stirring vigourously for 4 hours. This was then added to ethanol (1500 ml). The solid was collected and washed with diethyl ether (900 cm^3), toluene (900 cm^3) and sodium methoxide (2 mol dm^{-3}) solution (300 cm^3), and dried in vacuo. Orange crystals of 1,3-bis(*o*-nitrophenylamino)propane 5.1 (241.23 g, 0.76 mol, 61 %) were recrystallised from 1,2-dichloroethane, m.p. 152-153 °C. Found C, 56.11; H, 5.30; N, 17.56; requires C, 56.96; H, 5.06; N, 17.72 %, for $C_{15}H_{16}O_4N_4$, m_r = 316. ν/cm^{-1}: 760, 788, 1060, 1180, 1350, 1400, 1480, 1560, 1588, 1600, 1637, 2860, 2880, 3040, 3400. ^{1}H nmr (60 MHz, CDCl$_3$), δ /ppm: 2.35(p, *J* 6.6 Hz, 2H $\text{-NHCH}_2\underline{\text{CH}_2}$); 3.55(t, *J* 6.6 Hz, 4H $\text{-NH}\underline{\text{CH}_2}$); 6.50-8.40(mc, 10H-aromatic and $\text{-CH}_2\underline{\text{NH}}$). ^{13}C nmr (20.12 MHz, CDCl$_3$), δ /ppm: 28.5, 40.5, 113.6, 115.7, 127.0, 127.4, 136.4, 145.3.

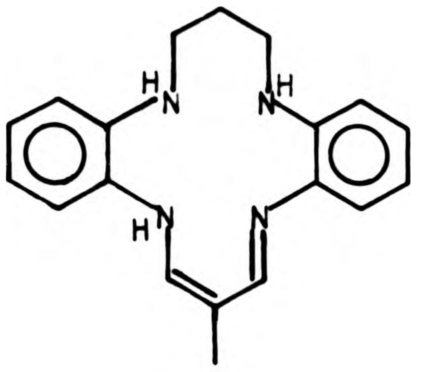
1,3-Bis(o-aminophenylamino)propane 5.2



5.2

To the refluxing orange solution of 1,3-bis(o-nitrophenylamino)propane 5.1 (10.0 g, 40.0 mmol) in 99 % ethanol (450 cm^3) was added 5 % palladium on activated carbon (0.5 g) as an ethanol slurry, and hydrazine hydrate (20 cm^3). These were added dropwise alternatively under a nitrogen atmosphere. When all the additions had been completed the solution was refluxed for 4 hours. On filtration a pale orange solution was obtained. After total evaporation under vacuum and on addition of 50 % aqueous ethanol, pale pink needles were obtained of 1,3-bis(o-aminophenylamino)propane 5.2 (8.85 g, 34.52 mmol, 87 %). Recrystallisation was from 50 % aqueous ethanol, m.p. 79.5-80.0 °C. Found C, 70.78; H, 7.60; N, 21.33; requires C, 70.28; H, 7.86; N, 21.86 %, for $C_{15}H_{20}N_4$, m_r = 265. ν/cm^{-1}: 738, 1146, 1225, 1272, 1313, 1342, 1380, 1455, 1465, 1505, 1595, 1605, 1625, 2850, 2870, 3260, 3380, 3400. ^{1}H nmr (60 MHz, CDCl$_3$), δ /ppm: 1.94(p, J 6.6 Hz, 2H-NHCH$_2$$\underline{CH_2}$); 3.19(t, J 6.6 Hz, 10H-NH$\underline{CH_2}$ and -CH$_2$$\underline{NH}$ and -C$\underline{NH_2}$); 6.66(s, 8H-aromatic). ^{13}C nmr (20.12 MHz, CDCl$_3$), δ /ppm: 29.0, 43.1, 118.8, 120.8, 134.4, 137.9.

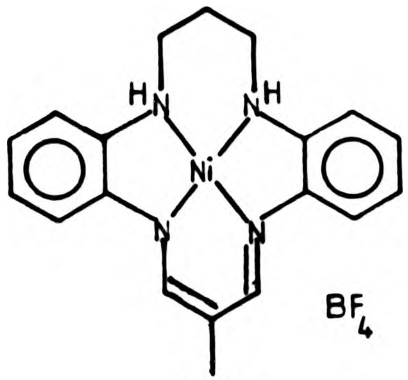
10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.3



5.3

3-Ethoxy-2-methylacrolein (1.1 cm^3, 10 mmol) was added to a refluxing solution of 1,3-bis(*o*-aminophenylamino)propane 5.2 (2.6 g, 10.0 mmol) in toluene (90 cm^3). The solution was refluxed with stirring under nitrogen for 4 hours. After cooling and evaporating under vacuum, cold methanol was added and orange microcrystals were obtained of 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.3 (1.16 g, 379 mmol, 38 %). Recrystallisation was from methanol, m.p. 193.5-195 °C. Found C, 73.5; H, 7.40; N, 18.00; requires C, 74.47; H, 7.24; N, 18.29 %; for $C_{19}H_{22}N_4$, m_r = 306. ν/cm^{-1}: 693, 751, 794, 1065, 1224, 1348, 1430, 1460, 1496, 1533, 2700, 2880, 3040, 3330. ^{1}H nmr (60 MHz, CDCl$_3$), δ /ppm: 2.00(p, *J* 5Hz, 2H-NHCH$_2$CH$_2$); 2.05(s, 5H-CCH$_3$); 3.41(t, *J* 5 Hz, 4H-NHCH$_2$); 4.72(s, 2H-CH$_2$NH); 6.50-7.40(mc, 9H-aromatic and -CHNH); 7.93(d, *J* 5 Hz, 2H-NHCH). ^{13}C nmr (20.12 MHz, CDCl$_3$), δ /ppm: 18.3, 28.7, 45.4, 103.1, 112.8, 113.6, 119.2, 124.1, 134.9, 139.8, 146.5. Mass spectrum m/z: 306(M*=35 %), 199(8), 185(23), 159(31), 145(44), 132(32), 119(100), 104(8), 92(31), 77(33), 65(40), 51(17), 39(25), 28(35), 18(21).

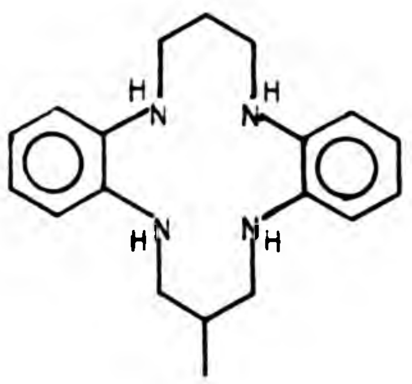
[(10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradeca-8,10-dienato)nickel(II)] monotetrafluoroborate 5.4



5.4

To the macrocycle 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.3 (0.51 g, 1.66 mmol) in methanol (50 cm^3) was added the pale blue solution of excess nickel(II)tetrafluoroborate (1.92 g, 8.28 mmol) in methanol(100 cm^3). This gave a deep orange solution which upon heating and cooling gave blue shiny crystals. These were filtered and washed with water to remove any unreacted $Ni(BF_4)_2$ and dried. Blue needles were obtained of [(10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradeca-8,10-dienato) nickel(II)] monotetrafluoroborate 5.4 (0.44 g, 0.97 mmol, 59 %), m.p. 274-276 °C. Found C, 50.70; H, 4.70; N, 12.50; Ni, 11.20; requires C, 50.61; H, 4.69; N, 12.43; Ni, 13.02 %, for $(C_{19}H_{21}N_4)BF_4Ni$, m_r = 450. V/cm^{-1}: 752, 1278, 1314, 1376, 1460, 1600, 2880, 2920, 3230. Mass spectrum m/z: 363(M* =10 %), 358(100), 334(15), 202(5), 178(25), 159(5), 119(5), 49(20), 20(10).

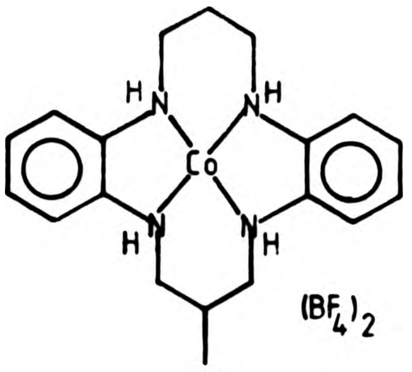
10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane 5.5



5.5

10-Methyl-1,5,8,11-tetra-aza-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.3 (5.6 g, 18.29 mmol) was suspended in toluene (600 cm^3) with 5 % palladium on activated carbon (3.24 g) in an autoclave (1000 cm^3). Reduction was carried out at 30 °C under 50 atmospheres of hydrogen gas for 18 hours with constant stirring. The filtered orange solution was evaporated to dryness, and ethyl acetate was added. Recrystallisation from ethyl acetate yielded pale yellow crystals of 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane 5.5 (3.24g, 10.44 mmol, 57 %), m.p. 180-182 °C. Found C, 74.10; H, 8.90; N, 16.00; requires C, 73.51; H, 8.44; N, 18.05 %, for $C_{19}H_{26}N_4$, m_r = 310. ν/cm^{-1}: 738, 903, 1047, 1142, 1227, 1242, 1378, 1460, 1504, 1580, 1603, 2880, 2920, 3040, 3284. ^{1}H nmr (220 MHz, $CDCl_3$), δ/ppm: 1.05(d, *J* 6.7 Hz, 3H-CH$\underline{CH_3}$); 1.95-2.45(mc, 3H-NHCH$_2\underline{CH_2}$ and CH$_3\underline{CH}$); 2.94(t, *J* 12 Hz, 2H-NH$\underline{CH_2}$); 3.10-3.26(mc, 2H-NH$\underline{CH_2}$); 3.36-3.60(mc, 4H-NH$\underline{CH_2}$); 4.35(s, 4H-CH$_2\underline{NH}$); 6.60-7.00(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ /ppm: 17.9, 26.7, 31.5, 45.7, 52.7, 111.1, 111.2, 119.3, 119.4, 137.7. Mass spectrum m/z: 310(M^*=96 %), 281(3), 267(15), 161(19), 147(15), 133(60), 119(100), 108(10), 92(28), 77(21), 65(21), 51(6), 39(10), 28(10), 18(8). X-ray (from toluene): $P2_1/c$, a=12.843, b=5.449, c=23.898 Å, β =101.522 °, Z=4, 2870 data with F >3 σ (F), R 0.1011.

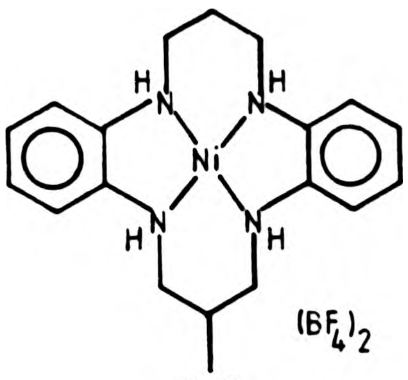
[(10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)-cobalt(II)] ditetrafluoroborate 5.6



5.6

The pink solution of cobalt(II) tetrafluoroborate (0.10 g, 0.28 mmol) in methanol (20 cm^3) was added to 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane 5.4 (0.08 g, 0.24 mmol) in methanol/dichloromethane (50 cm^3) to give a royal blue solution. A blue/purple solid was obtained on evaporation to a low volume. This was washed with cold methanol to yield [(10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)cobalt(II)] ditetrafluoroborate 5.6 (90.05 g, 0.10 mmol, 40 %), m.p. 247-250°C. Found C, 41.91; H, 4.85; N, 4.69; requires C, 42.03; H, 4.53; N, 5.16 %, for $C_{19}H_{26}N_4B_2F_8Co$, $m_r = 543$. ν /cm^{-1}: 725, 735, 1040-1085(b), 1145, 1150, 1230, 1245, 1263, 1341, 1465, 1475, 1505, 1518, 1535, 1595, 2848, 2928, 2960, 3285, 3400.

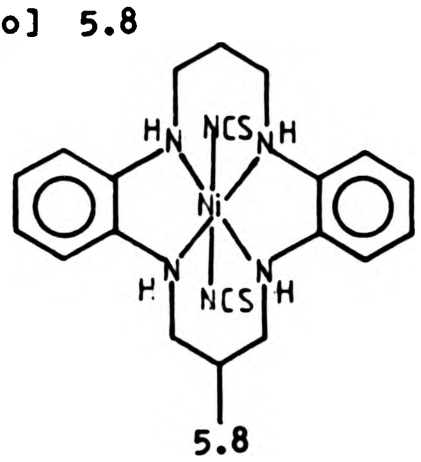
[(10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)-nickel(II)] ditetrafluoroborate 5.7



5.7

To a hot methanolic solution (20 cm^3) of 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane 5.5 (0.0126 g, 0.0406 mmol) under a nitrogen atmosphere was added nickel(II)tetrafluoroborate (0.0195 g, 0.0528 mmol) in hot methanol (20 cm^3). The resulting green solution was then evaporated gently under nitrogen to yield orange crystals of [(10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)nickel(II)] ditetrafluoroborate 5.7 (0.0125 g, 0.0230 mmol, 57 %), m.p. 272-274°C. Found C, 41.93; H, 4.72; N, 11.07; requires C, 42.04; H, 4.83; N, 10.33 % for $C_{19}H_{26}N_4B_2F_8Ni$, m_r=543. ν/cm^{-1}: 720, 760, 890, 1045, 1210, 1235, 1270, 1280, 1310, 1380, 1465, 1505, 1600, 1640, 2850, 2920, 2960, 3200, 3400. X-ray (from methanol): $P\bar{1}$, a=9.200, b=8.549, c=7.974 Å, α=109.105, β=112.902, γ=74.167° , Z=2, 1108 data with F >3σ(F), R 0.0722.

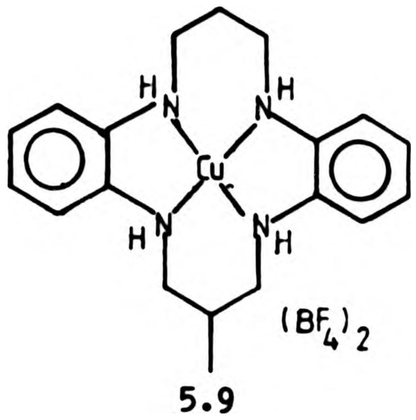
[(10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)-nickel(II) dithiocyanato] 5.8



5.8

Nickel(II) tetrafluoroborate (0.1686 g, 0.50 mmol) in hot methanol (20 cm^3) was added to a methanolic (20 cm^3) solution of 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane 5.5 (0.1001 g, 0.32 mmol) under nitrogen. Ammonium thiocyanate (0.0504g, 0.66 mmol) in methanol (5 cm^3) was added, to the resulting green solution, to yield a blue solution which was evaporated to a low volume under a nitrogen atmosphere. Pink needles were obtained of [(10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)nickel(II) dithiocyanato] 5.8 (0.0796 g, 0.16 mmol, 51 %), m.p. 284-285°C. Found C, 51.50; H, 5.40; N, 17.00; S, 12.50; Ni, 11.40; requires C, 51.97; H, 5.40; N, 17.32; S, 13.21; Ni, 12.10 %, for $C_{21}H_{26}N_2S_4Ni$, m_r=485. ν/cm^{-1}: 720, 790, 850, 870, 920, 965, 1000, 1045, 1068, 1120, 1140, 1190, 1205, 1235, 1270, 1370, 1410, 1460, 1492, 1600, 2085, 2880, 2940, 3180, 3240. Mass spectrum m/z: 358(100), 310(43), 267(12), 179(17), 160(15), 147(13), 133(53), 119(80), 108(10), 92(18), 77(23), 63(15), 59(15), 51(5), 34(43), 24(56), 18(57).

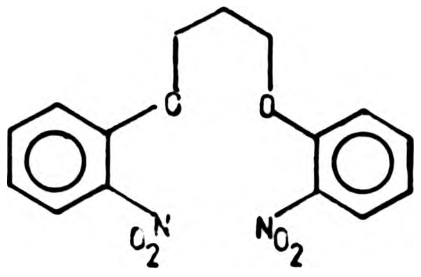
[(10-Methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane)-copper(II)] ditetrafluoroborate 5.9



5.9

To a solution of 10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane 5.5 (0.04 g, 0.13 mmol) in dichloromethane/methanol (50 cm^3) was added the blue solution of copper(II) tetrafluoroborate (0.04 g, 0.13 mmol) in methanol (20 cm^3). A pink solution was obtained and on evaporation to a low volume, a solid appeared, which was collected and washed with cold methanol. [(10-methyl-1,5,8,12-tetra-aza-6,7:13,14-dibenzocyclotetradecane) copper(II) ditetrafluoroborate 5.9 was obtained as a brown solid (0.04 g, 0.08 mmol, 51 %), m.p. 257-260°C. Found C, 41.60; H, 4.63; N, 4.59; requires C, 41.67; H, 4.79; N, 10.23 %, for $C_{19}H_{26}N_4B_2F_8Cu$, m_r = 548. ν/cm^{-1}: 723, 745, 770, 790, 813, 873, 893, 955, 995-1120(b), 1160, 1234, 1260, 1295, 1315, 1350, 1398, 1409, 1448, 1465, 1510, 1605, 2825, 2920, 2960, 3240.

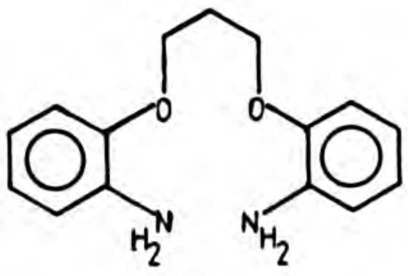
1,3-Bis(o-nitrophenyloxy)propane 5.10



5.10

To o-nitrophenol (478 g, 3.44 mol) in hot N,N-dimethylformamide (500 cm^3) was added potassium carbonate (239 g, 1.73 mol) in 10 g portions. On gentle boiling 1,3-dibromopropane (182 cm^3, 1.79mol) was added over 30 minutes. The solution was gently refluxed for 2 hours and the solvent (300 cm^3) was distilled from the mixture, which was then poured into deionised water (5 l). The yellow granular precipitate was filtered off, washed with dilute aqueous sodium hydroxide solution (0.25 mol dm^{-3}) and water then dried. The crystals of 1,3-bis(o-nitrophenyloxy)propane 5.10 (495.8 g, 1.56 mol, 87 %) were recrystallised from glacial acetic acid, m.p. 129-132 °C. Found: C, 56.80; H, 3.90; N, 9.10; requires C, 56.60; H, 4.40; N, 8.81 %, for $C_{15}H_{14}O_6N_2$, m_r=318. V/cm^{-1}: 690, 770, 795, 863, 893, 973, 990, 1007, 1073, 1114, 1170, 1280, 1300, 1377, 1490, 1540, 1607, 1627, 2800, 2880, 3040. ^{1}H nmr (60 MHz CDCl$_3$), δ/ppm: 2.30(p, J 5.3 Hz, 2H -OCH$_2$CH$_2$); 4.31(t, J 5.3 Hz, 4H -OCH$_2$); 6.81-8.12(mc, 8H -aromatic). ^{13}C nmr (20.12 MHz, CDCl$_3$), δ/ppm: 28.8, 65.4, 114.7, 120.5, 125.6, 134.5, 139.8, 152.4.

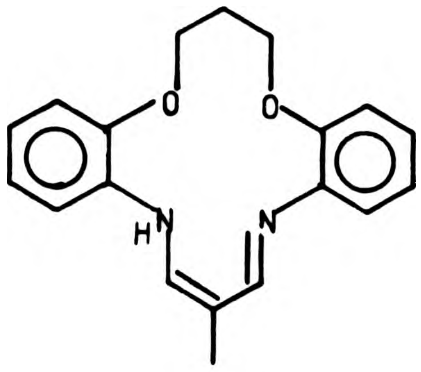
1,3-Bis(o-aminophenyloxy)propane 5.11



5.11

1,3-Bis(o-nitrophenyloxy)propane 5.10 (10.0 g, 39.33 mmol) was reduced under reflux in a nitrogen atmosphere with 5 % palladium on activated carbon (0.5 g) and hydrazine hydrate (20 cm^3). After filtration and evaporation to dryness 25 % aqueous ethanol was added. White crystals of 1,3-bis(o-aminophenyloxy)propane 5.11 were obtained (7.5 g, 29.03 mmol, 74 %), which were recrystallised from 25 % aqueous ethanol m.p. 47-49 °C. Found C, 71.06; H, 7.40; N, 10.94; requires C, 69.74; H, 7.02; N, 10.85 %, for $C_{15}H_{18}N_2O_2$, m_r = 258. ν/cm^{-1}: 734, 1030, 1140, 1220, 1271, 1337, 1400, 1460, 1503, 1615, 2870, 2910, 3353, 3348. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 2.22(p, J 6.6 Hz, 2H-OCH$_2\underline{CH_2}$); 3.65(s, 4H-CH$\underline{NH_2}$); 4.06(t, J 6.6 Hz, 4H-O$\underline{CH_2}$); 6.57(s, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 29.6, 65.2, 111.9, 115.3, 118.5, 121.4, 136.5, 146.5.

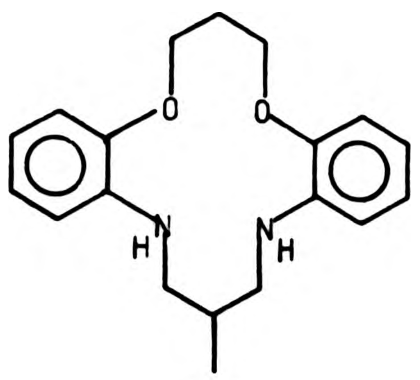
10-Methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.12



5.12

A solution of 3-ethoxy-2-methylacrolein (1.1 cm^3, 10 mmol) and 1,3-bis(*o*-aminophenyloxy)propane 5.11 (2.58 g, 10.0 mmol) in toluene (90 cm^3) was refluxed with stirring under nitrogen for 4 hours. After evaporating to dryness methanol was added and yellow needles were obtained of 10-methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.12 (1.26 g, 4.09 mmol, 41 %). Recrystallisation was from methanol, m.p. 237-238 °C. Found C, 74.30; H, 6.30; N, 8.80; requires C, 74.00; H, 6.53; N, 9.09 %, for $C_{19}H_{20}N_2O_2$, m_r = 308. ν/cm^{-1} : 748, 905, 1063, 1168, 1264, 1287, 1330, 1397, 1463, 1540, 1597, 1645, 2895, 2920, 3350. ^{1}H nmr (220 MHz, $CDCl_3$), δ/ppm: 2.05(s, 3H-$C\underline{CH_3}$); 2.33(p, *J* 5 Hz, 2H-$OCH_2\underline{CH_2}$); 4.23(t, *J* 5 Hz, 4H-$O\underline{CH_2}$); 6.70-7.35(mc, 9H-aromatic and $CH\underline{NH}$); 7.85(d, *J* 6.6 Hz, 2H-$N\underline{CH}$). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 18.1, 29.8, 67.8, 103.0, 111.9, 114.1, 121.1, 123.3, 136.0, 146.8, 150.2. Mass spectrum m/z: 308(M^*=5 %), 200(3), 120(1), 105(5), 44(58), 36(5), 28(10), 18(100).

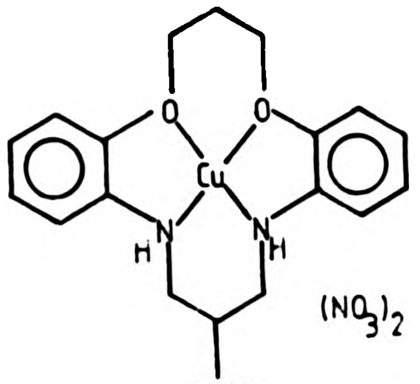
10-Methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.13



5.13

10-Methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradeca-8,10-diene 5.12 (9.34 g, 30.28 mmol) was placed with toluene (1000 cm^3) and 5 % palladium on activated carbon (5.00 g) in an autoclave (2000 cm^3). The macrocycle was then reduced under 50 atmospheres of hydrogen gas with stirring for 18 hours at 30 °C. After filtration the pale yellow solution was evaporated to dryness and ethyl acetate was added, yielding white crystals of 10-methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.13 (0.96 g, 25.49 mmol, 84 %). Recrystallisation was from ethyl acetate, m.p. 153.5-155.0 °C. Found C, 73.90; H, 7.80; N, 9.30; requires C, 73.04; H, 7.74; N, 8.97 %, for $C_{19}H_{24}N_2O_2$, m_r = 312. ν/cm^{-1}: 734, 1054, 1108, 1143, 1223, 1250, 1348, 1380, 1470, 1510, 1605, 2879, 2960, 3360. ^{1}H nmr (220 MHz, $CDCl_3$), δ/ppm: 1.05(d, *J* 6.7 Hz, 3H-CH$\underline{CH_3}$); 2.00-2.50(mc, 3H-OCH$_2\underline{CH_2}$ and -CH$_3\underline{CH}$); 3.03(t, *J* 12 Hz-2H-NH$\underline{CH_2}$); 3.35-3.54(mc, 2H-N$\underline{CH_2}$); 4.16-4.60(mc, 4H-O$\underline{CH_2}$); 5.05(s, 2H-CH$_2\underline{NH}$); 6.60-7.00(mc, 8H-aromatic). ^{13}C nmr (20.1 MHz, $CDCl_3$), δ/ppm: 17.8, 28.6, 31.4, 51.5, 67.8, 109.7, 110.1, 116.4, 121.3, 138.1, 146.5. Mass spectrum m/z: 312(M^{*}=96 %), 297(4), 270(6), 254(6), 204(10), 161(100), 150(15), 134(49), 120(41), 109(13), 93(17), 77(25), 65(30), 52(17), 41(27), 28(14), 18(7).

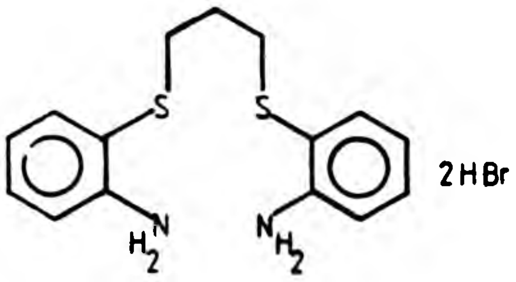
[(10-Methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane)copper(II)] dinitrate 5.14



5.14

To an acetone solution of 10-methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.13 (1.00 g, 3.20 mmol) was added copper(II) nitrate (0.78 g, 3.29 mmol). Immediately a green precipitate was obtained of [(10-methyl-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane) copper(II)] dinitrate 5.14 (0.91 g, 1.82 mmol, 57 %), m.p. 154°C(decomposes). Found C, 45.78; H, 4.86; N, 11.83; requires C, 45.64; H, 4.84; N, 11.21 % for $C_{19}H_{24}N_4O_8Cu$, m_r = 500. ν/cm^{-1}: 758, 768, 790, 805, 815, 840, 900, 973, 917, 1015, 1053, 1120, 1162, 1255, 1298, 1380, 1390, 1395, 1465, 1490, 1465, 1510, 1518, 1530, 1610, 2860, 2880, 2930, 2950, 2960, 3180, 3440.

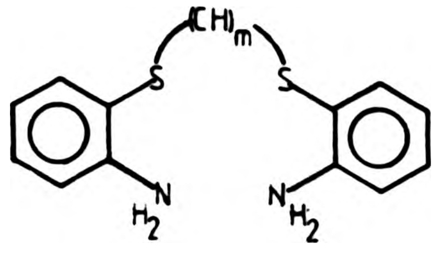
1,3-Bis(*o*-aminophenylthio)propane dibromide 5.15



5.15

Sodium (18.6 g, 0.81 mol) was dissolved in methanol (570 cm^3) and *o*-aminobenzenethiol (100 g, 0.74 mol) was added. The mixture was stirred under nitrogen for 10 minutes and a yellow solution was obtained. 1,3-Dibromopropane (78.0 g, 0.38 mol) in methanol (150 cm^3) was then added dropwise to the solution. The mixture was stirred overnight under nitrogen then refluxed for 6 hours. On cooling hydrobromic acid (80 cm^3, 48 %) was added to precipitate the white dibromide salt. This was filtered and washed with cold methanol and dried in vacuo. The 1,3-di-(*o*-aminophenylthio)propane dibromide 5.15 (168.6 g, 0.37 mol, 96 %) was recrystallised from methanol, (a few drops of 48 % HBr were added to prevent hydrolysis) and then dried in vacuo, m.p. 224-226 °C. Found C, 37.81; H, 4.43; N,5.68; S, 13.1; Br, 36.0; requires C, 39.82; H, 4.42; N, 6.19; S, 14.18; Br, 35.34 %, for $C_{15}H_{20}N_2S_2Br_2$, m_r = 452. V/cm^{-1}: 700, 740, 760, 980, 1150, 1380, 1490, 2880, 2900, 3040. ^{1}H nmr (60 MHz, d_6-DMSO), δ/ppm: 2.00(p, *J* 6.7 Hz, 2H -SCH$_2$CH$_2$); 2.95(t, *J* 6.7 Hz, 10H -SCH$_2$); 6.95-7.50(mc., 8H -aromatic). ^{13}C nmr (20.12 MHz, d_6-DMSO), δ/ppm: 27.8, 32.5, 123.3, 127.9, 128.3, 128.6, 132.7, 133.5.

Bis(o-aminophenylthio)alkanes 5.16-5.18



5.16, m=3

5.17, m=2

5.18, m=4

1,3-Bis(o-aminophenylthio)propane 5.16

1,3-Bis(o-aminophenylthio)propane dibromide 5.15 (20g, 44.22 mmol) was suspended in a saturated aqueous solution of sodium bicarbonate (100 cm^3). Dichloromethane was added and the organic phase was separated and washed with distilled water. The combined organic extracts were dried over anhydrous sodium sulphate and evaporated to dryness under pressure. A yellow oil was obtained of 1,3-bis(o-aminophenylthio)propane 5.16 (10.5g, 36.15 mmol, 82%). Found C, 61.90; H, 6.50; N, 9.60; S, 22.80; requires C, 62.06; H, 6.25; N, 9.65; S, 22.08 %, for $C_{18}H_{18}N_2S_2$, m_r = 290. ν/cm^{-1} 748, 853, 940, 1023, 1080, 1140, 1158, 1247, 1308, 1450, 1478, 1580, 1605, 2915, 3010, 3060, 3353, 3462. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 1.73(p, J 2H-$SCH_2\underline{CH_2}$); 2.78(t, J 7.3 Hz. 2H-$S\underline{CH_2}$); 4.22(s, 4H-$C\underline{NH_2}$); 6.45-7.50(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 22.8, 32.5, 123.3, 127.9, 128.3, 128.6, 132.7, 133.5. Mass spectrum m/z: 290(M^{*}=45 %), 198(15), 178(13), 166(100), 150(13), 138(60), 124(80), 118(5), 106(13), 94(50), 80(42), 73(5), 65(15), 53(5), 39(5), 18(37).

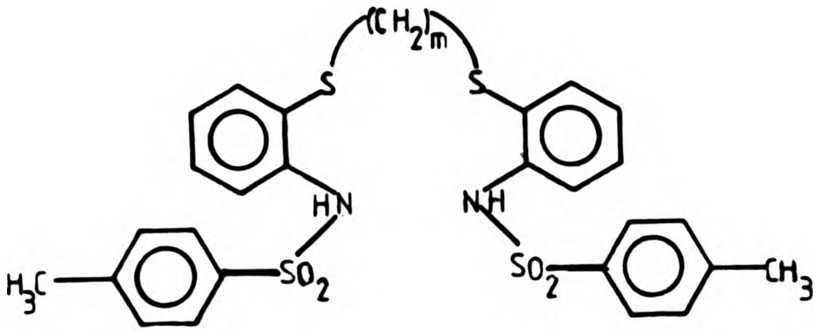
1,2-Bis(*o*-aminobenzenethio)ethane 5.17

The dihydrogenbromide salt was prepared in an analogous fashion to 1,3-bis(*o*-aminobenzenethio)propane dihydrogen bromide 5.15, this was not isolated but treated directly with saturated aqueous sodium bicarbonate and dichloromethane. The organic layer was extracted with dichloromethane, dried over anhydrous sodium sulphate and then evaporated to a low volume. A solid was obtained which was washed and recrystallised from methanol to yield purple crystals of 1,2-bis(*o*-amimophenylthio)ethane 5.17 (22 g, 79.59 mmol, 66 %), m.p. 77-78^{o}C. Found C, 61.40; H, 5.90; N, 10.30; S, 22.90; requires C, 60.82; H, 5.84; N, 10.14; S, 23.20 %, for $C_{14}H_{16}N_2S_2$, m_r = 276. ν/cm^{-1} 750, 852, 1165, 1448, 1480, 1583, 1618, 2880, 2930, 3060, 3180, 3358, 3390. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 2.85(s, 4H-$S\underline{CH}_2$); 4.10(s, 4H-$C\underline{NH}_2$); 6.50-7.40(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 34.5, 115.0, 116.8, 118.6, 130.0, 136.2, 148.6.

1,4-Bis(*o*-aminophenylthio)butane 5.18

This was prepared as above and gave a brown oil, 1,4-bis(*o*-aminophenylthio)butane 5.18 (32 g, 105.10 mmol, 88 %). Found C, 62.40; H, 6.80; N, 9.20; S, 21.60; requires C, 63.11; H, 6.62; N, 9.20; S, 21.06 %, for $C_{16}H_{20}S_2N_2$, m_r = 304. ν/cm^{-1}: 750, 1025, 1160, 1250, 1310, 1450, 1480, 1610, 2880, 2930, 3250, 3350. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 1.13-1.75(mc, 4H-$SCH_2\underline{CH}_2$); 2.38-2.75(mc, 4H-$S\underline{CH}_2$); 4.22(s, 4H-$C\underline{NH}_2$); 6.00-7.25(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 28.5, 34.2, 114.9, 117.9, 118.5, 129.6, 135.8, 148.3. Mass spectrum m/z: 304(M^{*} =85 %), 248(3), 180(30), 152(3), 138(10), 124(100), 109(3), 97(50), 88(75), 65(23), 39(15), 27(9).

Bis(2{p-tolylsulfonylamino}phenylthio)alkanes 5.19-5.21



5.19, m=3

5.20, m=2

5.21, m=4

1,3-Bis(2{p-tolylsulfonylphenylamino}phenylthio)propane 5.19

A solution of p-toluenesulfonylchloride (58.0 g, 304.2 mmol) in pyridine (200 cm^3) was added dropwise over three hours to a solution of 1,3-bis(o-aminophenylthio)propane 5.16 (35.5 g, 122.2 mmol) in pyridine (200 cm^3) at 30^{o}C. This was then heated at 50-60 ^{o}C for three hours. After cooling concentrated hydrochloric acid (100 cm^3) was added. The organic layer was extracted with dichloromethane and the combined extracts were dried over anhydrous sodium sulphate. 1,3-Bis(2{p-tolylsulfonylamino}phenylthio)propane 5.19 (67.7 g, 113.4 mmol, 68 %) was obtained as a brown oil after evaporation to dryness under vacuum. Found C, 57.70; H, 5.20; N, 4.80; S, 21.10; requires C, 58.16; H, 5.05; N, 4.68; S, 21.42 %, for $C_{29}H_{30}N_2O_4S_4$, m_r = 598. V/cm^{-1}: 623, 660, 703, 748, 755, 813, 913, 1038, 1060, 1090, 1165, 1183, 1210, 1265, 1335, 1380, 1447, 1470, 1572, 1587, 1598, 2920, 3060, 3260. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 1.49(p, J 7.3 Hz, 2H-$SCH_2\underline{CH_2}$); 2.27(s, 6H-$C\underline{CH_3}$); 2.47(t, J 7.3 Hz, 4H-$S\underline{CH_2}$); 6.60-7.90(mc, 18H-aromatic and -NH-). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.5, 28.5, 34.6, 119.6, 123.7, 124.8, 127.3, 129.8, 130.0, 135.6, 136.4, 138.8, 144.2. Mass spectrum m/z: 598(M^*=18 %), 444(18), 320(4), 290(2), 214(5), 199(10), 180(3), 164(100), 149(7), 136(63), 131(18), 124(25), 109(8), 91(38), 80(12), 65(13), 51(3), 39(7), 27(2).

1,2-Bis(2{p-tolylsulfonylamino}phenylthio)ethane 5.20

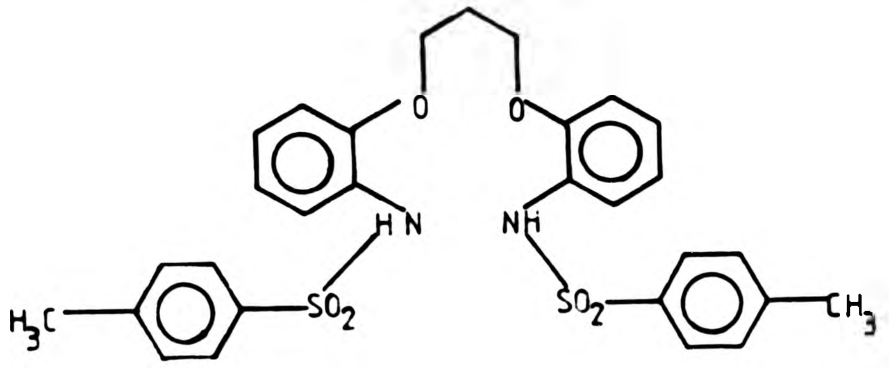
An analogous preparation was carried out as above but using 1,2-bis(o-aminophenylthio)ethane instead. A white solid was obtained which was recrystallised from dichloromethane/cyclohexane to yield crystals of 1,2-bis(2{p-tolylsulfonylamino}phenylthio)ethane 5.20 (24.5 g, 41.89 mmol, 77)%, m.p.181-182°C. Found C, 57.80; H, 4.90; N, 4.70; S, 21.80; requires C, 57.51; H, 4.83; N, 4.79; S, 21.93 %, for $C_{28}H_{28}N_2S_4O_4$, m_r = 584. ν/cm^{-1} 628, 670, 703, 763, 805, 912, 1038, 1062, 1095, 1168, 1188, 1211, 1275, 1343, 1396, 1450, 1475, 1575, 1600, 2860, 2930, 2960, 3040, 3070, 3270. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 2.33(s, 6H-C$\underline{CH}_3$); 2.42(s, 4H-S$\underline{CH}_2$); 7.20-7.70(mc, 18H-aromatic and -NH-). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 35.2, 119.9, 123.0, 124.9, 127.3, 129.9, 130.3, 135.4, 136.3, 139.0, 144.4.

1,4-Bis(2{p-tolylsulfonylamino}phenylthio)butane 5.21

The reaction was carried out as above and recrystallisation from dichloromethane/cyclohexane yielded white crystals of 1,4-bis(2{tolylsulfonylamino}phenylthio)butane 5.21 (40.25 g, 65.68 mmol, 80 %), m.p. 124-126°C. Found C, 57.50; H, 5.30; N, 4.50; S, 21.20;

requires, C, 58.79; H, 5.27; N, 4.57; S, 20.93 %, for $C_{30}H_{32}N_2S_4O_4$, m_r = 612. ν/ cm^{-1} 630, 675, 705, 732, 760, 820, 910, 948, 1040, 1068, 1092, 1158, 1170, 1190, 1270, 1338, 1390, 1445, 1473, 1585, 1597, 2850, 2930, 2950, 3020, 3040, 3240. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.43(p, $\underline{J}$ 7.3 Hz, 4H-$SCH_2\underline{CH_2}$); 2.35(s, 6H-$C\underline{CH_3}$); 2.46(t, $\underline{J}$ 7.3 Hz, 4H-$S\underline{CH_2}$); 6.75-7.88(mc, 18H-aromatic and -NH-). ^{13}C (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 28.3, 35.7, 119.6, 124.3, 124.8, 127.4, 129.8, 129.9, 135.5, 136.4, 138.8, 144.2.

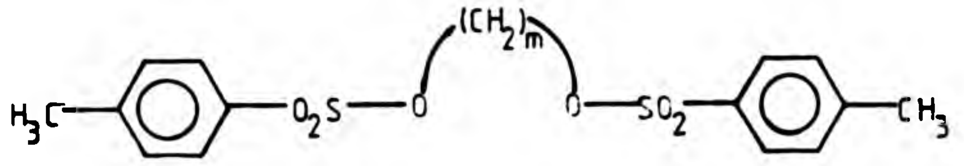
1,3-Bis(2{p-tolylsulfonylamino}phenyloxy)propane 5.22



5.22

To a solution of 1,3-bis(o-aminophenyloxy)propane 5.7 (29.00 g, 112.27 mmol) in pyridine (200 cm^3) was added a solution of p-toluenesulfonylchloride (66.00 g, 337.34 mmol) in pyridine (100 cm^3) at 30°C over 0.5 hours. The reaction temperature was then raised to 50-60°C for three hours. After cooling, dilute HCl (100 cm^3, 2 mol dm^{-3}) was added and the organic layer was extracted with dichloromethane. The combined dichloromethane extracts were dried over anhydrous sodium sulphate and evaporated to a low volume. The solid obtained was recrystallised from dichloromethane/cyclohexane to give pure 1,3-bis(2{p-tolylsulfonylamino}phenyloxy)propane 5.22 (55.00 g, 97.06 mmol, 86 %), m.p. 247-248 $^\circ$C. Found C, 61.30; H, 5.20; N, 5.00; requires C, 61.46; H, 5.34; N, 4.95 %, for $C_{29}H_{30}N_2O_6S_2$,m_r = 567. ν/cm^{-1} 670, 705, 752, 765, 815, 918, 992, 1052, 1093, 1113, 1160, 1185, 1252, 1290, 1338, 1385, 1400, 1465, 1475, 1500, 1598, 2890, 2948, 3020, 3060, 3090, 3280. ^{1}H nmr(60 MHz, d_6-DMSO), δ/ppm: 2.10-2.65(mc, 2H-$OCH_2\underline{CH_2}$); 3.30(s, 6H-$C\underline{CH_3}$); 3.60-4.10(mc, 4H-$O\underline{CH_2}$); 6.50-7.70(mc, 18H-aromatic and -NH-). ^{13}C nmr (20.12 MHz, d_6-DMSO), δ/ppm: 20.3, 28.0, 64.9, 112.4, 120.1. 123.9, 125.8, 126.3, 126.9, 138.0, 143.0, 149.0, 151.6.

Bis(p-tolylsulfonyloxy)alkanes 5.23-5.25



5.23, m=3

5.24, m=2

5.25, m=4

1,3-Bis(p-tolylsulfonyloxy)propane 5.23

p-Toluenesulfonyl chloride (130 g, 681.88 mmol) was added in portions (10 g) to a solution of propan-1,3-diol (20 g, 262.81 mmol) in pyridine (170 cm^3, 2110 mmol). The temperature was maintained below 10 °C. After all the additions the solution was left to stir for 3 hours at room temperature. The semi-solid mixture was then added to a 10M HCl (300 cm^3) and ice (1000 g) mixture. On vigorous stirring the oil solidified to give a white solid. Recrystallisation from 95 % aqueous ethanol yielded white needles of 1,3-bis(p-tolylsulfonyloxy)propane 5.23 (45 g, 117.05 mmol, 45 %), m.p. 92-93°C. Found C, 53.40; H, 5.30; S, 16.10; requires C, 53.11; H, 5.24; S, 16.68 %, for $C_{17}H_{20}O_6S_2$, m_r= 384. ν/cm^{-1} 658, 668, 708, 742, 792, 810, 855, 892, 942, 954, 1020, 1030, 1074, 1098, 1110, 1174, 1190, 1245, 1293, 1310, 1363, 1405, 1420, 1470, 1495, 1600, 2920, 2950, 2975. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 1.48(p, J 6.6 Hz, 2H-OCH$_2\underline{CH_2}$); 2.45(s, 6H-C$\underline{CH_3}$); 4.07(t, J 6.6 Hz, 4H-O$\underline{CH_2}$); 7.20-7.80(mc, 8H-aromatic). Mass spectrum m/z: 384(M^{*}=8 %), 262(2), 229(2), 213(32), 181(2), 173(12), 155(45), 139(3), 107(12), 91(100), 77(5), 65(25), 57(8), 51(4), 41(11), 29(3), 18(3).

1,2-Bis(*p*-tolylsulfonyloxy)ethane 5.24

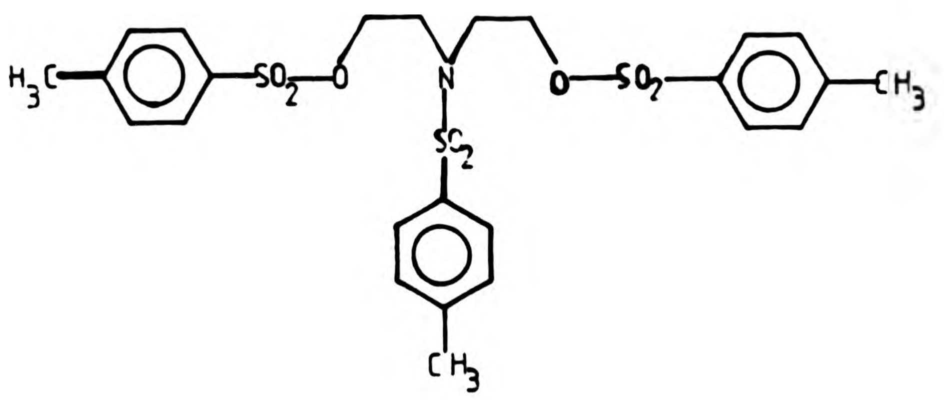
Prepared as above with ethan-1,2-diol instead of propan-1,3-diol. Recrystallisation from dichloromethane/IMS (95 %) yielded white shiny crystals of 1,2-bis(*p*-tolylsulfonyloxy)ethane 5.24, (80 g, 215.97 mmol, 79 %), m.p. 126-127°C. Found C, 51.60; H, 4.90; S, 20.80; requires C, 51.87; H, 4.90; S, 17.4 %, for $C_{15}H_{18}O_6S_2$, m_r =370. ν/cm^{-1} 612, 670, 803, 820, 920, 980, 1018, 1040, 1097, 1125, 1180, 1300, 1312, 1360, 1405, 1455, 1497, 1600, 1660, 1690, 1817, 1934, 2885, 2928, 2960, 2993, 3090. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 2.42(s, 6H-CC$\underline{H}_3$); 4.18(s, 4H-OC$\underline{H}_2$), 7.20-7.80(mc, 8H-aromatic). Mass spectrum m/z: 370(M^{*} =10 %), 119(10), 155(40), 139(10), 187(6), 91(100), 77(5), 65(35), 51(5), 39(10), 27(5).

1,2-Bis(*p*-tolylsulfonyloxy)butane 5.25

Prepared as above with butan-1,4-diol and recrystallisation from dichloromethane/IMS (95 %) yielded white needles of 1,4-bis(*p*-tolylsulfonyoxy)butane 5.25 (39.0 g, 97.78 mmol, 37 %), m.p. 77-78°C. Found C, 54.30; H, 6.00; S, 16.3; requires C, 54.25; H, 5.57; S, 16.09 %, for $C_{18}H_{22}O_6S_2$, m_r =398. ν/cm^{-1} 667, 733, 812, 852, 940, 1034, 1099, 1178, 1360, 1447, 1478, 1495, 1600, 2860, 2930, 2940, 2980, 3030, 3070, 3090. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 1.64(mc,4H-OCH$_2$C$\underline{H}_2$); 2.4(s, 6H-CC$\underline{H}_3$); 3.95(mc, 4H-OC$\underline{H}_2$); 7.55(mc, 8H-aromatic).

Mass spectrum m/z: 398(M* =6 %), 277(15), 226(5), 173(12), 172(8), 162(10), 155(45), 107(15), 91(100), 77(5), 65(25), 55(35).

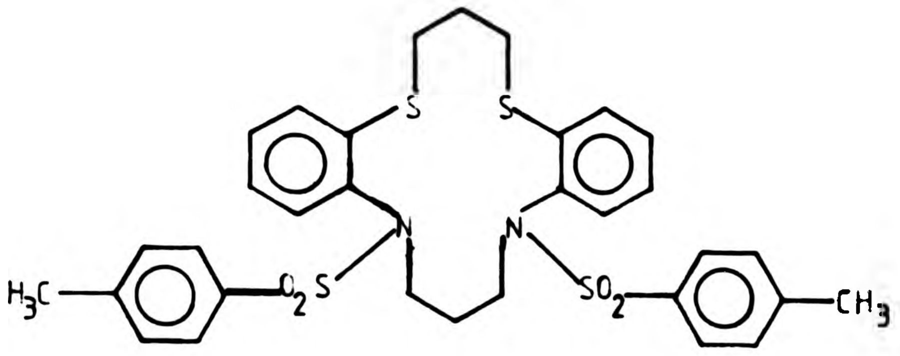
1,4,7-Tris(*p*-tolylsulfonyl)-4-aza-1,7-dioxoheptane 5.26



5.26

To a mechanically stirred solution of 2,2'-iminobisethanol (33.5 g, 300 mmol) in pyridine (310 cm^3) was added *p*-toluenesulphonyl chloride (183 g, 960 mmol) in portions at 0°C. The mixture was then stirred at 0°C for 0.5 hours then removed from the ice-bath and stirred at room temperature for a further 2 hours. To this was added HCl (600 cm^3, 2 mol dm^{-3}) maintaining the temperature of the reaction below 10°C. On standing the red oil crystallised to give a yellow product which was powdered in a mortar and washed with water. Recrystallisation from boiling methanol and decolourising charcoal, followed by washing with ethanol and ether yielded pale yellow crystals of 1,4,7-tris(*p*-tolylsulfonyl)-4-aza-1,7-dioxoheptane 5.26 (127.00 g, 223.72 mmol, 70 %), m.p. 96-98°C. Found C, 52.50; H, 5.00; N, 2.20; requires C, 52.90; H, 5.20; N, 2.50 %, for $C_{25}H_{29}NO_8S_3$, m_r = 568. ν/cm^{-1}: 655, 665, 707, 740, 820, 862, 912, 970, 990, 1003, 1020, 1040, 1093, 1123, 1160, 1195, 1193, 1272, 1295, 1310, 1340, 1360, 1400, 1450, 1459, 1468, 1495, 1598, 2900, 2930, 2957, 3040, 3090. ^{1}H nmr (60 MHz, CDCl$_3$), δ/ppm: 2.47(d, 9H-C$\underline{\text{CH}}_3$); 3.40(t, *J* 6 Hz, 4H-N$\underline{\text{CH}}_2$); 4.16(t, *J* 6 Hz, 4H-O$\underline{\text{CH}}_2$); 7.20-7.90(mc, 12H-aromatic).

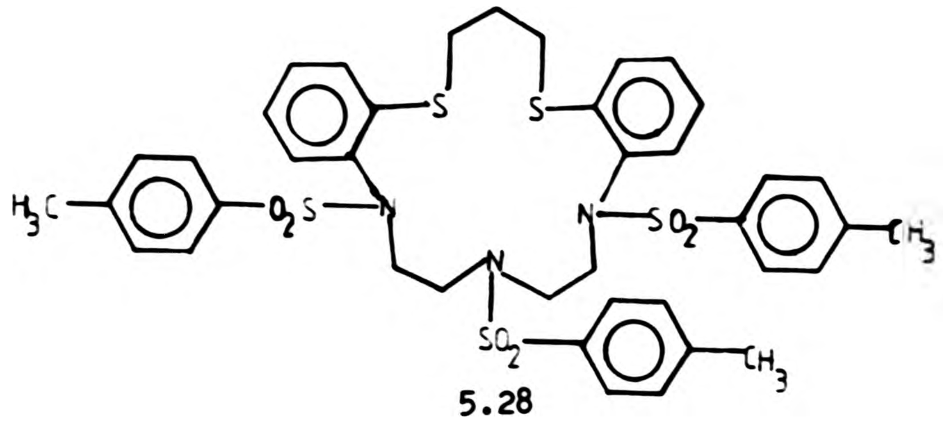
8,12-Bis(*p*-tolylsulfonyl)-8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane 5.27



5.27

1,3-Bis(*p*-tolylsulfonyloxy)propane 5.23 (6.52 g, 17.00 mmol) in N,N-dimethylformamide (80 cm^3) was added to 1,3-bis(2{*p*-tolylsulfonylamino}thio)propane 5.19 (10.15 g, 16.95 mmol) and anhydrous potassium carbonate (10 g, 72.35 mmol) in N,N-dimethylformamide (200 cm^3) at 100°C over four hours. Heating was maintained for a further 60 hours. After cooling, dichloromethane (200 cm^3) was added. The N,N-dimethylformamide was extracted with distilled water (4 x 600 cm^3) from the dichloromethane layer. The organic layer was dried over anhydrous sodium sulphate and evaporated to dryness under vacuum. A white solid was obtained which was recrystallised from dichloromethane/cyclohexane to give 8,12-bis(*p*-tolylsulfonyl)-8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane 5.27 (9.27 g, 14.51 mmol, 86 %), m.p. 217-220 $^\circ$C. Found C, 60.60; H, 5.50; N, 4.60; S, 19.30; requires C, 60.15; H, 5.36; N, 4.38; S, 20.08 %, for $C_{32}H_{34}N_2O_4S_4$, m_r= 638. ν/cm^{-1}: 655, 670, 725, 750, 765, 820, 907, 951, 1030, 1050, 1085, 1160, 1210, 1305, 1350, 1385, 1460, 1565, 1595, 1725, 2850, 2930, 2980, 3064. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.63-2.13(mc, 4H-$SCH_2\underline{CH}_2$ and -$CH_2\underline{CH}_2$); 2.38(s, 6H-$C\underline{CH}_3$); 2.60-3.33(mc, 6H-(4H-$S\underline{CH}_2$ and 2H-$N\underline{CH}_2$); 3.50-4.00(mc, 2H-$N\underline{CH}_2$); 6.37-7.75(mc, 16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 25.9, 28.8, 33.7, 50.4, 127.0, 127.9, 128.6, 129.1, 129.6, 131.5, 136.0, 140.0, 140.6, 143.6. Mass spectrum m/z: 638(M^{*}=22 %), 483(93), 328(5), 320(3), 295(8), 204(22), 192(18), 178(55), 164(22), 150(42), 144(10), 136(100), 130(18), 117(18), 109(32), 91(57), 77(12), 69(3), 65(24), 51(3), 41(10), 27(2), 18(43).

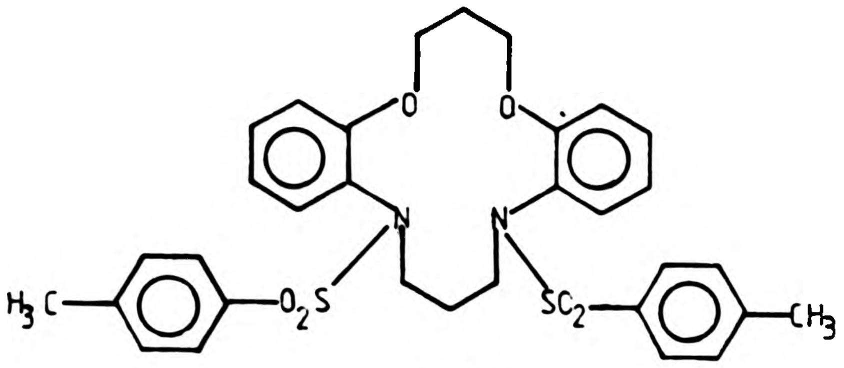
8,11,14-Tris(p-tolylsulfonyl)-8,11,14-triaza-1,5-dithio-6,7:15,16-dibenzocyclohexadecane 5.28



5.28

Cyclisation was carried out as above using 1,3-bis-(2{p-tolylsulfonylamiono}phenylthio)propane 5.25 (16.90 g, 28.22 mmol), 1,4,7-tris(p-tolylsulfonyl)-4-aza-1,7-dioxoheptane 5.26 (16.00 g, 28.19 mmol) and anhydrous potassium carbonate (15.60 g, 112.87 mmol). After work up and recrystallisation from dichloromethane/cyclohexane a white precipitate was obtained of 8,11,14-tris(p-tolylsulfonyl)-8,11,14-triaza-1,5-dithio-6,7:15,16-dibenzocyclohexadecane 5.28 (13.10 g, 15.32 mmol, 57 %), m.p. 245-246°C. Found C, 58.30; H, 5.20; N, 5.00; S, 19.30; requires C, 58.44; H, 5.27; N, 5.11; S, 19.50 %, for $C_{40}H_{43}N_3S_5O_6$, $m_r = 822$. V/cm^{-1}: 620, 655, 705, 723, 750, 768, 795, 815, 905, 980, 1020, 1040, 4057, 1073, 1095, 1160, 1261, 1295, 1305, 1350, 1380, 1437, 1452, 1470, 1495, 1598, 2665, 2730, 2755, 2780, 2820, 2856, 2890. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.38-2.00(mc, 2H-$SCH_2\underline{CH}_2$); 2.41(s, 6H-$C\underline{CH}_3$); 2.48(s, 3H-$C\underline{CH}_3$); 2.55-4.00(mc, 8H-$N\underline{CH}_2$ and -$S\underline{CH}_2$); 6.50-7.88(mc, 20H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.7, 33.2, 48.7, 49.8, 50.7, 127.1, 127.4, 128.0, 129.7, 131.1, 136.1, 137.4, 139.0, 140.0, 143.8. Mass spectrum m/z: 822(M^* =2), 666(5), 512(6), 378(6), 377(6), 221(15), 136(20), 91(100), 77(40), 65(56).

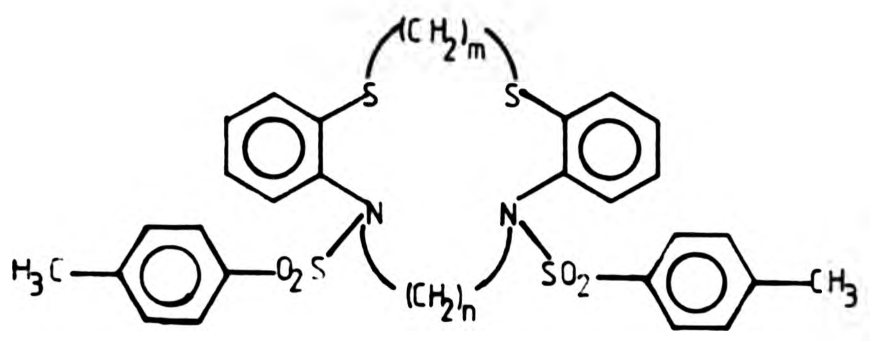
8,12-Bis(*p*-tolylsulfonyl)-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.29



5.29

The reaction was carried out as above but 1,3-bis(*p*-tolylsulfonyloxy)-propane 5.23 (20.0 g, 35.29 mmol), 1,3-bis(2{*p*-tolylsulfonylamino}-phenyloxo)propane 5.22 (13.60 g, 35.37 mmol) and anhydrous potassium carbonate (22.00 g, 159.18 mmol) were used instead, and recrystallisation after workup was from THF/methanol to give a white precipitate of 8,12-bis(*p*-tolylsulfony)-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.29 (19.80 g, 16.15 mmol, 46 %), m.p. 231-234°C. Found C, 63.20; H, 5.00; N, 4.60; requires C, 63.34; H, 5.15; N, 4.61 %, for $C_{32}H_{34}N_2S_2O_6$, m_r = 606. V/cm^{-1}: 655, 695, 712, 755, 818, 850, 915, 980, 1040, 1060, 1093, 1120, 1160, 1255, 1265, 1283, 1325, 1340, 1375, 1455, 1465, 1495, 1598, 2880, 2928, 2950, 3030, 3065. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.15-1.95(mc, 4H-$NCH_2\underline{CH_2}$ and -$OCH_2\underline{CH_2}$); 2.40(s, 6H-$C\underline{CH_3}$), 3.35-3.95(mc, 8H-$N\underline{CH_2}$ and $O\underline{CH_2}$); 6.65-7.75(mc, 16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.5, 28.5, 28.8, 48.5, 66.7, 113.1, 120.8, 127.7, 128.0, 129.2, 129.5, 136.8, 137.7, 142.9, 156.4. Mass spectrum m/z: 606(M^*=2 %), 345(47), 297(21), 296(35), 295(5), 246(9), 214(5), 188(17), 165(10), 162(14), 149(14), 134(15), 120(22), 92(22), 91(54), 83(100), 77(13), 65(18).

Bis(p-tolylsulfonyl)-diaza-dithio-dibenzocycloalkanes 5.30-5.35



5.30 m=3, n=4
5.31 m=2, n=3
5.32 m=2, n=4
5.33 m=4, n=2
5.34 m=4, n=3
5.35 m=4, n=4

General Synthetic Procedure for Ditosylated S_2N_2-Macrocycles of Various Ring-Sizes

The bis(p-tolylsulfonyloxy)alkane (1 mmol) in N,N'-dimethylformamide was added to the corresponding bis(2{p-tolylsulfonylamino)phenylthio)alkane (1 mmol) in the presence of excess anhydrous potassium carbonate (4 mmol) at 100°C over an hour then heated at 100°C for a further 3 hours. On cooling water and dichloromethane were added and the organic layer was extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulphate then evaporated to a low volume, and the solid obtained was recrystallised from dichloromethane/cyclohexane to give the pure ditosylated macrocycle.

8,13-Bis(*p*-tolylsulfonyl)-8,13-diaza-1,5-dithio-6,7:14,15-dibenzocyclopentadecane 5.30

1,4-Bis(*p*-tolylsulfonyoxy)butane 5.25 (4.0 g, 10.04 mmol,) 1,3-bis(2{*p*-tolylsulfonylamino}phenylthio)propane 5.19 (6.0 g, 10.01 mmol) and anhyrous potassium carbonate (6.3 g, 45.58 mmol) were used in this case and a white solid, 8,13-bis(*p*-tolylsulonyl)-8,13-diaza-1,5-dithio-6,7:14,15-dibenzocyclopentadecane 5.30 (4.65 g, 7.12 mmol, 71 %), m.p. 274-276°C was obtained. Found C, 58.90; H, 5.40; N, 4.50; S, 19.4; requires C, 60.70; H, 5.56; N, 4.29; S, 19.64 %, for $C_{33}H_{36}N_2S_4O_4$, m_r = 652. ν/cm^{-1} : 655, 677, 725, 763, 818, 915, 1020, 1040, 1053, 1090, 1165, 1263, 1310, 1343, 1441, 1470, 1478, 1497, 1585, 1605, 2860, 2930, 3060. ^{1}H (80 MHz, $CDCl_3$), δ/ppm: 1.12-1.68(mc, 4H-$\mathrm{NCH_2\underline{CH_2}}$); 1.68-2.19(mc, 4H-$\mathrm{SCH_2\underline{CH_2}}$); 2.40(s, 6H-$\mathrm{C\underline{CH_3}}$); 2.63-3.25(mc, 6H(4H-$\mathrm{S\underline{CH_2}}$ and 2H-$\mathrm{N\underline{CH_2}}$); 3.25-3.90(mc, 2H-$\mathrm{N\underline{CH_2}}$); 6.37-7.75(mc,16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.5, 25.1 25.6, 32.3, 50.7, 127.3, 128.2, 128.7, 129.4, 129.8, 136.4, 137.3, 140.5, 140.9, 143.6. Mass spectrum m/z: 652 (M^{+} =5 %), 497(2), 342(1).

7,11-Bis(*p*-tolylsulfonyl)-7,11-diaza-1,4-dithio-5,6:12,13-dibenzocyclotridecane 5.31

1,3-Bis(*p*-tolylsulfonyloxy)propane 5.23 (4.0 g, 10.40 mmol), was added to 1,2-bis(2{*p*-tolylsulfonylamino}phenylthio)ethane 5.20 (6.0 g, 10.26 mmol) and anhydrous potassium carbonate (6.40 g, 46.31 mmol) in N,N-dimethylformamide (120 cm^3). White crystals of 7,11-bis(*p*-

tolylsulfonyl)-7,11-diaza-1,4-dithio-5,6:12,13-dibenzocyclotridecane 5.31 (4.5 g, 7.20 mmol, 70 %), m.p. 145-146°C were yielded. Found C, 58.20; H, 5.30; N, 4.50; S, 20.70; requires C, 59.58; H, 5.16; N, 4.49; S, 20.52 %, for $C_{31}H_{32}N_2S_4O_4$, m_r =624. ν/cm^{-1}: 635, 710, 770, 815, 910, 1020, 1040, 1060, 1090, 1160, 1213, 1225, 1350, 1440, 1450, 1470, 1498, 1580, 1600, 2850, 2930, 3060. ^{1}H nmr (80 MHZ, $CDCl_3$), δ/ppm: 1.38-1.88(mc, 2H-$NCH_2\underline{CH_2}$); 2.25-2.50(mc, 4H-$S\underline{CH_2}$); 2.46(s, 6H-$C\underline{CH_3}$); 3.00-4.00(mc, 4H-$N\underline{CH_2}$); 6.50-7.75(mc, 16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 31.9, 35.2, 48.5, 126.2, 127.3, 128.0, 128.6, 129.6, 129.9, 136.1, 138.4, 143.6, 143.7. Mass spectrum m/z: 642(M^{+} =8 %), 469(40), 314(10), 214(20), 164(50), 150(70), 136(80), 109(30), 91(100), 77(10), 65(40), 39(20).

7,12-Bis(*p*-tolylsulfonyl)-7,12-diaza-1,4-dithio-5,6:13,14-dibenzocyclotetradecane 5.32

1,2-Bis(2{*p*-tolylsulfonylamino}phenylthio)ethane 5.20 (6.0 g, 10.26 mmol) in N,N-dimethylformamide (120 cm^3) and anhydrous potassium carbonate (6.4 g, 46.31 mmol) were reacted with 1,4-bis-(*p*-tolylsulfonyloxy)butane 5.25 (4.1 g, 10.29 mmol) and a white solid 7,12-bis(*p*-tolylsulfonyl)-7,12-diaza-1,4-dithio-5,6:13,14-dibenzocyclotetradecane 5.32 (4.55 g, 7.12 mmol, 69 %), m.p. 159-161°C was obtained. Found C, 59.10; H, 5.30; N, 4.50; S, 20.10; requires C, 58.50; H, 5.21; N, 4.26; S, 19.53 %, for $C_{32}H_{34}N_2S_4O_4$, m_r = 638. ν/cm^{-1} : 654, 678, 725, 730, 770, 814, 910, 1055, 1092, 1160, 1180, 1273, 1346, 1475, 1600, 2880, 2930, 2980, 3040. ^{1}H nmr(80 MHz, $CDCl_3$), δ/ppm: 1.25-1.83(mc, 4H-$NCH_2\underline{CH_2}$); 2.25-2.63(mc, 4H-$S\underline{CH_2}$); 2.40(s, 6H-

$C\underline{CH}_3$); 3.00-3.50(mc, 4H-$N\underline{CH}_2$); 6.00-7.75(mc, 16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 26.8, 30.0, 53.1, 128.3, 128.6, 129.5, 129.9, 135.5, 136.3, 137.6, 139.5, 140.3, 143.6. Mass spectrum m/z: 638(M^* =1 %), 483(30), 328(6), 246(3), 214(15), 204(10), 176(30), 162(20), 150(60), 149(50), 136(70), 124(40), 109(30), 91(100), 77(15), 69(15), 65(25), 51(20), 39(20).

9,12-Bis(*p*-tolylsulfonyl)-9,12-diaza-1,6-dithio-7,8:13,14-dibenzocyclotetradecane 5.33

The precursors used for this macrocycle were 1,2-bis(*p*-tolylsulfonyloxy)ethane 5.24 (4.85 g, 13.09 mmol) and 1,4-bis(2{*p*-tolylsulfonylamino} phenylthio)butane 5.21 (8.0 g, 13.05 mmol) in the presence of anhydrous potassium carbonate (8.20 g, 59.33 mmol). A white precipitate was obtained of 9,12-bis(*p*-tolylsulfony)-9,12-diaza-1,6-dithio-7,8:13,14-dibenzocyclotetradecane 5.33 (7.55 g, 11.82 mmol, 91 %), m.p. 112-114°C. Found C, 59.10; H, 5.70; N, 4.60; S, 23.90; requires C, 60.15; H, 5.36; N, 4.38; S, 20.08 %, for $C_{32}H_{34}N_2S_4O_4$, m_r = 638. ν/cm^{-1}: 658, 678, 698, 713, 735, 768, 820, 843, 920, 1023, 1040, 1092, 1096, 1165, 1190, 1213, 1260, 1268, 1293, 1325, 1343, 1350, 1385, 1455, 1475, 1485, 1560, 1603, 1700, 1718, 1735, 2870, 2910, 2930, 2970, 3070. ^1H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.30-2.00(mc, 4H-$SCH_2\underline{CH}_2$); 2.25-2.63(mc, 4H-$S\underline{CH}_2$); 2.40(s, 6H-$C\underline{CH}_3$); 2.87-3.00(mc, 4H-$N\underline{CH}_2$); 6.75-8.00(mc, 16H-aromatic) ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 25.8, 31.5, 44.6, 126.9, 127.2, 128.1, 128.2, 129.5, 131.0, 136.4, 138.7, 143.7, 144.2. Mass spectrum m/z: 638(M^*=3 %), 483(5), 457(10), 334(60), 328(2), 305(10), 192(30), 136(70), 91(100), 65(20), 39(25).

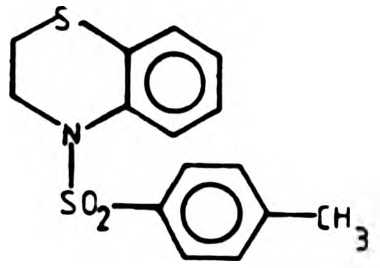
9,13-Bis(p-tolylsulfonyl)-9,13-diaza-1,6-dithio-7,8:14,15-dibenzocyclopentadecane 5.34

1,3-Bis (p-tolylsulfonyloxy)propane 5.23 (5.0 g, 13.00 mmol) was reacted with 1,4-bis(2{p-tolylsulfonylamino}phenylthio)butane 5.21 (8.0 g, 13.05 mmol) and anhydrous potassium carbonate (8.20 g, 59.33 mmol). After recrystallisation a white precipitate was obtained of 9,13-bis(p-tolylsulfonyl)-9,13-diaza-1,6-dithio-7,8:14,15-dibenzocyclopentadecane 5.34 (7.0 g, 10.72 mmol, 82 %), m.p. 244-246°C. Found C, 60.00; H, 5.70; N, 4.10; S, 21.00; requires C, 60.70; H, 5.56; N, 4.29; S, 19.64 %, for $C_{33}H_{36}N_2S_4O_4$, m_r = 652. V/cm^{-1}: 665, 683, 723, 762, 808, 830, 840, 903, 1030, 1052, 1090, 1145, 1167, 1350, 1355, 1385, 1435, 1470, 1495, 1585, 1600, 2850, 2920, 3040. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.25-1.85(mc, 6H-SCH$_2\underline{CH_2}$ and -NCH$_2\underline{CH_2}$); 2.40(s, 6H-C$\underline{CH_3}$); 2.60-3.00(mc, 4H-S$\underline{CH_2}$); 3.00-4.00(mc, 4H-N$\underline{CH_2}$); 6.25-7.87(mc, 16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 28.2, 30.7, 31.6, 50.0, 125.3, 127.3, 128.2, 129.1, 129.6, 129.8, 135.5, 137.4, 141.2, 143.8. Mass spectrum m/z: 652(M^* =1 %), 497(3), 343(6), 180(20), 136(20), 125(16), 122(30), 92(57), 91(100), 78(11), 65(28).

9,14-Bis(p-tolylsulfonyl)-9,14-diaza-1,6-dithio-7,8:15,16-dibenzocyclohexadecane 5.35

The reaction was carried out with 1,4-bis(p-tolylsulfonyloxy)butane 5.25 (5.2 g, 13.05 mmol, 1,4-bis(2{p-tolylsulfonylamino}phenylthio)-butane 5.21 (8.0 g, 13.05 mmol) and anhydrous potassium carbonate (8.8 g, 63.72 mmol). This synthesis yielded a white precipitate of 9,14-bis-(p-tolylsulfonyl)-9,14-diaza-1,6-thio-7,8:15,16-dibenzocyclohexadecane 5.35 (7.5 g, 11.26 mmol, 86 %), m.p.235-238°C. Found C, 60.00; H, 6.00; N, 4.60; S, 18.60; requires C, 61.32; H, 5.75; N, 4.21; S, 19.26 %, for $C_{34}H_{38}N_2S_4O_4$, m_r =666. ν/cm^{-1}: 650, 670, 725, 765, 820, 1055, 1090, 1160, 1347, 1435, 1470, 1495, 1580, 1600, 2850, 2920, 2950, 3050. ^1H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.25-2.00(mc, 8H-$SCH_2\underline{CH}_2$ and -$NCH_2\underline{CH}_2$); 2.63-3.10(mc, 4H-$S\underline{CH}_2$); 2.40(s, 6H-$C\underline{CH}_2$); 3.13-3.88(mc, 4H-$N\underline{CH}_2$); 6.50-8.00(mc, 16H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.6, 25.9, 28.4, 32.6, 50.9, 125.6, 127.3, 128.0, 128.2, 129.0, 129.5, 129.8, 129.9, 136.4, 143.5. Mass spectrum m/z: 666(M^{*} =20 %), 612(15), 511(56), 458(15), 356(48), 334(56), 304(16), 200(60), 149(25), 136(85), 109(20), 91(100), 80(20), 65(33), 39(27), 18(17).

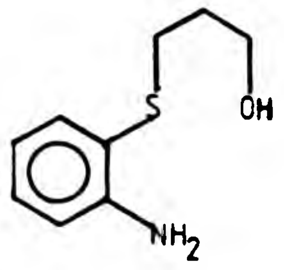
4-(*p*-Tolylsulfonyl)-4,1-aza-thio-5,6-benzocyclohexane 5.36



5.36

The same general procedure was used as for the cyclisation of the macrocycles above 5.30-5.35, 1,2-bis(*p*-tolylsulfonylamino)phenylthio)-ethane 5.20 (6.00 g, 10.26 mmol) was reacted with 1,2-bis(*p*-tolylsulfonyloxy)ethane 5.24 (3.80 g, 10.26 mmol) in N,N'-dimethylformamide in the presence of anhydrous potassium carbonate (6.40 g, 46.31 mmol) at 100°C. After work up, as above, white crystals of 4-(*p*-tolylsulfonyl)-4,1-aza-thio-5,6-benzocyclohexane 5.36 (4.90 g, 16.07 mmol, 78 %), m.p. 158-160°C were obtained. Found C, 58.20; H, 5.30; N, 4.40; S, 20.70; requires C, 58.90; H, 4.95; N, 4.60; S, 20.99 %, for $C_{15}H_{15}NS_2O_2$, m_r = 305. ν/cm^{-1}: 650, 668, 687, 708, 720, 732, 763, 803, 817, 840,915, 947, 1020, 1032, 1068, 1093, 1123, 1162, 1185, 1213, 1258, 1292, 1303, 1323, 1360, 1400, 1405, 1432, 1440, 1473, 1497, 1560, 1600, 2930, 2990, 3070. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 2.40(s, -C$\underline{H_3}$); 2.88(t, *J* 4.8Hz, 2H-S$\underline{CH}_2$); 3.97(t, *J* 4.8Hz, 2H-N$\underline{CH}_2$), 6.75-7.75(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.5, 25.8, 44.7, 119.9, 124.6, 126.5, 126.9, 128.0, 128.4, 129.8, 130.0, 135.4, 144.0 Mass spectrum m/z: 305(M^{*} =100 %), 240(5), 193(10), 150(100), 117(90), 91(80), 65(70), 45(60).

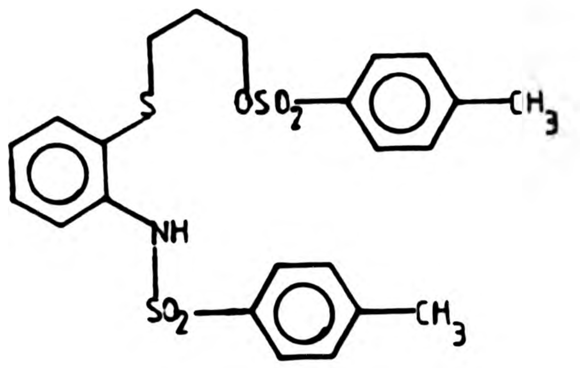
8,5-Aza-thio-6,7-benzo-octan-1-ol 5.37



5.37

Sodium pellets (5.00 g, 217.49 mmol) were dissolved in dry methanol (200 cm^3), keeping the reaction cool in an ice-bath, and to this was added *o*-aminothiophenol (26.35 g, 214.48 mmol), with stirring under a nitrogen atmosphere. After ten minutes 3-bromopropan-1-ol (29.25 g, 210.43 mmol) in methanol (50 cm^3) was added dropwise and an overnight stir preceeded a 6 hour reflux. On cooling and treating with saturated aqueous sodium bicarbonate the organic product was extracted with dichloromethane and dried over anhydrous sodium sulphate. Evaporation to dryness under vacuum yielded 8,5-aza-thio-6,7-benzo-octan-1-ol 5.37 (32.30 g, 176.25 mmol, 84 %), as a brown oil. Found C, 52.80; H, 8.20; N, 8.60; S, 20.00; requires C, 52.79; H, 8.23; N, 8.80; S, 20.14 %, for $C_7H_{13}NSO$, m_r = 159. V/cm^{-1}: 680, 750, 905, 1050, 1140, 1158, 1253, 1310, 1448, 1480, 1605, 2870, 2930, 3030, 3060, 3340. ^1H nmr (60 MHz, $CDCl_3$) δ/ppm: 1.70(p, *J* 2Hz, 2H-$SCH_2\underline{CH_2}$); 2.78(t, *J* 2Hz, 2H-$S\underline{CH_2}$); 3.60(t, *J*, 2Hz, 2H-$O\underline{CH_2}$); 3.83(s, 3H-OH- and -NH_2-); 6.50-7.50(mc, 4H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$) δ/ppm: 31.3, 32.3, 61.2, 115.2, 118.0, 118.8, 129.7, 135.8, 148.2. Mass spectrum m/z: 491($M^{\bullet}$ =2 %), 355(2), 336(11), 319(20), 213(5), 200(4), 181(2), 172(19), 164(91), 163(20), 155(18), 149(14), 136(49), 131(56), 130(50), 91(100), 65(40).

1,8-Di(*p*-tolylsulfonyl)-8,1,5-aza-oxo-thio-6,7-benzo-octane 5.38

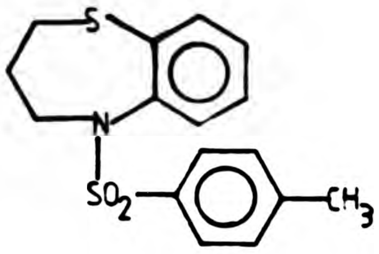


5.38

To 8,5-aza-thio-6,7-benzo-octan-1-ol 5.37 (60.00 g, 32.74 mmol) in pyridine (50 cm^3) was added *p*-toluenesulfonyl chloride (19.00 g, 99.66 mmol) in portions keeping the reaction temperature below 10°C. Stirring was maintained for 0.5 hours at this temperature then stirred at room temperature for a further 2.5 hours. This was then treated with a HCl/ice mixture and the product was extracted with dichloromethane and washed with sodium bicarbonate. The dichloromethane phase was dried over anhydrous sodium carbonate and evaporated to dryness to give an oil (12.05 g). A tlc of the oil (using dichloromethane as elutant) showed 2 spots on the plate. The oil was purified using a silica column and the impurities came down with toluene. The desired product was removed from the column using toluene/dichloromethane (1:1) and 1,8-(*p*-tolylsulfonyl)-8,1,5-aza-oxo-thio-6,7-benzo-octane 5.38 (11.00 g, 22.37 mmol, 68 %) was obtained as an oil. Found C, 5.50; H, 5.00; N, 2.65; S, 19.33; requires C, 5.62; H, 5.13; N, 2.85; S, 19.57 %, for $C_{23}H_{25}NS_3O_5$, m_r = 491. ν/cm^{-1}: 630, 668, 735, 763, 817, 925, 990, 1095, 1170, 1215, 1270, 1340, 1360, 1390, 1480, 1600, 2930, 2970, 3065, 3250. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.76(p, *J* 4.8 Hz, 2H-$SCH_2\underline{CH}_2$); 2.25(s, 3H-$C\underline{CH}_3$); 2.36(s, 3H-$C\underline{CH}_3$); 2.55(t, *J* 4.8 Hz, 2H-$S\underline{CH}_2$); 4.00(t, *J*, 4.8 Hz, 2H-

O$\underline{CH_2}$); 6.90-7.90(mc, 13H-aromatic and -NH-). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.5, 21.7, 28.6, 32.0, 68.3, 119.7, 123.5, 124.8, 127.3, 128.0, 129.8,130.1, 133.0, 135.41, 136.63, 136.4, 138.8, 144.3, 145.2. Mass spectrum m/z: 491(M^{*} =2 %), 355(20), 336(1), 319(19), 181(2), 166(6), 165(13), 164(91).

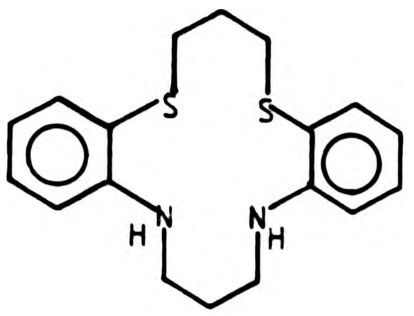
5-(p-Tolylsulfonyl)-5,1-aza-thio-6,7-benzocycloheptane 5.39



5.39

The ditosylated alcohol/amine 5.38 (3.00 g, 6.12 mmol) in N'N-dimethylformamide with anhydrous potassium carbonate (28.94 mmol) was heated at 100°C for 3 hours after which water was added. The desired product was extracted with dichloromethane, dried over anhydrous sodium sulphate and then evaporated to a low volume under vacuum giving a white solid. This was recrystallised from dichloromethane/cyclohexane to yield white crystals of 5-(p-tolylsulfonyl)-5,1-aza-thio-6,7-benzocycloheptane 5.39 (1.50 g, 4.70 mmol, 77 %), m.p. 131-133°C. Found C, 61.95; H, 5.57; N, 4.50; requires C, 60.16; H, 5.36; N, 4.38 %, for $C_{16}H_{17}NS_2O_2$, m_r = 319. ν/cm^{-1}: 665, 680, 728, 742, 753, 810, 825, 863, 883, 898, 964, 1020, 1030, 1040, 1070, 1095, 1127, 1153, 1193, 1245, 1255, 1287, 1305, 1325, 1340, 1373, 1415, 1443, 1458, 1498, 1580, 1600, 1735, 2840, 2920, 2960, 3045. ^{1}H nmr(80 MHz, $CDCl_3$), δ/ppm: 1.75-2.25(mc, 2H-SCH$_2\underline{\text{CH}}_2$); 2.38(s, 3H-C$\underline{\text{CH}}_3$); 2.73(t, $\underline{J}$ Hz, 2H-S$\underline{\text{CH}}_2$); 3.75(t, $\underline{J}$ 5 Hz, 2H-N$\underline{\text{CH}}_2$); 7.05-7.80(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 21.5, 30.9, 31.4, 49.8, 127.7, 128.2, 128.5, 129.4, 130.6, 133.7, 136.4, 138.3, 143.1, 143.3. Mass spectrum m/z: 319(M* = 100 %), 223(4), 164(2), 149(100), 136(2), 135(3), 95(5), 83(8), 71(10), 59(11), 56(21), 54(17).

8,12-Diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane 5.40



5.40

Method A -Via Detosylation with Sodium/Naphthalene in THF

Sodium wire (1.5 g, 65.25 mmol) was dissolved in a solution of naphthalene (9.2 g, 71.78 mmol) in dried THF (70 cm^3) under a nitrogen atmosphere for one hour. The resulting green solution was cooled in a cardice/acetone bath until the solution almost solidified (0.5 hours) then solid 8,12-bis(*p*-tolylsulfonyl)-8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane 3.27 (8.0 g, 12.52 mmol) was added. This mixture was maintained at cardice/acetone temperature for 20 minutes, then allowed to warm to room temperature with stirring for an hour. Acetic acid (20 cm^3) was added slowly keeping the reaction cool in an ice-bath followed by 20 % ammonium chloride solution. Distilled water (50 cm^3) was added to the brown solution and the organic layer was extracted with dichloromethane and dried over anhydrous sodium sulphate. After evaporation to dryness under vacuum the naphthalene was removed by using a silica column with cyclohexane. The macrocycle was removed from the column with dichloromethane. This was evaporated to dryness and the residual naphthalene was removed by sublimation under vacuum at 50-60 °C, and an oil was obtained (3.30 g). The oil required purification by gel filtration.

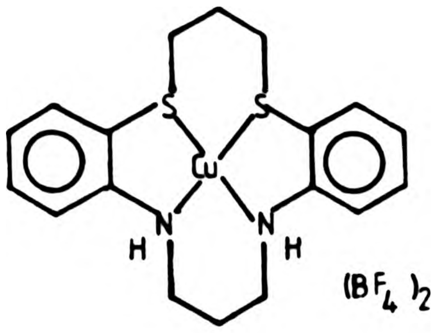
A Sephadex LH-20 column (length-25cm, diameter-1cm) was packed with dichloromethane after swelling the Sephadex LH-20 for 24 hours in dichloromethane. The sample (0.5 g) was loaded on with dichloromethane and eluted with the same solvent. Approximately 15 cm^3 of dichloromethane was required for complete removal of the sample from the column. The first fraction (5 cm^3) contained the pure detosylated macrocycle (0.1 g, 16 %), the remaining fractions still contained impurities. (Note the column needed to be eluted several times with dichloromethane before loading of next sample was possible). 8,12-Diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane 5.40 was obtained as a brown oil. Found C, 64.10; H, 6.90; N, 8.50; S, 18.60; requires C, 65.41; H, 6.71; N, 8.48; S, 19.40 %, for $C_{18}H_{22}N_2S_2$, $m_r = 330$. ν/cm^{-1} 755, 1176, 1213, 1280, 1300, 1330, 1435, 1464, 1493, 1515, 1583, 1600, 1620, 2880, 2950, 2980, 3040, 3080, 3390. ^{1}H nmr (60 MHz, $CDCl_3$) δ/ppm: 1.35-2.00(mc, 4H-$\mathrm{SCH_2\underline{CH}_2}$ and -$\mathrm{NHCH_2\underline{CH}_2}$); 2.65(t, $\underline{J}$ 7.3 Hz, 4H-$\mathrm{S\underline{CH}_2}$); 3.15(t, $\underline{J}$ 5.3 Hz, 4H-$\mathrm{N\underline{CH}_2}$); 5.12(s, 2H-$\mathrm{CH_2\underline{NH}}$); 6.30-7.50(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 29.1, 33.4, 41.5, 110.2, 116.9, 117.5, 130.2, 136.4, 149.3. Mass spectrum m/z: 330(M*=49 %), 290(4), 206(13), 181(14), 178(16), 178(16), 176(13), 169(12), 167(20), 166(29), 165(26), 164(36), 163(12), 162(13), 151(11), 150(25), 149(35), 144(10), 141(19), 138(30), 131(26), 136(100), 132(28), 128(75)

Method B -Via Direct Alkylation Methods With 1,3-Dibromopropane

1,3-Bis(*o*-aminophenylthio)propane 5.16 (25.00 g, 86.08 mmol), anhydrous sodium carbonate (32.90 g, 369.84 mmol) and 1,3-dibromopropane (17.40 g, 86.18 mmol) were refluxed neat for 90 hours at an oil-bath temperature of 160°C with mechanical stirring. After cooling the brown solid was extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulphate and evaporated to dryness under vacuum at 50°C. A brown oil (25.8 g) was obtained and this was purified by column chromatography.

A silica column (25cm × 1.1cm) was packed with toluene and the sample (1.25 g) was loaded on with toluene. The impurities were removed first with neat toluene then with dichloromethane. The desired fraction was removed from the column with 10 % THF in dichloromethane. This was evaporated to dryness to an oil (0.72 g) and further purified via gel filtration. A Sephadex LH-20 column (30 cm 1.1 cm) was packed with chloroform (swelling and eluting agent), and the sample (0.5 g) was loaded on with chloroform. The first fraction was collected (5 cm^3) and evaporated to yield the pure oil 5.40 (0.35 g, 25 %).

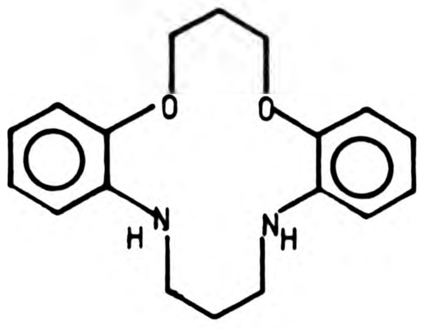
[(8,12-Diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane)copper(II)] ditetrafluoroborate 5.41



5.41

Copper(II) tetrafluoroborate (0.21 g, 0.89 mmol) in methanol (20 cm^3) was added to 8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane 5.40 (0.17 g, 0.51 mmol) in acetonitrile/dichloromethane (50 cm^3), resulting in a green solution which was evaporated to a low volume under vacuum. [(8,12-Diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradecane) copper(II)] difluoroborate 5.41 was thus obtained as a green solid (0.12 g, 0.22 mmol, 42 %), m.p. 300-305°C. Found C, 37.11; H, 3.72; N, 4.18; requires C, 38.07; H, 3.91; N, 4.93 %, for $C_{18}H_{22}N_2S_2B_2F_8Cu$, $m_r = 568$. ν/cm^{-1}: 760, 960, 1030-1150(b), 1300, 1343, 1420, 1440, 1478, 1500, 1560, 1580, 1590, 1620, 1630, 2850, 2920, 2960, 3140, 3400.

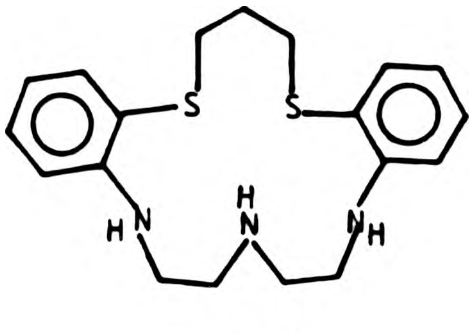
8,12-Diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.42



5.42

Detosylation of 8,12-bis(p-tolylsulfonyl)-8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.29 (8.00 g, 13.18 mmol) was carried out as reported above for 5.40, using naphthalene (9.5 g, 74.12 mmol) and sodium wire (1.60 g, 69.50 mmol). After work-up a pale pink solid was obtained of 8,12-diaza-1,5-dioxo-6,7:13,14-dibenzocyclotetradecane 5.42 (91.6 g, 5.3623 mmol, 41 %), m.p. 203-204°C. (No attempt was made to purify this ligand and the yield calculated was based on the pure product as judged from the ^{13}C and ^{1}H nmr spectra). Found C, 72.38; H, 7.20; N, 9.00; requires C, 72.45; H, 7.43; N, 9.39 %, for $C_{18}H_{22}N_2O_2$, m_r = 298. ν/cm^{-1}: 732, 963, 1013, 1048, 1060, 1100, 1125, 1140, 1210, 1235, 1250, 1305, 1345, 1450, 1510, 1600, 2860, 2920, 2950, 3040, 3400. ^{1}H nmr (80 MHz, $CDCl_3$), δ/ppm: 1.80-2.50(mc, 4H-$OCH_2\underline{CH_2}$ and -$NHCH_2\underline{CH_2}$); 3.00-3.50(mc, 4H-$NH\underline{CH_2}$); 3.90-4.40(mc, 4H-$O\underline{CH_2}$); 4.75(s, 2H-$CH_2\underline{NH}$); 6.50-7.10(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 26.8, 28.7, 44.6, 67.9, 110.1, 111.6, 116.6, 121.8, 138.8, 146.7. Mass spectrum m/z: 298 (M^{*} =100 %), 254911), 190(36), 176(9), 162(67), 150(26), 149(33), 148(24), 134(42), 91(15), 65(20).

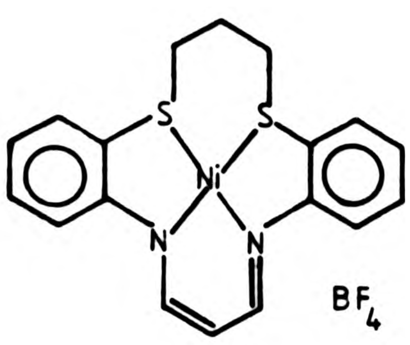
8,11,14-Triaza-1,5-dithio-6,7:15,16-dibenzocyclohexadecane 5.43



5.43

8,11,14-Tris(p-tolylsulfonyl)-8,11,14-triaza-1,5-dithio-6,7:15,16-dibenzocyclohexadecane 5.28 (8.00 g, 9.73 mmol) was treated (as in the preparation of 5.40 above) with naphthalene (10.10 g, 78.02 mmol) and sodium wire (1.70 g,73.95 mmol) in THF. An oil was produced consisting mainly of the detosylated macrocycle 8,11,14-triaza-1,5-dithio-6,7:15,16-dibenzocyclohexadecane 5.43 (2.10 g, 5.84 mmol, 60 %). No attempt was made to purify this oil by gel filtration because of similar purification problems expected for this oil as in the purification of 5.40. V/cm^{-1}: 610, 668, 685, 750, 785, 815, 955, 1012, 1035, 1082, 1105, 1125, 1163, 1255, 1285, 1315, 1380, 1450, 1480, 1500, 1590, 1610, 2860, 2930, 2960, 3030, 3060, 3350, 3460. ^{1}H nmr (60 MHz, CDCl$_3$), δ/ppm: 1.20-1.85(mc, 2H-SCH$_2\underline{CH_2}$); 2.10-4.00(mc, 12H-S$\underline{CH_2}$ and -N$\underline{CH_2}$); 5.35(s, 3H-CH$_2\underline{NH}$); 6.40-7.70(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, CDCl$_3$), δ/ppm: 29.1, 36.9, 40.0, 47.0, 114.8, 116.8, 118.8, 131.6, 136.2, 148.8. Mass spectrum m/z: 359(M* = 5 %), 319(24), 268(4), 260(40, 215(5), 211(12), 180(8), 167(12), 164(58), 163(25), 149(16), 141(12), 137(9), 131(39), 130(58), 129(34), 128(33), 125(33), 124(35), 109(25), 108(16), 93(25), 91(100), 80(15), 79(35), 78(10), 77(19), 65(38).

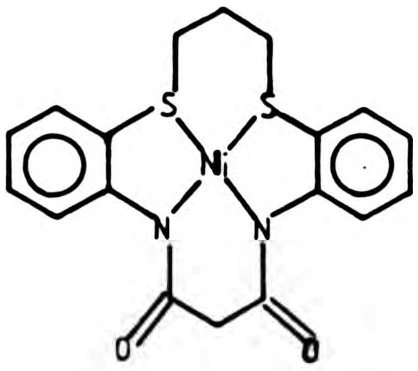
[(10-Methyl-8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradeca-8,10-dienato)nickel(II)] monotetrafluoroborate 5.44



5.44

1,3-Bis(o-aminophenylthio)propane 5.16 (4.14 g, 14.25 mmol), nickel(II)acetate (1.90 g, 7.63 mmol) and nickel(II)tetrafluoroborate (2.60 g, 7.64 mmol) were heated under nitrogen in dimethylacetamide (100 cm^3). When refluxing commenced 2-methyl-3-ethoxyacrolein (1.63 g, 14.28 mmol) was added. Refluxing was maintained for four hours. After cooling and evaporating to a low volume shiny green crystals were obtained of [(10-methyl-8,12-diaza-1,5-dithio-6,7;13,14-dibenzocyclotetradeca-8,10-dienato)nickel(II)] monotetrafluoroborate 5.44 (3.65 g, 7.53 mmol, 53 %), m.p. 300-305°C. Found C, 43.90; H, 4.60; N, 5.30; S, 13.0; requires C, 42.07; H, 3.95; N, 5.78; S, 13.22 % for $C_{19}H_{19}N_2S_2BF_4Ni$, m_r=485. ν/cm^{-1}:632, 753, 906, 953, 1050, 1170, 1210, 1255, 1310, 1360, 1465, 1500, 1575, 1615, 2920. Mass spectrum m/z: 398(M^{*} =4 %), 397(3), 368(1), 341(5), 290(4), 235(4), 233(15), 204(15), 176(12), 165(20), 149(15), 136(70), 109(20), 87(48), 72(14), 44(100).

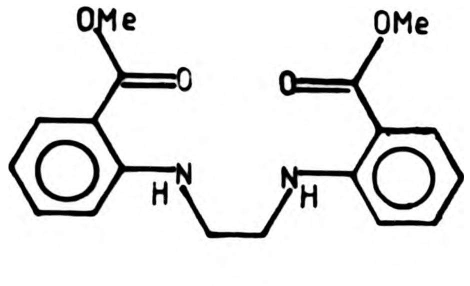
[(8,12-Diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradeca-9,11-dionato)-nickel(II)] 5.45



5.45

1,3-Bis(o-aminophenylthio)propane 5.16 (7.85 g, 27.03 mmol) was refluxed for 113 hours under nitrogen in xylene (100 cm^3) with nickel(II) acetate (6.8 g, 27.32 mmol) and dimethyl malonate (4.4 g, 33.30 mmol). After cooling a brown solid of [(8,12-diaza-1,5-dithio-6,7:13,14-dibenzocyclotetradeca-9,11-dionato)nickel(II)] 5.45 (9.75 g, 23.49 mmol, 87 %), m.p. 294-296^{o}C was obtained. Found C, 52.60; H, 3.80; N, 5.90; S, 13.50; Ni, 11.10; requires C, 52.07; H, 3.88; N, 6.75; S, 15.44; Ni, 14.14 %, for $C_{18}H_{16}N_2O_2S_2Ni$, m_r=415. V/cm^{-1}: 720, 745, 755, 766, 885, 910, 945, 995, 1030, 1160, 1225, 1270, 1290, 1320, 1370, 1405, 1440, 1470, 1500, 1560, 1575, 1590, 1605, 1645, 1675, 2910, 2930, 2970, 3000, 3040. Mass spectrum m/z: 414(M^{*}= 15 %), 358(15), 316(5), 290(20), 165(80), 151(70), 136(85), 132(30), 124(45), 108(25), 96(57), 93(100), 80(27), 77(23), 69(50), 65(40), 58(15), 51(20).

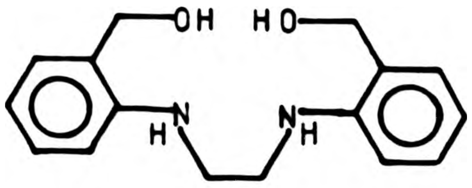
N,N-Bis(o-carbomethoxyphenyl)-1,2-diaminoethane 5.46



5.46

In a reaction vessel under nitrogen gas was placed methylanthranilate (302 g, 2 mol) and with stirring was added 1,2-dibromoethane (187 g, 1 mol). Then fine grain anhydrous sodium carbonate (500 g) was added. A gentle reflux was maintained for 60 hours. The oil bath temperature was maintained in the range 140-150 °C. The mixture was constantly stirred and the solid dislodged from the sides of the reaction flask. On cooling the mixture solidified and was extracted 6 times with hot tetrahydrofuran (350 cm^3 portions each time). The collective extracts were evaporated under vacuum almost to dryness and methanol (200 cm^3) was added. After cooling to 0 °C the white solid was collected, washed with cold methanol and dried, (165.52 g, 0.504 mol 48 %). On recrystallisation from methanol, white needles were obtained of N,N-bis(o-carbomethoxyphenyl)-1,2-diaminoethane 5.46, m.p. 117-119 °C. Found C, 66.40; H, 6.20; N, 8.20; requires C, 65.84; H, 6.14; N, 8.53 %, for $C_{18}H_{20}N_2O_4$, m_r = 328. ν/cm^{-1}: 740, 1233, 1258, 1377, 1457, 1513, 1578, 1682, 2880, 2920, 3330. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 3.50(t, J 2.7 Hz, 4H-NHCH$_2$); 3.80(s, 6H-OCH$_3$); 6.50-7.60(mc, 8H-aromatic); 7.8(d, J 6.7 Hz, 2H-CH$_2$NH). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 42.1, 51.4, 110.4, 114.9, 131.8, 134.6, 150.8, 169.0. Mass spectrum m/z: 328(M^{*}=13 %), 177(11), 164(45), 148(10), 132(100), 119(5), 105(17), 92(6), 77(33), 65(4), 45(13), 39(4), 18(5).

4,7-Diaza-2,3:8,9-dibenzodeca-1,10-diol 5.47

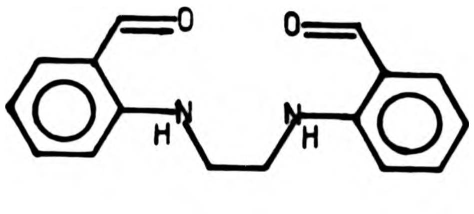


5.47

In a reaction flask (2 l) was placed lithium aluminium hydride (25 g) and to this was added calcium hydride, dried tetrahydrofuran (500 cm^3). With rapid stirring n,n-bis(o-carbomethoxyphenyl)1,2-diaminoethane 5.46 (120 g in 600 cm^3 THF; 0.37 mol) was added slowly to the reaction mixture via a quickfit dropping funnel. After addition the mixture was refluxed for 1 hour then allowed to cool to room temperature. Then slowly with fast stirring distilled water was added (25 cm^3), followed by 15 % sodium hydroxide solution (25 cm^3) and then again with distilled water (75 cm^3). The mixure was heated and filtered while hot. The filtrate contained the dialcohol. Five further extractions were carried out using THF (350 cm^3 portions) and the combined six extracts were evaporated almost to dryness. Methanol was added (200 cm^3), and the solution was cooled to 0 °C yielding white needles of 4,7-diaza-2,3:8,9-dibenzodeca-1,10-diol 5.47 (78.97 g, 0.26 mol, 72 %) which were washed with cold methanol. Recrystallisation was from methanol, m.p. 123-125 °C. Found C, 71.10; H, 7.80; N, 10.30; requires C, 70.56; H, 7.40; N,10.37 %, for $C_{16}H_{20}N_2O_2$, m_r = 272. V/cm^{-1}: 615, 742, 767, 824, 854, 868, 930, 943, 970, 1008, 1060, 1123, 1160, 1193, 1223, 1250. 1296, 1337, 1378, 1403, 1460, 1510, 1588, 1610, 2905, 3200, 3300. ^{1}H nmr (60 MHz, $CDCl_3$),

δ/ppm: 3.47(s, 4H-NH$\underline{CH_2}$); 4.60(s, 4H-HO$\underline{CH_2}$); 4.80(s, 2H-$CH_2\underline{NH}$ and -CH_2OH); 6.50-7.35(mc, 8H-aromatic). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 42.1, 63.8, 110.4, 116.4, 125.6, 128.9, 129.9, 147.2. Mass spectrum m/z: 272(M^{*}=15 %), 150(4), 137(45), 118(100), 106(9), 91(27), 77(6), 65(5), 30(6), 18(10).

4,7-Diaza-2,3:8,9-dibenzodeca-1,10-dione 5.48



5.48

Type "B" Manganese Dioxide

Manganese(II)carbonate (2 Kg, 17.4 mol) was spread out on aluminium foil and placed in a furnace for 48 hours at 280-300 °C until the powder was completely black. After cooling, 15 % nitric acid (4 l) was added and with regular stirring the reaction took place (nitric acid was used to react with any unreacted $MnCO_3$). The black solid was filtered and washed with deionised water until the solid was acid free. The activated MnO_2 was placed in the furnace again for a further 24 hours at the same temperature, then removed and stored (1212 g, 13.94 mol).

In a reaction flask (2 l) the above type "B" MnO_2 (300 g, 3.45 mol) was placed and with fast stirring under a nitrogen atmosphere was added 4,7-diaza-2,3:8,9-dibenzodeca-1,10-diol 5.47 (35.0 g, 0.117 mol) as a suspension in anhydrous sodium dried diethyl ether (1500 cm^3). After refluxing for 18 hours the MnO_2 was filtered and extracted 10 times with hot chloroform (400 cm^3 portions each time). The combined extracts were evaporated approximately to 50 cm^3 and methanol (300 cm^3) was added and the mixture was cooled to 0 °C. The yellow product was filtered and washed with cold methanol and dried in a vacuum oven at 50 °C. The dried product 4,7-diaza-2,3:8,9-dibenzodeca-1,10-dione 5.48 (23.4 g, 0.87 mol, 75 %) was collected. Recrystallisation was from methanol m.p. 176-178 °C. Found C, 71.60; H, 6.20; N, 10.10; requires C, 71.62; H, 6.01; N, 10.44 %, for $C_{16}H_{16}N_2O_2$, m_r = 268. ν/cm^{-1}: 793, 848, 1015, 1043, 1100, 1130, 1152, 1203, 1280, 1320, 1358, 1443, 1505, 1555, 1593, 1645, 2707, 2905, 3310. ^{1}H nmr (60 MHz, $CDCl_3$), δ/ppm: 3.55(t, $\underline{J}$ 3Hz, 4H-NH$\underline{CH_2}$); 6.55-7.65(mc, 8H-aromatic); 9.80(s, 2H-O$\underline{CH_2}$). ^{13}C nmr (20.12 MHz, $CDCl_3$), δ/ppm: 41.5, 110.63, 115.40, 118.7, 135.9, 136.8, 150.4, 194.0. Mass spectrum m/z: 268(M^*=18 %), 147(4), 134(100), 116(11), 106(27), 91(15), 77(32), 65(6), 44(8), 39(4), 28(4), 18(12).

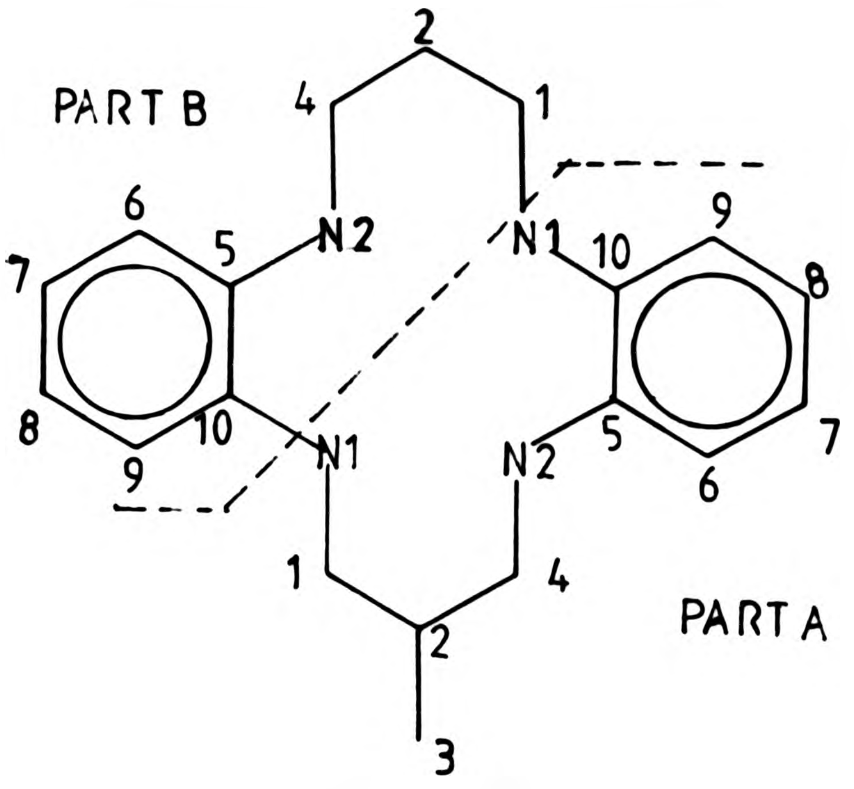
References

1. Tasker, P.A., Fleischer, E.B., J. Amer. Chem. Soc., 92, 7072 (1970).
2. Behr, H, Breitmaier, E., Chem. Ber., 111, 913 (1978).
3. Cannon, R.D., Chiswell, B., Venazi, L.M., J. Chem. Soc., A, 1277 (1967).
4. Hay, R.W., Lawrence, G.A., Shone, U.R., J. Chem. Soc. Dalton, 942 (1976).
5. Marvel, C.S., Sekera, V.C., Org. Synth. Coll. Vol. 3, 366 (1955).
6. Sugimoto, B.M., Nonoyama, M., Ito, T., Fujita, J.Inorg. Chem., 22, 950 (1983).
7. Green, M., Smith, J., Tasker, P.A., Inorg. Chim. Acta., 17 (1971).

APPENDIX

Appendix 1 X-Ray Crystallography Data

Appendix 2 X-Ray Structure Factors



$(C_{19}H_{26}N_4)$

Hydrogen atom labelling is H1A1 and H1A2 for atoms on C1A and H1B1 and H1B2 on C1B etc. Anilino protons are H1AN, H1BN, H2BN and H2BN

TABLE 2 **Fractional atomic coordinates for the hydrogen atoms for $C_{19}H_{26}N_4$**

Atom	x	y	z
H(1A1)	0.8335	0.3308	0.0552
H(1A2)	0.7660	0.1081	0.0376
H(2A)	0.7072	0.4565	0.1057
H(3A1)	0.6557	0.4881	0.0075
H(3A2)	0.7196	0.7174	0.0260
H(3A3)	0.6150	0.6593	0.0380
H(4A1)	0.5416	0.3769	0.0955
H(4A2)	0.5821	0.1463	0.0658
H(6A)	0.4027	0.1005	0.0777
H(7A)	0.2613	-0.2306	0.0824
H(8A)	0.3322	-0.6057	0.1531
H(9A)	0.4783	-0.5874	0.2053
H(1B1)	0.6667	-0.6367	0.2245
H(1B2)	0.6600	-0.3851	0.2774
H(2B1)	0.8108	-0.5702	0.3119
H(2B2)	0.7985	-0.2324	0.2904
H(4B1)	0.9577	-0.4568	0.2681
H(4B2)	0.8677	-0.6267	0.2223
H(6B)	1.0018	-0.5772	0.1802
H(7B)	1.0757	-0.5845	0.1065
H(8B)	1.0275	-0.3757	0.0158
H(9B)	0.9276	0.0009	0.0365
H(1AN)	0.8255	0.1633	0.1375
H(2AN)	0.6917	0.0550	0.1310
H(1BN)	0.6569	-0.1042	0.2241
H(2BN)	0.8767	-0.1154	0.2029

TABLE 3 Anisotropic thermal parameters (Å) for $C_{19}H_{26}N_4$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1A)	0.021(6)	0.052(8)	0.037(7)	0.009(7)	0.003(6)	0.004(6)
N(2A)	0.018(6)	0.062(8)	0.031(7)	0.011(7)	-0.003(6)	-0.005(6)
N(1B)	0.015(6)	0.054(7)	0.043(7)	0.009(7)	-0.003(6)	0.008(7)
N(2B)	0.032(6)	0.050(8)	0.031(7)	0.011(7)	-0.004(6)	0.004(7)
C(1A)	0.028(8)	0.060(10)	0.041(9)	0.021(9)	0.005(8)	0.009(8)
C(2A)	0.029(8)	0.052(10)	0.030(8)	0.004(8)	0.004(8)	0.000(8)
C(3A)	0.039(9)	0.053(10)	0.064(10)	0.010(10)	0.002(9)	0.002(9)
C(4A)	0.026(8)	0.048(9)	0.054(10)	0.009(9)	0.006(8)	0.001(8)
C(5A)	0.018(8)	0.054(10)	0.036(9)	0.009(9)	0.003(8)	0.007(9)
C(6A)	0.021(8)	0.075(11)	0.045(10)	0.003(10)	-0.002(9)	0.007(9)
C(7A)	0.013(8)	0.086(12)	0.038(9)	0.009(10)	-0.002(8)	-0.006(10)
C(8A)	0.020(9)	0.055(11)	0.065(12)	0.001(10)	-0.003(10)	-0.008(9)
C(9A)	0.025(9)	0.050(9)	0.059(10)	0.009(10)	0.006(9)	-0.002(9)

table 3 continued

C(10A)	0.016(8)	0.054(10)	0.039(9)	0.013(10)	-0.006(8)	0.010(9)
C(1B)	0.032(9)	0.065(11)	0.043(10)	0.008(9)	0.001(9)	0.010(9)
C(2B)	0.012(7)	0.067(10)	0.033(8)	0.012(9)	-0.008(8)	0.008(8)
C(4B)	0.022(8)	0.049(9)	0.041(8)	0.010(8)	-0.007(8)	0.015(7)
C(5B)	0.008(7)	0.050(10)	0.029(8)	0.003(8)	-0.011(7)	-0.001(7)
C(6B)	0.021(7)	0.059(11)	0.045(9)	-0.001(9)	0.001(8)	0.008(8)
C(7B)	0.015(8)	0.083(13)	0.065(11)	-0.003(11)	0.005(9)	0.001(9)
C(8B)	0.033(10)	0.084(14)	0.044(10)	0.002(10)	0.000(9)	0.012(10)
C(9B)	0.030(8)	0.058(11)	0.043(9)	0.008(9)	0.003(8)	0.011(9)
C(10B)	0.013(7)	0.046(9)	0.043(9)	0.005(9)	-0.004(8)	0.007(8)

TABLE 4 Bond lengths (Å) for $C_{19}H_{26}N_4$

N(1A) -C(1A)	1.469(17)	N(1A) -C(10B)	1.402(17)
N(2A) -C(4A)	1.463(18)	N(2A) -C(5A)	1.390(18)
N(1B) -C(10A)	1.427(15)	N(1B) -C(1B)	1.485(18)
N(2B) -C(4B)	1.436(17)	N(2B) -C(5B)	1.408(17)
C(1A) -C(2A)	1.494(19)	C(2A) -C(3A)	1.529(20)
C(2A) -C(4A)	1.501(18)	C(5A) -C(6A)	1.385(17)
C(5A) -C(10A)	1.411(20)	C(6A) -C(7A)	1.372(22)
C(7A) -C(8A)	1.353(23)	C(8A) -C(9A)	1.386(18)
C(9A) -C(10A)	1.386(20)	C(1B) -C(2B)	1.511(16)
C(2B) -C(4B)	1.524(19)	C(5B) -C(6B)	1.359(19)
C(5B) -C(10B)	1.412(19)	C(6B) -C(7B)	1.386(22)
C(7B) -C(8B)	1.363(23)	C(8B) -C(9B)	1.361(21)
C(9B) -C(10B)	1.380(20)		

TABLE 5 Bond Angles (°) for $C_{19}H_{26}N_4$

C(10B)-N(1A) -C(1A)	120(1)	C(5A) -N(2A) -C(4A)	117.7(9)
C(1B) -N(1B) -C(10A)	117(1)	C(5B) -N(2B) -C(4B)	119(1)
C(2A) -C(1A) -N(1A)	112(1)	C(3A) -C(2A) -C(1A)	109(1)
C(4A) -C(2A) -C(1A)	119(1)	C(4A) -C(2A) -C(3A)	108(1)
C(2A) -C(4A) -N(2A)	110.5(9)	C(6A) -C(5A) -N(2A)	126(1)
C(10A)-C(5A) -N(2A)	115(1)	C(10A)-C(5A) -C(6A)	118(1)
C(7A) -C(6A) -C(5A)	121(1)	C(8A) -C(7A) -C(6A)	120(1)
C(9A) -C(8A) -C(7A)	121(1)	C(10A)-C(9A) -C(8A)	120(1)
C(5A) -C(10A)-N(1B)	115(1)	C(9A) -C(10A)-N(1B)	125(1)
C(9A) -C(10A)-C(5A)	120(1)	C(2B) -C(1B) -N(1B)	108(1)
C(4B) -C(2B) -C(1B)	116(1)	C(2B) -C(4B) -N(2B)	109(1)
C(6B) -C(5B) -N(2B)	125(1)	C(10B)-C(5B) -N(2B)	116(1)
C(10B)-C(5B) -C(6B)	119(1)	C(7B) -C(6B) -C(5B)	120(1)
C(8B) -C(7B) -C(6B)	122(1)	C(9B) -C(8B) -C(7B)	118(1)
C(10B)-C(9B) -C(8B)	122(1)	C(5B) -C(10B)-N(1A)	117(1)
C(9B) -C(10B)-N(1A)	124(1)	C(9B) -C(10B)-C(5B)	119(1)

TABLE 6 Intermolecular distances (Å) for $C_{19}H_{26}N_4$

Atom1	Atom2	dist	S	a	b	c
H(3A2)...	N(1A)	2.85	1	0.0	1.0	0.0
H(1B1)...	N(2A)	2.74	1	0.0	-1.0	0.0
H(9A) ...	N(1B)	2.99	2	1.0	-1.0	0.0
H(4B1)...	N(2B)	2.82	2	2.0	-1.0	0.0
H(2B1)...	C(7A)	3.08	2	1.0	-1.0	0.0
H(4A1)...	C(8A)	3.02	1	0.0	1.0	0.0
H(4A1)...	C(9A)	2.69	1	0.0	1.0	0.0
H(4A1)...	C(10A)	2.78	1	0.0	1.0	0.0
H(9A) ...	C(10A)	3.01	2	1.0	-1.0	0.0
H(8A) ...	C(1B)	3.01	2	1.0	-1.0	0.0
H(8A) ...	C(2B)	3.05	2	1.0	-1.0	0.0
H(6B) ...	C(4B)	3.04	2	2.0	-1.0	0.0
H(4B1)...	C(5B)	2.77	2	2.0	-1.0	0.0
H(1AN)...	C(6B)	3.06	1	0.0	1.0	0.0
H(2B2)...	C(6B)	3.03	2	2.0	0.0	0.0
H(7A) ...	C(8B)	2.96	1	-1.0	0.0	0.0
H(8B) ...	C(8B)	2.58	-1	2.0	-1.0	0.0
H(9B) ...	C(8B)	3.03	-1	2.0	0.0	0.0
H(3A2)...	C(9B)	3.06	1	0.0	1.0	0.0
H(3A2)...	C(10B)	2.87	1	0.0	1.0	0.0

Symmetry Transformations:

The second atom is related to the first atom, at (x,y,z), by the symmetry operation S with (a,b,c) added to the (x',y',z') of S.

Where S

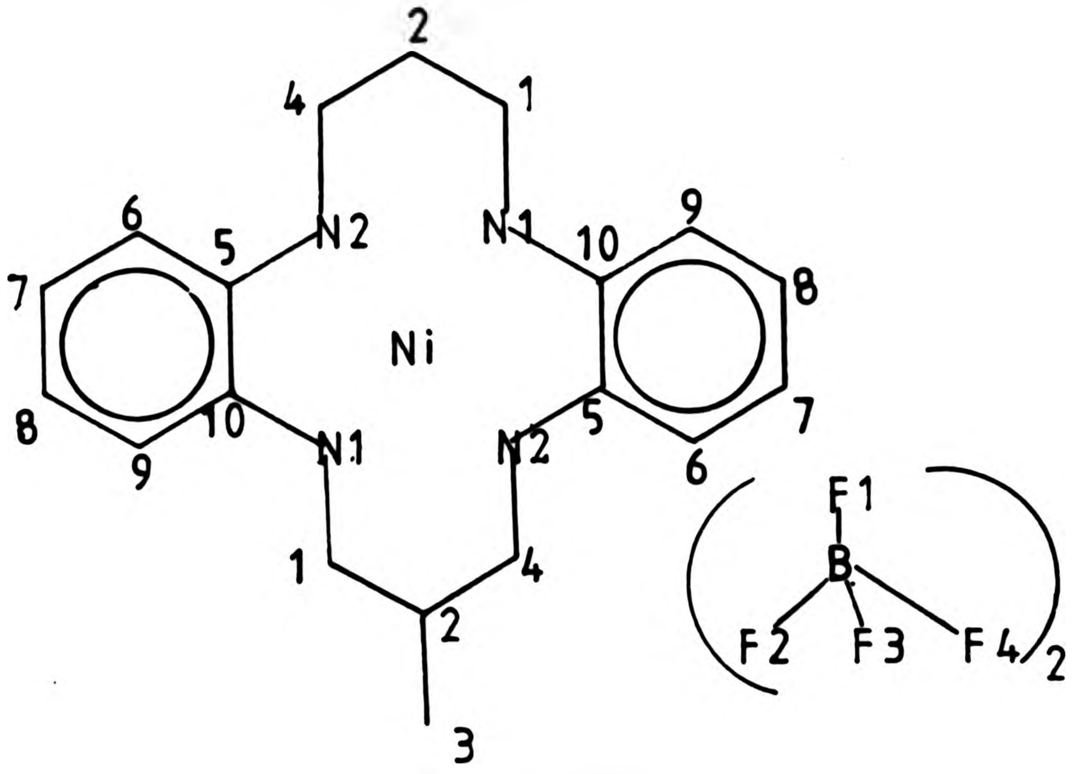
1 x, y, z

TABLE 7 Intramolecular distances (Å) for $C_{19}H_{26}N_4$

N(2A) ...N(1A)	2.86	N(2B) ...N(1A)	2.66
C(2A) ...N(1A)	2.46	C(4A) ...N(1A)	3.09
C(5B) ...N(1A)	2.40	C(9B) ...N(1A)	2.46
H(1A1)...N(1A)	2.11	H(1A2)...N(1A)	1.83
H(2A) ...N(1A)	2.61	H(9B) ...N(1A)	2.56
H(2AN)...N(1A)	1.73	H(2BN)...N(1A)	2.30
N(1B) ...N(2A)	2.62	C(1A) ...N(2A)	3.08
C(2A) ...N(2A)	2.44	C(6A) ...N(2A)	2.48
C(10A)...N(2A)	2.37	H(2A) ...N(2A)	2.59
H(4A1)...N(2A)	1.91	H(6A) ...N(2A)	2.60
H(1AN)...N(2A)	2.88	H(1BN)...N(2A)	2.45
N(2B) ...N(1B)	2.85	C(5A) ...N(1B)	2.40
C(9A) ...N(1B)	2.49	C(2B) ...N(1B)	2.43
C(4B) ...N(1B)	3.09	H(9A) ...N(1B)	2.83
H(1B1)...N(1B)	2.12	H(1B2)...N(1B)	1.75
H(2B2)...N(1B)	2.44	H(2AN)...N(1B)	2.66
C(1B) ...N(2B)	3.07	C(2B) ...N(2B)	2.42
C(6B) ...N(2B)	2.45	C(10B)...N(2B)	2.39
H(2B2)...N(2B)	2.50	H(4B1)...N(2B)	2.08
H(4B2)...N(2B)	2.02	H(6B) ...N(2B)	2.52
H(1AN)...N(2B)	2.78	H(1BN)...N(2B)	3.00
C(3A) ...C(1A)	2.46	C(4A) ...C(1A)	2.58
C(9B) ...C(1A)	2.93	C(10B)...C(1A)	2.49
H(2A) ...C(1A)	1.92	H(3A1)...C(1A)	2.39
H(3A2)...C(1A)	2.91	H(4A2)...C(1A)	2.58

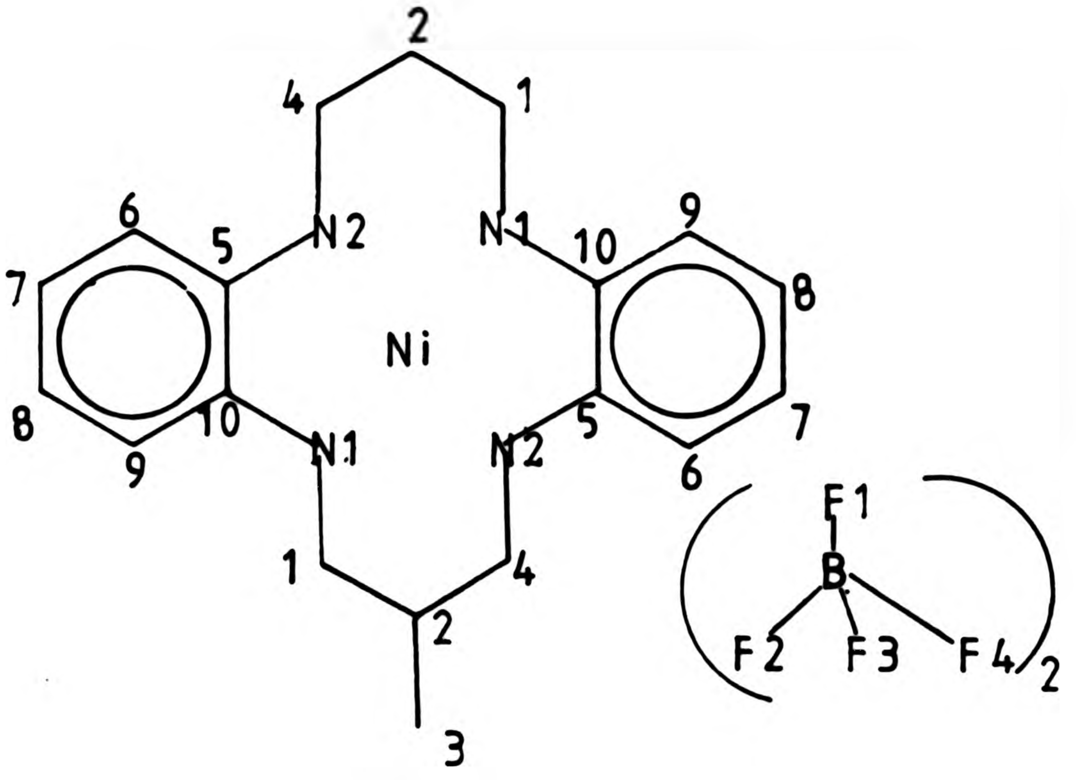
table 7 continued

H(2AN)...C(10A)	2.94	H(1BN)...C(10A)	1.86
C(4B) ...C(1B)	2.57	H(9A) ...C(1B)	2.69
H(2B1)...C(1B)	2.08	H(2B2)...C(1B)	2.03
H(4B2)...C(1B)	2.79	H(1BN)...C(1B)	2.03
H(1B1)...C(2B)	2.22	H(1B2)...C(2B)	1.74
H(4B1)...C(2B)	2.16	H(4B2)...C(2B)	2.11
H(1BN)...C(2B)	2.64	H(2BN)...C(2B)	2.82
C(5B) ...C(4B)	2.44	C(6B) ...C(4B)	2.88
H(1B1)...C(4B)	2.80	H(2B1)...C(4B)	2.11
H(2B2)...C(4B)	2.10	H(6B) ...C(4B)	2.46
H(2BN)...C(4B)	2.10	C(7B) ...C(5B)	2.37
C(8B) ...C(5B)	2.78	C(9B) ...C(5B)	2.40
H(4B1)...C(5B)	2.78	H(4B2)...C(5B)	2.64
H(6B) ...C(5B)	1.89	H(7B) ...C(5B)	2.94
H(1AN)...C(5B)	2.76	H(2BN)...C(5B)	1.67
C(8B) ...C(6B)	2.40	C(9B) ...C(6B)	2.74
C(10B)...C(6B)	2.39	H(4B1)...C(6B)	2.89
H(4B2)...C(6B)	2.77	H(7B) ...C(6B)	1.76
H(2BN)...C(6B)	2.85	C(9B) ...C(7B)	2.34
C(10B)...C(7B)	2.74	H(6B) ...C(7B)	2.07
H(8B) ...C(7B)	2.21	C(10B)...C(8B)	2.40
H(7B) ...C(8B)	1.89	H(9B) ...C(8B)	2.10
H(1A1)...C(9B)	2.91	H(1A2)...C(9B)	2.68
H(7B) ...C(9B)	3.01	H(8B) ...C(9B)	2.15
H(1AN)...C(9B)	3.03	H(1A1)...C(10B)	2.82
H(1A2)...C(10B)	2.50	H(9B) ...C(10B)	1.98
H(1AN)...C(10B)	1.97	H(2AN)...C(10B)	2.95
H(2BN)...C(10B)	2.28		



$[\mathrm{Ni}(\mathrm{C}_{19}\mathrm{H}_{26}\mathrm{N}_4)](\mathrm{BF}_4)_2$

Hydrogen atom labelling is H1A1 and H1A2 for atoms on C1A and H1B1 and H1B2 on C1B etc. Anilino protons are H1AN, H1BN, H2AN and H2BN



$[Ni(C_{19}H_{26}N_4)](BF_4)_2$

Hydrogen atom labelling is H1A1 and H1A2 for atoms on C1A and H1B1 and H1B2 on C1B etc. Anilino protons are H1AN, H1BN, H2AN and H2BN

TABLE 2 Fractional atomic coordinates for the hydrogen atoms for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

Atom	x	y	z
H(1A1)	-0.3265	0.1735	0.0194
H(1A2)	-0.3371	0.3881	0.0379
H(2A1)	-0.0676	0.4320	0.2862
H(2A2)	-0.2182	0.4231	0.3450
H(4A1)	0.0321	0.2422	0.4963
H(4A2)	-0.1107	0.1205	0.3411
H(6A)	0.2740	0.1737	0.6173
H(7A)	0.4967	-0.0328	0.7834
H(8A)	0.5602	-0.3226	0.5750
H(9A)	0.3779	-0.4126	0.2604
H(1AN)	-0.0507	0.3070	-0.0233
H(2AN)	0.1421	0.1988	0.2372

TABLE 3 Anisotropic thermal parameters ($Å^2$) for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.050(1)	0.036(1)	0.028(1)	0.013(1)	0.005(1)	-0.002(1)
N(1A)	0.055(5)	0.037(4)	0.044(5)	0.022(4)	0.008(4)	0.007(4)
N(2A)	0.043(5)	0.038(4)	0.024(4)	0.007(3)	0.003(4)	-0.009(4)
C(1A)	0.052(6)	0.042(6)	0.041(6)	0.008(5)	0.007(5)	0.004(5)
C(2A)	0.071(7)	0.045(6)	0.054(7)	0.011(5)	0.017(6)	0.005(5)
C(3A)	0.077(15)	0.068(15)	0.046(13)	0.010(11)	0.039(12)	0.022(12)
C(4A)	0.055(6)	0.047(6)	0.036(5)	0.007(5)	0.009(5)	-0.012(5)
C(5A)	0.041(6)	0.048(6)	0.027(5)	0.012(4)	0.002(5)	-0.008(4)
C(6A)	0.058(7)	0.056(7)	0.040(6)	0.009(5)	0.009(5)	-0.012(5)
C(7A)	0.053(7)	0.088(9)	0.038(6)	0.028(6)	0.007(5)	-0.010(6)
C(8A)	0.056(7)	0.065(7)	0.061(8)	0.032(6)	-0.005(6)	-0.007(6)
C(9A)	0.064(7)	0.054(6)	0.050(7)	0.021(5)	-0.004(6)	-0.001(5)
C(10A)	0.042(6)	0.052(6)	0.034(5)	0.022(5)	-0.010(5)	-0.017(5)

table 3 continued

F(1)	0.104(5)	0.066(4)	0.061(4)	0.000(3)	0.045(4)	-0.013(3)
F(2)	0.079(5)	0.169(7)	0.074(5)	0.077(5)	0.010(4)	0.019(5)
F(3)	0.132(6)	0.045(4)	0.105(5)	0.014(4)	0.064(5)	-0.005(3)
F(4)	0.089(5)	0.082(5)	0.099(5)	0.014(4)	0.046(4)	-0.021(4)
B	0.050(8)	0.047(7)	0.049(8)	0.012(6)	0.018(6)	-0.008(6)

TABLE 4 Bond lengths (Å) for [Ni($C_{19}H_{26}N_4$)](BF_4)$_2$

Ni	-N(1A)	1.931(7)	Ni	-N(2A)	1.920(6)
N(1A)	-C(1A)	1.490(14)	N(2A)	-C(4A)	1.475(13)
N(2A)	-C(5A)	1.447(10)	C(1A)	-C(2A)	1.505(12)
C(2A)	-C(3A)	1.430(24)	C(2A)	-C(4A)	1.534(13)
C(5A)	-C(6A)	1.354(11)	C(5A)	-C(10A)	1.383(12)
C(6A)	-C(7A)	1.388(14)	C(7A)	-C(8A)	1.373(15)
C(8A)	-C(9A)	1.364(14)	C(9A)	-C(10A)	1.391(13)
N(1A)	-C(10B)	1.440(10)	F(1)	-B	1.381(15)
F(2)	-B	1.370(12)	F(3)	-B	1.371(14)
F(4)	-B	1.370(12)			

TABLE 5 Bond angles (°) for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

N(1A)	-Ni	-N(1B)	180.0	N(1A)	-Ni	-N(2B)	88.0(3)
N(2A)	-Ni	-N(1A)	92.0(3)	C(1A)	-N(1A)	-Ni	112.3(7)
Ni	-N(1A)	-C(10B)	108.9(7)	C(1A)	-N(1A)	-(C10B)	111.4(7)
C(4A)	-N(2A)	-Ni	113.6(5)	C(5A)	-N(2A)	-Ni	109.9(5)
C(5A)	-N(2A)	-C(4A)	111.5(8)	C(2A)	-C(1A)	-N(1A)	110.0(8)
C(3A)	-C(2A)	-C(1A)	111(1)	C(4A)	-C(2A)	-C(1A)	112.7(7)
C(4A)	-C(2A)	-C(3A)	112(1)	C(2A)	-C(4A)	-N(2A)	110.0(9)
C(6A)	-C(5A)	-N(2A)	123.7(7)	C(10A)	-C(5A)	-N(2A)	115.7(7)
C(10A)	-C(5A)	-C(6A)	120.6(8)	C(7A)	-C(6A)	-C(5A)	119.9(8)
C(8A)	-C(7A)	-C(6A)	119.6(8)	C(9A)	-C(8A)	-C(7A)	121.0(1)
C(10A)	-C(9A)	-C(8A)	119.3(9)	C(9A)	-C(10A)	-C(5A)	119.6(7)
N(1A)	-C(10B)	-C(5B)	117.5(8)	N(1A)	-C(10B)	-C(9B)	122.9(10)
F(2)	-B	-F(1)	108.2(9)	F(3)	-B	-F(1)	106(1)
F(3)	-B	-F(2)	106.4(8)	F(4)	-B	-F(1)	113.2(8)
F(4)	-B	-F(2)	112(1)	F(4)	-B	-F(3)	110.7(9)

TABLE 6 Intermolecular distances (Å) for [Ni($C_{19}H_{26}N_4$)](BF_4)$_2$

atom1	atom2	dist	S	a	b	c
F(2)	...Ni	3.75	1	0.0	1.0	0.0
F(2)	...N(1A)	3.09	1	0.0	1.0	0.0
N(2A)	...N(1A)	2.68	-1	0.0	0.0	0.0
C(5A)	...N(1A)	2.41	-1	0.0	0.0	0.0
C(9A)	...N(1A)	2.49	-1	0.0	0.0	0.0
C(10A)	...N(1B)	1.44	-1	0.0	0.0	0.0
H(9A)	...N(1A)	2.75	-1	0.0	0.0	0.0
F(4)	...C(1A)	3.38	1	1.0	0.0	0.0
C(5A)	...C(1A)	3.49	-1	0.0	0.0	0.0
C(9A)	...C(1A)	2.97	-1	0.0	0.0	0.0
C(10A)	...C(1A)	2.42	-1	0.0	0.0	0.0
F(3)	...C(1A)	3.25	-1	0.0	0.0	0.0
H(9A)	...C(1A)	2.86	-1	0.0	0.0	0.0
H(8A)	...C(3A)	2.84	1	1.0	-1.0	0.0
C(8A)	...C(3A)	3.36	-1	0.0	0.0	1.0
H(4A2)	...C(6A)	3.04	-1	0.0	0.0	1.0
F(3)	...C(7A)	3.38	1	0.0	0.0	-1.0
H(4A2)	...C(7A)	3.05	-1	0.0	0.0	1.0
H(1A2)	...C(9A)	2.80	-1	0.0	0.0	0.0
H(1AN)	...C(9A)	2.96	-1	0.0	0.0	0.0
H(1A1)	...C(10A)	2.59	-1	0.0	0.0	0.0
H(1A2)	...C(10A)	2.79	-1	0.0	0.0	0.0
H(1AN)	...C(10A)	2.25	-1	0.0	0.0	0.0
F(2)	...F(1)	2.23	1	0.0	1.0	0.0
H(9A)	...F(1)	2.65	1	0.0	-1.0	0.0

table 6 continued

H(8A) ...F(1)	2.41	-1	1.0	0.0	1.0
F(3) ...F(2)	2.19	1	0.0	-1.0	0.0
F(4) ...F(2)	2.22	1	0.0	-1.0	0.0
H(4A1)...F(2)	2.55	1	0.0	-1.0	1.0
H(6A) ...F(2)	2.69	1	0.0	-1.0	1.0
H(1AN)...F(2)	2.06	1	0.0	-1.0	0.0
H(2A1)...F(2)	2.60	-1	0.0	2.0	0.0
H(7A) ...F(3)	2.97	1	0.0	0.0	1.0
H(1A1)...F(3)	2.35	-1	0.0	0.0	0.0
H(4A2)...F(3)	2.77	-1	0.0	0.0	0.0
H(7A) ...F(3)	2.42	-1	1.0	0.0	1.0
H(1A1)...F(4)	2.76	1	-1.0	0.0	0.0
H(1A2)...F(4)	2.85	1	-1.0	0.0	0.0
H(6A) ...F(4)	2.79	1	0.0	0.0	1.0
H(9A) ...F(4)	2.50	1	0.0	-1.0	0.0
H(1A2)...F(4)	2.54	-1	0.0	1.0	0.0
H(6A) ...B	3.02	1	0.0	0.0	1.0
H(9A) ...B	3.02	1	0.0	-1.0	0.0

Symmetry Transformations:

The second atom is related to the first atom, at (x,y,z), by the symmetry operation S with (a,b,c) added to the (x',y',z') of S.

Where S

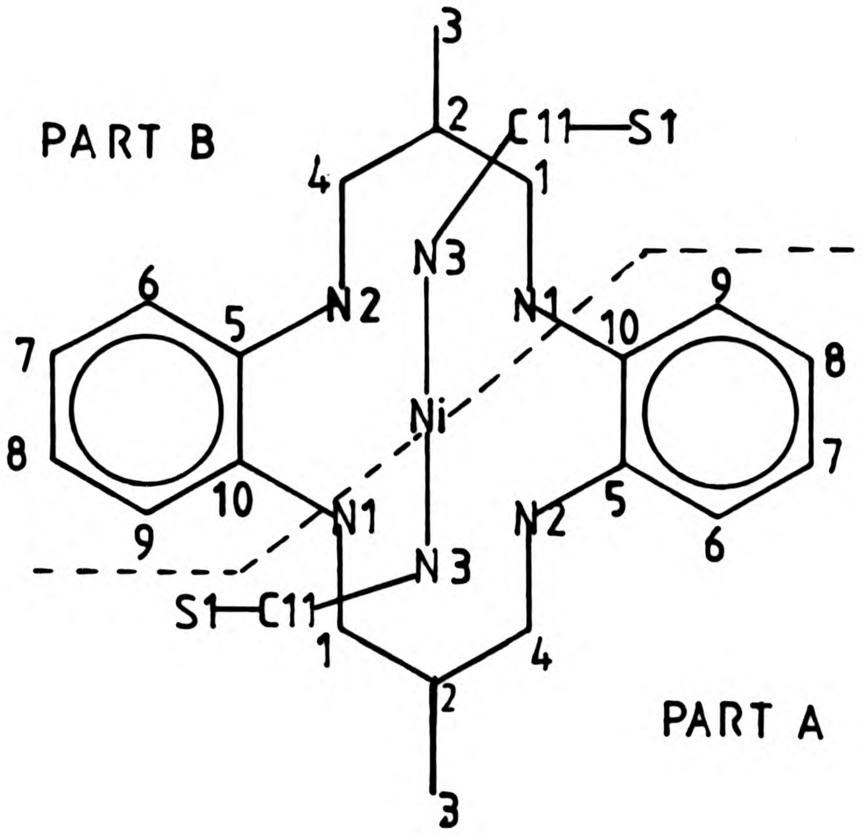
1	x, y, z

TABLE 7 Intramolecular distances (Å) for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

C(1A) ...Ni	2.85	C(2A) ...Ni	3.27
C(4A) ...Ni	2.85	C(5A) ...Ni	2.77
C(9A) ...Ni	4.11	C(10A)...Ni	2.76
F(1) ...Ni	3.59	F(3) ...Ni	2.85
B ...Ni	3.64	H(1A1)...Ni	3.00
H(2A1)...Ni	3.68	H(4A1)...Ni	3.75
H(4A2)...Ni	3.04	H(1AN)...Ni	2.59
N(2A) ...N(1A)	2.77	C(2A) ...N(1A)	2.45
C(4A) ...N(1A)	3.04	F(1) ...N(1A)	3.34
H(1A1)...N(1A)	2.12	H(1A2)...N(1A)	2.25
H(2A1)...N(1A)	2.77	H(2AN)...N(1A)	2.76
C(1A) ...N(2A)	3.03	C(2A) ...N(2A)	2.47
C(6A) ...N(2A)	2.47	C(10A)...N(2A)	2.40
F(1) ...N(2A)	2.93	F(3) ...N(2A)	3.15
H(2A1)...N(2A)	2.68	H(4A1)...N(2A)	2.04
H(4A2)...N(2A)	2.16	H(6A) ...N(2A)	2.66
H(1AN)...N(2A)	2.90	C(3A) ...C(1A)	2.42
C(4A) ...C(1A)	2.53	H(2A1)...C(1A)	2.23
H(2A2)...C(1A)	2.15	H(4A2)...C(1A)	2.68
H(1AN)...C(1A)	2.25	H(1A1)...C(2A)	2.36
H(1A2)...C(2A)	2.03	H(4A1)...C(2A)	2.19
H(4A2)...C(2A)	2.09	H(1AN)...C(2A)	2.63
H(2AN)...C(2A)	2.64	C(4A) ...C(3A)	2.46
H(1A1)...C(3A)	3.00	H(1A2)...C(3A)	2.38
H(2A1)...C(3A)	1.92	H(4A1)...C(3A)	2.69

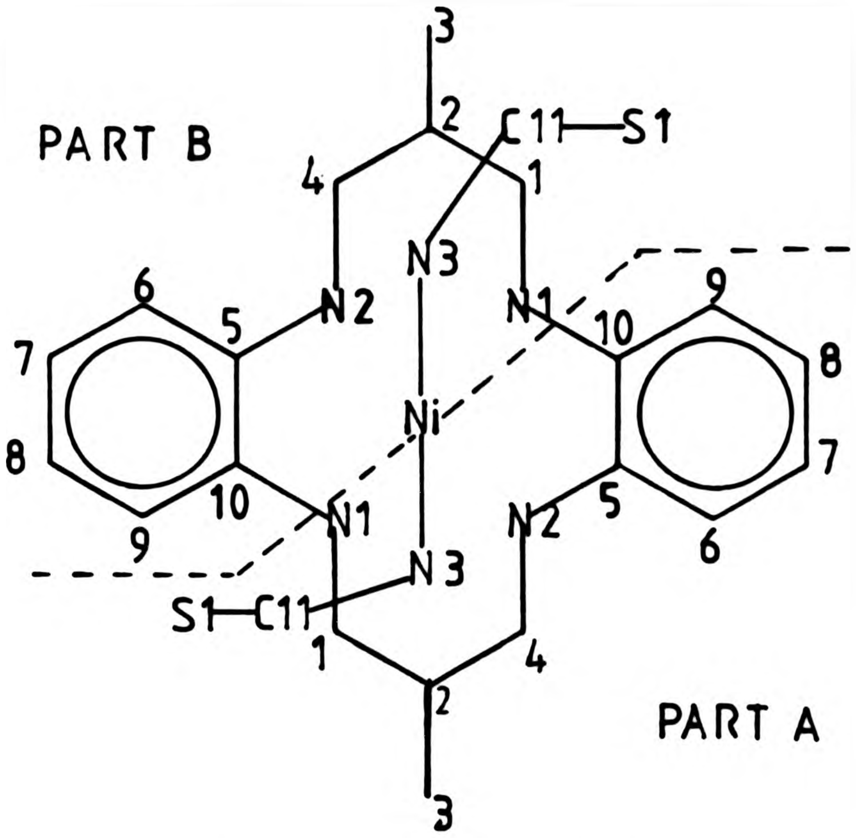
table 7 continued

H(4A2)...C(3A)	2.71	C(5A) ...C(4A)	2.41
C(6A) ...C(4A)	2.97	C(10A)...C(4A)	3.48
H(1A1)...C(4A)	2.96	H(2A1)...C(4A)	2.13
H(2A2)...C(4A)	2.19	H(6A) ...C(4A)	2.79
H(2AN)...C(4A)	2.13	C(7A) ...C(5A)	2.37
C(8A) ...C(5A)	2.74	C(9A) ...C(5A)	2.40
H(4A1)...C(5A)	2.50	H(4A2)...C(5A)	2.82
H(6A) ...C(5A)	2.07	H(2AN)...C(5A)	2.06
C(8A) ...C(6A)	2.39	C(9A) ...C(6A)	2.76
C(10A)...C(6A)	2.38	H(4A1)...C(6A)	2.53
H(7A) ...C(6A)	2.21	H(2AN)...C(6A)	2.85
C(9A) ...C(7A)	2.38	C(10A)...C(7A)	2.75
H(6A) ...C(7A)	2.16	H(8A) ...C(7A)	2.20
C(10A)...C(8A)	2.38	H(7A) ...C(8A)	2.18
H(9A) ...C(8A)	2.14	H(8A) ...C(9A)	2.12
H(9A) ...C(10A)	2.18	H(2AN)...C(10A)	3.01
F(3) ...F(1)	2.20	F(4) ...F(1)	2.25
H(2A1)...F(1)	2.82	H(1AN)...F(1)	2.26
H(2AN)...F(1)	1.89	F(4) ...F(3)	2.21
H(1AN)...F(3)	2.86	H(2AN)...F(3)	2.48
H(1AN)...B	2.51	H(2AN)...B	2.69



$[Ni(C_{19}H_{26}N_4)(NCS)_2]$

(Hydrogen atom labelling is H1A1 and H1A2 for atoms on C1A and H1B1 and H1B2 on C1B etc. Anilino protons are H1AN, H2AN, H1BN and H2BN).



$[Ni(C_{19}H_{26}N_4)(NCS)_2]$

(Hydrogen atom labelling is H1A1 and H1A2 for atoms on C1A and H1B1 and H1B2 on C1B etc. Anilino protons are H1AN, H2AN. H1BN and H2BN).

table 1 continued

C(8B)	0.0581(15)	-0.1767(13)	0.1907(20)	0.076(7)
C(9B)	0.1084(14)	-0.1077(12)	0.1486(20)	0.073(5)
C(10B)	0.1645(13)	-0.0510(11)	0.2401(18)	0.052(5)
C(11B)	0.4624(13)	0.1100(11)	0.3732(15)	0.048(5)
C(3AE)	0.22530	0.15360	-0.07160	0.0600
C(3BE)	0.20960	0.06430	0.77260	0.0600

TABLE 2 Fractional atomic coordinates for the hydrogen atoms for [Ni($C_{19}H_{26}N_4$)(NCS)$_2$]

Atom	x	y	z
H(1A1)	0.1950	0.0080	0.0163
H(1A2)	0.0901	0.0572	0.0618
H(2A1)	0.1918	0.0828	0.0682
H(2A2)	0.3086	0.1402	0.1096
H(4A1)	0.0913	0.1986	0.1010
H(4A2)	0.1802	0.2731	0.0687
H(6A)	0.0918	0.3590	0.1402
H(7A)	0.0083	0.4539	0.2580
H(8A)	0.0153	0.4415	0.4710
H(9A)	0.1220	0.3211	0.5939
H(1B1)	0.1958	0.2127	0.6656
H(1B2)	0.0983	0.1563	0.5633
H(2B1)	0.3184	0.0871	0.6537
H(2B2)	0.2047	0.0323	0.5823
H(4B1)	0.0962	0.0141	0.5338
H(4B2)	0.1973	-0.0533	0.6067
H(6B)	0.1202	-0.1484	0.4970
H(7B)	0.0186	-0.2419	0.3305
H(8B)	0.0157	-0.2204	0.1240
H(9B)	0.1042	-0.0983	0.0519
H(1AN)	0.2853	0.0140	0.2031
H(2AN)	0.2898	0.2424	0.2439
H(1BN)	0.2862	0.2339	0.4764
H(2BN)	0.2980	-0.0200	0.4844

TABLE 3 Anisotropic thermal parameters (Å) for [Ni($C_{19}H_{26}N_4$)$(NCS)_2$]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.045(1)	0.029(1)	0.078(2)	0.002(2)	0.007(1)	0.001(1)
S(1A)	0.063(4)	0.146(6)	0.159(7)	0.079(6)	0.000(4)	0.017(4)
S(1B)	0.050(3)	0.052(3)	0.118(5)	0.001(4)	0.018(3)	0.008(3)
N(1A)	0.076(12)	0.049(10)	0.083(15)	0.002(11)	0.017(11)	-0.007(8)
N(2A)	0.080(12)	0.039(10)	0.069(14)	0.020(10)	0.025(11)	-0.004(8)
N(3A)	0.055(9)	0.039(8)	0.093(13)	0.021(10)	-0.009(9)	-0.002(8)
N(1B)	0.053(10)	0.035(8)	0.075(12)	-0.015(9)	0.021(9)	-0.009(7)
N(2B)	0.048(9)	0.030(8)	0.062(11)	0.009(8)	0.003(9)	0.012(7)
N(3B)	0.050(9)	0.045(8)	0.110(14)	0.004(11)	0.019(9)	0.005(9)
C(1A)	0.213(31)	0.078(18)	0.071(21)	-0.020(17)	0.036(22)	-0.003(19)
C(2A)	0.279(38)	0.078(19)	0.072(20)	0.014(16)	0.022(23)	-0.095(23)
C(4A)	0.152(26)	0.050(15)	0.118(28)	0.046(18)	0.028(22)	-0.029(16)

TABLE 4 Bond lengths (Å) for [Ni($C_{19}H_{26}N_4$)$(NCS)_2$]

Ni	-N(1A)	2.106(18)	Ni	-N(2A)	2.129(14)
Ni	-N(3A)	2.040(14)	Ni	-N(1B)	2.079(15)
Ni	-N(2B)	2.114(13)	Ni	-N(3B)	2.119(13)
S(1A)	-C(11A)	1.606(18)	S(1B)	-C(11B)	1.619(18)
N(1A)	-C(1A)	1.48(3)	N(1A)	-C(10B)	1.445(25)
N(2A)	-C(4A)	1.42(3)	N(2A)	-C(5A)	1.46(3)
N(3A)	-C(11A)	1.138(22)	N(1B)	-C(10A)	1.486(21)
N(1B)	-C(1B)	1.48(3)	N(2B)	-C(4B)	1.43(3)
N(2B)	-C(5B)	1.486(20)	N(3B)	-C(11B)	1.150(23)
C(1A)	-C(2A)	1.64(4)	C(2A)	-C(4A)	1.59(4)
C(2A)	-C(3AE)	1.446(25)	C(5A)	-C(6A)	1.46(3)
C(5A)	-C(10A)	1.31(3)	C(6A)	-C(7A)	1.40(3)
C(7A)	-C(8A)	1.29(3)	C(8A)	-C(9A)	1.47(3)
C(9A)	-C(10A)	1.43(3)	C(1B)	-C(2B)	1.56(3)
C(2B)	-C(4B)	1.63(3)	C(2B)	-C(3BE)	1.578(23)
C(5B)	-C(6B)	1.445(25)	C(5B)	-C(10B)	1.33(3)
C(6B)	-C(7B)	1.42(3)	C(7B)	-C(8B)	1.31(3)
C(8B)	-C(9B)	1.42(3)	C(9B)	-C(10B)	1.44(3)

TABLE 5 Bond angles (°) for [Ni($C_{19}H_{26}N_4$)(NCS)$_2$]

N(2A) -Ni -N(1A)	98.0(7)	N(3A) -Ni -N(1A)	90.7(6)
N(3A) -Ni -N(2A)	89.8(6)	N(1B) -Ni -N(1A)	177.6(6)
N(1B) -Ni -N(2A)	80.7(6)	N(1B) -Ni -N(3A)	91.3(6)
N(2B) -Ni -N(1A)	80.9(6)	N(2B) -Ni -N(2A)	178.5(6)
N(2B) -Ni -N(3A)	91.1(6)	N(2B) -Ni -N(1B)	100.4(6)
N(3B) -Ni -N(1A)	87.8(6)	N(3B) -Ni -N(2A)	89.6(6)
N(3B) -Ni -N(3A)	178.3(7)	N(3B) -Ni -N(1B)	90.1(6)
N(3B) -Ni -N(2B)	89.5(5)	C(1A) -N(1A) -Ni	117(1)
C(10B)-N(1A) -Ni	105(1)	C(10B)-N(1A) -C(1A)	115(2)
C(4A) -N(2A) -Ni	116(1)	C(5A) -N(2A) -Ni	102(1)
C(5A) -N(2A) -C(4A)	117(2)	C(11A)-N(3A) -Ni	156(2)
C(10A)-N(1B) -Ni	106(1)	C(1B) -N(1B) -Ni	114(1)
C(1B) -N(1B) -C(10A)	115(1)	C(4B) -N(2B) -Ni	114(1)
C(5B) -N(2B) -Ni	104(1)	C(5B) -N(2B) -C(4B)	116(1)
C(11B)-N(3B) -Ni	163(1)	C(2A) -C(1A) -N(1A)	110(2)
C(4A) -C(2A) -C(1A)	108(2)	C(3AE)-C(2A) -C(1A)	110(2)
C(3AE)-C(2A) -C(4A)	113(2)	C(2A) -C(4A) -N(2A)	112(2)
C(6A) -C(5A) -N(2A)	118(2)	C(10A)-C(5A) -N(2A)	121(2)
C(10A)-C(5A) -C(6A)	121(2)	C(7A) -C(6A) -C(5A)	113(2)
C(8A) -C(7A) -C(6A)	127(2)	C(9A) -C(8A) -C(7A)	119(2)
C(10A)-C(9A) -C(8A)	114(2)	C(5A) -C(10A)-N(1B)	116(2)
C(9A) -C(10A)-N(1B)	118(2)	C(9A) -C(10A)-C(5A)	125(2)
N(3A) -C(11A)-S(1A)	177(2)	C(2B) -C(1B) -N(1B)	112(2)
C(4B) -C(2B) -C(1B)	109(1)	C(3BE)-C(2B) -C(1B)	109(1)
C(3BE)-C(2B) -C(4B)	103(1)	C(2B) -C(4B) -N(2B)	111(2)

table 5 continued

C(6B) -C(5B) -N(2B)	118(2)	C(10B)-C(5B) -N(2B)	118(1)
C(10B)-C(5B) -C(6B)	124(2)	C(7B) -C(6B) -C(5B)	114(2)
C(8B) -C(7B) -C(6B)	123(2)	C(9B) -C(8B) -C(7B)	122(2)
C(10B)-C(9B) -C(8B)	117(2)	C(5B) -C(10B)-N(1A)	119(2)
C(9B) -C(10B)-N(1A)	121(2)	C(9B) -C(10B)-C(5B)	119(2)
N(3B) -C(11B)-S(1B)	179(2)		

TABLE 6 Intermolecular distances (Å) for [Ni($C_{19}H_{26}N_4$)$(NCS)_2$]

atom1	atom2	dist	S	a	b	c
H(1A1)...	S(1A)	3.35	-1	0.0	0.0	0.0
H(4B2)...	S(1A)	3.00	-1	0.0	0.0	1.0
H(9B) ...	S(1A)	2.94	-1	0.0	0.0	0.0
C(3BE)...	S(1A)	3.58	-1	0.0	0.0	1.0
N(1B) ...	S(1A)	3.50	-2	1.0	1.0	1.0
C(9A) ...	S(1A)	3.44	-2	1.0	1.0	1.0
H(9A) ...	S(1A)	3.07	-2	1.0	1.0	1.0
C(10A)...	S(1A)	3.63	-2	1.0	1.0	1.0
C(1B) ...	S(1A)	3.73	-2	1.0	1.0	1.0
H(1B1)...	S(1A)	3.02	-2	1.0	1.0	1.0
H(1BN)...	S(1A)	2.97	-2	1.0	1.0	1.0
N(2B) ...	S(1B)	3.47	-1	1.0	0.0	1.0
H(2BN)...	S(1B)	2.54	-1	1.0	0.0	1.0
C(4B) ...	S(1B)	3.59	-1	1.0	0.0	1.0
H(4B2)...	S(1B)	3.00	-1	1.0	0.0	1.0
H(7A) ...	S(1B)	2.94	2	0.0	0.0	0.0
H(7B) ...	S(1B)	3.24	2	0.0	-1.0	0.0
C(8B) ...	S(1B)	3.84	2	0.0	-1.0	0.0
H(8B) ...	S(1B)	3.01	2	0.0	-1.0	0.0
H(4A2)...	S(1B)	3.04	-2	0.0	1.0	0.0
H(6A) ...	S(1B)	3.16	-2	0.0	1.0	0.0
H(9A) ...	S(1B)	3.31	-2	0.0	1.0	1.0
C(8B) ...	N(2A)	3.37	2	0.0	-1.0	0.0
C(6B) ...	H(2AN)	2.99	2	0.0	-1.0	0.0
C(7B) ...	H(2AN)	2.44	2	0.0	-1.0	0.0

table 6 continued

C(8B) ...H(2AN)	2.36	2	0.0	-1.0	0.0
C(9B) ...H(2AN)	2.87	2	0.0	-1.0	0.0
C(3BE)...H(1A1)	2.92	1	0.0	0.0	1.0
C(3BE)...C(2A)	3.37	1	0.0	0.0	1.0
C(6B) ...H(4A2)	3.02	2	0.0	-1.0	0.0
C(9B) ...C(5A)	3.48	2	0.0	-1.0	0.0
C(10B)...C(6A)	3.46	2	0.0	-1.0	0.0
H(1AN)...C(6A)	3.03	2	0.0	-1.0	0.0
H(1AN)...C(7A)	2.80	2	0.0	-1.0	0.0
C(11B)...H(7A)	2.96	2	0.0	-1.0	0.0
H(8A) ...C(8A)	3.05	-1	0.0	1.0	1.0
C(3AE)...H(1B1)	3.03	1	0.0	0.0	-1.0
C(6B) ...H(1B2)	2.96	-1	0.0	0.0	1.0
C(7B) ...H(1B2)	2.86	-1	0.0	0.0	1.0
C(3AE)...C(2B)	3.40	1	0.0	0.0	-1.0
C(11B)...C(8B)	3.47	2	0.0	0.0	0.0
C(11B)...H(8B)	2.72	2	0.0	0.0	0.0
C(3BE)...C(3AE)	2.22	1	0.0	0.0	1.0

Symmetry Transformations:

The second atom is related to the first atom, at (x,y,z), by the symmetry operation S with (a,b,c) added to the (x',y',z') of S.

Where S

1 x, y, z

TABLE 7 Intramolecular distances (Å) for [Ni($C_{19}H_{26}N_4$)(NCS)$_2$]

H(2AN)...Ni	2.71	H(2BN)...Ni	2.67
C(1A) ...Ni	3.08	H(1A2)...Ni	3.36
C(2A) ...Ni	3.34	H(2A1)...Ni	3.11
H(2A2)...Ni	3.23	C(4A) ...Ni	3.04
H(4A1)...Ni	3.19	C(5A) ...Ni	2.83
C(6A) ...Ni	4.18	C(9A) ...Ni	4.19
C(10A)...Ni	2.87	C(11A)...Ni	3.12
C(1B) ...Ni	3.00	H(1B2)...Ni	3.21
C(2B) ...Ni	3.28	H(2B1)...Ni	3.41
H(2B2)...Ni	2.93	C(4B) ...Ni	3.00
H(4B1)...Ni	3.24	C(5B) ...Ni	2.86
C(6B) ...Ni	4.20	C(9B) ...Ni	4.19
C(10B)...Ni	2.85	C(11B)...Ni	3.24
H(1AN)...Ni	2.57	H(1BN)...Ni	2.50
N(3A) ...S(1A)	2.74	N(3B) ...S(1B)	2.77
N(2A) ...N(1A)	3.19	N(3A) ...N(1A)	2.95
N(2B) ...N(1A)	2.74	N(3B) ...N(1A)	2.93
H(1A1)...N(1A)	2.10	H(1A2)...N(1A)	2.10
C(2A) ...N(1A)	2.55	H(2A1)...N(1A)	1.78
H(2A2)...N(1A)	2.61	C(4A) ...N(1A)	3.22
C(5B) ...N(1A)	2.39	C(9B) ...N(1A)	2.51
H(9B) ...N(1A)	2.78	N(3A) ...N(2A)	2.94
N(1B) ...N(2A)	2.73	N(3B) ...N(2A)	2.99
C(1A) ...N(2A)	3.24	C(2A) ...N(2A)	2.50
H(2A1)...N(2A)	2.93	H(2A2)...N(2A)	2.54

table 7 continued

H(4A1)...N(2A)	2.02	H(4A2)...N(2A)	2.07
C(6A) ...N(2A)	2.50	H(6A) ...N(2A)	2.78
C(10A)...N(2A)	2.41	H(1BN)...N(2A)	2.58
N(3B) ...H(2AN)	2.73	C(2A) ...H(2AN)	2.61
C(4A) ...H(2AN)	1.92	C(5A) ...H(2AN)	2.11
C(6A) ...H(2AN)	3.03	C(10A)...H(2AN)	2.96
N(1B) ...N(3A)	2.94	N(2B) ...N(3A)	2.97
C(1A) ...N(3A)	3.41	H(1A2)...N(3A)	3.01
C(4A) ...N(3A)	3.37	H(4A1)...N(3A)	2.84
C(5A) ...N(3A)	3.06	C(10A)...N(3A)	3.11
C(1B) ...N(3A)	3.37	H(1B2)...N(3A)	2.88
C(4B) ...N(3A)	3.35	H(4B1)...N(3A)	2.90
C(5B) ...N(3A)	3.12	C(10B)...N(3A)	3.13
N(2B) ...N(1B)	3.22	N(3B) ...N(1B)	2.97
C(5A) ...N(1B)	2.37	C(9A) ...N(1B)	2.51
H(9A) ...N(1B)	2.75	H(1B1)...N(1B)	2.10
H(1B2)...N(1B)	2.08	C(2B) ...N(1B)	2.52
H(2B1)...N(1B)	2.70	H(2B2)...N(1B)	2.88
C(4B) ...N(1B)	3.25	N(3B) ...N(2B)	2.98
C(1B) ...N(2B)	3.22	C(2B) ...N(2B)	2.53
H(2B1)...N(2B)	2.76	H(2B2)...N(2B)	1.63
H(4B1)...N(2B)	2.05	H(4B2)...N(2B)	2.01
C(6B) ...N(2B)	2.51	H(6B) ...N(2B)	2.77
C(10B)...N(2B)	2.42	N(3B) ...H(2BN)	2.68
C(2B) ...H(2BN)	2.69	C(4B) ...H(2BN)	1.97
C(5B) ...H(2BN)	2.12	C(6B) ...H(2BN)	3.01
C(10B)...H(2BN)	2.94	H(1AN)...N(3B)	2.61
H(1BN)...N(3B)	2.65	H(2A2)...C(1A)	2.23

table 7 continued

C(4A) ...C(1A)	2.61	H(4A1)...C(1A)	2.60
C(9B) ...C(1A)	2.86	H(9B) ...C(1A)	2.57
C(10B)...C(1A)	2.46	C(3AE)...C(1A)	2.53
H(1AN)...C(1A)	1.88	C(2A) ...H(1A1)	2.20
C(9B) ...H(1A1)	2.77	C(10B)...H(1A1)	2.79
C(3AE)...H(1A1)	2.59	C(2A) ...H(1A2)	2.29
C(4A) ...H(1A2)	2.74	C(9B) ...H(1A2)	2.79
C(10B)...H(1A2)	2.65	C(3AE)...H(1A2)	3.00
H(4A1)...C(2A)	2.18	H(4A2)...C(2A)	2.20
H(1AN)...C(2A)	2.61	C(4A) ...H(2A1)	2.19
C(10B)...H(2A1)	2.95	C(3AE)...H(2A1)	2.06
C(4A) ...H(2A2)	2.16	C(3AE)...H(2A2)	2.09
C(5A) ...C(4A)	2.46	C(6A) ...C(4A)	2.83
H(6A) ...C(4A)	2.58	C(3AE)...C(4A)	2.53
C(5A) ...H(4A1)	2.65	C(6A) ...H(4A1)	2.83
C(11A)...H(4A1)	2.80	C(3AE)...H(4A1)	2.99
C(5A) ...H(4A2)	2.76	C(6A) ...H(4A2)	2.66
C(3AE)...H(4A2)	2.62	H(6A) ...C(5A)	2.26
C(7A) ...C(5A)	2.39	C(8A) ...C(5A)	2.79
C(9A) ...C(5A)	2.43	C(11A)...C(5A)	3.42
H(1BN)...C(5A)	2.34	H(7A) ...C(6A)	2.10
C(8A) ...C(6A)	2.42	C(9A) ...C(6A)	2.88
C(10A)...C(6A)	2.40	C(7A) ...H(6A)	2.18
H(8A) ...C(7A)	2.08	C(9A) ...C(7A)	2.39
C(10A)...C(7A)	2.69	C(8A) ...H(7A)	2.04
H(9A) ...C(8A)	2.25	C(10A)...C(8A)	2.43
C(9A) ...H(8A)	2.20	C(1B) ...C(9A)	2.87
H(1B1)...C(9A)	2.69	H(1B2)...C(9A)	2.87

table 7 continued

H(1BN)...C(9A)	2.79	C(10A)...H(9A)	2.21
C(1B) ...H(9A)	2.58	C(1B) ...C(10A)	2.51
H(1B1)...C(10A)	2.80	H(1B2)...C(10A)	2.68
H(1BN)...C(10A)	1.73	H(2B1)...C(1B)	2.19
H(2B2)...C(1B)	2.17	C(4B) ...C(1B)	2.59
H(4B1)...C(1B)	2.69	C(3BE)...C(1B)	2.54
H(1BN)...C(1B)	2.37	C(2B) ...H(1B1)	2.16
C(3BE)...H(1B1)	2.64	C(2B) ...H(1B2)	2.17
C(4B) ...H(1B2)	2.63	C(3BE)...H(1B2)	2.87
H(4B1)...C(2B)	2.25	H(4B2)...C(2B)	2.25
C(4B) ...H(2B1)	2.30	C(3BE)...H(2B1)	2.20
C(5B) ...H(2B2)	2.89	C(3BE)...H(2B2)	2.18
C(5B) ...C(4B)	2.47	C(6B) ...C(4B)	2.85
H(6B) ...C(4B)	2.62	C(3BE)...C(4B)	2.52
C(5B) ...H(4B1)	2.66	C(6B) ...H(4B1)	2.84
C(3BE)...H(4B1)	2.87	C(5B) ...H(4B2)	2.73
C(6B) ...H(4B2)	2.65	C(3BE)...H(4B2)	2.62
H(6B) ...C(5B)	2.24	C(7B) ...C(5B)	2.40
C(8B) ...C(5B)	2.74	C(9B) ...C(5B)	2.39
H(1AN)...C(5B)	2.88	H(7B) ...C(6B)	2.17
C(8B) ...C(6B)	2.40	C(9B) ...C(6B)	2.84
C(10B)...C(6B)	2.45	C(7B) ...H(6B)	2.19
H(8B) ...C(7B)	2.06	C(9B) ...C(7B)	2.39
C(10B)...C(7B)	2.78	C(8B) ...H(7B)	2.04
H(9B) ...C(8B)	2.18	C(10B)...C(8B)	2.44
C(9B) ...H(8B)	2.16	H(1AN)...C(9B)	2.99
C(10B)...H(9B)	2.21	H(1AN)...C(10B)	2.02
H(1AN)...C(11B)	3.07		

Observed and Calculated Structure Factors for $C_{19}H_{26}N_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	704	576	4	4	0	64	-51	3	2	1	135	-144	-2	0	2	420	-376	3	2	2	332	-331
3	0	0	633	592	5	4	0	73	66	4	2	1	239	-255	2	0	2	539	431	4	2	2	145	-151
4	0	0	748	-596	10	4	0	93	-115	5	2	1	372	-417	3	0	2	963	827	5	2	2	327	-364
5	0	0	142	136	4	5	0	93	-87	7	2	1	92	-100	4	0	2	60	62	10	2	2	102	-169
6	0	0	422	391	5	5	0	109	94	9	2	1	114	-126	5	0	2	255	238	-9	3	2	104	191
7	0	0	353	-324	6	5	0	125	132	11	2	1	118	-178	6	0	2	720	-578	-4	3	2	149	145
8	0	0	190	-184	8	5	0	90	99	-10	3	1	128	177	7	0	2	73	-77	-3	3	2	189	187
9	0	0	258	262	0	6	0	256	-201	1	3	1	88	-53	8	0	2	332	-278	-2	3	2	160	146
11	0	0	118	-125	1	6	0	133	97	2	3	1	93	-64	9	0	2	407	-406	-1	3	2	92	95
13	0	0	84	-88	4	6	0	90	43	6	3	1	92	96	-11	1	2	139	134	1	3	2	164	-156
2	1	0	562	-645	-13	1	1	184	-184	7	3	1	97	116	-10	1	2	413	-407	2	3	2	387	365
3	1	0	299	-341	-11	1	1	106	-99	10	3	1	82	-103	-9	1	2	77	55	3	3	2	234	-244
4	1	0	296	-329	-10	1	1	417	462	-10	4	1	95	-101	-8	1	2	201	195	4	3	2	149	134
5	1	0	128	141	-9	1	1	287	-283	-6	4	1	107	-116	-7	1	2	313	-278	6	3	2	105	-133
6	1	0	309	328	-7	1	1	78	-38	-2	4	1	79	111	-6	1	2	144	138	8	3	2	144	186
8	1	0	337	316	-6	1	1	551	-482	0	4	1	148	-164	-5	1	2	425	-371	-5	4	2	113	115
9	1	0	152	-149	-3	1	1	952	-1029	5	4	1	135	-151	-3	1	2	112	100	-4	4	2	218	254
10	1	0	146	175	-2	1	1	59	41	8	4	1	113	110	-2	1	2	602	681	0	4	2	165	-156
13	1	0	108	134	1	1	1	253	-277	-3	5	1	123	141	-1	1	2	413	-453	4	4	2	89	-83
0	2	0	142	151	3	1	1	242	-276	-2	5	1	104	-85	0	1	2	744	817	5	4	2	118	112
2	2	0	64	90	4	1	1	221	-242	1	5	1	105	-113	1	1	2	1186	1037	-1	5	2	164	-160
4	2	0	117	120	5	1	1	464	497	2	5	1	126	-112	2	1	2	600	682	0	5	2	99	91
5	2	0	56	64	6	1	1	99	-107	3	5	1	118	-85	3	1	2	394	430	2	5	2	138	131
6	2	0	173	159	7	1	1	62	63	6	5	1	92	86	4	1	2	193	-225	3	5	2	164	129
7	2	0	69	53	10	1	1	110	-119	-1	6	1	158	-134	5	1	2	409	-481	5	5	2	96	-97
9	2	0	114	-101	-11	2	1	72	54	0	6	1	163	-148	6	1	2	140	168	-14	1	3	137	182
10	2	0	171	223	-9	2	1	115	119	-13	0	2	154	-188	7	1	2	130	-124	-13	1	3	151	157
14	2	0	96	-108	-7	2	1	202	214	-12	0	2	274	267	9	1	2	121	124	-12	1	3	88	-82
1	3	0	71	75	-6	2	1	115	-114	-11	0	2	240	-261	-10	2	2	124	-160	-10	1	3	139	-137
2	3	0	148	-142	-5	2	1	136	-105	-10	0	2	116	127	-7	2	2	164	-163	-8	1	3	176	150
3	3	0	230	229	-4	2	1	397	386	-8	0	2	102	-124	-5	2	2	151	134	-6	1	3	312	-280
4	3	0	163	-150	-3	2	1	96	100	-7	0	2	139	103	-4	2	2	331	-327	-5	1	3	99	-84
8	3	0	104	111	-2	2	1	259	273	-6	0	2	93	-42	-3	2	2	384	400	-4	1	3	161	138
10	3	0	154	-223	-1	2	1	68	-78	-5	0	2	379	354	-1	2	2	99	73	-3	1	3	79	-72
13	3	0	84	-79	0	2	1	356	-394	-4	0	2	788	633	0	2	2	139	-149	-2	1	3	250	-286
0	4	0	151	152	2	2	1	131	-147	-3	0	2	306	254	1	2	2	281	-243	-1	1	3	280	-320

Observed and Calculated Structure Factors for $C_{19}H_{26}N_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	1	3	1231	974	0	4	3	88	75	-2	1	4	438	-514	4	3	4	105	-117	7	1	5	161	-177
2	1	3	1097	1111	4	4	3	177	161	-1	1	4	993	1189	6	3	4	252	-278	-11	2	5	81	56
3	1	3	508	489	6	4	3	79	-66	0	1	4	710	-717	7	3	4	107	-100	-9	2	5	261	-243
4	1	3	256	284	7	4	3	112	123	1	1	4	155	-172	8	3	4	123	-168	-6	2	5	83	74
5	1	3	57	-33	0	5	3	103	98	2	1	4	760	657	-7	4	4	118	137	-5	2	5	101	115
6	1	3	225	247	3	5	3	77	-67	3	1	4	332	336	-5	4	4	127	-134	-4	2	5	529	-511
7	1	3	119	127	-13	0	4	91	-73	4	1	4	255	293	-3	4	4	98	112	-3	2	5	83	88
8	1	3	95	89	-11	0	4	236	-247	5	1	4	375	436	-1	4	4	101	117	0	2	5	60	91
9	1	3	72	53	-10	0	4	195	-196	6	1	4	154	-167	1	4	4	173	-156	2	2	5	318	281
-11	2	3	122	-140	-9	0	4	583	544	7	1	4	72	-87	3	4	4	164	-125	3	2	5	228	227
-10	2	3	110	120	-8	0	4	205	210	8	1	4	111	-81	4	4	4	243	-262	4	2	5	312	303
-8	2	3	187	161	-7	0	4	97	-41	-11	2	4	89	-82	6	4	4	82	67	5	2	5	99	109
-6	2	3	71	58	-5	0	4	621	-496	-8	2	4	120	103	-5	5	4	107	-111	6	2	5	139	-164
-5	2	3	376	-334	-4	0	4	223	205	-7	2	4	306	-284	-3	5	4	126	126	8	2	5	89	-104
-2	2	3	149	157	-3	0	4	596	540	-6	2	4	77	66	-2	5	4	116	-105	-3	3	5	144	125
-1	2	3	72	-57	-2	0	4	635	-619	-5	2	4	149	-129	-1	5	4	168	173	-2	3	5	120	154
0	2	3	259	258	-1	0	4	193	-217	-4	2	4	269	-273	0	5	4	155	-163	-1	3	5	258	265
1	2	3	96	82	0	0	4	1227	-1152	-3	2	4	131	-143	1	5	4	183	-166	3	3	5	110	-118
2	2	3	129	-108	1	0	4	696	652	-2	2	4	215	-220	-13	1	5	127	111	4	3	5	98	-93
3	2	3	141	-117	2	0	4	1199	-1069	-1	2	4	268	-254	-12	1	5	165	-151	5	3	5	126	-141
5	2	3	322	-343	3	0	4	573	-495	0	2	4	119	-102	-11	1	5	82	79	6	3	5	135	-157
6	2	3	64	-75	4	0	4	272	-245	1	2	4	329	278	-10	1	5	75	-90	7	3	5	100	-128
8	2	3	230	-304	5	0	4	148	-158	2	2	4	220	-183	-8	1	5	249	-259	-8	4	5	89	120
9	2	3	138	224	6	0	4	474	473	3	2	4	269	273	-6	1	5	130	-136	-5	4	5	242	220
-6	3	3	109	105	7	0	4	174	176	4	2	4	89	79	-5	1	5	471	-468	-4	4	5	118	-118
-5	3	3	142	142	-14	1	4	182	-217	5	2	4	357	-397	-4	1	5	202	218	-3	4	5	116	115
-3	3	3	146	146	-13	1	4	144	-156	7	2	4	126	197	-3	1	5	416	466	-2	4	5	83	57
-2	3	3	115	119	-12	1	4	83	60	8	2	4	190	-257	-2	1	5	561	-672	-1	4	5	87	79
1	3	3	163	159	-11	1	4	115	-94	-10	3	4	77	-55	-1	1	5	1040	1193	4	4	5	202	199
2	3	3	73	44	-10	1	4	187	190	-9	3	4	90	-86	0	1	5	644	-652	5	4	5	168	213
4	3	3	113	92	-9	1	4	144	-133	-4	3	4	243	-227	1	1	5	499	-413	-2	5	5	148	125
5	3	3	101	-102	-7	1	4	71	62	-2	3	4	75	-77	2	1	5	124	117	-1	5	5	86	-110
7	3	3	120	160	-6	1	4	286	242	-1	3	4	265	256	3	1	5	67	45	1	5	5	118	74
-5	4	3	83	-79	-5	1	4	328	-296	0	3	4	309	311	4	1	5	228	238	2	5	5	89	46
-3	4	3	134	-144	-4	1	4	177	205	1	3	4	211	-205	5	1	5	239	246	-14	0	6	146	154
-1	4	3	76	-89	-3	1	4	360	404	3	3	4	152	-135	6	1	5	76	77	-13	0	6	529	493

Observed and Calculated Structure Factors for $C_{19}H_{26}N_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-11	0	6	786	751	-3	2	6	202	194	5	1	7	182	-191	-1	0	8	59	-47	4	2	8	161	-181
-10	0	6	447	-403	-2	2	6	91	-77	6	1	7	136	-204	1	0	8	170	-165	-11	3	8	113	115
-9	0	6	344	-321	-1	2	6	246	226	-8	2	7	209	-185	2	0	8	268	-235	-9	3	8	231	250
-8	0	6	423	389	1	2	6	712	-571	-7	2	7	154	-153	3	0	8	125	91	-8	3	8	146	-177
-7	0	6	72	-50	2	2	6	171	154	-5	2	7	87	106	4	0	8	479	-388	-5	3	8	95	-103
-6	0	6	199	152	3	2	6	264	256	-4	2	7	128	-149	5	0	8	316	316	-4	3	8	106	77
-5	0	6	413	353	4	2	6	429	428	-3	2	7	85	-74	-15	1	8	108	88	-3	3	8	144	162
-4	0	6	428	-409	5	2	6	409	446	-2	2	7	180	-181	-14	1	8	117	102	-2	3	8	183	-181
-3	0	6	470	-473	-9	3	6	117	-118	-1	2	7	55	-78	-13	1	8	247	225	0	3	8	195	189
-2	0	6	902	1024	-3	3	6	177	-179	0	2	7	239	-243	-11	1	8	158	176	1	3	8	143	-111
-1	0	6	688	-691	-2	3	6	161	-153	1	2	7	469	397	-10	1	8	217	216	2	3	8	206	-185
0	0	6	782	-764	-1	3	6	258	-295	2	2	7	144	-132	-9	1	8	163	-168	3	3	8	118	98
1	0	6	160	164	0	3	6	119	-133	4	2	7	128	138	-8	1	8	214	-201	4	3	8	112	-105
4	0	6	862	768	1	3	6	217	190	5	2	7	206	200	-7	1	8	78	-61	5	3	8	107	134
5	0	6	477	-480	2	3	6	116	-74	6	2	7	116	114	-6	1	8	119	-112	-7	4	8	79	-46
6	0	6	107	125	3	3	6	286	259	-11	3	7	80	-47	-5	1	8	268	319	-6	4	8	98	118
-15	1	6	116	97	5	3	6	160	184	-3	3	7	189	-198	-4	1	8	225	265	-5	4	8	105	-106
-12	1	6	167	-171	-3	4	6	79	-70	6	3	7	187	-283	-3	1	8	262	-317	-4	4	8	81	-97
-10	1	6	70	-77	1	4	6	192	179	-4	4	7	76	45	-2	1	8	176	195	-3	4	8	107	94
-9	1	6	158	-155	3	4	6	112	100	-1	4	7	73	84	-1	1	8	110	-127	-1	4	8	72	89
-8	1	6	88	77	5	4	6	145	-174	0	4	7	89	103	0	1	8	217	198	3	4	8	161	131
-7	1	6	290	277	-4	5	6	154	-148	1	4	7	230	190	3	1	8	126	143	4	4	8	165	155
-6	1	6	89	100	3	5	6	102	-96	2	4	7	127	-94	4	1	8	231	216	-4	5	8	88	64
-5	1	6	243	243	-14	1	7	148	-161	3	4	7	112	-122	5	1	8	132	-131	0	5	8	89	67
-4	1	6	296	-299	-11	1	7	138	-139	4	4	7	157	-170	-14	2	8	98	93	-12	1	9	134	119
-3	1	6	228	264	-10	1	7	106	-105	-13	0	8	134	-123	-11	2	8	111	-102	-11	1	9	116	82
-1	1	6	403	453	-9	1	7	161	-177	-12	0	8	350	329	-10	2	8	98	-106	-10	1	9	369	365
0	1	6	179	168	-7	1	7	131	130	-11	0	8	167	138	-8	2	8	68	-60	-9	1	9	170	165
1	1	6	447	-386	-6	1	7	306	279	-10	0	8	294	280	-7	2	8	93	74	-8	1	9	106	-119
2	1	6	319	279	-5	1	7	365	-371	-8	0	8	121	97	-6	2	8	76	-72	-7	1	9	157	156
4	1	6	109	-103	-3	1	7	256	-303	-7	0	8	319	-278	-5	2	8	133	153	-5	1	9	255	264
5	1	6	146	-136	-2	1	7	300	282	-6	0	8	158	-121	-3	2	8	152	-158	-4	1	9	193	201
6	1	6	136	172	-1	1	7	269	-302	-5	0	8	715	-590	-2	2	8	136	172	-3	1	9	108	-112
-9	2	6	124	117	1	1	7	319	-312	-4	0	8	482	-477	0	2	8	840	824	-2	1	9	177	169
-6	2	6	62	49	2	1	7	233	-220	-3	0	8	83	109	1	2	8	177	142	-1	1	9	193	-197
-4	2	6	123	-118	3	1	7	335	-295	-2	0	8	190	-199	2	2	8	143	-132	0	1	9	583	551

Observed and Calculated Structure Factors for $C_{19}H_{26}N_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	1	9	168	-160	2	0	10	261	-216	-2	3	10	74	87	-1	3	11	99	-84	-9	2	12	261	294
2	1	9	261	-238	3	0	10	209	-172	-1	3	10	97	-97	1	3	11	93	104	-8	2	12	259	296
4	1	9	265	-240	4	0	10	306	-294	0	3	10	123	-123	-8	4	11	161	136	-7	2	12	106	72
-8	2	9	111	-120	5	0	10	225	-272	1	3	10	192	167	-7	4	11	106	101	-4	2	12	202	-188
-7	2	9	120	-126	-14	1	10	152	154	2	3	10	149	156	-5	4	11	86	-74	-3	2	12	319	369
-4	2	9	234	261	-13	1	10	151	-141	-10	4	10	85	-96	-3	4	11	89	82	-2	2	12	69	-46
-3	2	9	395	-434	-12	1	10	247	220	-7	4	10	99	-95	-14	0	12	167	-153	1	2	12	250	223
-2	2	9	274	294	-10	1	10	151	134	-5	4	10	117	115	-13	0	12	176	151	2	2	12	157	-153
0	2	9	373	-363	-9	1	10	312	309	-4	4	10	174	-178	-12	0	12	307	-269	4	2	12	82	-78
3	2	9	223	-237	-7	1	10	204	-181	-3	4	10	120	113	-11	0	12	201	-170	5	2	12	183	-253
4	2	9	132	146	-5	1	10	278	-296	1	4	10	97	-80	-8	0	12	165	-133	-10	3	12	136	127
-6	3	9	86	-93	-4	1	10	310	-321	1	5	10	76	45	-7	0	12	310	262	-7	3	12	113	-127
-4	3	9	87	115	-3	1	10	143	155	3	5	10	100	78	-6	0	12	128	-129	-5	3	12	149	-160
-3	3	9	85	-100	-2	1	10	121	-129	-13	1	11	131	-123	-5	0	12	163	180	-4	3	12	83	-91
-2	3	9	117	-74	-1	1	10	99	-114	-12	1	11	130	134	-4	0	12	319	334	-3	3	12	106	113
1	3	9	154	-155	0	1	10	68	71	-9	1	11	230	225	-3	0	12	394	405	-1	3	12	98	113
-5	4	9	100	-81	1	1	10	365	-321	-8	1	11	94	99	-1	0	12	72	69	1	3	12	98	-104
-4	4	9	249	251	2	1	10	420	-368	-7	1	11	93	87	0	0	12	137	-123	2	3	12	68	31
-3	4	9	179	-195	3	1	10	237	210	-6	1	11	132	120	2	0	12	290	296	-4	4	12	79	71
-2	4	9	102	109	4	1	10	89	-64	-4	1	11	225	-271	4	0	12	123	108	-2	4	12	80	89
0	4	9	173	-166	-9	2	10	131	-150	-2	1	11	329	-340	5	0	12	294	-350	1	4	12	82	-52
0	5	9	83	-60	-8	2	10	128	-149	0	1	11	249	-242	-11	1	12	118	-99	3	4	12	88	-71
2	5	9	90	85	-7	2	10	135	-129	1	1	11	410	341	-10	1	12	83	-88	-12	1	13	177	-171
-13	0	10	432	-383	-6	2	10	140	-153	2	1	11	173	173	-9	1	12	118	147	-11	1	13	94	-76
-12	0	10	130	-99	-5	2	10	72	78	3	1	11	233	185	-7	1	12	73	77	-7	1	13	132	-147
-11	0	10	101	-91	-4	2	10	429	482	4	1	11	121	-133	-5	1	12	100	116	-6	1	13	93	-90
-9	0	10	189	-180	-3	2	10	287	-338	-14	2	11	88	72	-4	1	12	99	-132	-5	1	13	124	-136
-8	0	10	146	-130	-2	2	10	186	198	-10	2	11	94	88	-3	1	12	164	-164	-4	1	13	196	208
-7	0	10	128	139	-1	2	10	93	-101	-9	2	11	82	90	-2	1	12	123	-142	-3	1	13	129	154
-6	0	10	68	53	0	2	10	201	-200	-8	2	11	109	183	-1	1	12	474	-460	-2	1	13	183	-212
-5	0	10	324	312	1	2	10	451	378	-6	2	11	148	-166	0	1	12	307	284	-1	1	13	116	121
-4	0	10	266	-259	-10	3	10	109	-126	2	2	11	205	196	2	1	12	325	-290	0	1	13	268	-232
-3	0	10	492	-529	-7	3	10	91	-103	4	2	12	90	-101	3	1	12	176	-173	1	1	13	234	-253
-2	0	10	106	-87	-6	3	10	142	129	-6	3	11	89	-80	4	1	12	120	-143	2	1	13	255	263
-1	0	10	231	-239	-5	3	10	269	-292	-3	3	11	72	-25	-12	2	12	87	-80	3	1	13	180	-196
1	0	10	192	-175	-4	3	10	100	104	-2	3	11	95	-108	-11	2	12	84	81	4	1	13	93	96

Observed and Calculated Structure Factors for $C_{19}H_{26}N_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-10	2	13	133	167	-8	1	14	78	-96	-8	2	15	74	-81	1	3	16	86	-95	-9	2	18	107	-101
-8	2	13	116	119	-4	1	14	116	122	-7	2	15	204	219	-7	4	16	99	74	-7	2	18	121	140
-7	2	13	173	189	0	1	14	119	-114	-4	2	15	129	128	-3	4	16	117	-92	-6	2	18	133	-146
-5	2	13	108	101	-13	2	14	167	147	1	2	15	158	-99	-2	4	16	82	-75	-5	2	18	220	237
-4	2	13	106	-86	-11	2	14	107	115	3	2	15	90	-61	-12	1	17	112	106	-4	2	18	116	-127
-2	2	13	253	-254	-9	2	14	110	-117	-7	3	15	79	89	-10	1	17	97	109	-3	2	18	242	-275
-1	2	13	211	201	-8	2	14	107	149	-6	3	15	104	121	-4	1	17	136	154	1	2	18	176	177
1	2	13	131	-214	-6	2	14	161	180	-4	3	15	134	-127	0	1	17	139	162	-7	3	18	143	-145
2	2	13	123	84	-5	2	14	80	108	-8	4	15	120	-115	2	1	17	158	-173	-5	3	18	129	-132
3	2	13	86	79	-1	2	14	112	-101	-5	4	15	125	-119	3	1	17	160	178	-3	3	18	122	-113
4	2	13	86	-93	0	2	14	324	-291	-4	4	15	108	-78	-4	2	17	242	261	2	3	18	88	-71
5	2	13	233	347	1	2	14	143	-120	-10	0	16	145	-132	1	2	17	79	80	-6	4	18	114	91
-8	3	13	87	-96	2	2	14	173	161	-5	0	16	87	-65	-6	3	17	151	122	-4	4	18	117	123
-7	3	13	113	-120	3	2	14	79	-90	-3	0	16	335	-299	-5	3	17	95	132	-3	4	18	91	78
-6	3	13	142	-127	4	2	14	134	130	-2	0	16	365	348	-4	3	17	99	65	-9	1	19	141	146
-5	3	13	230	-257	-8	3	14	165	157	-1	0	16	212	-219	-5	4	17	93	70	-8	1	19	118	-137
-3	3	13	78	69	-7	3	14	202	223	0	0	16	146	150	-10	0	18	84	-98	-5	1	19	88	-78
-9	4	13	139	-125	-5	3	14	441	463	1	0	16	148	145	-9	0	18	91	93	-4	1	19	134	-125
-5	4	13	80	78	-4	3	14	477	-473	2	0	16	164	-163	-8	0	18	179	-201	-3	1	19	158	-177
-4	4	13	111	-104	-2	3	14	84	95	-12	1	16	94	-51	-7	0	18	99	-135	-2	1	19	168	-180
-1	4	13	90	58	-1	3	14	87	-73	-8	1	16	192	198	-6	0	18	102	-98	-7	2	19	84	-110
0	4	13	80	-79	0	3	14	119	115	1	1	16	264	271	-5	0	18	85	98	-6	2	19	92	94
1	4	13	105	-98	2	3	14	75	-96	3	1	16	77	-71	-4	0	18	234	239	-5	2	19	149	-172
2	5	13	108	-75	3	3	14	90	84	-12	2	16	107	118	-3	0	18	94	-66	-4	2	19	79	-68
-14	0	14	131	125	4	3	14	132	125	-9	2	16	80	-88	-2	0	18	116	125	-3	2	19	138	162
-8	0	14	165	202	-8	4	14	88	58	-7	2	16	133	-112	-1	0	18	101	106	-3	4	19	91	88
-7	0	14	225	-172	-6	4	14	119	-112	-5	2	16	373	-377	1	0	18	382	368	-8	0	20	117	185
-6	0	14	154	147	-10	1	15	114	-129	-4	2	16	104	-127	-12	1	18	106	-88	-5	0	20	77	-79
-5	0	14	158	150	-9	1	15	128	-173	-1	2	16	81	96	-10	1	18	112	-97	-4	0	20	157	-129
-4	0	14	105	-107	-4	1	15	91	-89	1	2	16	255	-250	-9	1	18	123	-147	-3	0	20	149	123
-3	0	14	202	199	-3	1	15	72	57	4	2	16	83	-136	-4	1	18	151	152	-2	0	20	111	-80
-1	0	14	255	242	-2	1	15	261	270	-8	3	16	81	-50	-2	1	18	89	93	-1	0	20	186	167
1	0	14	144	-113	-1	1	15	101	106	-7	3	16	80	-74	0	1	18	174	-172	1	0	20	180	190
3	0	14	141	149	0	1	15	157	159	-6	3	16	83	106	2	1	18	155	168	2	0	20	139	141
4	0	14	283	343	1	1	15	105	-122	-5	3	16	93	129	3	1	18	134	-134	-7	1	20	94	-85
-14	1	14	114	-112	-13	2	15	88	65	-4	3	16	268	267	4	1	18	144	200	-3	1	20	253	253

Observed and Calculated Structure Factors for $C_{19}H_{26}N_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	1	20	142	151	-3	4	20	92	98	-4	0	22	141	132	-3	1	22	96	-82	-4	0	24	101	-88
-1	1	20	148	165	1	4	20	86	57	-3	0	22	84	-79	0	1	22	146	157	-2	0	24	106	113
0	1	20	102	127	-6	1	21	108	-102	-2	0	22	264	-230	-8	1	23	144	151	1	0	24	220	-257
3	1	20	129	157	-3	1	21	133	143	-1	0	22	164	-170	-7	1	23	101	-78	-4	1	24	121	107
-8	2	20	88	-83	-2	1	21	114	-111	0	0	22	265	-272	-6	1	23	101	105	-1	1	24	87	-80
-4	2	20	120	129	-1	1	21	108	-114	1	0	22	324	-312	-2	1	23	118	120	1	1	24	151	-175
-3	2	20	88	66	2	1	21	119	139	2	0	22	297	370	0	1	23	109	100	0	1	25	90	-89
-7	3	20	110	94	-6	2	21	103	-97	-10	1	22	126	90	-4	2	23	106	-102	-3	0	26	97	-73
-6	3	20	205	-191	-4	2	21	100	-126	-7	1	22	123	137	-10	0	24	120	104	-4	2	26	110	98
0	3	20	93	-90	-8	0	22	95	105	-5	1	22	85	73	-9	0	24	105	-123	-5	1	27	85	62
1	3	20	129	111	-6	0	22	79	-17	-4	1	22	148	-138	-5	0	24	107	-88	-3	1	27	95	-64

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

H	K	L	10FO	10FC
2	0	0	256	-245
3	0	0	92	105
4	0	0	124	133
5	0	0	159	169
8	0	0	102	92
-6	1	0	63	60
-5	1	0	79	88
-4	1	0	344	357
-3	1	0	182	175
-2	1	0	274	257
-1	1	0	254	263
1	1	0	176	200
2	1	0	94	103
3	1	0	254	280
4	1	0	181	192
5	1	0	123	123
7	1	0	139	130
8	1	0	87	81
-7	2	0	68	61
-5	2	0	139	140
-4	2	0	349	352
-3	2	0	80	81
-2	2	0	160	175
-1	5	0	81	70
0	2	0	269	-259
1	2	0	200	187
2	2	0	142	163
3	2	0	235	301
4	2	0	84	94
5	2	0	73	77
6	2	0	156	171
7	2	0	94	86
-6	3	0	81	79
-5	3	0	155	156
-4	3	0	89	85
-3	3	0	96	93
-2	3	0	116	119
-1	3	0	342	323
0	3	0	480	442
1	3	0	155	-131
3	3	0	169	198
5	3	0	117	138
6	3	0	149	167
-6	4	0	79	76
-5	4	0	150	145
-4	4	0	176	180
-3	4	0	147	153
-2	4	0	271	261
-1	4	0	305	307
0	4	0	90	85
1	4	0	174	-173
2	4	0	155	169
3	4	0	201	197
4	4	0	98	125
5	4	0	94	113
6	4	0	77	83
7	4	0	77	74
8	4	0	49	57
-6	5	0	76	88
-5	5	0	83	83
-4	5	0	120	128
-2	5	0	194	199
-1	5	0	89	91
0	5	0	52	45
1	5	0	317	287
2	5	0	164	147
3	5	0	129	119
4	5	0	100	98
5	5	0	129	138
6	5	0	142	159
7	5	0	74	79
-1	6	0	123	124
0	6	0	166	157
1	6	0	214	192
2	6	0	129	114
3	6	0	142	137
4	6	0	76	80
5	6	0	128	128
6	6	0	81	86
-4	7	0	85	99
-3	7	0	75	100
-2	7	0	50	-46
0	7	0	93	85
1	7	0	113	105
2	7	0	118	108
3	7	0	82	80
4	7	0	132	117
5	7	0	100	91
-2	8	0	52	59
0	8	0	69	70
1	8	0	89	96
4	8	0	99	76
5	8	0	78	51
-1	9	0	73	86
0	9	0	65	75
-3	-9	1	55	56
-6	-8	1	58	50
-5	-8	1	71	69
-4	-8	1	121	113
-3	-8	1	99	87
-2	-8	1	59	62
-1	-8	1	114	114
4	-8	1	58	71
-5	-7	1	128	123
-4	-7	1	136	127
-3	-7	1	114	111
-2	-7	1	97	97
-1	-7	1	109	120
0	-7	1	72	82
2	-7	1	92	97
-6	-6	1	126	128
-5	-6	1	150	157
-2	-6	1	136	141
-1	-6	1	214	211
0	-6	1	180	182
1	-6	1	47	-66
2	-6	1	163	165
3	-6	1	173	189
5	-6	1	55	76
-7	-5	1	84	84
-6	-5	1	85	84
-5	-5	1	39	36
-2	-5	1	311	303
-1	-5	1	263	261
2	-5	1	136	138
3	-5	1	176	181
4	-5	1	71	82
5	-5	1	75	84
6	-5	1	71	74
-8	-4	1	88	120
-7	-4	1	117	133
-5	-4	1	149	159
-4	-4	1	119	126
-3	-4	1	71	-61
-2	-4	1	116	113
0	-4	1	38	39
1	-4	1	338	337
2	-4	1	182	186
3	-4	1	81	89
4	-4	1	89	95
5	-4	1	94	84
6	-4	1	59	52
-7	-3	1	100	98
-6	-3	1	129	150
-5	-3	1	125	145
-3	-3	1	172	191
-1	-3	1	114	127
0	-3	1	517	513
1	-3	1	390	380
2	-3	1	459	453
3	-3	1	160	162
5	-3	1	101	92
-7	-2	1	110	111
-6	-2	1	96	110
-5	-2	1	75	-75
-4	-2	1	89	95
-3	-2	1	467	520
-2	-2	1	1031	1145
-1	-2	1	292	295
0	-2	1	184	-162
1	-2	1	74	77
2	-2	1	526	525
3	-2	1	245	235
4	-2	1	39	17
5	-2	1	112	112
6	-2	1	81	83
-7	-1	1	83	87
-5	-1	1	136	146
-4	-1	1	319	357
-3	-1	1	54	-36
-2	-1	1	685	788
-1	-1	1	268	289
0	-1	1	151	138
1	-1	1	579	542
2	-1	1	89	-85
3	-1	1	192	176
4	-1	1	191	177
5	-1	1	171	160
6	-1	1	158	153
7	-1	1	119	118

Observed and Calculated Structure Factors for [Ni(C$_{19}$H$_{26}$N$_4$)](BF$_4$)$_2$

H	K	L	10FO	10FC
-8	0	1	69	69
-6	0	1	171	187
-5	0	1	81	81
-3	0	1	48	-38
-2	0	1	94	-113
-1	0	1	613	590
1	0	1	379	313
2	0	1	113	-92
3	0	1	246	245
4	0	1	157	168
5	0	1	126	116
8	0	1	137	168
-6	1	1	144	142
-5	1	1	89	96
-4	1	1	192	197
-3	1	1	321	329
-2	1	1	218	223
-1	1	1	619	535
0	1	1	131	-123
1	1	1	183	-191
2	1	1	89	74
3	1	1	124	118
4	1	1	152	151
7	1	1	117	98
8	1	1	134	154
-7	2	1	85	98
-6	2	1	151	153
-5	2	1	324	336
-4	2	1	279	279
-3	2	1	61	66
-2	2	1	284	249
0	2	1	49	-41
1	2	1	331	270
2	2	1	96	82
3	2	1	109	122
4	2	1	258	261
5	2	1	48	56
6	2	1	152	144
7	2	1	93	85
-6	3	1	127	144
-5	3	1	177	186
-4	3	1	111	111
-3	3	1	63	60
-2	3	1	201	207
-1	3	1	237	227
0	3	1	133	124
1	3	1	93	97
2	3	1	226	206
3	3	1	441	385
4	3	1	268	278
5	3	1	121	132
-5	4	1	56	-63
-4	4	1	65	53
-3	4	1	231	237
-2	4	1	204	202
-1	4	1	286	285
0	4	1	56	-41
1	4	1	147	145
2	4	1	341	312
3	4	1	156	144
4	4	1	168	147
5	4	1	178	171
6	4	1	72	70
7	4	1	73	64
-4	5	1	107	-127
-2	5	1	178	184
-1	5	1	150	147
1	5	1	206	197
2	5	1	181	175
3	5	1	75	68
4	5	1	92	67
6	5	1	140	131
7	5	1	92	84
-5	6	1	72	78
-2	6	1	100	120
0	6	1	98	99
1	6	1	113	112
2	6	1	157	135
3	6	1	136	120
4	6	1	78	72
-3	7	1	91	118
0	7	1	94	104
1	7	1	93	85
2	7	1	93	80
4	7	1	84	75
0	8	1	100	112
1	8	1	71	74
3	9	1	58	60
-2	-9	2	51	31
-4	-8	2	136	118
-3	-8	2	97	90
0	-8	2	110	115
1	-8	2	93	100
-5	-7	2	95	73
4	-7	2	161	141
-2	-7	2	55	47
0	-7	2	75	71
1	-7	2	176	181
2	-7	2	49	58
3	-7	2	77	99
-6	-6	2	126	120
-3	-6	2	83	77
-2	-6	2	135	127
-1	-6	2	164	175
1	-6	2	56	49
2	-6	2	139	139
3	-6	2	143	150
6	-6	2	57	49
-9	-5	2	94	94
-7	-5	2	90	84
-6	-5	2	115	104
-3	-5	2	169	168
-2	-5	2	296	311
-1	-5	2	350	349
0	-5	2	96	79
1	-5	2	97	97
2	-5	2	189	187
3	-5	2	66	69
-8	-4	2	69	68
-7	-4	2	50	50
-6	-4	2	77	64
-5	-4	2	263	263
-4	-4	2	234	262
-3	-4	2	82	101
-2	-4	2	195	214
-1	-4	2	77	76
0	-4	2	429	408
1	-4	2	468	446
3	-4	2	57	59
4	-4	2	90	91
6	-4	2	62	67
-6	-3	2	189	190
-4	-3	2	150	166
-3	-3	2	301	328
-2	-3	2	196	203
0	-3	2	206	212
1	-3	2	457	433
2	-3	2	254	263
3	-3	2	227	240
4	-3	2	149	150
5	-3	2	98	95
-7	-2	2	61	54
-6	-2	2	73	76
-5	-2	0	210	-220
-4	-2	2	279	258
-3	-2	2	604	668
-2	-2	2	87	86
-1	-2	2	369	351
0	-2	2	107	-102
1	-2	2	309	303
2	-2	2	249	256
3	-2	2	40	-23
4	-2	2	52	42
5	-2	2	100	80
6	-2	2	124	128
7	-2	2	98	89
-8	-1	2	94	89
-7	-1	2	111	108
-5	-1	2	172	182
-4	-1	2	336	361
-3	-1	2	598	625
-2	-1	2	114	-114
-1	-1	2	249	-201
0	-1	2	159	159
1	-1	2	253	208
2	-1	2	205	-176
3	-1	2	60	-63
4	-1	2	206	177
5	-1	2	153	138
6	-1	2	240	326
7	-1	2	79	-65
-8	0	2	153	148
-7	0	2	170	177
-6	0	2	107	111
-5	0	2	171	170
-4	0	2	151	153
-3	0	2	419	430
-2	0	2	37	37
-1	0	2	55	-59
0	0	2	398	386

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	0	2	93	-87	-3	3	2	187	175	1	7	2	122	128	-6	-4	3	112	95	2	-2	3	360	344
2	0	2	96	85	-1	3	2	64	70	2	7	2	71	63	-5	-4	3	271	270	4	-2	3	144	129
3	0	2	263	256	0	3	2	212	219	3	7	2	64	60	-4	-4	3	88	90	5	-2	3	89	78
4	0	2	285	256	2	3	2	166	185	-4	-8	3	108	111	-3	-4	3	86	99	7	-2	3	77	64
5	0	2	115	107	3	3	2	329	345	-2	-8	3	61	-80	-2	-4	3	216	217	-9	-1	3	71	75
6	0	2	127	112	4	3	2	162	186	-1	-8	3	113	117	-1	-4	3	311	276	-8	-1	3	50	53
7	0	2	76	69	5	3	2	111	94	0	-8	3	107	113	0	-4	3	126	130	-7	-1	3	90	101
-8	1	2	94	84	6	3	2	77	53	1	-8	3	85	106	1	-4	3	121	129	-5	-1	3	245	239
-7	1	2	144	151	-4	4	2	81	87	2	-8	3	61	66	2	-4	3	66	45	-4	-1	3	364	354
-6	1	2	101	94	-3	4	2	95	99	-5	-7	3	168	168	4	-4	3	71	66	-3	-1	3	154	170
-4	1	2	262	261	-2	4	2	123	116	-4	-7	3	164	156	5	-4	3	138	132	-2	-1	3	420	367
-3	1	2	178	180	-1	4	2	170	178	-3	-7	3	76	72	6	-4	3	77	87	-1	-1	3	159	146
-1	1	2	481	448	0	4	2	174	159	-1	-7	3	100	98	-8	-3	3	65	57	0	-1	3	327	312
0	1	2	372	284	1	4	2	153	151	0	-7	3	171	162	-7	-3	3	65	39	1	-1	3	104	106
1	1	2	288	301	2	4	2	239	233	1	-7	3	75	79	-6	-3	3	220	213	2	-1	3	69	-57
2	1	2	480	508	5	4	2	124	110	3	-7	3	55	62	-5	-3	3	315	335	3	-1	3	104	90
3	1	2	77	82	6	4	2	51	53	4	-7	3	71	90	-4	-3	3	153	-161	4	-1	3	261	232
5	1	2	87	85	-6	5	2	62	65	-6	-6	3	91	78	-3	-3	3	209	233	5	-1	3	277	248
6	1	2	89	88	-5	5	2	52	63	-5	-6	3	109	118	-2	-3	3	181	185	-8	0	3	153	149
7	1	2	176	156	-4	5	2	58	65	-3	-6	3	147	151	-1	-3	3	40	47	-7	0	3	85	95
-6	2	2	99	112	-2	5	2	202	209	-2	-6	3	267	257	1	-3	3	104	-87	-6	0	3	59	64
-5	2	2	267	279	-1	5	2	155	170	-1	-6	3	227	238	2	-3	3	188	185	-4	0	3	85	89
-4	2	2	187	193	0	5	2	83	84	0	-6	3	83	93	3	-3	3	165	176	-3	0	3	469	433
-3	2	2	96	-80	1	5	2	127	120	2	-6	3	131	127	4	-3	3	159	148	-2	0	3	147	130
-1	2	2	366	331	2	5	2	134	135	3	-6	3	114	107	5	-3	3	121	99	-1	0	3	86	-73
0	2	2	233	233	5	5	2	73	62	4	-6	3	81	89	6	-3	3	71	80	0	0	3	494	489
1	2	2	153	171	6	5	2	75	61	-6	-5	3	82	82	-10	-2	3	71	60	1	0	3	277	296
2	2	2	227	239	-3	6	2	128	141	-5	-5	3	89	80	-9	-2	3	94	92	3	0	3	216	223
3	2	2	320	348	-2	6	2	151	179	-4	-5	3	161	157	-7	-2	3	125	118	4	0	3	229	194
4	2	2	107	105	1	6	2	96	103	-3	-5	3	54	60	-6	-2	3	120	119	5	0	3	310	279
5	2	2	67	63	2	6	2	126	129	-2	-5	3	216	237	-5	-2	3	240	242	6	0	3	77	68
6	2	2	138	117	3	6	2	107	104	-1	-5	3	402	389	-4	-2	3	214	219	8	0	3	65	47
7	2	2	117	94	4	6	2	60	-55	0	-5	3	132	132	-3	-2	3	48	29	-7	1	3	77	68
-8	3	2	80	101	6	6	2	85	76	1	-5	3	191	174	-2	-2	3	102	99	-6	1	3	115	113
-5	3	2	119	125	-4	7	2	63	91	2	-5	3	205	182	0	-2	3	133	125	-5	1	3	88	79
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	5	-5	3	62	69	1	-2	3	316	304	-3	1	3	150	-142

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	1	3	44	-58	-2	4	3	74	75	-1	-7	4	154	133	-6	-3	4	283	287	-7	0	4	71	65
-1	1	3	231	243	-1	4	3	204	202	0	-7	4	112	120	-4	-3	4	96	106	-5	0	4	50	-49
0	1	3	343	371	0	4	3	182	185	1	-7	4	60	51	-3	-3	4	275	282	-4	0	4	201	186
1	1	3	537	545	1	4	3	136	132	3	-7	4	75	82	-2	-3	4	237	232	-3	0	4	376	347
2	1	3	261	290	3	4	3	67	72	-6	-6	4	116	106	0	-3	4	84	83	-2	0	4	79	71
3	1	3	85	97	4	4	3	96	88	-5	-6	4	110	106	1	-3	4	133	125	-1	0	4	137	118
4	1	3	86	79	5	4	3	69	71	-4	-6	4	75	72	2	-3	4	256	237	0	0	4	250	249
5	1	3	68	62	-5	5	3	58	64	-3	-6	4	193	177	3	-3	4	210	207	1	0	4	109	107
6	1	3	91	81	-3	5	3	85	81	-2	-6	4	139	141	5	-3	4	88	87	2	0	4	98	99
7	1	3	77	48	-2	5	3	208	222	-1	-6	4	125	131	-10	-2	4	62	64	3	0	4	59	51
-5	2	3	172	180	-1	5	3	164	169	0	-6	4	56	62	-7	-2	4	94	94	4	0	4	107	92
-4	2	3	92	97	1	5	3	82	86	2	-6	4	63	60	-6	-2	4	253	252	5	0	4	90	71
-3	2	3	132	-117	3	5	3	79	77	3	-6	4	142	168	-5	-2	4	77	80	6	0	4	67	63
-2	2	3	284	273	4	5	3	126	133	-7	-5	4	111	102	-4	-2	4	141	137	-7	1	4	74	60
-1	2	3	318	307	5	5	3	58	46	-6	-5	4	70	53	-2	-2	4	65	54	-6	1	4	138	133
0	2	3	175	176	6	5	3	62	66	-5	-5	4	99	95	-1	-2	4	152	145	-5	1	4	83	88
1	2	3	90	103	-3	6	3	75	81	-4	-5	4	111	107	0	-2	4	72	71	-4	1	4	237	212
2	2	3	74	64	0	6	3	71	78	-3	-5	4	111	101	1	-2	4	311	284	-1	1	4	286	286
3	2	3	132	131	1	6	3	69	75	-2	-5	4	81	81	2	-2	4	347	338	0	1	4	230	234
4	2	3	129	125	2	6	3	67	50	0	-5	4	83	88	3	-2	4	412	400	1	1	4	51	64
7	2	3	88	62	4	6	3	65	74	1	-5	4	102	111	4	-2	4	101	83	2	1	4	118	122
-6	3	3	57	66	0	7	3	87	92	2	-5	4	93	89	6	-2	4	63	54	3	1	4	92	82
-5	3	3	99	100	1	7	3	83	77	3	-5	4	83	97	-8	-1	4	83	75	-8	2	4	65	72
-4	3	3	158	151	-2	-9	4	75	87	4	-5	4	81	104	-7	-1	4	110	108	-7	2	4	100	94
-3	3	3	187	184	0	-9	4	67	74	-7	-4	4	220	223	-6	-1	4	82	-63	-4	2	4	103	99
-2	3	3	216	200	-7	-8	4	68	64	-6	-4	4	79	82	-5	-1	4	51	-66	-3	2	4	139	133
-1	3	3	109	106	-5	-8	4	81	74	-5	-4	4	64	62	-4	-1	4	105	109	-2	2	4	321	310
0	3	3	155	156	-4	-8	4	115	113	-3	-4	4	75	69	-3	-1	4	161	162	-1	2	4	292	281
2	3	3	46	44	3	-8	4	71	71	-2	-4	4	389	378	-2	-1	4	364	318	0	2	4	61	53
3	3	3	142	148	-1	-8	4	67	62	-1	-4	4	145	145	-1	-1	4	428	374	1	2	4	96	99
4	3	3	54	60	0	-8	4	119	124	0	-4	4	128	126	0	-1	4	188	183	2	2	4	71	74
5	3	3	74	61	1	-8	4	87	103	1	-4	4	107	102	1	-1	4	202	211	3	2	4	108	116
-6	4	3	92	99	-5	-7	4	110	118	4	-4	4	71	69	3	-1	4	214	200	6	2	4	77	83
-5	4	3	119	123	-4	-7	4	147	139	5	-4	4	82	79	4	-1	4	233	203	7	2	4	75	47
-4	4	3	151	153	-3	-7	4	113	103	-8	-3	4	66	58	6	-1	4	71	58	-5	3	4	143	151
-3	4	3	68	78	-2	-7	4	152	148	-7	-3	4	182	167	-8	0	4	96	90	-4	3	4	175	188

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)](BF_4)_2$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-3	3	4	194	173	-9	-6	5	84	82	0	-3	5	99	94	-4	1	5	154	133	-6	-7	6	72	82
-2	3	4	69	68	-6	-6	5	75	78	1	-3	5	319	300	-3	1	5	147	132	-5	-7	6	75	72
-1	3	4	109	111	-5	-6	5	153	157	2	-3	5	224	220	-2	1	5	117	109	-3	-7	6	53	53
0	3	4	65	62	-4	-6	5	168	160	4	-3	5	75	60	-1	1	5	248	244	0	-7	6	82	115
1	3	4	107	110	-3	-6	5	49	64	-6	-2	5	153	147	0	1	5	132	121	-6	-6	6	95	92
2	3	4	151	154	-2	-6	5	74	63	-5	-2	5	88	93	4	1	5	127	139	-5	-6	6	126	118
3	3	4	76	82	-1	-6	5	79	77	-4	-2	5	71	78	5	1	5	81	89	-4	-6	6	58	65
4	3	4	55	62	2	-6	5	109	119	-3	-2	5	143	135	-7	2	5	76	79	-3	-6	6	112	107
5	3	4	57	43	3	-6	5	69	87	-2	-2	5	56	43	-5	2	5	90	95	-2	-6	6	108	107
6	3	4	78	87	-9	-5	5	108	107	-1	-2	5	121	122	-4	2	5	71	80	-1	-6	6	144	138
-5	4	4	99	89	-8	-5	5	75	84	0	-2	5	52	50	-3	2	5	71	63	0	-6	6	70	78
-4	4	4	75	72	-6	-5	5	117	117	1	-2	5	133	120	-1	2	5	61	49	-7	-5	6	64	55
-3	4	4	61	73	-5	-5	5	102	112	2	-2	5	267	259	0	2	5	180	180	-6	-5	6	67	64
-2	4	4	69	66	-4	-5	5	169	169	3	-2	5	52	42	1	2	5	123	125	-5	-5	6	90	81
-1	4	4	147	150	-2	-5	5	58	67	4	-2	5	115	100	2	2	5	123	117	-3	-5	6	75	67
2	4	4	165	182	-1	-5	5	160	162	5	-2	5	66	67	3	2	5	86	73	-2	-5	6	103	109
3	4	4	92	98	0	-5	5	60	71	-8	-1	5	86	84	4	2	5	62	87	-1	-5	6	225	227
4	4	4	100	98	1	-5	5	56	65	-7	-1	5	111	102	-5	3	5	89	100	0	-5	6	85	96
5	4	4	77	77	2	-5	5	94	87	-3	-1	5	303	282	-4	3	5	132	133	2	-5	6	77	74
6	4	4	58	58	3	-5	5	96	120	-2	-1	5	320	286	-3	3	5	107	100	3	-5	6	67	82
-2	5	4	172	175	4	-5	5	65	100	0	-1	5	166	157	-2	3	5	60	-40	-7	-4	6	85	72
-1	5	4	109	104	-8	-4	5	174	173	1	-1	5	197	189	-1	3	5	120	-121	-5	-4	6	74	65
2	5	4	95	96	-7	-4	5	72	79	2	-1	5	119	117	0	3	5	164	172	-3	-4	6	82	83
3	5	4	110	115	-5	-4	5	45	41	-8	0	5	83	78	1	3	5	151	153	-2	-4	6	100	114
0	6	4	69	62	-3	-4	5	86	76	-5	0	5	175	172	2	3	5	63	62	-1	-4	6	118	132
1	6	4	90	87	-2	-4	5	218	213	-4	0	5	254	237	3	3	5	60	49	0	-4	6	210	213
1	7	4	72	75	-1	-4	5	189	195	-3	0	5	377	343	-2	4	5	96	87	1	-4	6	75	70
-4	-8	5	123	129	0	-4	5	211	218	-2	0	5	169	141	-1	4	5	59	56	2	-4	6	118	120
-3	-8	5	85	86	1	-4	5	342	329	0	0	5	177	198	-2	5	5	79	84	-9	-3	6	54	52
0	-8	5	57	73	2	-4	5	67	61	1	0	5	121	130	-1	5	5	66	73	-6	-3	6	86	69
-7	-7	5	64	51	-6	-3	5	93	87	4	0	5	69	61	1	5	5	60	75	-5	-3	6	180	170
-5	-7	5	113	115	-5	-3	5	119	113	5	0	5	75	67	2	5	5	71	77	-4	-3	6	90	87
-4	-7	5	77	73	-4	-3	5	54	57	-8	1	5	52	26	-2	6	5	60	39	-3	-3	6	66	75
-2	-7	5	76	78	-3	-3	5	251	252	-7	1	5	58	70	0	6	5	84	106	-2	-3	6	155	145
-1	-7	5	74	75	-2	-3	5	126	126	-6	1	5	112	115	1	6	5	69	77	-1	-3	6	162	158
1	-7	5	70	94	-1	-3	5	113	107	-5	1	5	140	127	-7	-7	6	66	74	0	-3	6	249	259

Observed and Calculated Structure Factors for [Ni($C_{19}H_{26}N_4$)](BF_4)$_2$

H	K	L	10FO	10FC
-7	-2	6	142	135
-6	-2	6	168	157
-5	-2	6	134	115
-4	-2	6	168	165
-3	-2	6	65	73
-2	-2	6	158	162
-1	-2	6	153	152
0	-2	6	61	65
3	-2	6	73	74
-7	-1	6	134	132
-6	-1	6	50	42
-5	-1	6	105	100
-4	-1	6	216	210
-3	-1	6	175	172
-2	-1	6	66	69
0	-1	6	60	79
1	-1	6	148	150
2	-1	6	120	129
3	-1	6	85	94
4	-1	6	66	71
-5	0	6	90	87
-4	0	6	118	118
-3	0	6	178	164
-2	0	6	109	109
-1	0	6	90	88
0	0	6	146	159
-6	1	6	74	96
-3	1	6	64	-64
-2	1	6	140	142
-1	1	6	172	186
0	1	6	58	55
-5	2	6	68	73
-4	2	6	106	113
-3	2	6	63	-60
-1	2	6	64	75
1	2	6	83	112
-5	3	6	75	77
-4	3	6	60	68
0	3	6	76	108
-5	-7	7	59	66
-4	-7	7	75	77
-3	-7	7	51	60
-5	-6	7	75	73
-3	-6	7	62	73
-2	-6	7	96	109
-1	-6	7	64	88
-7	-5	7	70	69
-4	-5	7	79	84
-3	-5	7	110	115
-2	-5	7	191	208
-7	-4	7	79	64
-6	-4	7	76	71
-5	-4	7	67	74
-4	-4	7	112	113
-3	-4	7	84	89
-2	-4	7	155	173
1	-4	7	72	100
-6	-3	7	172	173
-5	-3	7	102	93
-3	-3	7	54	76
-2	-3	7	126	149
-1	-3	7	163	198
0	-3	7	55	84
1	-3	7	64	74
-7	-2	7	75	79
-6	-2	7	157	143
-5	-2	7	87	74
-3	-2	7	107	102
-2	-2	7	119	116
-1	-2	7	91	96
1	-2	7	67	72
-7	-1	7	69	68
-4	-1	7	132	135
-3	-1	7	119	123
-1	-1	7	83	-89
1	-1	7	135	170
2	-1	7	71	87
-6	0	7	77	76
-3	0	7	84	86
-2	0	7	61	68
1	0	7	90	106
-3	1	7	115	125
-2	1	7	64	72
-1	1	7	100	107
2	1	7	69	82
-3	2	7	108	107
-2	2	7	81	84
0	2	7	76	86
-1	3	7	76	83
0	3	7	82	95
1	3	7	59	56
-5	-7	8	70	72
-4	-7	8	88	96
-6	-6	8	78	76
-5	-6	8	73	80
-4	-6	8	94	110
-1	-6	8	80	88
0	-6	8	57	68
-4	-5	8	145	145
-3	-5	8	158	156
-1	-5	8	62	62
-7	-4	8	58	54
-5	-4	8	93	86
-4	-4	8	103	97
-3	-4	8	123	123
0	-4	8	58	61
-6	-3	8	82	83
-5	-3	8	69	65
-1	-3	8	102	112
0	-3	8	86	93
-4	-2	8	59	65
-1	-2	8	72	83
-5	-1	8	71	80
-4	-1	8	75	68
-3	-1	8	79	77
-5	0	8	88	82
-3	0	8	55	68
-2	0	8	66	66
-1	0	8	61	81
0	0	8	80	116
-4	1	8	102	107
-3	1	8	76	79
-2	1	8	81	88
-1	1	8	75	81
0	1	8	66	78
-5	-6	9	94	115
-2	-5	9	58	66
-2	-2	9	90	108
-2	-1	9	84	95

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)(NCS)_2]$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	1778	-1889	3	4	0	284	-255	12	8	0	230	-156	1	15	0	188	139	-10	2	1	169	-161
4	0	0	145	-142	4	4	0	263	239	13	8	0	167	-188	8	15	0	217	-288	-8	2	1	531	495
6	0	0	241	-228	6	4	0	662	686	1	9	0	291	-271	3	16	0	169	-202	-6	2	1	400	-361
8	0	0	430	-447	7	4	0	145	130	2	9	0	141	135	2	17	0	208	210	-5	2	1	335	-393
12	0	0	237	-244	9	4	0	180	-153	3	9	0	208	-172	6	17	0	147	186	-4	2	1	127	-26
14	0	0	282	252	12	4	0	204	207	5	9	0	626	642	0	18	0	428	466	-3	2	1	173	-218
2	1	0	850	-926	14	4	0	160	-137	7	9	0	465	-480	-13	0	1	265	-216	-2	2	1	455	456
3	1	0	1797	-1957	1	5	0	714	586	9	9	0	537	525	-11	0	1	436	408	-1	2	1	175	132
4	1	0	876	928	2	5	0	295	-279	0	10	0	1025	871	-9	0	1	430	-404	0	2	1	1090	-1066
5	1	0	1388	1505	3	5	0	429	382	1	10	0	418	-410	-7	0	1	733	722	2	2	1	535	541
6	1	0	902	-962	5	5	0	419	-431	2	10	0	202	-215	-5	0	1	390	-353	4	2	1	688	-650
7	1	0	391	-434	6	5	0	143	198	3	10	0	335	344	-3	0	1	512	476	6	2	1	477	477
8	1	0	720	758	8	5	0	346	-342	4	10	0	434	413	3	0	1	740	766	8	2	1	387	-377
9	1	0	293	325	9	5	0	275	-275	5	10	0	223	-213	5	0	1	1310	-1338	-13	3	1	240	214
11	1	0	310	-292	11	5	0	173	135	6	10	0	404	-400	7	0	1	162	142	-9	3	1	272	-284
1	2	0	908	-761	0	6	0	386	-352	8	10	0	229	-239	13	0	1	231	202	-8	3	1	383	391
2	2	0	236	-357	1	6	0	176	155	10	10	0	202	162	-10	1	1	225	-237	-7	3	1	391	355
3	2	0	2861	2807	3	6	0	590	-587	12	10	0	180	-170	-9	1	1	227	-258	-6	3	1	694	-700
4	2	0	437	416	4	6	0	293	-269	2	11	0	439	-443	-8	1	1	422	-415	-5	3	1	889	-880
5	2	0	619	-644	7	6	0	285	260	4	11	0	378	343	-6	1	1	779	748	-4	3	1	187	-177
7	2	0	152	-152	8	6	0	221	205	5	11	0	167	130	-5	1	1	707	-688	-3	3	1	439	-408
9	2	0	202	192	1	7	0	189	183	6	11	0	497	-476	-4	1	1	646	-658	-2	3	1	481	433
10	2	0	157	110	2	7	0	473	448	7	11	0	177	-156	-3	1	1	876	897	-1	3	1	189	-130
11	2	0	418	-446	5	7	0	169	132	8	11	0	271	322	-2	1	1	1012	1112	1	3	1	230	175
13	2	0	307	272	6	7	0	727	661	12	11	0	248	167	2	1	1	130	38	3	3	1	536	-518
1	3	0	251	-224	8	7	0	328	-339	0	12	0	419	-401	3	1	1	701	638	4	3	1	568	515
2	3	0	136	89	11	7	0	167	-129	1	12	0	526	-494	4	1	1	202	103	5	3	1	285	-262
4	3	0	572	-491	12	7	0	258	-240	3	12	0	381	372	5	1	1	707	-679	6	3	1	291	255
5	3	0	424	-441	0	8	0	1116	1043	5	12	0	148	113	6	1	1	378	-337	7	3	1	465	412
6	3	0	986	-1042	1	8	0	577	570	2	13	0	204	-151	7	1	1	126	132	8	3	1	538	-549
7	3	0	125	103	2	8	0	212	-215	3	13	0	181	123	8	1	1	714	689	11	3	1	458	415
8	3	0	791	831	3	8	0	395	-337	5	13	0	284	-310	10	1	1	170	-141	-11	4	1	422	-394
11	3	0	296	278	4	8	0	239	221	7	13	0	172	177	11	1	1	367	329	-9	4	1	250	264
0	4	0	2777	-2328	6	8	0	296	-295	0	14	0	410	-405	13	1	1	166	-152	-8	4	1	382	384
1	4	0	506	-450	10	8	0	204	197	4	14	0	148	-112	-14	2	1	311	-293	-7	4	1	137	-161
2	4	0	766	-686	11	8	0	266	256	6	14	0	237	248	-12	2	1	319	325	-6	4	1	379	390

Observed and Calculated Structure Factors for $[\mathrm{Ni}(\mathrm{C}_{19}\mathrm{H}_{26}\mathrm{N}_{4})(\mathrm{NCS})_{2}]$

H	K	L	10FO	10FC
-4	4	1	197	-212
-2	4	1	420	-350
-1	4	1	320	-274
0	4	1	222	-239
1	4	1	205	-271
2	4	1	261	-220
3	4	1	146	76
5	4	1	791	763
6	4	1	228	251
7	4	1	336	-298
13	4	1	257	-232
-8	5	1	410	372
-7	5	1	306	297
-4	5	1	258	233
-3	5	1	197	-185
-2	5	1	435	-403
-1	5	1	436	411
0	5	1	675	619
1	5	1	196	-171
2	5	1	449	398
3	5	1	267	-242
4	5	1	588	-515
5	5	1	265	298
8	5	1	409	-382
-10	6	1	195	-128
-9	6	1	210	-160
-8	6	1	341	-359
-7	6	1	308	-287
-6	6	1	245	249
-5	6	1	609	590
-4	6	1	261	-233
-3	6	1	178	210
-2	6	1	522	478
-1	6	1	791	-762
0	6	1	1343	1241
1	6	1	389	372
2	6	1	579	-567
4	6	1	446	402
7	6	1	224	206
-7	7	1	243	-221
-5	7	1	908	873
-4	7	1	261	229
-3	7	1	452	-495
-2	7	1	370	-347
-1	7	1	622	591
0	7	1	356	-310
1	7	1	319	-328
2	7	1	283	251
3	7	1	131	120
5	7	1	594	580
6	7	1	147	-173
7	7	1	564	-503
8	7	1	299	290
11	7	1	318	-294
-11	8	1	333	346
-10	8	1	337	335
-8	8	1	586	-625
-3	8	1	427	-381
-1	8	1	549	523
0	8	1	486	489
1	8	1	322	-336
2	8	1	160	-191
3	8	1	707	665
4	8	1	272	281
5	8	1	588	-550
6	8	1	476	-471
7	8	1	328	294
8	8	1	204	197
13	8	1	199	183
-8	9	1	574	-577
-6	9	1	609	685
-5	9	1	175	138
-4	9	1	421	-456
-2	9	1	591	619
0	9	1	733	-735
1	9	1	457	-403
3	9	1	180	165
5	9	1	232	-185
8	9	1	662	609
10	9	1	341	-327
12	9	1	256	230
-11	10	1	264	332
-8	10	1	365	354
-7	10	1	366	364
-5	10	1	225	-276
-4	10	1	338	-332
-2	10	1	157	164
-1	10	1	444	453
0	10	1	863	-847
1	10	1	434	-437
2	10	1	301	344
3	10	1	466	482
4	10	1	350	-317
5	10	1	662	-610
6	10	1	313	267
7	10	1	173	174
-5	11	1	727	-730
-3	11	1	554	556
-2	11	1	413	380
-1	11	1	341	-325
0	11	1	355	-355
1	11	1	319	333
2	11	1	251	232
5	11	1	504	-513
7	11	1	350	345
11	11	1	252	237
-8	12	1	272	301
-4	12	1	222	134
-3	12	1	276	260
-1	12	1	439	-420
0	12	1	534	-551
1	12	1	210	246
2	12	1	503	514
3	12	1	237	-194
4	12	1	316	-325
6	12	1	263	300
-6	13	1	289	-305
-2	13	1	436	-441
-1	13	1	159	-139
0	13	1	343	369
1	13	1	246	260
2	13	1	293	235
8	13	1	248	-252
-1	14	1	265	-285
5	14	1	372	329
6	14	1	160	-139
-5	15	1	32	277
1	15	1	271	-272
0	16	1	245	320
6	16	1	232	-259
-2	17	1	281	244
-1	17	1	197	151
-1	18	1	176	240
3	18	1	233	256
-14	0	2	186	-217
-12	0	2	319	363
-8	0	2	534	605
-6	0	2	438	-558
-2	0	2	1142	-1275
0	0	2	1051	-1133
2	0	2	349	408
6	0	2	416	479
8	0	2	252	-249
12	0	2	219	-218
-6	1	2	577	-588
-4	1	2	343	381
-3	1	2	529	534
-2	1	2	681	716
-1	1	2	577	-545
0	1	2	662	679
1	1	2	158	-95
2	1	2	140	-122
3	1	2	381	-375
4	1	2	340	332
5	1	2	213	-270
6	1	2	200	-223
8	1	2	432	-459
11	1	2	355	335
13	1	2	208	-210
-11	2	2	311	-344
-9	2	2	562	640
-7	2	2	385	-453
-6	2	2	190	-233
-5	2	2	582	636
-4	2	2	165	-171
-3	2	2	707	667
-2	2	2	251	261
-1	2	2	681	-678
1	2	2	1362	-1387
3	2	2	245	-331
5	2	2	915	931
6	2	2	230	232
7	2	2	574	-599
9	2	2	246	274
-10	3	2	162	218
-6	3	2	863	-897
-3	3	2	202	-222
-2	3	2	284	266
-1	3	2	993	950
0	3	2	1291	1182

Observed and Calculated Structure Factors for [Ni($C_{19}H_{26}N_4$)(NCS)$_2$]

H	K	L	10FO	10FC
2	3	2	460	437
3	3	2	145	170
4	3	2	433	432
6	3	2	319	-288
8	3	2	515	-524
10	3	2	289	311
11	3	2	286	-279
12	3	2	245	-253
-8	4	2	546	-606
-6	4	2	515	586
-4	4	2	228	-252
-3	4	2	306	-301
-2	4	2	1006	912
-1	4	2	568	-512
0	4	2	785	748
1	4	2	341	323
2	4	2	629	-623
3	4	2	501	-499
4	4	2	296	300
5	4	2	443	451
6	4	2	494	-519
8	4	2	340	341
-11	5	2	175	183
-10	5	2	225	-258
-9	5	2	208	186
-7	5	2	186	178
-5	5	2	193	185
-4	5	2	377	-311
-3	5	2	960	-922
-1	5	2	986	922
0	5	2	359	-325
1	5	2	798	-775
2	5	2	220	257
3	5	2	446	405
4	5	2	344	-397
5	5	2	622	639
6	5	2	287	293
7	5	2	439	-463
8	5	2	199	173
11	5	2	301	-282
-8	6	2	199	-258
-7	6	2	428	430
-6	6	2	433	423
-5	6	2	869	-863
-3	6	2	592	573
-2	6	2	123	-137
-1	6	2	285	223
0	6	2	508	478
2	6	2	720	-727
3	6	2	613	596
4	6	2	396	388
5	6	2	779	-771
6	6	2	557	-496
7	6	2	230	236
8	6	2	142	54
10	6	2	234	255
-6	7	2	511	482
-5	7	2	176	157
-4	7	2	188	-184
-3	7	2	194	-188
-2	7	2	921	867
-1	7	2	452	-419
0	7	2	1836	-1696
1	7	2	407	429
2	7	2	268	-260
3	7	2	155	-141
8	7	2	319	356
9	7	2	178	146
10	7	2	237	-203
12	7	2	276	228
-10	8	2	219	-161
-9	8	2	328	-271
-8	8	2	393	373
-7	8	2	219	237
-6	8	2	284	-327
-5	8	2	392	-410
-3	8	2	319	281
-2	8	2	473	-445
-1	8	2	538	497
0	8	2	160	-159
1	8	2	196	-188
2	8	2	418	398
3	8	2	428	391
4	8	2	353	-324
5	8	2	370	-351
6	8	2	390	419
8	8	2	356	-355
9	8	2	272	-266
11	8	2	176	110
-13	9	2	236	254
-11	9	2	287	-284
-5	9	2	458	-466
-3	9	2	618	570
-1	9	2	385	-349
0	9	2	250	-244
1	9	2	415	387
3	9	2	668	-638
7	9	2	271	232
8	9	2	151	-152
11	9	2	317	294
-9	10	2	197	202
-8	10	2	441	432
-7	10	2	270	-251
-6	10	2	429	-368
-5	10	2	230	267
-2	10	2	258	-253
-1	10	2	418	-388
2	10	2	153	101
3	10	2	154	-199
4	10	2	143	-181
5	10	2	382	363
6	10	2	599	583
8	10	2	262	-266
-6	11	2	233	-269
-5	11	2	260	224
-4	11	2	224	186
-2	11	2	438	-437
0	11	2	934	921
3	11	2	247	-284
5	11	2	224	183
-8	12	2	253	-181
-6	12	2	161	163
-5	12	2	376	398
-3	12	2	348	-331
-1	12	2	189	-154
0	12	2	226	195
1	12	2	130	152
2	12	2	272	-226
3	12	2	490	-449
5	12	2	313	324
-6	13	2	165	-189
-3	13	2	328	-339
-1	13	2	415	396
0	13	2	345	351
1	13	2	162	-206
3	13	2	234	276
7	13	2	250	-209
-8	14	2	314	-352
-6	14	2	226	244
0	14	2	160	198
1	14	2	158	99
6	14	2	331	-354
-3	15	2	355	-327
0	15	2	389	-467
2	15	2	181	172
-2	16	2	212	-158
3	16	2	200	241
-1	17	2	299	-245
0	17	2	314	-334
-9	0	3	376	375
-7	0	3	435	-419
-5	0	3	759	786
-1	0	3	180	-211
1	0	3	817	-854
5	0	3	908	950
7	0	3	421	-406
11	0	3	276	-270
-13	1	3	234	-220
-10	1	3	308	280
-9	1	3	252	305
-8	1	3	394	-435
-7	1	3	241	263
-6	1	3	319	-373
-5	1	3	309	-312
-4	1	3	248	264
-3	1	3	344	-317
-1	1	3	1064	1080
0	1	3	791	795
1	1	3	131	-138
2	1	3	275	-256
3	1	3	276	256
4	1	3	263	281
5	1	3	180	-175
6	1	3	306	-296
-8	2	3	455	-484
-6	2	3	572	550
-5	2	3	324	322
-4	2	3	217	-188
-3	2	3	240	-192
-2	2	3	1122	1141

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)(NCS)_2]$

H	K	L	10FO	10FC
2	3	2	460	437
3	3	2	145	170
4	3	2	433	432
6	3	2	319	-288
8	3	2	515	-524
10	3	2	289	311
11	3	2	286	-279
12	3	2	245	-253
-8	4	2	546	-606
-6	4	2	515	586
-4	4	2	228	-252
-3	4	2	306	-301
-2	4	2	1006	912
-1	4	2	568	-512
0	4	2	785	748
1	4	2	341	323
2	4	2	629	-623
3	4	2	501	-499
4	4	2	296	300
5	4	2	443	451
6	4	2	494	-519
8	4	2	340	341
-11	5	2	175	183
-10	5	2	225	-258
-9	5	2	208	186
-7	5	2	186	178
-5	5	2	193	185
-4	5	2	377	-311
-3	5	2	960	-922
-1	5	2	986	922
0	5	2	359	-325
1	5	2	798	-775
2	5	2	220	257
3	5	2	446	405
4	5	2	344	-397
5	5	2	622	639
6	5	2	287	293
7	5	2	439	-463
8	5	2	199	173
11	5	2	301	-282
-8	6	2	199	-258
-7	6	2	428	430
-6	6	2	433	423
-5	6	2	869	-863
-3	6	2	592	573
-2	6	2	123	-137
-1	6	2	285	223
0	6	2	508	478
2	6	2	720	-727
3	6	2	613	596
4	6	2	396	388
5	6	2	779	-771
6	6	2	557	-496
7	6	2	230	236
8	6	2	142	54
10	6	2	234	255
-6	7	2	511	482
-5	7	2	176	157
-4	7	2	188	-184
-3	7	2	194	-188
-2	7	2	921	867
-1	7	2	452	-419
0	7	2	1836	-1696
1	7	2	407	429
2	7	2	268	-260
3	7	2	155	-141
8	7	2	319	356
9	7	2	178	146
10	7	2	237	-203
12	7	2	276	228
-10	8	2	219	-161
-9	8	2	328	-271
-8	8	2	393	373
-7	8	2	219	237
-6	8	2	284	-327
-5	8	2	392	-410
-3	8	2	319	281
-2	8	2	473	-445
-1	8	2	538	497
0	8	2	160	-159
1	8	2	196	-188
2	8	2	418	398
3	8	2	428	391
4	8	2	353	-324
5	8	2	370	-351
6	8	2	390	419
8	8	2	356	-355
9	8	2	272	-266
11	8	2	176	110
-13	9	2	236	254
-11	9	2	287	-284
-5	9	2	458	-466
-3	9	2	618	570
-1	9	2	385	-349
0	9	2	250	-244
1	9	2	415	387
3	9	2	668	-638
7	9	2	271	232
8	9	2	151	-152
11	9	2	317	294
-9	10	2	197	202
-8	10	2	441	432
-7	10	2	270	-251
-6	10	2	429	-368
-5	10	2	230	267
-2	10	2	258	-253
-1	10	2	418	-388
2	10	2	153	101
3	10	2	154	-199
4	10	2	143	-181
5	10	2	382	363
6	10	2	599	583
8	10	2	262	-266
-6	11	2	233	-269
-5	11	2	260	224
-4	11	2	224	186
-2	11	2	438	-437
0	11	2	934	921
3	11	2	247	-284
5	11	2	224	183
-8	12	2	253	-181
-6	12	2	161	163
-5	12	2	376	398
-3	12	2	348	-331
-1	12	2	189	-154
0	12	2	226	195
1	12	2	130	152
2	12	2	272	-226
3	12	2	490	-449
5	12	2	313	324
-6	13	2	165	-189
-3	13	2	328	-339
-1	13	2	415	396
0	13	2	345	351
1	13	2	162	-206
3	13	2	234	276
7	13	2	250	-209
-8	14	2	314	-352
-6	14	2	226	244
0	14	2	160	198
1	14	2	158	99
6	14	2	331	-354
-3	15	2	355	-327
0	15	2	389	-467
2	15	2	181	172
-2	16	2	212	-158
3	16	2	200	241
-1	17	2	299	-245
0	17	2	314	-334
-9	0	3	376	375
-7	0	3	435	-419
-5	0	3	759	786
-1	0	3	180	-211
1	0	3	817	-854
5	0	3	908	950
7	0	3	421	-406
11	0	3	276	-270
-13	1	3	234	-220
-10	1	3	308	280
-9	1	3	252	305
-8	1	3	394	-435
-7	1	3	241	263
-6	1	3	319	-373
-5	1	3	309	-312
-4	1	3	248	264
-3	1	3	344	-317
-1	1	3	1064	1080
0	1	3	791	795
1	1	3	131	-138
2	1	3	275	-256
3	1	3	276	256
4	1	3	263	281
5	1	3	180	-175
6	1	3	306	-296
-8	2	3	455	-484
-6	2	3	572	550
-5	2	3	324	322
-4	2	3	217	-188
-3	2	3	240	-192
-2	2	3	1122	1141

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)(NCS)_2]$

H	K	L	10FO	10FC
0	2	3	252	-299
2	2	3	779	-751
4	2	3	210	225
5	2	3	154	-185
8	2	3	515	533
-13	3	3	252	-268
-11	3	3	348	353
-10	3	3	306	-296
-8	3	3	210	208
-7	3	3	213	178
-6	3	3	538	593
-4	3	3	313	-324
-3	3	3	367	-382
-1	3	3	1492	1460
0	3	3	668	-635
1	3	3	467	-447
2	3	3	457	470
3	3	3	668	676
4	3	3	409	-368
5	3	3	544	-626
6	3	3	200	176
13	3	3	230	188
-9	4	3	435	-473
-8	4	3	300	-337
-7	4	3	527	569
-6	4	3	184	154
-5	4	3	1038	-1074
-3	4	3	445	403
-2	4	3	258	238
-1	4	3	128	-106
0	4	3	387	-368
1	4	3	668	647
2	4	3	213	294
4	4	3	208	192
5	4	3	941	-878
6	4	3	436	-478
7	4	3	605	613
8	4	3	255	247
9	4	3	180	-168
11	4	3	282	305
-14	5	3	251	-257
-8	5	3	443	432
-7	5	3	370	-388
-5	5	3	282	235
-4	5	3	339	-367
-3	5	3	556	582
-2	5	3	645	644
-1	5	3	986	-1001
0	5	3	1693	-1662
2	5	3	934	975
4	5	3	585	-607
6	5	3	424	414
9	5	3	182	127
10	5	3	258	-222
-8	6	3	387	440
-6	6	3	662	-693
-5	6	3	307	-349
-4	6	3	598	613
-3	6	3	409	422
-2	6	3	1194	-1147
-1	6	3	463	-466
0	6	3	206	140
2	6	3	533	491
3	6	3	501	460
4	6	3	343	-339
5	6	3	448	-391
6	6	3	285	284
7	6	3	227	242
8	6	3	397	-363
10	6	3	156	152
12	6	3	193	-159
-13	7	3	234	229
-11	7	3	300	-332
-4	7	3	213	201
-3	7	3	328	318
-2	7	3	130	157
-1	7	3	1181	-1123
1	7	3	541	538
3	7	3	733	-724
5	7	3	455	481
6	7	3	142	-121
11	7	3	184	185
-9	8	3	354	365
-8	8	3	391	415
-7	8	3	216	-217
-6	8	3	345	-358
-5	8	3	517	557
-3	8	3	118	-124
0	8	3	165	222
1	8	3	330	-275
5	8	3	253	264
6	8	3	332	348
7	8	3	294	-285
8	8	3	366	-334
11	8	3	195	-200
-8	9	3	311	-309
-4	9	3	213	229
-1	9	3	220	225
0	9	3	586	574
4	9	3	271	251
6	9	3	370	-380
-8	10	3	169	-239
-6	10	3	225	252
-5	10	3	257	283
-3	10	3	264	-293
-2	10	3	235	200
4	10	3	187	145
5	10	3	230	204
-4	11	3	163	-215
-3	11	3	150	-140
-1	11	3	418	401
0	11	3	151	159
1	11	3	167	-184
3	11	3	348	355
-8	12	3	242	-239
-6	12	3	210	269
-2	12	3	255	249
-1	12	3	171	-108
2	12	3	208	-193
8	12	3	199	212
-8	13	3	186	197
-3	13	3	162	-223
0	13	3	484	-505
-5	14	3	247	-346
0	14	3	172	232
2	14	3	175	-164
5	14	3	277	-313
7	14	3	186	157
-2	15	3	200	234
0	15	3	208	-237
1	15	3	166	173
3	15	3	287	-294
5	15	3	212	196
-8	16	3	202	236
-2	16	3	254	-229
0	17	3	225	272
1	17	3	162	173
-10	0	4	196	-172
-8	0	4	177	186
-6	0	4	337	388
-2	0	4	947	1045
0	0	4	824	-872
2	0	4	465	-540
4	0	4	371	409
-9	1	4	232	-254
-8	1	4	239	270
-7	1	4	366	341
-6	1	4	151	-211
-5	1	4	481	-487
-3	1	4	330	362
-1	1	4	582	623
0	1	4	383	-361
1	1	4	208	-232
3	1	4	431	446
4	1	4	339	-351
5	1	4	147	-102
6	1	4	376	432
9	1	4	163	-174
-13	2	4	256	231
-9	2	4	232	-344
-7	2	4	218	183
-6	2	4	199	274
-5	2	4	429	-455
-3	2	4	603	618
-2	2	4	160	202
-1	2	4	766	-756
0	2	4	278	-304
1	2	4	358	335
2	2	4	122	68
3	2	4	263	-299
5	2	4	191	-181
7	2	4	492	477
11	2	4	252	227
-12	3	4	244	212
-10	3	4	189	-222
-8	3	4	688	685
-6	3	4	392	-409
-5	3	4	132	49
-3	3	4	154	-187
-1	3	4	551	-525

Observed and Calculated Structure Factors for $[Ni(C_{19}H_{26}N_4)(NCS)_2]$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	3	4	707	-742	-8	6	4	286	314	0	8	4	557	-596	3	0	5	471	-534	5	3	5	479	515
1	3	4	504	486	-7	6	4	224	-176	4	8	4	174	92	5	0	5	192	171	6	3	5	335	-338
2	3	4	256	240	-6	6	4	529	-542	11	8	4	195	-209	7	0	5	295	338	-13	4	5	243	-214
3	3	4	549	-589	-5	6	4	621	569	-7	9	4	197	176	-8	1	5	368	390	-11	4	5	303	321
4	3	4	461	-399	-3	6	4	740	-736	-5	9	4	135	-153	-6	1	5	267	-274	-8	4	5	223	-229
6	3	4	641	631	-2	6	4	232	-204	-1	9	4	316	270	-5	1	5	373	419	-5	4	5	302	308
8	3	4	206	-209	-1	6	4	556	555	3	9	4	382	397	-4	1	5	208	-189	-3	4	5	472	-479
-6	4	4	791	-752	0	6	4	746	768	5	9	4	413	-461	-3	1	5	260	-321	-1	4	5	681	653
-5	4	4	269	-318	1	6	4	304	-295	-6	10	4	282	301	-2	1	5	444	-495	0	4	5	258	290
-4	4	4	531	491	2	6	4	132	-118	-5	10	4	189	-137	-1	1	5	662	-761	1	4	5	394	-435
-3	4	4	675	738	3	6	4	485	482	-3	10	4	254	252	0	1	5	411	421	3	4	5	662	686
-2	4	4	1070	-1045	6	6	4	133	167	-2	10	4	171	147	2	1	5	182	264	5	4	5	191	-198
-1	4	4	292	-280	7	6	4	385	-366	0	10	4	441	-450	4	1	5	112	-194	7	4	5	244	-255
0	4	4	1226	1245	8	6	4	204	-233	11	10	4	142	122	5	1	5	155	212	11	4	5	226	-231
3	4	4	209	-212	9	6	4	162	146	-8	11	4	200	255	6	1	5	304	334	-8	5	5	655	-625
4	4	4	239	-181	11	6	4	333	-273	0	11	4	324	-359	8	1	5	203	-190	-6	5	5	624	623
8	4	4	298	-261	-12	7	4	226	-206	2	11	4	279	278	-14	2	5	277	220	-5	5	5	250	-243
10	4	4	289	256	-10	7	4	224	177	-6	12	4	184	-193	-8	2	5	265	-294	-3	5	5	328	292
12	4	4	266	-238	-8	7	4	561	-529	-5	12	4	195	-150	-6	2	5	207	-169	-2	5	5	317	295
-11	5	4	400	-374	-6	7	4	189	192	-3	12	4	353	388	-5	2	5	204	268	-1	5	5	190	217
-9	5	4	362	397	-3	7	4	155	171	-1	12	4	217	-280	-2	2	5	590	-601	2	5	5	365	-375
-8	5	4	223	-223	-1	7	4	147	101	0	12	4	194	207	0	2	5	753	791	3	5	5	176	170
-7	5	4	391	-388	0	7	4	516	529	-8	13	4	224	209	6	2	5	191	-218	4	5	5	240	235
-5	5	4	344	339	1	7	4	156	-108	-1	13	4	225	-254	10	2	5	234	211	5	5	5	213	-182
-4	5	4	186	132	2	7	4	327	-335	3	13	4	284	-313	-9	3	5	297	297	6	5	5	387	-386
-1	5	4	720	-722	4	7	4	308	310	5	13	4	317	398	-8	3	5	399	-430	8	5	5	418	387
0	5	4	121	149	5	7	4	178	120	-6	14	4	296	-338	-7	3	5	296	-324	-14	6	5	219	-227
1	5	4	271	258	6	7	4	509	-561	0	14	4	309	336	-6	3	5	180	172	-11	6	5	170	159
3	5	4	941	-995	8	7	4	296	332	0	15	4	191	234	-5	3	5	644	637	-6	6	5	205	226
4	5	4	376	362	9	7	4	149	-131	2	15	4	212	-228	-4	3	5	469	487	-3	6	5	381	-337
5	5	4	740	758	-9	8	4	191	201	-3	16	4	219	-284	-3	3	5	629	-637	-2	6	5	456	490
6	5	4	401	-406	-8	8	4	186	-113	-1	16	4	270	278	-1	3	5	160	-226	-1	6	5	446	471
7	5	4	173	-174	-6	8	4	407	385	0	18	4	199	-220	1	3	5	154	-198	0	6	5	759	-752
9	6	4	206	200	-5	8	4	222	205	-11	0	5	260	-260	2	3	5	391	-411	2	6	5	199	197
-13	6	4	259	-202	-3	8	4	474	-488	-1	0	5	282	-280	3	3	5	209	-271	4	6	5	155	-179
-9	6	4	293	252	-2	8	4	230	217	1	0	5	133	-126	4	3	5	300	351	6	6	5	205	188

Observed and Calculated Structure Factors for [Ni($C_{19}H_{26}N_4$)(NCS)$_2$]

A5C

H	K	L	10FO	10FC
10	6	5	191	-133
-9	7	5	380	-372
-8	7	5	152	141
-7	7	5	299	276
-5	7	5	354	-333
-4	7	5	193	-163
-3	7	5	246	267
-2	7	5	145	-143
0	7	5	271	268
1	7	5	180	173
3	7	5	277	314
5	7	5	492	-500
-11	8	5	226	-200
-6	8	5	200	197
-4	8	5	171	-184
-3	8	5	153	149
-1	8	5	232	-230
0	8	5	244	-249
1	8	5	175	127
3	8	5	354	-305
-8	9	5	321	289
-6	9	5	328	-338
-3	9	5	194	-205
-2	9	5	264	-260
2	9	5	329	296
6	9	5	193	139
8	9	5	247	-159
-3	10	5	291	279
-2	10	5	189	-231
-1	10	5	510	-505
0	10	5	361	379
-5	11	5	304	301
-3	11	5	232	-225
3	11	5	280	-266
5	11	5	328	343
-3	12	5	200	-189
-1	12	5	146	163
0	12	5	339	376
2	12	5	196	-242
4	12	5	236	210
-8	13	5	285	-332
-6	13	5	279	283
6	13	5	210	-196
-3	14	5	232	-254
-1	14	5	300	377
3	14	5	195	228
0	16	5	260	-301
-14	0	6	255	242
-8	0	6	396	-347
0	0	6	304	291
6	0	6	320	-305
8	0	6	194	175
-9	1	6	195	219
-8	1	6	256	-271
-6	1	6	337	341
-3	1	6	261	-225
-1	1	6	193	237
0	1	6	177	-166
5	1	6	206	150
7	1	6	214	-233
8	1	6	186	140
11	1	6	215	-154
-11	2	6	370	315
-9	2	6	166	-136
-4	2	6	198	-196
-3	2	6	194	-214
-2	2	6	232	171
-1	2	6	297	312
2	2	6	262	-307
3	2	6	534	518
4	2	6	213	219
5	2	6	452	-456
-8	3	6	182	-222
-7	3	6	190	179
-6	3	6	495	479
-5	3	6	308	-302
-3	3	6	381	373
-2	3	6	391	439
0	3	6	415	-393
1	3	6	132	-118
6	3	6	271	-222
8	3	6	250	187
11	3	6	182	155
-14	4	6	258	-218
-12	4	6	174	103
-8	4	6	453	426
-7	4	6	211	215
-6	4	6	121	-76
-2	4	6	302	322
-1	4	6	313	326
0	4	6	597	-564
2	4	6	426	446
5	4	6	148	-131
-13	5	6	185	148
-9	5	6	319	-290
-7	5	6	151	113
-5	5	6	400	-408
-3	5	6	637	628
-1	5	6	285	-300
0	5	6	267	311
3	5	6	167	155
5	5	6	268	-224
6	5	6	178	161
11	5	6	203	178
-11	6	6	245	-231
-7	6	6	210	-177
-1	6	6	386	-423
0	6	6	243	-238
2	6	6	186	228
3	6	6	363	-313
4	6	6	221	-266
5	6	6	363	389
-8	7	6	234	184
-6	7	6	458	-467
-2	7	6	323	-332
0	7	6	247	240
6	7	6	186	179
-8	8	6	313	-296
-3	8	6	187	227
-1	8	6	372	-338
0	8	6	235	177
2	8	6	228	-251
3	8	6	217	-214
-5	9	6	236	234
-3	9	6	442	-449
-1	9	6	183	227
5	9	6	237	249
-2	10	6	205	-234
-1	10	6	203	226
0	10	6	307	382
5	10	6	232	-230
-6	11	6	333	361
-4	11	6	211	-272
-2	11	6	343	356
0	11	6	282	-279
-8	12	6	185	167
-1	12	6	291	287
1	12	6	159	-193
2	12	6	215	166
3	12	6	301	355
-5	13	6	245	-247
-3	13	6	260	277
0	14	6	243	-267
4	14	6	176	-214
-13	0	7	167	-103
-11	0	7	254	216
-9	0	7	437	-457
-7	0	7	291	347
-3	0	7	189	245
-1	0	7	219	287
3	0	7	452	479
5	0	7	598	-631
-6	1	7	397	353
-5	1	7	285	-275
-3	1	7	555	594
-2	1	7	371	390
-1	1	7	269	-341
0	1	7	551	-623
1	1	7	172	172
2	1	7	257	259
3	1	7	138	-89
11	1	7	159	182
-8	2	7	478	437
-6	2	7	438	-425
-4	2	7	228	238
0	2	7	206	-155
2	2	7	439	504
3	2	7	164	222
5	2	7	140	-152
6	2	7	268	259
8	2	7	302	-283
-6	3	7	276	-253
-3	3	7	605	575
-2	3	7	248	-292
-1	3	7	586	-591
0	3	7	278	284
1	3	7	163	182
2	3	7	169	-145
-9	4	7	307	261
-8	4	7	256	272

Observed and Calculated Structure Factors for [Ni($C_{19}H_{26}N_4$)($NCS)_2$]

H	K	L	10FO	10FC
-7	4	7	295	-263
-5	4	7	296	257
-3	4	7	187	-220
-1	4	7	207	-193
3	4	7	359	-398
5	4	7	442	453
-6	5	7	258	-242
-4	5	7	248	313
-3	5	7	244	-209
-2	5	7	312	-277
-1	5	7	172	185
0	5	7	459	437
-8	6	7	308	-249
-5	6	7	320	340
0	6	7	187	209
2	6	7	306	-302
-6	7	7	263	286
-3	7	7	339	-257
-1	7	7	290	322
-9	8	7	191	-134
-7	8	7	179	142
-5	8	7	128	-57
-1	8	7	208	259
4	8	7	241	223

H	K	L	10FO	10FC
5	8	7	241	-192
-6	9	7	218	223
0	9	7	259	-252
-9	10	7	144	-189
-5	10	7	204	-175
-1	10	7	247	338
2	10	7	187	228
-3	11	7	245	230
-2	11	7	176	101
-1	11	7	283	-291
1	11	7	180	205
3	11	7	224	-202
-8	12	7	216	213
2	12	7	180	208
-2	13	7	221	-206
0	13	7	221	209
-8	0	8	300	342
-6	0	8	444	-400
-4	0	8	383	354
-2	0	8	259	-245
2	0	8	237	218
4	0	8	205	-236
-8	1	8	222	-283
-3	1	8	348	326

H	K	L	10FO	10FC
-1	1	8	404	-381
0	1	8	270	283
1	1	8	142	176
2	1	8	202	-171
3	1	8	224	-241
-9	2	8	315	258
-7	2	8	186	-90
-5	2	8	261	305
-3	2	8	363	-314
5	2	8	264	168
-5	3	8	224	-206
-2	3	8	215	-237
0	3	8	242	198
3	3	8	189	179
-8	4	8	200	-135
-7	4	8	225	-204
-6	4	8	239	160
-2	4	8	176	137
-1	4	8	167	-217
0	4	8	203	-199
2	4	8	155	-112
-3	5	8	168	-172
2	5	8	189	249
3	5	8	175	127

H	K	L	10FO	10FC
-2	6	8	206	172
0	6	8	150	-205
-8	7	8	179	157
-3	7	8	318	352
0	7	8	176	-144
4	7	8	208	-228
-9	8	8	152	-105
-6	8	8	215	-213
-3	8	8	245	191
-1	8	8	159	-235
1	9	8	154	212
3	9	8	239	-267
-8	10	8	214	243
-1	13	8	150	158
-3	0	9	337	-443
-1	0	9	219	246
1	0	9	186	-106
-5	1	9	197	-144
2	1	9	267	-303
4	1	9	153	226
-6	2	9	179	171
-4	2	9	194	-214
-2	2	9	255	136
0	2	9	173	-268

H	K	L	10FO	10FC
-11	3	9	146	117
-4	3	9	132	202
-2	3	9	143	-117
1	4	9	206	159
-8	5	9	257	209
-4	6	9	155	136
-1	7	9	197	-258
-2	8	9	159	-155
-8	9	9	290	-254
4	9	9	195	151
-3	10	9	190	-232
-2	10	9	211	191
-2	0	10	252	285
0	0	10	268	-202
3	2	10	232	-166
-5	5	10	187	179
-3	6	10	204	-222
-1	6	10	184	177
-8	7	10	226	-180
-6	7	10	152	147
4	7	10	146	142
3	4	11	160	115
3	7	11	172	34

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END