

**The Hydrogen Bonding of  $Zn(SCN)_2L$  where  
 $L = Me_xH_{2-x}N(CH_2)_2NH_{2-y}Me_y$ ,  $x,y \leq 2$   
and the Hydrogen Bonding of Organo-  
ammonium Thiocyanates**

**by**

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**Submitted in partial fulfillment of the requirements  
for the degree of Master of Science**

**at**

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## Abstract

An x-ray crystallographic analysis of the hydrogen bonding that occurs with the thiocyanate anion is reported. The first study examines the hydrogen bonding that can occur exclusively at the sulphur end of the thiocyanate ion. Complexes of tetrahedral four-coordinate zinc were used. These complexes all had two coordination sites of the zinc occupied by the thiocyanate anion, and the remaining two by the bidentate ligand ethylenediamine, or its methylated derivative. This complex is then  $Zn(NCS)_2Me_xH_{2-x}N(CH_2)_2NH_{2-y}Me_y$ , where  $x,y \leq 2$ . In all cases, the nitrogen atom of the thiocyanate anion is coordinated to the zinc, leaving the sulphur available for intermolecular hydrogen bonding. The conclusion to this section is that all available hydrogens are involved in the hydrogen bonds, while not all sulfurs are involved. Branching occurs even when not strictly required, and results in a hydrogen bonding system of a centrosymmetric cyclic dimer or an infinite helix.

With the behaviour of the sulphur end of the thiocyanate ion in exclusively N-H...S hydrogen bonding systems established, the next study is of the preference of the thiocyanate system towards N-H...NCS or N-H...SCN bonding. In these systems, the thiocyanate ion is no longer bonded to a metal, and so has both ends free to form hydrogen bonds. A series of organoammonium thiocyanates were prepared, such that the ratio of available H(N) atoms to thiocyanate ions was varied. The series was also geometrically varied so that the cation/NCS<sup>-</sup> system was presented with a series of packing situations in the expectation that one of these variables might force an ion pair to use the less favoured N-H...S interaction. The findings of this study was that in the group of cations that form a n:n ratio with the thiocyanate ions (so that there is a single N-H bond for one thiocyanate ion), the overwhelming preference of the SCN<sup>-</sup> ion is to form a single N-H...NCS bond. In the cases where the number of H(N) atoms is larger than the number of thiocyanate ions, the ion will first form two separate bonds to the nitrogen atom of the thiocyanate ion before forming an N-H...SCN bond. Thus somewhat weaker (N-H)<sub>2</sub>..NCS bonds are preferred to a single N-H....SCN bond.

## Abbreviations and Definitions

$\text{\AA}$	Angstrom
ACP	Absolute configuration parameter
B	Thermal motion value
CSD	Cambridge Structural Database
$d$	Specific bond distance
F(000)	Total number of electrons in the unit cell
GOF	Goodness of fit
L	Ligand (usually the methylated ethylenediamine)
Max/min	Empirical absorption coefficient
R ( $R^2$ )	Residual/reliability index
Residual ed	Residual electron density max. and min. values
T	Thiocyanate ion
U(eq)	Thermal motion parameters, expressed in terms of mean-square amplitudes of vibration in angstroms.
V	Volume of unit cell
X	Any atom (often donor atom in hydrogen bonding)
Z	Number of molecules per unit cell
$^\circ$	Degrees
$\phi$	Specific bond angle
$\mu$	Linear absorption coefficient
a,b,c	Unit cell dimensions
$\alpha, \beta, \gamma$	Unit cell angles

### Drawings:

Zn, N, O, C, S, H	Zinc, Nitrogen, Oxygen, Carbon, Sulphur and Hydrogen atoms
-	Bond
...	Hydrogen bond, or long distance contact
..	Electron pair
+/-	Positive/negative charge

Zinc and Hydrogen atoms are not shaded

Nitrogen atoms are the darkest

Sulphur atoms are lighter than carbon atoms, which are lighter than oxygen atoms

## Abbreviations of compounds

1MenZ2T,  $(\text{MeNH}(\text{CH}_2)_2\text{NH}_2)\text{Zn}(\text{NCS})_2$

3enZ2T, Tris(ethylenediamine)zinc(2+)  $(\text{SCN})_2$

3Men2T, Trimethylethylenediammonium thiocyanate

3MenZ2T,  $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe})\text{Zn}(\text{NCS})_2$

3spg3T, The classical proton sponge

4Men2T, Tetramethylethylenediammonium thiocyanate

4Mbn2T, Tetramethylbutylenediammonium thiocyanate

4Mpn2T, Tetramethylpropylenediammonium thiocyanate

BeT, Betaine thiocyanate

Cy2T, Cystamine hydrothiocyanate

Da2Tw, Dabco thiocyanate

en2T, Ethylenediammonium thiocyanate

enZ2T,  $(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)\text{Zn}(\text{NCS})_2$

enZ4Tw, Ethylenediammonium zinc( $\text{SCN}$ )<sub>4</sub>

g2MenZ2T,  $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{NH}_2)\text{Zn}(\text{NCS})_2$

QT, Quinuclidinium thiocyanate

s2MenZ2T,  $(\text{MeNH}(\text{CH}_2)_2\text{NHMe})\text{Zn}(\text{NCS})_2$

s2MenZ4T, sym-Dimethylethylenediammonium zinc( $\text{SCN}$ )<sub>4</sub>

s2Mpiz2T, Dimethylpiperazinium thiocyanate

T3pT, Terpyridinium thiocyanate

u2Men2T, unsym-Dimethylethylenediammonium thiocyanate

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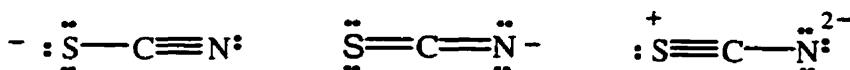
**Full crystal data and a record of the structure determination for  
each structure that is reported in this thesis are available on CD-ROM.**

## Chapter 1 Introduction

The influence of hydrogen bonding on the packing of binary ion-pairs in crystals is a long-term research interest in the Dalhousie Crystallographic Centre. An important supplementary interest is an examination of how this hydrogen bonding influences the individual geometry of the ions concerned. Most recent studies have involved salts of the polyhalides, particularly the rod-like  $I_3^-$  and  $Br_3^-$  anions. In this instance the study has been of organoammonium cations and the polyhalide anions and one aspect of the study has been to examine the effect of the hydrogen bonding on the linear (or slightly bent) geometry of the polyhalides [1]. There is no option for the hydrogen bonding in a trihalide, except whether the bond is formed to the terminal or central halogen atom.

The study of the linear homoatomic  $X_3^-$  anions is here extended to a linear triatomic anion in which the two terminal atoms are different and thus have different hydrogen bonding requirements. The ion of choice is the thiocyanate ion,  $NCS^-$ . This ion is often classed as a pseudo-halogen.

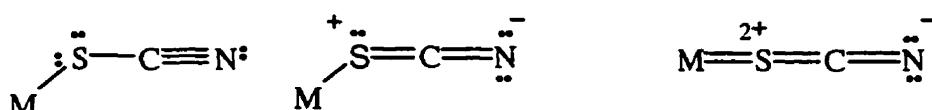
There are a number of possible Lewis Structures that can be drawn for this anion [2].



**Figure 1.** Possible Lewis structures of the thiocyanate anion

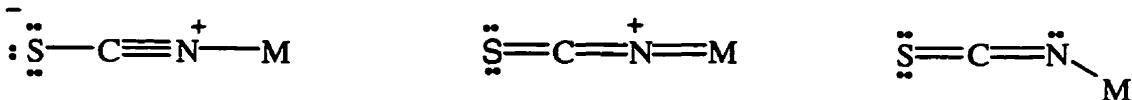
However the structure of the thiocyanate anion has been very carefully examined in a deformation density study of sodium thiocyanate [3] and ammonium thiocyanate [4]. The difference between the C-N bond lengths in the two structures is statistically insignificant, as is the difference between the C-S bond lengths. The SCN angle in  $\text{NH}_4\text{SCN}$  is slightly larger than in  $\text{NaSCN}$  ( $179.60^\circ$  and  $179.09^\circ$  respectively). The C-N bond length in  $\text{NaSCN}$ ,  $1.178(1)\text{\AA}$  is slightly longer than the expected  $1.153\text{\AA}$  for a  $\text{C}\equiv\text{N}$  triple bond. Similarly, the C-S bond length of  $1.647(1)\text{\AA}$  is between a single and double bond. This suggests that the  $\pi$ -bonding occurs mostly in the CN bond. Therefore, the bonding in the thiocyanate ion is most closely represented by the first structure drawn above.

The anion can coordinate to metal atoms at either the sulphur end [2]:



**Figure 2.** Possible Lewis structures of M-SCN

or the nitrogen end [2]:



**Figure 3.** Possible Lewis structures of M-NCS

The primary coordination site can be predicted from hard/soft acid/base criteria [5]. Similarly the anion can form hydrogen bonds at either end and again the preference is, to some extent, predictable from the nature of the hydrogen bond donor.

There is a wealth of information on N-H...N hydrogen bonds [6], but much less on N-H...S hydrogen bonds, and no really systematic experimental study appears to have been undertaken (Tchertanov and Pascard have done a statistical analysis based on thiocyanate compounds) [7]. The first aim of this work, therefore, is to examine the hydrogen bonding where it occurs exclusively at the sulphur end of the thiocyanate. Once this has been achieved, the study will be extended to circumstances where either the nitrogen or sulphur of the thiocyanate can take part in hydrogen bonding. The investigation will then be to determine criteria to predict which end of the anion will form the hydrogen bond.

Chapter 2 examines the hydrogen bonding in conditions where this bonding is exclusively to the sulphur end of the ion. Complexes of tetrahedral four-coordinate zinc were used. These are all complexes of which two of the coordination sites on the Zn atom are occupied by  $\text{NCS}^-$  groups, and the remaining two by the chelating (bidentate) ligand ethylenediamine (*en*) or its N-methylated derivative. The resulting complex is thus  $\text{Zn}(\text{NCS})_2\text{L}$ , where  $\text{L} = \text{Me}_x\text{H}_{2-x}\text{NCH}_2\text{CH}_2\text{NH}_{2-y}\text{Me}_y$  ( $x, y = 0, 1, 2$ ;  $x \geq y$ )<sup>1</sup>.

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<sup>1</sup> In addition, the  $[(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)^{2+} (\text{Zn}(\text{SCN})_4)^{2-}]$  and  $[(\text{Zn}(\text{en})_3)^{2+} (\text{NCS})_2]$  were prepared. All attempts to prepare the tetrahedrally coordinated  $\text{Zn}(\text{en})_2 (\text{SCN})^2$  with either pure ethylenediamine or the symmetrically N,N' dimethylated ethylene diamine produced octahedral zinc complexes with two chelate rings and two trans-dithiocyanato groups.

In all these complexes the nitrogen atom of the NCS group is coordinated to the zinc. Intermolecular hydrogen bonding between the N-H hydrogen atoms and the thiocyanate group must be of the N-H...S variety.

The zinc complexes were chosen for three main reasons. (1) The  $Zn^{2+}$  ( $d^{10}$ ) ion does not change its oxidation state. (2) The tetrahedral complexes do not have the variety of geometric isomers that would be encountered in the octahedral complexes. (3) The constant stoichiometric ratio of  $((Me)_{x+y}en):SCN$  of 1:2 allows the hydrogen bonding to the sulphur atoms to be manipulated neatly. Thus when  $x+y = 2$ , there are exactly the same number of N-H hydrogen atoms to donate the hydrogen to the bond as there are NCS sulphur atoms to receive the hydrogen. When  $x+y < 2$ , there is a surplus of N-H hydrogen atoms and, on the general principle a crystal seeks to maximize its hydrogen bonding engagement, the N-H hydrogen atoms will have to share the sulphur atoms. On the other hand, when  $x+y = 3$ , there is now a deficit of N-H hydrogen atoms and the two sulphur atoms will have to share the one hydrogen<sup>2</sup>.

Thus the selection of these complexes provides a systematic variation of the hydrogen bonding conditions for the N-H...S system.

With the behavior of the sulphur end of the thiocyanate ion in exclusively N-H...S hydrogen bonding systems established, the question of chapter 3 is the preference of the  $NCS^-$  system towards N-H...NCS and N-H...SCN bonding. In these systems the  $NCS^-$  group is not bound to a metal and has both ends free to

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<sup>2</sup> When  $x+y = 4$  there is of course no hydrogen bonding possible.

form hydrogen bonds. Intuitively, it would be expected that the N-H...NCS arrangement will dominate the field. An examination of the literature confirms this perception [8]. The question then becomes: under what circumstances will an N-H...SCN bond form when the same thiocyanate ion can also form an N-H...NCS bond?

To examine this question a series of organoammonium thiocyanates were prepared and their crystal structures were determined (Chapter 3). The intention here was to vary the ratio of available N-H hydrogen atoms to one thiocyanate ion, and to vary the geometry of the cation to present the cation/NCS<sup>-</sup> system with a series of packing situations. It was thought that both or either of the variables might force an ion pair to use the less favoured N-H...S interaction.

In order to vary the N-H : NCS ratio a series of compounds similar to those mentioned above  $\{(Me_xH_{3-x}NCH_2CH_2NH_{3-y}Me_y)^{2+} (SCN^-)_2 \}$  [x, y = 0,1,2; x ≥ y] were prepared <sup>3</sup>. The N-H:NCS<sup>-</sup> ratio was further extended by an examination of the structure of the guanidinium  $[(NH_2)_3C]^+$  thiocyanate.

To vary the geometric conditions, the diamine chain was lengthened and the  $\{(Me_2HN(CH_2)_xNHMe_2\)^{2+} (SCN^-)_2 \}$ , x = 3, 4, structures were examined. The

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<sup>3</sup> Interestingly only *en*, N,N'-Me<sub>2</sub>*en* and Me<sub>4</sub>*en* in this series crystallised. The rest remained stubbornly as oils even after a year of recrystallisation effort.

geometric conditions were further extended in the structures of the thiocyanate ion with the organoammonium cations derived from N,N'-dimethylpiperazine (essentially removing much of the flexibility from the conformation of Me<sub>4</sub>en), Dabco <sup>4</sup> and quinuclidine (removing all the flexibility), and terpyridine.

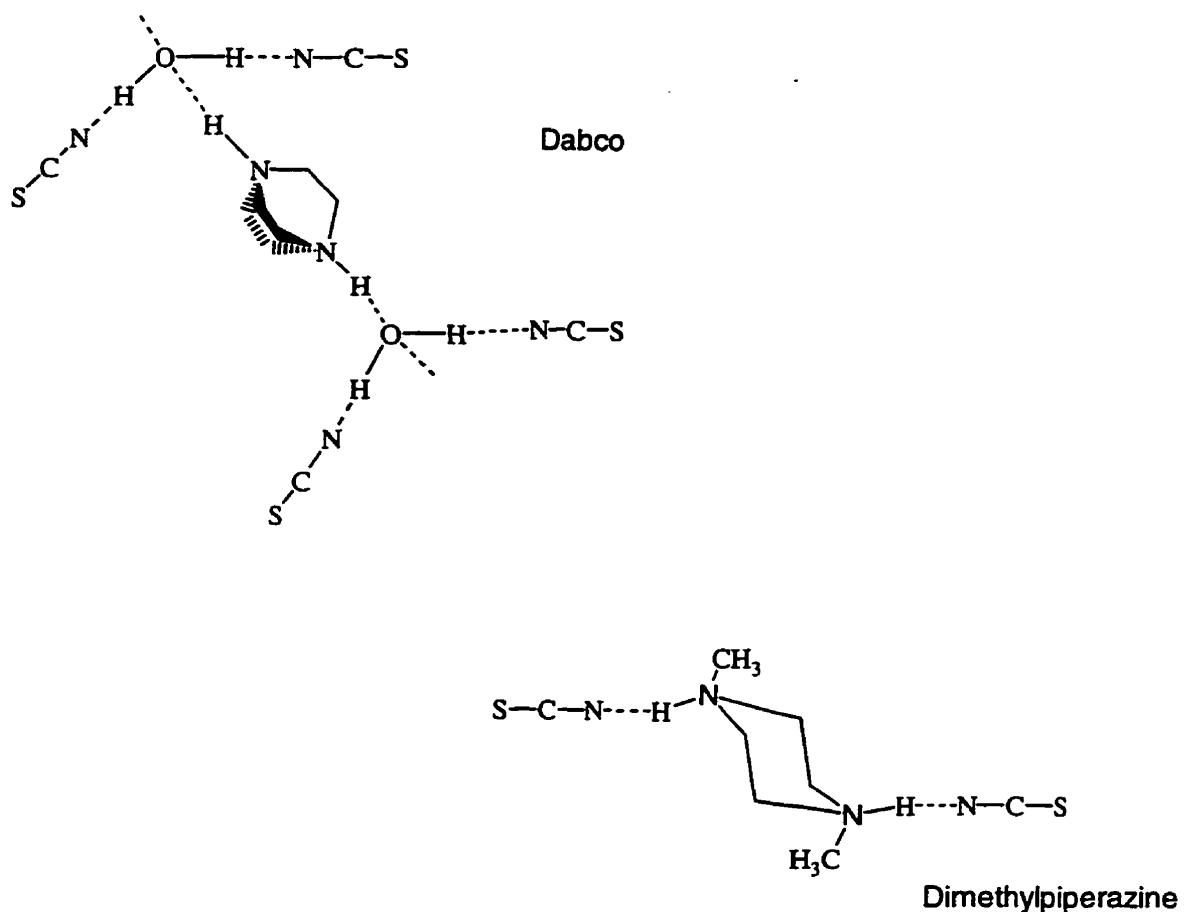


Figure 4. Diagram of Dabco and dimethylpiperazine thiocyanates

<sup>4</sup> The DabcoH<sub>2</sub><sup>2+</sup> thiocyanate turned out to be hydrated (see Chapter 3) and, unfortunately for the intended purpose, contained only N-H...OH<sub>2</sub> and not N-H...SCN or N-H...NCS bonds.

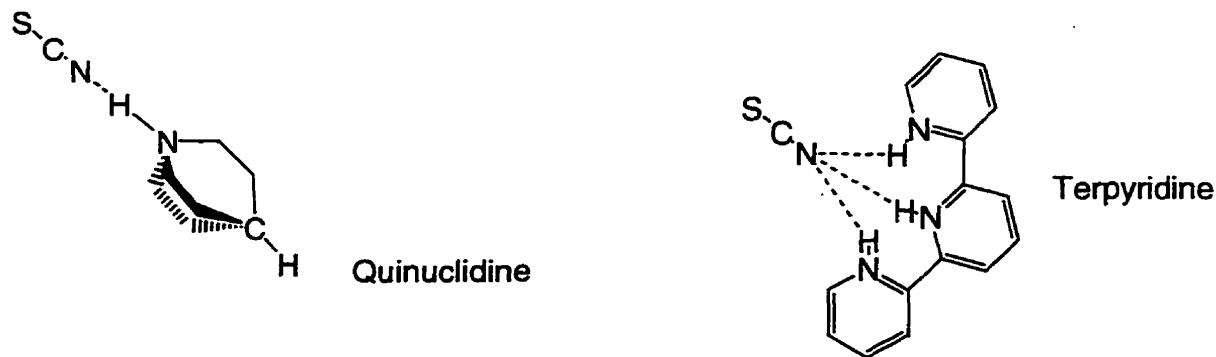


Figure 5. Diagrams of quinuclidine and terpyridine thiocyanates

Finally, attempts were made to adjust the nature of the hydrogen donor cations by the introduction of some “soft” groups into the ion. For this the structures of the thiocyanato salts derived from aminoethanethiol ( $\text{NH}_2(\text{CH}_2)_2\text{SH}$ ) and the permanent zwitterion betaine ( $(\text{CH}_3)_3\text{NCH}_2\text{COO}$ ) were examined.

## Chapter 2

When the thiocyanate anion forms a salt with a cation that contains a hydrogen atom capable of hydrogen bonding, then this hydrogen atom will form a hydrogen bond. While the bond could be formed to an acceptor atom somewhere in the cation itself, it is more likely that the bond will be formed to the thiocyanate ion itself. In structures where the thiocyanate ion is present as an isolated ion, i.e. where it is not coordinated to a metal atom, there is a choice of acceptor atoms for the donating hydrogen atom. The bond can form either at the nitrogen end or at the sulphur end. The Cambridge Structural Database (CSD) currently contains 217 structures of thiocyanate salts where the thiocyanate ion is an isolated ion. Of these, 49 have hydrogen bonds to the nitrogen end of the ion (maximum H...N distance of 2.4Å), while fifteen have hydrogen bonds to the sulphur end of the ion (maximum H...N distance of 2.5Å). Of the fifteen structures with X-H...SCN hydrogen bonds only one does not contain, in addition, a strong X-H...NCS interaction as well. This confirms the intuitive notion that O-H... and N-H... hydrogen bonds to the thiocyanate ion have a very strong preference for forming at the nitrogen end of the anion. This one anomalous structure is a special case<sup>1</sup>. An examination of the structures extracted from the CSD, and more particularly, an examination of the structures reported in Chapter 3 shows that the thiocyanate sulphur atom seems to be oriented in such a fashion as to get out of the way of any potential hydrogen bonding system. In fact, an

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<sup>1</sup> For more details see Chapter 3

examination of the structures where both X-H...N and X-H...S hydrogen bonds occur simultaneously leaves a strong suspicion that any X-H...S interaction is an unavoidable accident rather than a crucial part of the packing within the crystal. In ammonium thiocyanate [3], for example, there are three N-H...N and one N-H...S hydrogen bonds. In this instance, it seems that the N-H...N bonds are the primary bonds and the N-H...S bond is an accidental extra. This is possibly caused by a combination of too many N-H systems seeking to form a hydrogen bond and too little packing flexibility for the sulphur to get out of the way. There is thus little or no information available about the preferences of the X-H...S hydrogen bond in the absence of the dominant X-H...N bond.

The aim of this first part of the investigation was to design a series of compounds which would provide the information about the preferences of the thiocyanate sulphur atom when it is in a structure which provides for the formation of X-H...S hydrogen bonds exclusively. The series of compounds chosen were the neutral, tetrahedrally coordinated,  $Zn^{2+}$  complexes containing two thiocyanate ions and a chelated ethylenediamine or methyl substituted ethylenediamine,  $Me_xH_{2-x}N(CH_2)_2NH_{2-y}Me_y$  (where  $x,y \leq 2$ ,  $x>y$ ).

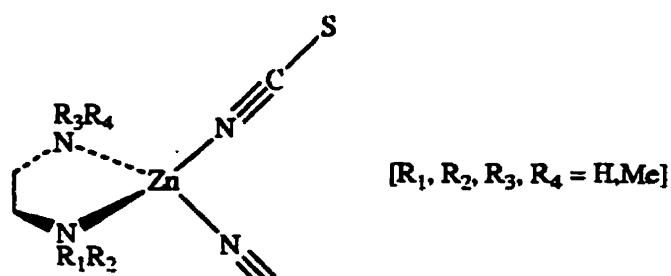


Figure 6. Diagram of  $Me_xH_{2-x}N(CH_2)_2NH_{2-y}Me_y$

In addition, the  $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]^{2+} [\text{Zn}(\text{NCS})_4]^{2-}$  salt was prepared. In all these complexes, the nitrogen end of the thiocyanate ion coordinates to the zinc atom. In these crystal structures, hydrogen bonds can be only be formed intermolecularly to the thiocyanate ion using the N-H hydrogen atoms on one molecule and the thiocyanate groups on another. However, the coordination geometry of the complex is such that the nitrogen atoms, close to the zinc atom, are protected from any intermolecular N-H approach and therefore only the sulphur atoms are available for hydrogen bonding. The expected weak hydrogen bond would then occur between the H(N) of the ethylenediamine and the sulphur of the thiocyanate. However, the exact direction of bonding, any branching that may occur and the general packing is difficult to predict, even if it is assumed that i) every H(N) is used in this H...S bond, ii) the atoms seek to maximize their participation in hydrogen bonding, and iii) the geometry of the  $\text{ZnT}_2$ , where T= thiocyanate, portion is constant to control the spatial distribution of sulphur atoms. For  $x=y=0$ , the ratio is  $R= \text{H}(\text{N})/\text{S}=(4-x-y)/2=2$ . There is thus an excess of H(N) and they must each share a sulphur atom or atoms. For  $x=1$ ,  $y=0$ , and for the  $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]^{2+} [\text{Zn}(\text{NCS})_4]^{2-}$  salt  $R= 3/2$  i.e. there is an excess of H(N). For  $x+y=2$ , where two methyl groups exist together on one nitrogen or separated symmetrically, R would be  $(4-x-y)/2=1$ . This means there would be one sulfur for every H(N) atom. This is consistent with the formation of *unbranched* N-H...S bonds; in this case there are two. In the case of  $x+y=3$ ,  $R=1/2$ , so branched hydrogen bonding is expected because of the deficit of H(N) atoms. The only hydrogen atom must now be shared between two sulphur atoms. For

$x+y=4$ , where there are now two pairs of Me groups, R=0 since there are no H(N) atoms available, and there can be no hydrogen bonding.

The consideration of the geometry of these interactions is helped by the fact that the zinc complexes have tetrahedral geometry. There is thus no primary complication of possible *cis* and *trans* thiocyanato- ligands that could arise in an octahedral system. In addition, since a series of methyl substituted ethylenediamines are used as ligands, the unsymmetrically substituted ligands ( $m > n$ ) would, in an octahedral system, give rise to several geometric isomers which could then be further complicated by *cis* and *trans* isomers of the (NCS)<sup>-</sup> group.

All the compounds  $(Me_xH_{2-x}NCH_2-CH_2NH_{2-y}Me_y)Zn(NCS)_2$  [ $x \geq y$ ,  $x,y = 0,1,2$ ] and  $[NH_3CH_2CH_2NH_3]^{2+} [Zn(NCS)_4]^{2-}$  were prepared<sup>2</sup> by methods which are described in Chapter 4. For each compound, crystals suitable for single crystal X-ray diffraction were obtained and a full set of X-ray reflection data was collected.

For the following discussion, the compounds are coded as follows: enZ2T,  $(NH_2(CH_2)_2NH_2)Zn(NCS)_2$  where  $x,y=0$ ; 1MenZ2T,  $(MeNH(CH_2)_2NH_2)Zn(NCS)_2$  for  $x=1$ ,  $y=0$ ; s2MenZ2T, (*sym N,N*)  $(MeNH(CH_2)_2NHMe)Zn(NCS)_2$  for  $x, y=1$ ; g2MenZ2T, (*gem, N,N*)  $(Me_2N(CH_2)_2NH_2)Zn(NCS)_2$  for  $x=2$ ,  $y=0$ ; 3MenZ2T,  $(Me_2N(CH_2)_2NHMe)Zn(NCS)_2$  for  $x=2$ ,  $y=1$ ; 4MenZ2T,  $(Me_2N(CH_2)_2NHMe)Zn(NCS)_2$  for  $x,y=2$ ; and enZ4T,  $[NH_3CH_2CH_2NH_3]^{2+} [Zn(NCS)_4]^{2-}$ .

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<sup>2</sup> Originally the  $(Me_mH_{2-m}NCH_2-CH_2NH_{2-n}Me_n)Zn(NCS)_2$  salts were prepared for this project by W. Louch (Dalhousie Chemistry Honours Project 1996/97). He was not involved however in any of

The crystal data are summarized in Table 7. The positional parameters, isotropic temperature factors of non-hydrogen atoms and H(N), interatomic distances and bond angles are presented in Tables 4-6, 8. The following consistent atom numbering is used: the thiocyanate ligands are labeled S1 C1 N1 and S2 C2 N2 and the methylated ethylenediamine units are numbered N3 C4 C5 N6. Where the Me substitution is asymmetric, N3 carries more Me groups. These carbons and hydrogens are then numbered according to the parent atom, eg. H61 and H62 on N6, C31 on N3.

The thermal parameters and the estimated standard deviations of some of the positional parameters in Table 8 are larger than desired. An explanation for this is the existence of a positional disorder of the carbon atoms in ethylenediamine, which arises from the flexibility of the *en* group. Thus the average  $U_{\text{eq}}$  per atom is  $0.048\text{\AA}^2$  in enZ2T,  $0.071 \text{\AA}^2$  in 1MenZ2T but 0.079 and higher for other structures. Attempts were made to resolve the disorder through modeling as a superposition of two arrangements through SHELXL or TeXsan. However, some of the thiocyanate atoms also had relatively high  $U_{\text{eq}}$ , displaying an overall looseness of the less hydrogen-bonded structures.  $U_{\text{eq}}(\text{S})/U_{\text{eq}}(\text{Zn}) = 1.08$  for en, 1.24 1Men, 1.17 for s2Men, 1.35 for g2Men and 1.57 for 3Men.

**enZ2T**

enZ2T has  $x,y=0$ , so  $L = \text{Me}_x\text{H}_{2-x}\text{N}(\text{CH}_2)_2\text{NH}_{2-y}\text{Me}_y$  becomes  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$  and the ligand is simply ethylenediamine.

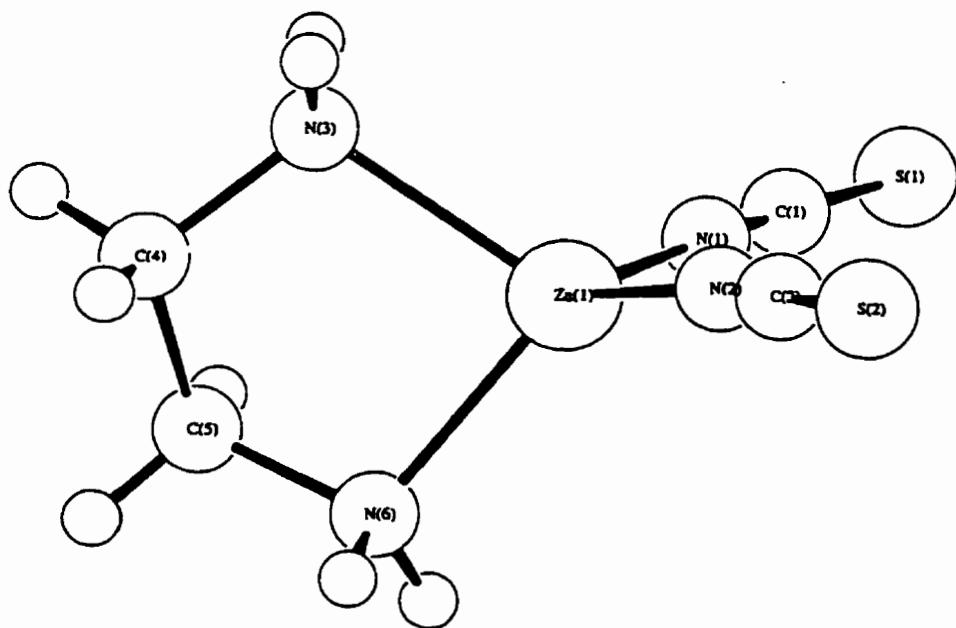


Figure 7. enZ2T

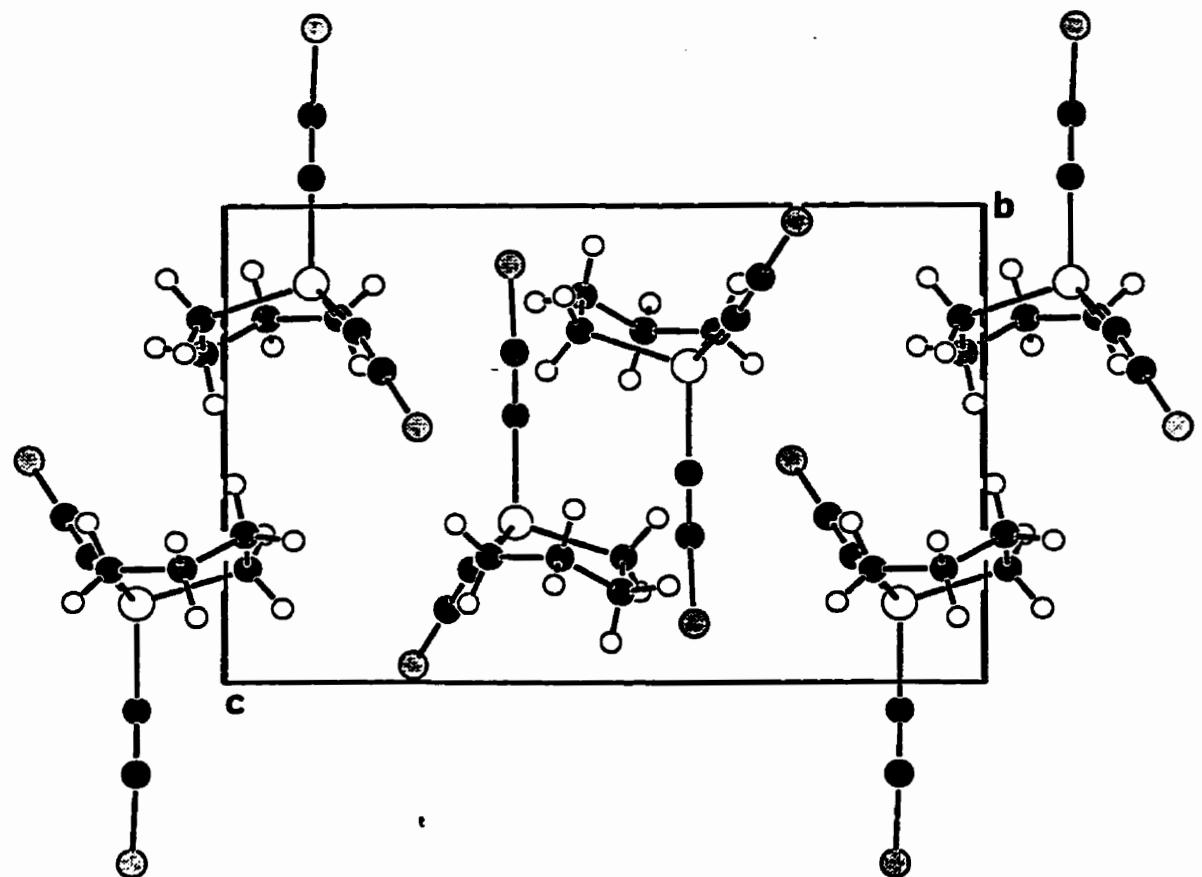


Figure 8. Packing of enZ2T

enZ2T is a centrosymmetric structure where all the H(N) and sulphur atoms are utilized in H(N)..S bonds. Each sulphur atom is coordinated to three H(N) atoms. The H(61) and H(62) atoms are donors in bifurcated N(6)-H(61)...S(1), S(2) and N(6)-H(62)...S(1), S(2) bonds; and the H(31) and H(32) atoms form short unbranched N(3)-H(31)..S(1) and N(3)-H(32)..S(2) bonds. The sequence ...H(62B')...S(1B')...H(61) ... S(2B)...H(62B'') forms an infinite pseudo- $2_1$  helix parallel to  $a$ , with the S(1B')...H(31C'') and S(2B)...H(32A') bonds extending radially from the helix.

### 1MenZ2T

1MenZ2T has one methyl group off N3. This gives L=MeHN(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>.

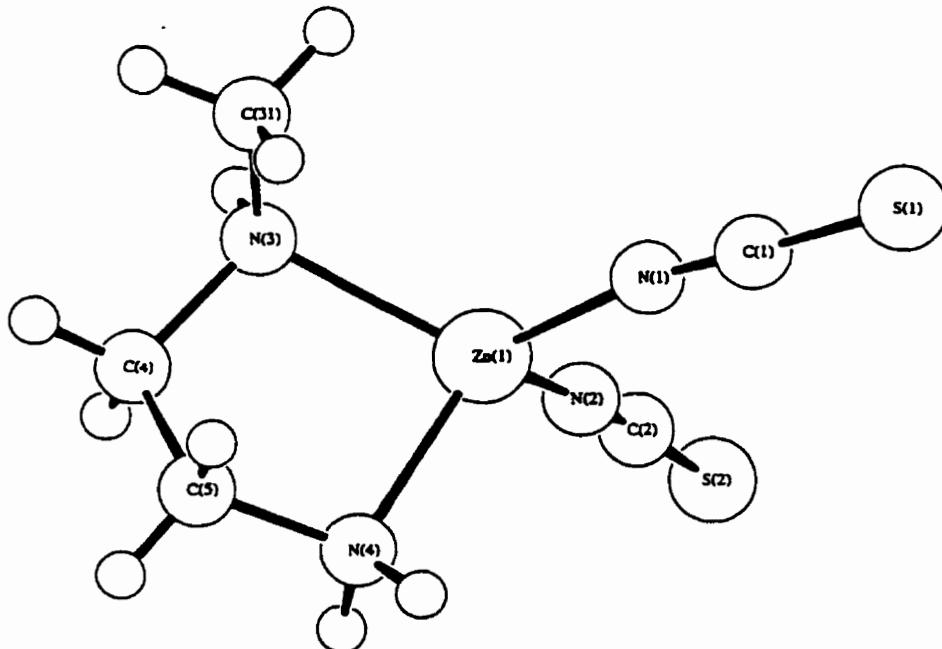


Figure 9. 1MenZ2T

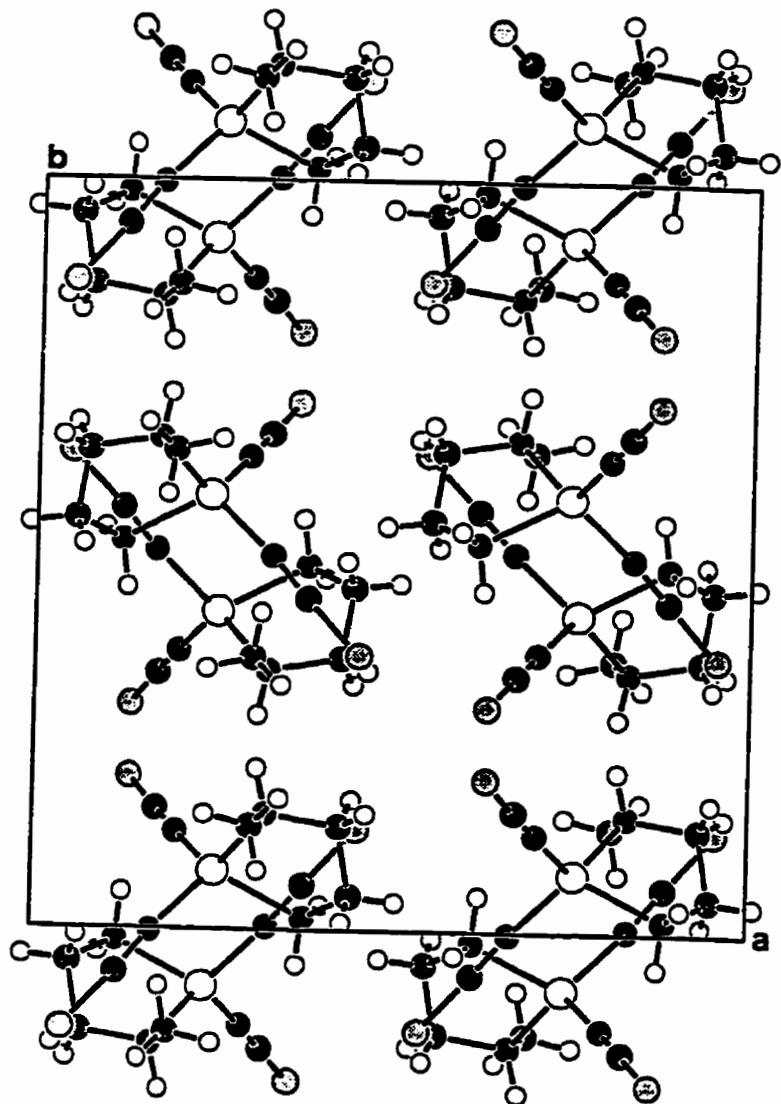


Figure 10. Packing of 1MenZ2T

The centroids of the molecules are located in planes parallel to (002) at  $z=\pm\frac{1}{4}$ .

Each molecule has six nearest neighbors, those in the plane parallel to (002) nearly equidistant and those perpendicular to (002) at a somewhat shorter distance. The molecules are packed in columns with  $2_1\text{llc}$  as axes. The nearest neighbor sulphur atoms form irregular S1, S1, S2, S2 tetrahedra in which the four S1...S2 contacts are at  $\sim 4\text{\AA}$ , S2...S2  $\sim 5.16\text{\AA}$  and S1...S1  $\sim 6.60$ . These tetrahedra create columns of sulphur atoms parallel to  $c$ . All the H(N) and sulphur atoms are engaged in N-H(N)..S bonds. These bonds are asymmetrically bifurcated, with one H(N)..S component much shorter than the other. The S2 atom has contacts to H3 and H62 at fairly short distances of comparable length,  $\sim 2.83$  and  $2.70\text{\AA}$ . The S1 atoms are 4 coordinated by H3, H62 and two H61 atoms. The shortest is to H61,  $-2.62\text{\AA}$ ,  $\text{NHS}\sim 158^\circ$ , with the other contacts between 3 and  $3.3\text{\AA}$ . The C4 and C5 atoms (the carbons on L) are disordered.

### s2MenZ2T

s2MenZ2T has one methyl group on each nitrogen and packs as follows:

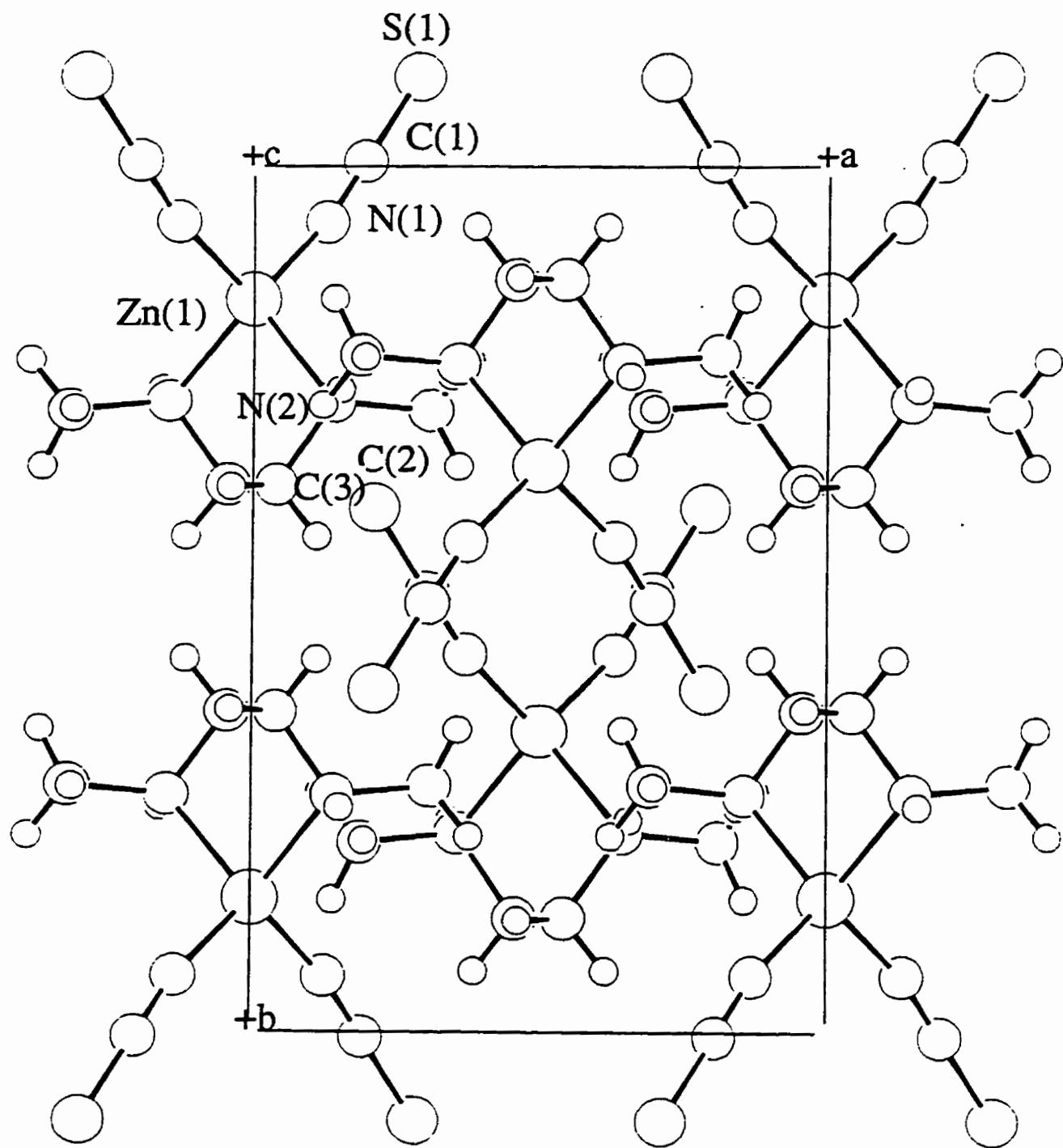


Figure 11. Packing of s<sub>2</sub>MenZ<sub>2</sub>T

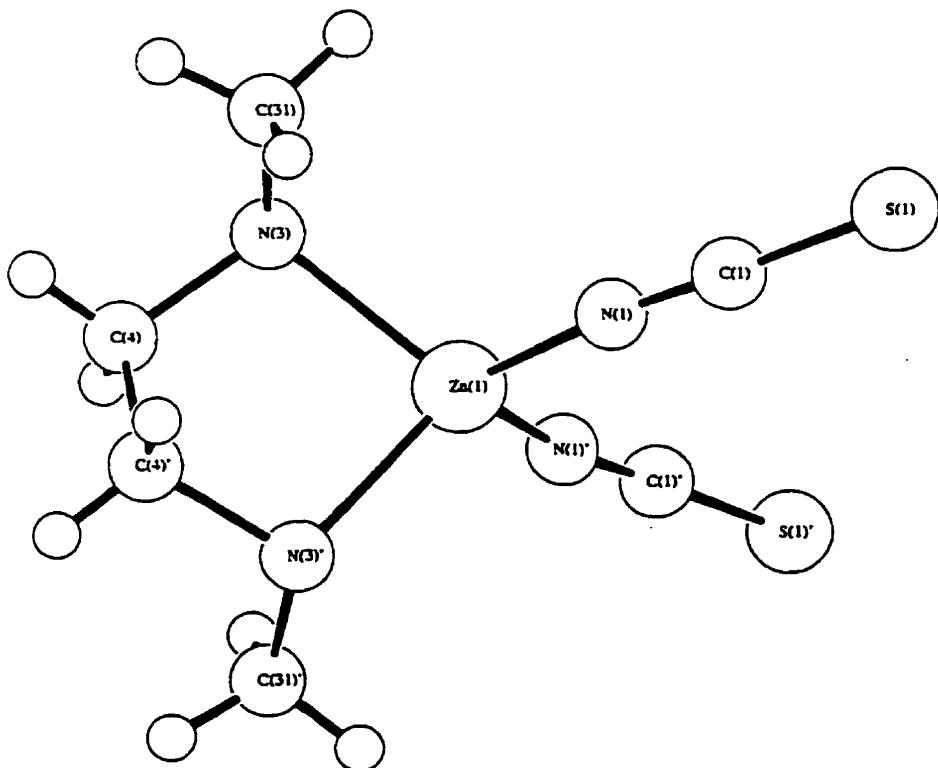


Figure 12. s2MenZ2T

A routine operation of TeXsan to 25 suitable reflections resulted in a triclinic cell. However, further refinement of this  $a=11.549$ ,  $b=7.590$ ,  $c=8.667$ ,  $\alpha=124.86$ ,  $\beta=112.31$   $\gamma=77.42$  cell produced an indication of a  $C_2$  axis. Re-examination of the cell determination revealed that the triclinic cell could be transformed into another triclinic cell of twice the volume, in which the angles deviate from  $90^\circ$  by only  $0.04^\circ$ . This difference is apparently far enough from  $90^\circ$  for the program to conclude a triclinic cell (no dimensions equivalent, no angles of  $90^\circ$ ) instead of the monoclinic cell where  $\alpha$  and  $\gamma$  are  $90^\circ$ ,  $\beta \neq 90^\circ$ ,  $a$ ,  $b$  and  $c$ , non-equivalent. The monoclinic cell was determined and this  $C$ -centered cell was then refined on the basis of a  $C2/c$  cell. The triclinic cell is converted to the monoclinic cell by the

matrix ( $a_M/b_M/c_M$ ) = (0,0, -1/0, 2, 1/1, 0, 1)( $a_T, b_T, -c_T$ ). The existence of this C2 axis through the Zn atoms greatly simplifies the structure of s2enZ2T. The molecules are arranged in sheets parallel to (001) which are cross-linked with H(N)..S bonds. Two essentially straight, symmetry-equivalent N-H(N)...S bonds might be expected due to the ratio, R=2/2=1. However, a single-type, asymmetrically bifurcated N3-H3..SA, SB bond forms a centro-symmetric [...]H3...S...]<sub>2</sub> ring dimer, in which H3...SA ~2.68Å, H3...SB ~2.93Å, SA-H3-SB ~85°, H2-SA-H3c ~95°, SA..SB 3.78Å, H3..H3C~4.14Å. Each sulphur atom is therefore engaged in two H(3)..sulphur bonds. The C4 (and therefore C4') atoms are disordered.

### g2MenZ2T

g2MenZ2T has two methyl groups on N3, and no methyl groups on N6. This obviously removes the symmetry of the previous example that also contained two methyl groups.

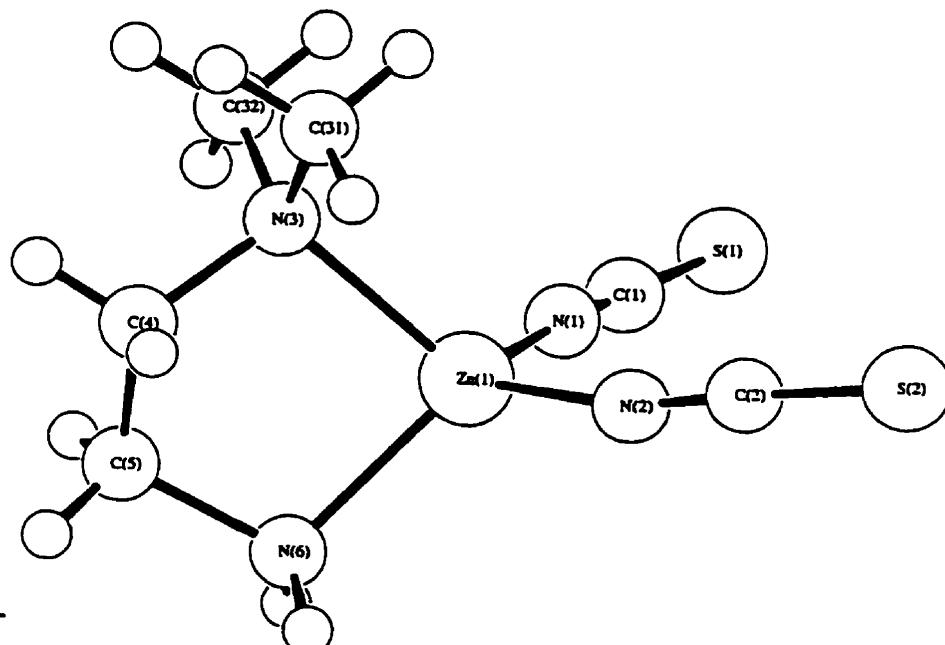


Figure 13. g2MenZ2T

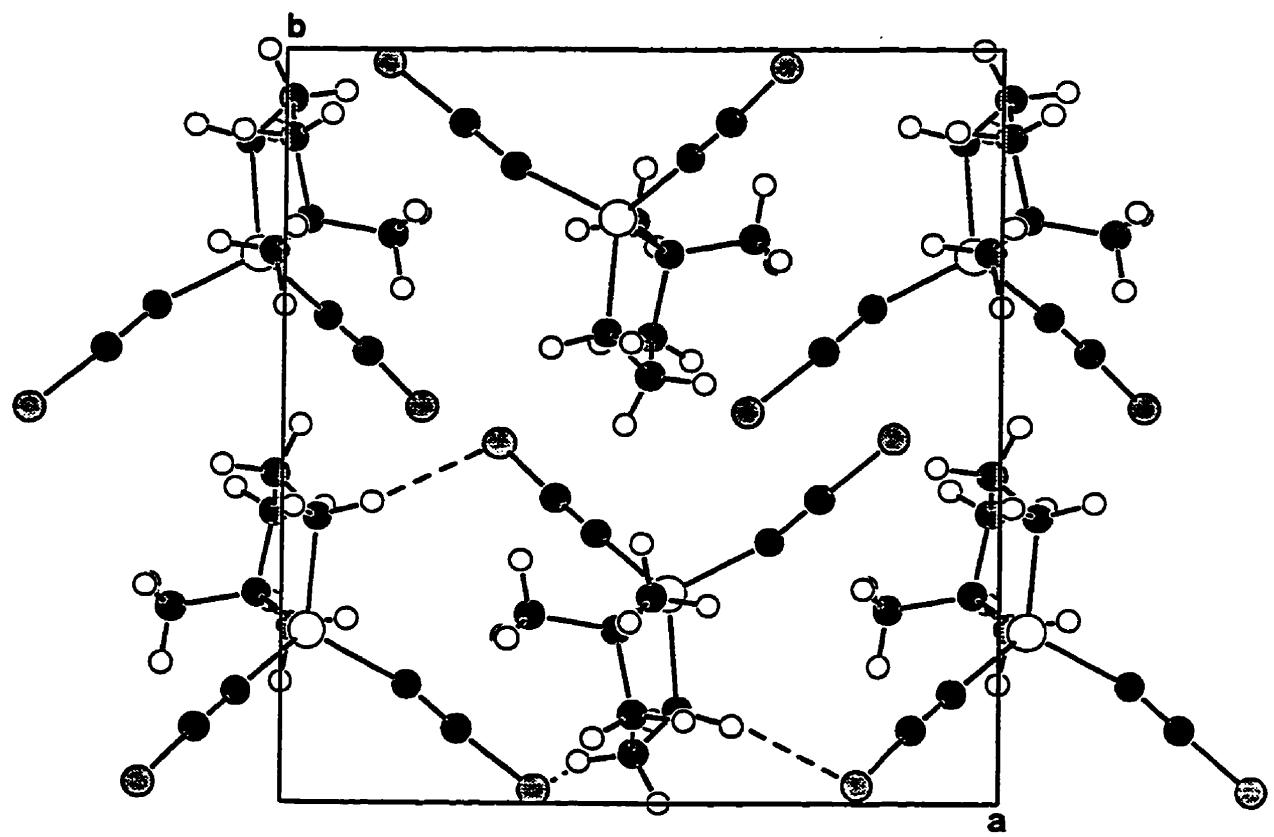


Figure 14. Packing of g2MenZ2T

The molecules are arranged in chiral packing of symmetry  $P2_12_12_1$ . The overall symmetry is not far from  $Pnma$ , which has  $P2_12_12_1$  as a subset. The oriented pseudo  $C_2$  axes bisecting the S1-Zn-S2 angle are roughly parallel to  $b$  and are situated on thin bands parallel to (200). In each band, they point in the same direction but the directions in adjacent bands are anti-parallel. The Zn atoms (the centroid of the molecule) are approximately at points of an orthorhombically distorted diamond lattice deriving from the aristo type by descent in subgroups:  $Fd\ \bar{3}\ m(8(a))\supset F41/ddm(I41/amd)\supset F\ \bar{4}d2(I\ \bar{4}2d)\supset I2_12_12_1\supset P2_12_12_1$ . Each molecule is thus tetrahedrally coordinated; the coordination tetrahedra of the centroids are considerably flattened perpendicular to  $c$ .

As with the symmetric dimethyl, the  $R = 2/2=1$  allows for the formation of two unbranched N-H(N)..S bonds per Zn atom. Instead, each H(N) is utilized in an asymmetrically bifurcated N-H(N)..S bond in which each sulphur atom comes from a different neighboring molecule. However, while each of the two H(N) atoms is two-coordinated by sulfur (H61B..S2, S1A; H62B...S1A, S1'), the S1 atom is the recipient of three hydrogen bonds, to H62B, H61B, H62C. The S2 atom is H(N) coordinated only singly, by a short S2..H61B ~2.69A bond; the N6-H61..S2B' bond is strongly bent,  $NHS\sim 145^\circ$ , with the H61-S2B'-C2B' ~101°. It is probable, however, that this asymmetry at H61 is balanced somewhat as the S2 atoms is involved also in weak C-H(C).. S interactions with the methylene hydrogen (C) atoms on the en ring, where these H(C)...S2 distances in the range of 2.8-3.2A. The certainty of these interactions is in question owing to the

disordered C4 and C5, resulting in question in the location of the appropriate hydrogen atoms.

A similar situation may also exist with S1. These hydrogen bonds are arranged helically about the  $2_{111}a$  axes at  $x,y=\frac{1}{4}, \frac{1}{2}; \frac{3}{4}, 0$  which localize the disjoint hydrogen bond regions of the structure. The H62...S1B ~2.66A and H61...S2B' ~2.69A are substantially shorter than the H62...S1C" ~3.11A and H61...S1C" ~3.21A bonds. The geometry of these strong/weak bifurcation components is shown in the following figure:

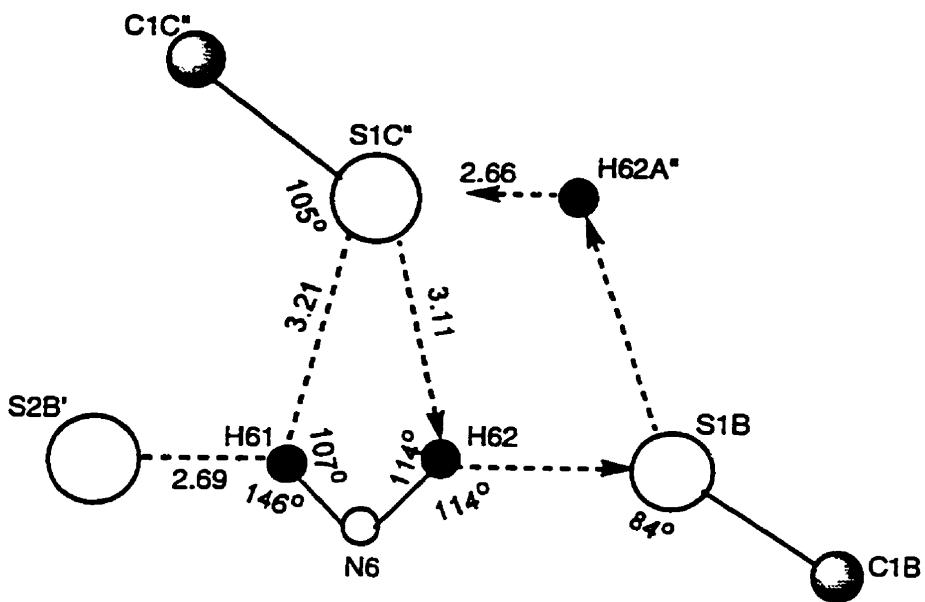


Figure 15. Geometry of strong, weak bifurcation of g2MenZ2T

**3MenZ2T** This is the only one of the compounds which contains two non-equivalent molecules. N13 and N23 have a single methyl group, N16 and N26 have two groups.

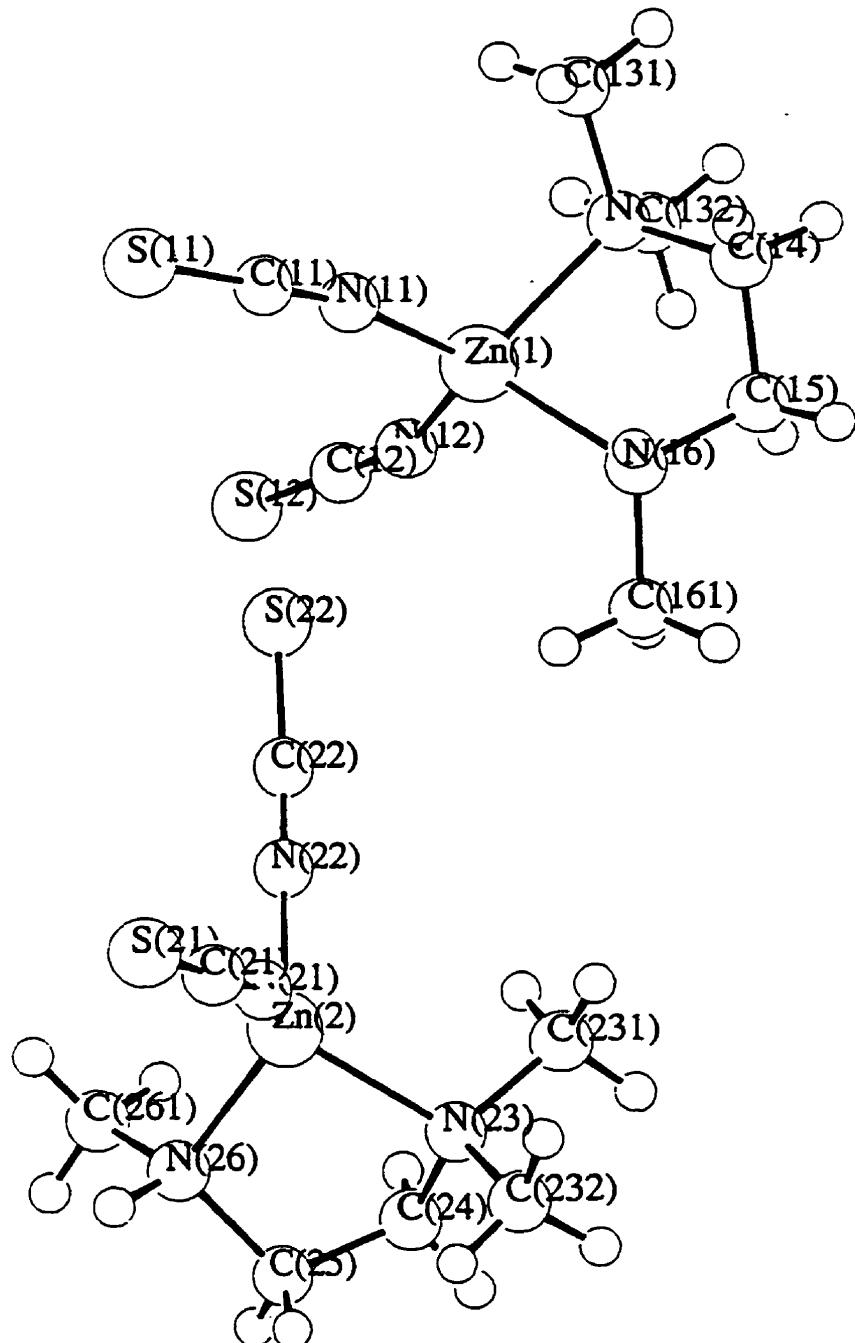


Figure 16. 3MenZ2T

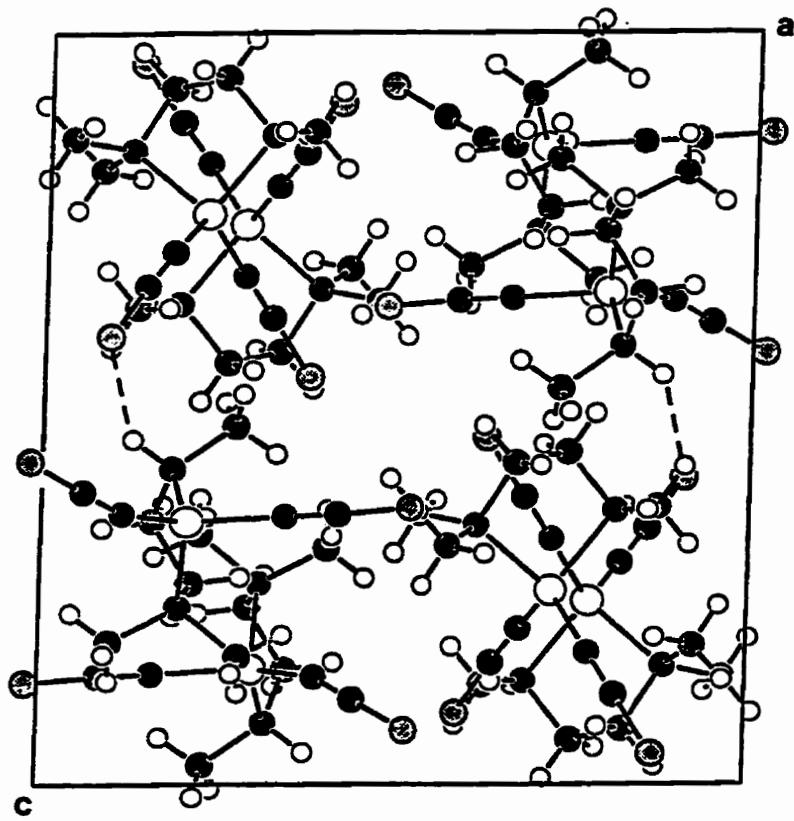


Figure 17. Packing diagram of 3MnZ<sub>2</sub>T

At an R=½ value, branched N-H(N)..S bonds will be expected, and it may be the scarcity of H(N) atoms in the structure that is responsible for the existence of these two molecules. The Zn(NCS)<sub>2</sub> portion of the first molecule is roughly parallel to (100), and the same portion of the second molecule is roughly perpendicular to (100). The hydrogen bond regions are concentrated, in a ring-dimer-like fashion, about inversion centres at 2(b) of *P2<sub>1</sub>/n*, while the centers at 2(a) and 2(d) relate the non-hydrogen bonded S11 atoms as well as the Me groups on N16 and N23 in the columns parallel to *a*.

The hydrogen bond at H26 is nearly symmetrically trifurcated, N16-H16...S12A, S12'', S21A''. H16 is bonded to S12B at ~2.70A, NHS~152°. There are two other sulphur atoms, S(21C') at ~3.83A, NHS~164°, and S22 at 3.95A, NHS~91°. These are too far away for an effective hydrogen-bonding interaction. If the value of 3.55A is used as the cut-off for N-H(N)..S bonding, then S22 must be considered as non-hydrogen bonded, and similarly for S11. The S12 atom is the recipient of 3 hydrogen bonds, H16B' at ~2.70A, NHS~152°, H26A' at ~2.93A, NHS~128° and H26' at ~3.11A, NHS~128° and so is the most strongly hydrogen bonded of the sulphur atoms in 3MenZ2T. This is reflected in the value of U<sub>eq</sub> that is significantly smaller than the U<sub>eq</sub> of the other three sulphur atoms (Table 2). Finally, S21 has only one weak bond to H26A'' at ~3.11A, NHS~126°.

#### 4MenZ2T

4MenZ2T has two methyl groups on both N3 and N6. From systematic absences and intensity statistics, this compound appears to crystallize in the non-centrosymmetric space group *Pba2*. The structure must be considerably disordered, as attempts to refine it did not bring its R below ~14% and so further attempts were discontinued. However, the unit cell volume of 4MenZ2T fits in well with the other members of the title series.

#### Molecular geometry and crystal packing

Tables 5 and 6 describe the geometry of the thiocyanato group in the title compounds. The means of the bond lengths are 1.149Å for the N-C bond and 1.614Å for the C-S bond; the group is close to linear, the mean N-C-S angle being 178.3°. The mean Zn-N bond length involving the T group is 1.929Å; the Zn-N bond length in the *en* portion of the molecule is 2.045Å. The Zn-N-C angle of the thiocyanate group has a mean of 169.5° and shows a larger variation. In Zn(NCS)<sub>2</sub>, where the four thiocyanate groups tetrahedrally coordinating the Zn(2) atom are bonded to Zn at both ends, the Zn(2)-N-C mean is 169.9° [9]. The above mean geometries in the thiocyanate group are also statistically indistinguishable from values determined by Tchertanov and Pascard [10] in a CSD search of 905 M-NCS fragments. However, the mean Zn-N bond length and mean Zn-N-C angle reported in the same reference of 33 Zn-NCS monodentate ligands are less related to those found for our compounds,

although the mean Zn-N-C angles are again statistically indistinguishable. This seems to confirm the general finding of Tchertanov and Pascard that the internal geometry of the covalently N-coordinated thiocyanate group remains essentially constant regardless of the circumstances, whereas the M-N distance and the M-N-C angles are determined by the nature and coordination number of the metal, and the crystal packing.

The N-Zn-N angles between the thiocyanate groups range from 110.7 to 116.5°, with a mean of 113.1°; this is a somewhat narrower range than in  $Zn(NCS)_2$ , 106.5-113.7°. The N-Zn-N angle involving the *en* nitrogens is considerably smaller, with a mean of 87.3°, and its variation also is significantly smaller, 85.7-88.4°. This is consistent with the smaller  $U_{eq}$  of the *en* nitrogens; a paired *t* statistic shows, at 95% confidence, that the means  $U_{eq} = \frac{1}{2} \{U_{eq}N(1) + U_{eq}N(2)\}$  and  $U_{eq} = \frac{1}{2} \{U_{eq}N(3) + U_{eq}N(6)\}$  do not come from the same population ( $t=2.55$ ,  $t_{0.05}=2.57$ ). The range of the  $N_T\text{-Zn-}N_L$  angles is considerable, 107.1-119.5°. The volume per formula unit,  $V_1 = V/Z$ , of the title compounds can be represented by  $V_1 = 231 + 31.10(x+y)$ , ( $n=6$ ,  $r^2=0.998$ ,  $\sigma = 1.5\text{Å}^3 \sim 1.2\%$  of range), where  $x+y \leq 4$  is again the total number of Me groups on the *en*. The space filling thus closely conforms to additivity. The volume increment  $31.1\text{Å}^3/\text{Me}$  for a Me group attached to an aliphatic N atom coordinated to Zn considerably exceeds that for a typical Me group attached to a C atom,  $23.5\text{Å}^3/\text{Me}$  [11].

The difference  $V_1(\text{calc}) - V_1(\text{obs})$  is largest for  $s2\text{MenZ2T}$ ,  $\sim 4\text{Å}^3$ . When  $V_1(s2\text{MenZ2T})$  is not included in the regression,  $V_1 = 231.8 + 31.10(x+y)$  ( $n=5$ ,  $r^2=1.00$ ,  $\sigma = 0.4\text{Å}^3 \sim 0.3\%$  of range) and  $V_1(\text{calc}) - V_1(\text{obs})$  for  $s2\text{MenZ2T}$  increases

to  $5\text{ \AA}^3$ . This confirms that the packing in s2MenZ2T is in fact denser than that in the *gem* isomer.

### Hydrogen bonding

Of these six structures, five are incompletely methylated, and are examples of neutral metal thiocyanato complexes with exhaustive intermolecular hydrogen bonding. The main feature of the hydrogen bonded system that is common to these five structures is the ...S...H...S...H... group which occurs as a helix or as a dimer. The [...S...H...]<sub>n</sub> helix forms about a twofold screw axis in g2MenZ2T and a pseudo screw axis in enZ2T. The cyclic [...S...H...]<sub>2</sub> dimer forms in the remaining three structures.

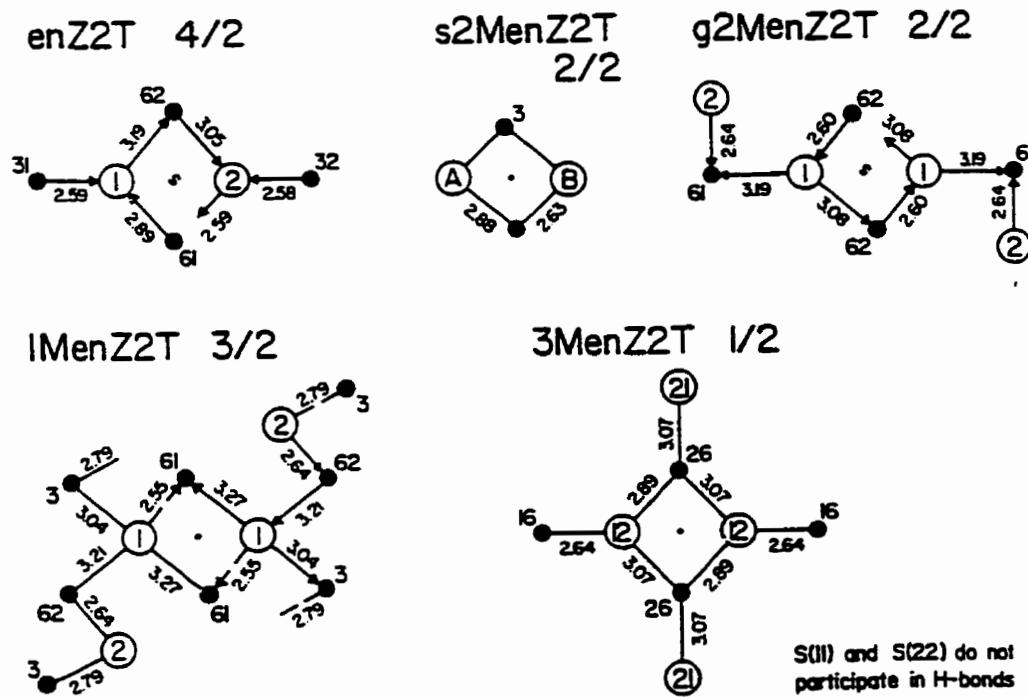


Figure 18. Helix and dimer hydrogen bonded systems

The hydrogen bond in the later group is thus bifurcated or trifurcated and so alternates between long and short bonds.

s2MenZ2T has the simplest hydrogen bonded system, and since the H(N)/S ratio of 2/2 means it has one sulfur for each (N)H, its hydrogen bonds are all of the same type and components of the centrosymmetric dimer. Conflicting with the R-value of one, is that each H(N) is coordinated by two sulfurs, and two H(N) atoms coordinate each sulfur. Unbranched bonds are expected, but the space filling with bifurcated bonds is more efficient.

The g2MenZ2T also has a ratio of 2/2, but has a mixed 1 and 3 coordination of sulfur. This is due to the asymmetry of the methyl substitution which gives uneven distribution of hydrogen bonds and that leads to a less uniform coordination of the sulfurs. It is worth noting, that of all the H(N)...S bonds in these compounds, the only unbranched bonds exist in enZ2T and 3MenZ2T, and not in the previous two compounds in which the number of H(N) atoms matches the number of sulfur atoms.

enZ2T and 1MenZ2T have H(N)/S ratios of less than one, suggesting the higher coordination of sulfur by H(N). In the H(N) deficient 3MenZ2T, the centrosymmetric dimer is expanded to  $S_4H(N)_4$  by attaching a hydrogen bond terminating atom of the opposite kind to the dimer. The ratio of the resulting group then rises to  $4/4= 1$ , from  $1/2$ . When the non-hydrogen bonding sulfurs are included, the ratio becomes  $4/(4+4)=1/2$  as required.

It seems that the H(N) atoms in these structures attempt to bond to as many sulfur atoms as possible. The formation of branched hydrogen bonds maximizes the total number of possible bonds. The following tables outline the location of the branched and unbranched N-H(N)...S bonds:

Table 1. Location of N-H...S bonds and number of H(N) atoms coordinated to S

	Normal	N-H(N)...S bond bifurcated	N-H(N)...S bond Trifurcated
enZ2T	H(31), H(32)	H(61), H(62)	-
1MenZ2T	-	H(3), H(61), H(62)	-
s2MenZ2T	-	H(3)	-
g2MenZ2T	-	H(61), H(62)	-
3MenZ2T	H(16)	-	H(26)

	0	1	2	3	4
enZ2T	-	-	-	S(1), S(2)	-
1MenZ2T	-	-	S(2)	-	S(1)
s2MenZ2T	-	-	S	-	-
g2MenZ2T	-	S(2)	-	S(1)	-
3MenZ2T	S(11),S(22)	S(21)	-	S(12)	-

The 23 angles of H(N)-S-C where H(N)...S<3.8A, range from ~71° to ~141°. Creating a histogram from 60-150° at intervals of 7.5° gives a bivariate distribution. The smaller group of just four examples, with a mean of 133°, is too small for meaningful statistics to be done. The larger group of 19, has a mean of 91° and is only slightly skewed. There is no obvious correlation between the H(N)-S-C angle and the H(N)...S distance or the H(N) coordination number of the sulfur atoms. However, the mean of the H(N)-S-C angels at the three singly H(N) coordinated S atoms is 91°. For the four quadruply H(N) coordinate sulfur atoms it is only 83°. In NH<sub>4</sub>SCN [4], where the S atom is coordinated by two H(N) atoms, the angles are 92.05 and 95.22°. The closeness of these values to 90° points towards the substantial interaction of the p orbital of sulfur with H(N).

### N-H(N)-S angles vs H(N)...S distances

Table 2 shows the N-H(N)-S =  $\phi$  angles and H(N)...S =  $d$  distances. It is immediately obvious that the table suggests the existence of a trend:  $\phi$  decreases with increasing  $d$ .

Table 2 H...S bond distances and N-H...S, H...S-C angles

Bond	H...S distance, Å	N-H-S angle, °	H-S-C angle
<b>enZ2T</b>			
N(1)-H(31)...S(1A)	2.59	150	77
N(3)-H(32)...S(2C)	2.58	148	105
N(6)-H(61)...S(2B)	2.59	152	92
N(6)-H(61)...S(1B')	2.89	112	84
N(6)-H(62)...S(2')	3.05	115	104
N(6)-H(62)...S(1")	3.19	129	141
<b>1MeZ2T</b>			
N(3)-H(3)...S(2C)	2.79	127	81
N(3)-H(3)...S(1F)	3.04	120	93
N(6)-H(61)...S(1H)	2.55	157	71
N(6)-H(61)...S(1G)	3.27	103	76
N(6)-H(62)...S(2H')	2.64	150	86
N(6)-H(62)...S(1G)	3.21	107	91
<b>s2MenZ2T</b>			
N(3)-H(3)...S(A)	2.63	135	128
N(3)-H(3)...S(B)	2.88	132	104
<b>g2MenZ2T</b>			
N(6)-H(61)...S(2B')	2.64	145	100
N(6)-H(61)...S(1C")	3.19	106	105
N(6)-H(62)...S(1B)	2.60	143	84
N(6)-H(62)...S(1C")	3.08	113	130
<b>3MenZ2T</b>			
N(16)-H(16)...S(12B)	2.64	151	111
N(16)-H(16)...S(21C')	3.76	164	84
N(16)-H(16)...S(22)	3.95	90	114
N(16)-H(26)...S(12A)	2.89	127	85
N(16)-H(26)...S(12")	3.07	127	134
N(16)-H(26)...S(21A")	3.07	125	90

Five regression functions were examined; linear ( $\phi = a_0 + a_1 d$ ), quadratic ( $\phi = a_0 + a_1 d + a_2 d^2$ ), power ( $\phi = a_0 d^{a_1}$ ), exponential ( $\phi = a_0 e^{a_1 d}$ ) and logarithmic ( $\phi = a_0 + a_1 \ln(d)$ ). These functions were assessed for their suitability to represent the preceding trend. Based on their  $r^2$  and  $\sigma$  values, the quadratic regression was slightly better than the others. However, this function is not suitable as a description of the trend because a parabola is not monotonic, and the increasing trend of the parabola at longer distance values does not describe the relationship. The linear function may also be ruled out because the values on extrapolation are not suitable. The distance value obtained through extrapolation to  $180^\circ$  is 2.06A, even smaller than the 2.16A estimated from the linear fit determined by Allen [12], where the geometries come from  $X-H(X)\dots S=CR_1R_2$  and thus from stronger H-bonds than examined here. A preference for the remaining three functions cannot be determined because of the small number of data points and the closeness of their  $r^2$  and  $\sigma$  values. To determine which function is statistically and physically best suited, external points are needed to determine the correct curvature of the regression. In the structure of ammonium thiocyanate, there are two closely spaced values that have been determined by low-temperature neutron diffraction. The power regression with the two ammonium thiocyanate points at triple weight was then accepted as the regression equation increasing the values of  $r^2$  (by ~7%) and  $\sigma$ . The fitted expression then becomes  $\phi = 582.8d^{-1.430}$ , with  $r^2$  at 0.903 and  $\sigma$  at 4.7°. Extrapolation to  $\phi=180^\circ$  gives  $d$  at 2.29A as the limit below which the  $\phi$  can be

expected to be straight. The following table shows the regression values for the previous functions:

**Table 3**

Regressions of  $\phi = N-H(N)-S$  on  $d = H(N) \dots S \text{ \AA}$ <sup>a</sup>

Function	$r^2$	Q <sup>b</sup>	$\sigma$	$d(180)$	$d(90)$
Linear	0.805		5.7	2.06	3.53
	0.856	1.063	5.6	2.14	3.49
Quadratic	0.820		5.8	2.29	c
	0.883	1.077	5.4	2.29	c
Power	0.803		5.8	2.24	3.74
	0.860	1.071	5.3	2.26	3.71
Exponential	0.799		5.6	2.17	3.64
	0.853	1.068	5.4	2.21	3.61
Logarithmic	0.811		5.6	2.16	3.60
	0.868	1.070	5.4	2.21	3.55

<sup>a</sup> First line are values from table 2, second line are set of table 2 plus NH<sub>4</sub>SCN; extrapolation to  $\phi=180^\circ$  and  $90^\circ$  respectively.

<sup>b</sup> Ratio of the two  $r^2$  values

<sup>c</sup>  $\phi_{\min}=108.1^\circ$  at  $d=3.49 \text{ \AA}$

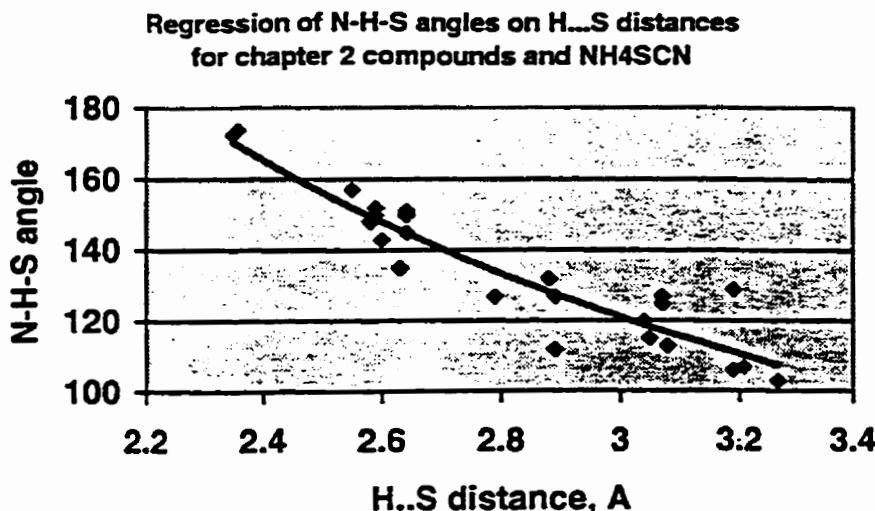


Figure 19. Regression of N-H...S angles on H...S distances of title compounds

The distances and angles of these N-H(N)...S bonds and of similar bonds in other structures may be compared in a more graphic way. A polar plot may be created, superimposing the bonds on a fixed N-H(N) vector. The short components of the bifurcated bonds and the unbranched bonds are shown at A. The long components of the bifurcated bonds are shown at B.

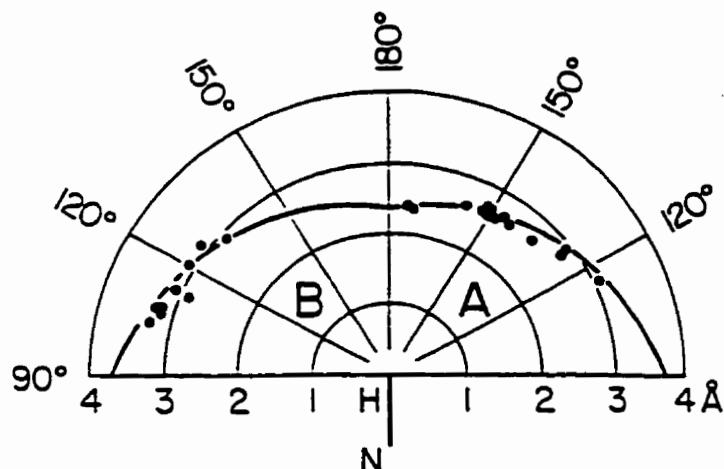


Figure 20. Polar plot of  $\phi$  vs  $d$  of title compounds

To further expand this selection of bonds and angles, the CSD was searched for further structures containing Zn-NCS and H(N). Nine structures had coordinates available, and in these nine, 23 N-H(N)...S bonds existed. These 23  $d,\phi$  pairs, along with the ammonium thiocyanate pair at triple weight, were again fitted to a power function with the equation  $\phi=460.3d^{1.142}$  ( $r^2=0.630$ ,  $\sigma=8.4$ ). This sample was not as consistent as the previous regression. It is unknown if this was due to the inadequacy and inconsistency of the data set or due to a dissimilar data set.

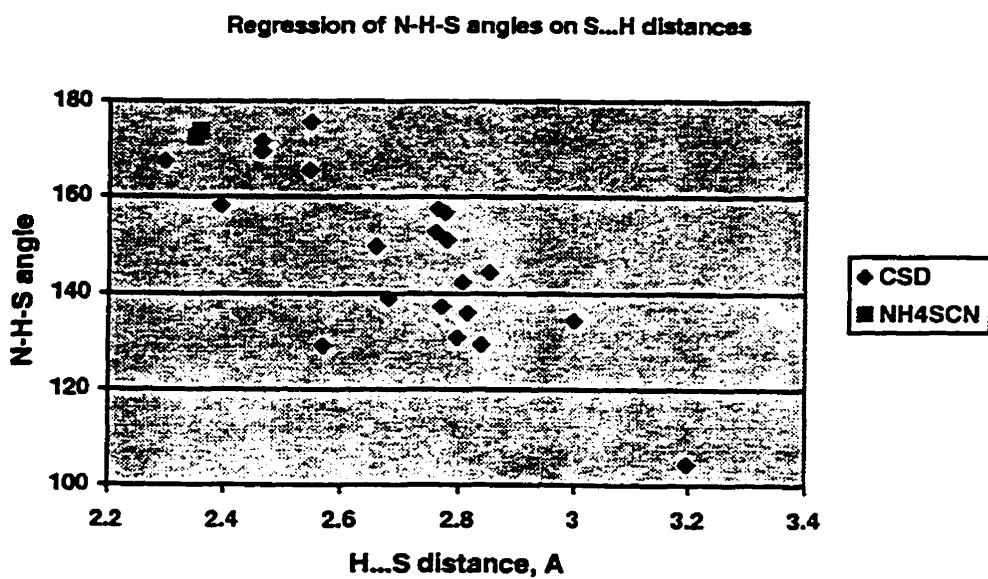


Figure 21. Regression of angles vs distances of CSD data and NH<sub>4</sub>SCN

Many of the data pairs in the determined structures come from bifurcated bonds. It was of interest to see to what magnitude the *means* of the bonds and angles could be used to represent the bifurcated bond. Nine means were used along with three points for the unbranched bonds and the two ammonium thiocyanate points for a new regression. These 14 points gave a considerably better fit than the original set. This result may show a strengthening of the  $d,\phi$  correlation, or show that the branches of the bifurcated bond are not independent. C represents the unbranched N-H(N) bonds and the *means* of the bifurcated N-H(N)...S bonds. D is the CSD data for structures containing Zn-NCS groups.

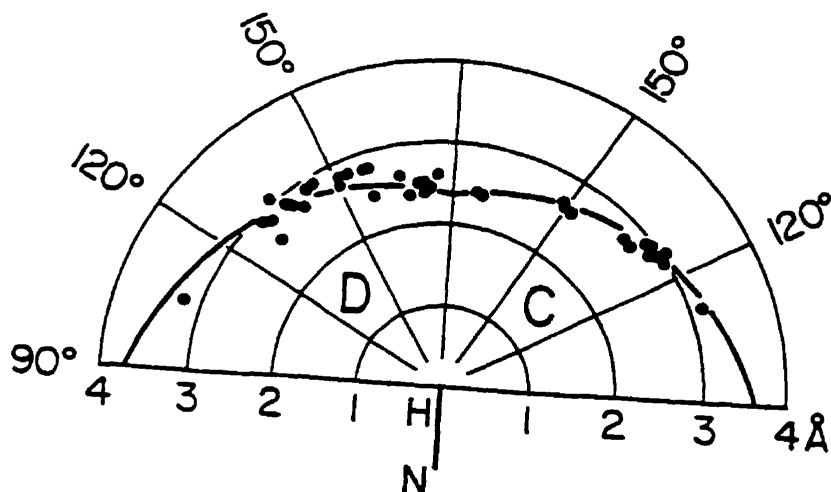


Figure 22. Polar plot of CSD data and the unbranched and means of the bifurcated bonds of the title compounds.

The overall H(N)...S and N-H(N)-S means for the branches of the bifurcated bonds are 2.71 Å, 139° and 3.09 Å, 116°. The following graph shows the values of the distances (H...S) and angles (N-H...S) for the title compounds, the means

and NH<sub>4</sub>SCN. The following ellipse represents them and their standard deviations.

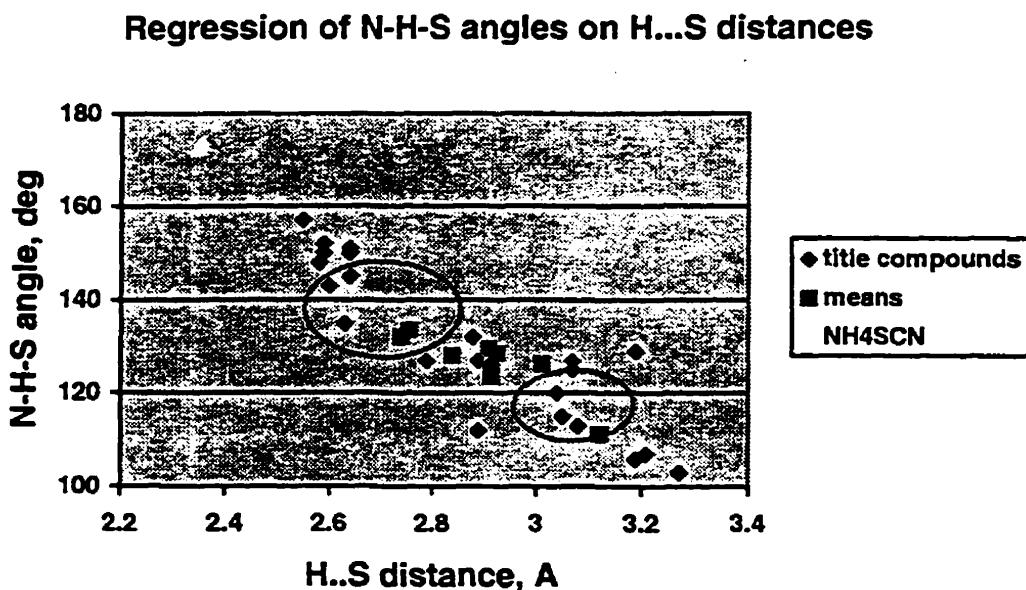


Figure 23. Regression using title compounds, means of bifurcated bonds and NH<sub>4</sub>SCN.

However, if the previous indication is true, that the branches are not independent, then the elliptic domains represent the areas in which the data points for the bifurcated bonds would be expected to fall. Geometric criteria may not be enough to determine if a long bond of  $d>3.2\text{A}$  still qualifies as a true hydrogen bond. If the previous findings are factual, then this determination may be made normatively, and thus define a cut-off limit for assigning effective N-H(N)...S

interactions. Since there is not sufficient reliable data to make a firm conclusion, further investigation is necessary.

## Conclusions

Figure 18 shows much of the coordination between H(N) and sulfur. It is evident that all the hydrogens are involved in hydrogen bonds to the sulfur atoms. It is also apparent that not all the sulfurs are involved in these bonds. These hydrogen bonds do not follow the stoichiometric expectations in respect to branching. Branching occurs even when not strictly required, and provides the basis for the main feature of the core, which is either the centrosymmetric cyclic dimer of 1MenZ2T, s2MenZ2T and 3MenZ2T, or the infinite helix of enZ2T or g2MenZ2T. When the ratio of H(N)/S is greater than one, i.e. the structure is hydrogen abundant, the bonds tend to be shorter and less branched. In these cases, the larger number of hydrogen atoms has a better chance of finding the sulfur acceptors.

From the regressions, it is apparent that the H(N)...S distances are strongly correlated to the N-H(N)-S angles. This is represented by the power regression  $\phi=582.8d^{1430}$ , with a strong  $r^2$  value of 0.90. The power regression, and the extrapolation taken from it, gave us the following results:

- a) N-H(N)..S bonds will be 180° for distances below ~2.3A.
- b) H(N)...S interactions are no longer effective at distances greater than 3.5A.
- c) H(N)...S distances longer than 2.7A, which corresponds to an angle of approximately 140°, occur as the longer branch of an often bifurcated N-H(N)...S bond.

When the geometries of the branched bonds are averaged to the mean distances and mean angles, the overall means have small standard deviations. This means that the elliptical domain defined in the plot is relatively small. When a particularly bent bond is determined, this ellipse may help to determine if it is part of a branched system, and therefore the partner branch may be searched for and found since there is an indication that the geometries of the pair are also related.

## **Experimental**

In both chapter 2 and in the following chapter 3, all the H(N) atoms were seen in the difference maps, but in the refinements, were placed geometrically 0.95Å from the nitrogen or carbon atoms, and not refined. No estimated standard deviations are therefore quoted. All atoms in all the structures are fairly mobile at room temperatures, and so have large  $U_{\text{ii}}$  values. In several cases, an unusually large U value suggested a positional disorder. This disorder was attempted to be resolved by modelling it as two alternative equally populated positions. The resulting improvement was not dramatic, owing to the simplicity of the model, but more complicated modelling would have resulted in a data/parameter ratio that would be too small, and so was not attempted.

**Table 4** Bond lengths and angles of the H...SCN<sup>-</sup> contact

Bond	H...S distance	N-H...S angle	N...S distance	H...C distance	H...S-C angle
enZ2T					
N(1)-H(31)...S(1A)	2.59	150	3.506(7)	2.77	77
N(3)-H(32)...S(2C)	2.58	148	3.492(7)	3.44	105
N(6)-H(61)...S(2B)	2.59	152	3.513(7)	3.16	92
N(6)-H(61)...S(1B')	2.89	112	3.400(6)	3.19	84
N(6)-H(62)...S(2')	3.05	115	3.601(7)	3.82	104
N(6)-H(62)...S(1")	3.19	129	3.912(7)	4.59	141
1MeZ2T					
N(3)-H(3)...S(2C)	2.79	127	3.502(9)	3.03	81
N(3)-H(3)...S(1F)	3.04	120	3.658(10)	3.53	93
N(6)-H(61)...S(1H)	2.55	157	3.519(10)	2.60	71
N(6)-H(61)...S(1G)	3.27	103	3.633(10)	3.29	76
N(6)-H(62)...S(2H')	2.64	150	3.562(11)	3.30	86
N(6)-H(62)...S(1G)	3.21	107	3.633(11)	3.64	91
S2MenZ2T					
N(3)-H(3)...S(A)	2.63	135	3.44(3)	3.88	128
N(3)-H(3)...S(B)	2.88	132	3.65(3)	3.68	104
G2MenZ2T					
N(6)-H(61)...S(2B')	2.64	145	3.522(16)	3.39	100
N(6)-H(61)...S(1C")	3.19	106	3.604(13)	3.96	105
N(6)-H(62)...S(1B)	2.60	143	3.472(16)	2.96	84
N(6)-H(62)...S(1C")	3.08	113	3.604(13)	4.34	130
3MenZ2T					
N(16)-H(16)...S(12B)	2.64	151	3.569(7)	3.62	111
N(16)-H(16)...S(21C')	3.76	164	4.749(9)	3.98	84
N(16)-H(16)...S(22)	3.95	90	4.079(8)	4.83	114
N(16)-H(26)...S(12A)	2.89	127	3.594(8)	3.21	85
N(16)-H(26)...S(12")	3.07	127	3.769(9)	3.11	134
N(16)-H(26)...S(21A")	3.07	125	3.750(8)	3.50	90

**Table 5** Distances and angles in the title compounds of Chapter 2

Atom	Zn-N distances	N-C in T	C-S in T	N-C-S angles	Zn-N-C angles
EnZ2t					
N(1)	1.955(10)	1.167(12)	1.594(10)	178.3(8)	178.2(7)
N(2)	1.936(8)	1.164(11)	1.614(9)	179.0(8)	168.7(8)
N(3)	2.078(7)				
N(6)	2.037(7)				
1MenZ2T					
N(1)	1.931(11)	1.136(13)	1.636(13)	177.6(13)	170.3(12)
N(2)	1.921(10)	1.146(13)	1.633(13)	178.8(10)	176.7(12)
N(3)	2.038(9)				
N(6)	2.045(8)				
S2MenZ2T					
N	1.91(3)	1.16(2)	1.62(3)	178(1)	164(1)
N(3)	2.05(2)				
G2MenZ2T					
N(1)	1.92(2)	1.15(2)	1.62(2)	177(2)	176(2)
N(2)	1.928(14)	1.13(2)	1.63(2)	178(2)	166.7(14)
N(3)	2.045(11)				
N(6)	2.022(12)				
3MenZ2T					
N(11)	1.927(8)	1.152(9)	1.599(9)	179.8(8)	168.6(7)
N(12)	1.936(7)	1.159(9)	1.616(10)	178.1(9)	162.6(7)
N(13)	2.060(7)				
N(16)	2.037(7)				
N(21)	1.923(8)	1.15(1)	1.59(1)	179.3(9)	161.6(8)
N(22)	1.933(9)	1.12(1)	1.60(1)	177(1)	171.0(9)
N(23)	2.059(7)				
N(26)	2.022(8)				

Table 6 N-Zn-N angles

Angle	EnZ2t	1MenZ2T	S2MenZ2T	G2MenZ2T	3MenZ2T		Mean
					Mol. 1	Mol. 2	
N(1)-Zn-N(2)	116.5(3)	111.5(4)	111(1)	112.2(6)	116.5(3)	110.7(3)	113.1{25}
N(1)-Zn-N(3)	109.0(3)	113.5(4)	110.7(9)	111.9(6)	112.5(3)	116.4(3)	
N(1)-Zn-N(6)	108.8(3)	110.0(4)	117.4(8)	116.6(7)	112.7(3)	122.4(3)	
N(2)-Zn-N(3)	113.3(3)	119.5(4)	117.4(8)	112.3(5)	110.9(3)	107.1(4)	
N(2)-Zn-N(6)	119.1(3)	113.3(4)	110.7(4)	114.1(6)	112.5(3)	110.0(4)	
N(3)-Zn-N(6)	85.9(2)	86.4(4)	87.8(6)	87.4(4)	88.4(3)	87.7(4)	87.3{9}
Mean	108.8{3}	109.0{4}	109.2{8}	109.1{6}	108.9{3}	109.1{4}	

Table 7 Crystal Data

Parameter	EnZT	1MenZT	S2MenZT	G2MenZT	3MenZT
Formula	C <sub>4</sub> H <sub>8</sub> N <sub>4</sub> S <sub>2</sub> Zn	C <sub>5</sub> H <sub>10</sub> N <sub>4</sub> S <sub>2</sub> Zn	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> S <sub>2</sub> Zn	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> S <sub>2</sub> Zn	C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> S <sub>2</sub> Zn
FW	241.6	255.7	269.7	269.7	283.7
Crystal size.	0.03,0.25,0.25	0.07,0.15,0.30	0.06,0.2,0.35	0.1,0.15,0.27	0.07,0.07,0.3
$\mu$ , cm	74.6	66.2	60.6	59.5	54.1
Max/min	1.00-0.84	1.00-0.32	1.00-0.60	1.00-0.65	1.00-0.63
$\theta$ range	6-60.0/22	5.9-60.0/25	4.2-60.2/25	5.1-62/25	2.5-62/25
A, Å	7.963(2)	14.076(1)	8.667(5)	11.827(2)	13.378(2)
B, Å	8.736(3)	15.084(2)	12.46(2)	12.928(2)	12.965(5)
C, Å	13.389(2)	9.906(1)	11.51(1)	7.696(2)	14.969(2)
$\alpha$ , °	90	90	90	90	90
$\beta$ , °	95.34(2)	90	112(1)	90	91.85(1)
$\gamma$ , °	90	90	90	90	90
V, Å <sup>3</sup>	927.5(7)	2103.5(6)	1154(6)	1176.4(7)	2594(2)
Z	4	8	4	4	8
$\rho_c$ , g/cm <sup>3</sup>	1.730(2)	1.615(1)	1.553(5)	1.522(1)	1.452(1)
F(000)	488	1040	552	552	1168
Space	Pbca	C2/c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> /n	

Parameter	EnZ2T	1MenZ2T	S2MenZ2T	G2MenZ2T	3MenZ2T
$h, k, l$ ranges	0/8 0/9 –15/14	0/15 0/16 0/11	0/12 –8/8 –9/8	0/13 0/14 0/8	0/15 0/14 -16/16
Reflections:					
Total	1379	1563	3602	1037	4252
Unique total	1379	1563	900	1037	4058
Unique used			374		1486
Program	SHELXL	SHELXL	TEXSAN	SHELXL	TEXSAN
100R merge			4.2		5.1
weighting	SHELXL	SHELXL	unit	SHELXL	sigma
data/param	13.8	14.3	6.1	8.2	5.9
100R;100R <sub>w</sub>	100R1;100 <sub>w</sub>	5.0, 12.9	3.7; 8.6	5.1; 5.5	3.3 3.5
R2	100R1;100 <sub>w</sub>	11.5; 16.5	20.7; 15.5	4.4; 10.9 15.3; 15.2	
GOF	1.03	0.92	0.99	1.05	1.27
Residual std	-0.51/0.84	-0.45/0.38	-0.38/0.37	-0.50/0.59	-0.24/0.29

**Table 8 Positional parameters and isotropic temperature factors of nonhydrogen and H(N) atoms in the title compounds**

Atom	x	y	z	Ueq
<b>enZ2T</b>				
Zn	0.1841(1)	0.3366(2)	0.6140(1)	0.045(1)
N(1)	0.1802(10)	0.5604(11)	0.6151(6)	0.062(2)
C(1)	0.1825(g)	0.6939(11)	0.6162(6)	0.041(2)
S(1)	0.1818(3)	0.8762(3)	0.6203(2)	0.050(1)
N(2)	0.0014(9)	0.2342(10)	0.6727(5)	0.052(2)
C(2)	-0.0925(9)	0.1512(11)	0.7065(6)	0.040(2)
S(2)	-0.2237(3)	0.0348(3)	0.7515(2)	0.047(1)
N(3)	0.2172(8)	0.2615(8)	0.4699(5)	0.047(2)
H(31)	0.133	0.190	0.449	0.056
H(32)	0.212	0.347	0.425	0.056
C(4)	0.3856(11)	0.1886(11)	0.4740(7)	0.052(2)
C(5)	0.5056(10)	0.2629(11)	0.5548(6)	0.047(2)
N(6)	0.4253(8)	0.2648(8)	0.6508(5)	0.040(2)
H(61)	0.483	0.333	0.696	0.048
H(62)	0.426	0.165	0.678	0.048
<b>1MenZ2T</b>				
Zn	0.2559(1)	0.4228(1)	0.2647(1)	0.059(1)
N(1)	0.1686(7)	0.5037(8)	0.3511(11)	0.074(4)
C(1)	0.1190(8)	0.5584(9)	0.3862(12)	0.054(3)
S(1)	0.0458(2)	0.6345(2)	0.4414(4)	0.074(1)
N(2)	0.2012(7)	0.3705(7)	0.1059(10)	0.062(3)
C(2)	0.1727(7)	0.3398(8)	0.0081(13)	0.049(3)
S(2)	0.1335(2)	0.2975(2)	-0.1330(3)	0.071(1)
N(3)	0.3288(6)	0.3450(6)	0.3973(10)	0.064(3)
H(3)	0.314	0.285	0.378	0.077
C(31)	0.3057(10)	0.3618(9)	0.5400(12)	0.095(5)
C(4)	0.4303(7)	0.3609(9)	0.3656(15)	0.088(5)
C(5)	0.4465(8)	0.4571(9)	0.3350(14)	0.091(5)
N(6)	0.3825(6)	0.4850(7)	0.2289(9)	0.065(3)
H(61)	0.407	0.469	0.143	0.078
H(62)	0.375	0.548	0.231	0.078

**s2MenZ2T**

Zn	0	0.15329(6)	3/4	0.071(1)
N	0.1276(5)	0.0669(3)	0.8895(4)	0.085(1)
C	0.1920(6)	-0.0047(4)	0.9544(5)	0.063(1)
S	0.2872(2)	-0.10360(9)	1.0445(1)	0.083(1)
N(3)	0.1439(4)	0.2717(3)	0.7191(3)	0.061(1)
H(3)	0.153	0.257	0.639	0.073
C(31)	0.3097(6)	0.2820(4)	0.8144(5)	0.085(3)
C(4)	0.0423(6)	0.3707(3)	0.7045(5)	0.076(1)

**g2MenZ2T<sup>a</sup>**

Zn	0.9625(2)	0.7252(2)	0.1245(3)	0.055(1)
N(1)	1.0641(14)	0.6446(12)	-0.0146(21)	0.076(5)
C(1)	1.1202(16)	0.5967(13)	-0.1055(26)	0.059(5)
S(1)	1.1970(4)	0.5239(4)	-0.2297(7)	0.074(2)
N(2)	0.8209(11)	0.6553(11)	0.1644(19)	0.065(5)
C(2)	0.7510(14)	0.5980(14)	0.1900(24)	0.059(5)
S(2)	0.6475(4)	0.5179(4)	0.2261(7)	0.074(2)
N(3)	1.0365(8)	0.7734(8)	0.3507(14)	0.055(3)
C(31a)	0.9649	0.7495	0.4947	0.142(27)
C(31b)	0.9967	0.7183	0.5077	0.096(16)
C(32a)	1.1562	0.7432	0.3847	0.121(28)
C(32b)	1.1609	0.7654	0.3357	0.129(18)
C(4a)	1.0436	0.8824	0.3420	0.136(32)
C(4b)	0.9900	0.8830	0.3728	0.086(13)
C(5)	1.0014(17)	0.9374(11)	0.1900(14)	0.103(9)
N(6)	0.9462(13)	0.8762(9)	0.0604(15)	0.059(4)
H(61)	0.979	0.889	-0.050	0.071
H(62)	0.868	0.894	0.054	0.071

**3MenZ2T**

Zn(I)	0.22355(9)	0.21577(9)	0.24297(7)	0.062(1)
N(11)	0.2767(5)	0.3172(5)	0.3258(5)	0.063(3)
C(11)	0.3163(6)	0.3640(6)	0.3819(6)	0.057(3)
S(11)	0.3713(2)	0.4286(2)	0.4602(2)	0.092(1)
N(12)	0.1789(6)	0.0871(5)	0.2939(5)	0.072(3)
C(12)	0.1417(7)	0.0272(7)	0.3397(6)	0.062(3)
S(12)	0.0919(2)	-0.0547(2)	0.4064(2)	0.078(1)
Zn(2)	0.79657(9)	0.01667(6)	0.34808(6)	0.061(1)
N(21)	0.8869(6)	0.1317(6)	0.3587(5)	0.073(3)
C(21)	0.9419(8)	0.1913(8)	0.3883(6)	0.066(4)
S(21)	1.0176(2)	0.2753(2)	0.4290(2)	0.107(1)
N(22)	0.6595(7)	0.0623(7)	0.3550(7)	0.096(4)
C(22)	0.5847(8)	0.1013(7)	0.3580(7)	0.072(4)
S(22)	0.4805(2)	0.1601(2)	0.3668(2)	0.109(1)
N(13)	0.1161(5)	0.2760(6)	0.1562(5)	0.067(3)
C(131)	0.0756(9)	0.3764(8)	0.1825(9)	0.125(5)
C(132)	0.0329(7)	0.2042(8)	0.1401(6)	0.084(4)
C(14)	0.1714(9)	0.2897(6)	0.0730(7)	0.096(4)

C(15)	0.2444(8)	0.2057(9)	0.0588(6)	0.090(4)
N(16)	0.3123(6)	0.1938(5)	0.1365(5)	0.068(3)
H(16)	0.358	0.250	0.136	0.079
C(161)	0.3711(9)	0.0980(9)	0.1317(7)	0.100(4)
N(23)	0.8054(7)	-0.0711(7)	0.2340(3)	0.082(3)
C(231)	0.9010(9)	-0.0569(8)	0.1878(6)	0.101(4)
C(232)	0.722(1)	-0.046(1)	0.1683(8)	0.161(6)
C(24)	0.790(1)	-0.1748(10)	0.266(1)	0.147(6)
C(25)	0.844(1)	-0.1919(8)	0.349(1)	0.136(6)
N(26)	0.8171(6)	-0.1147(6)	0.4192(5)	0.082(3)
H(26)	0.874	-0.105	0.458	0.098
C(261)	0.7316(9)	-0.1410(10)	0.4751(8)	0.125(5)

a) In the final refinement, the positional parameters of the atoms in split positions (a, b) were kept fixed but their U(eq) were refined.

## Chapter 3

In Chapter 2, the structures of a series of compounds containing the thiocyanate ion coordinated to a Zn atom were examined. The special feature of these compounds was that they contained hydrogen bonding which was exclusively between an N-H group and the sulphur atom of the thiocyanate group. However, when the nitrogen atom is not coordinated to a metal<sup>1</sup>, both the nitrogen and the sulphur end of the thiocyanate ion are capable of hydrogen bonding. The subject therefore to be examined in this chapter is the normal preference of the thiocyanate ion in hydrogen bonding when both the nitrogen and the sulphur ends of the ion are available for this type of bonding.

The Cambridge Structural Database (Jan. 1998 Issue) contains 1925 structures which contain the thiocyanate ion. Of these, only 217 do not have the ion coordinated<sup>2</sup> to a metal atom. The 217 structures were scanned to see how many had an X-H...NCS interaction and how many had an X-H...SCN interaction. The maximum H...N distance in the search was set at 2.4Å, which is the lower limit of the Van der Waals interaction, and the

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<sup>1</sup> In one of the structures that follows, an N-H hydrogen atom "creeps in" and manages to form a hydrogen bond to a nitrogen atom which itself is coordinated to a metal.

<sup>2</sup> The "coordinated to a metal criterion" does not exclude the compounds containing the groups 1 and 2 metals, since the CSD does not classify the interactions between (say) K<sup>+</sup> and (SCN) as a bond represented by a line in a conventional structural diagram.

maximum H...S distance was set at 2.5Å which represents a reasonable upper limit of a significant bond. The X atom of the X-H system was set to "any atom" but in both searches only interactions involving the C-H, O-H and N-H groups were found. From the 217 structures, 51 contained at least one X-H...N interaction, but two of these structures were repeat determinations to give only 49 uniquely different structures with the interaction. Of the 49 structures, three were co-crystallisations of an organic molecule with a group 1 or group 2 metal thiocyanate ( $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$ ). The histogram of the results of this search is shown in Figure 58, on page 116.

The search for the X-H...S bonds found only 17 structures with interactions within the range. Again two of these were the same repeat structure determinations, giving just 15 uniquely different structures. Three of these 15 structures are co-crystallisations of an organic molecule with a group 1 or 2 metal thiocyanate ( $\text{K}^+$ ,  $\text{Cs}^+$  or  $\text{Ca}^{2+}$ ). The histogram of this search is on p.117, Figure 59. 14 of the 15 structures also contained X-H...N(thiocyanate) interactions. The one structure that seems at first glance to contain an exclusive X-H...S interaction is the structure of phenacyl-kojate cesium thiocyanate [13]. In this structure the  $\text{Cs}^+$  ion is 7-coordinate with short contacts between both a nitrogen end and two sulphur ends of three symmetry-related ( $\text{SCN}^-$ ) ions. In addition there are five contacts to oxygen atoms of the organic molecule. Under these circumstances, the thiocyanate ion is not an isolated ion. This example (and the other examples of co-crystallisation of an organic molecule with a group 1 or 2 metal

thiocyanate) should be removed from the list for both X-H...N and X-H...S interactions. The final count then becomes 46 structures with the X-H...N interaction and 12 with the X-H...S interaction. All the structures with the X-H...S interaction now all also contain at least one X-H...N interaction. In 10 of these 12 cases the X-H...N interaction has an H...N distance shorter than 2.2Å which represents a strong hydrogen bond. Thus in at least 10 of the 12 cases, the X-H...N interaction can be regarded as the dominant hydrogen bonding interaction in the structure and the X-H...S interaction as a convenient, but not crucial, addition.

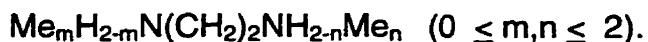
The structure of ammonium thiocyanate is not recorded in the CSD. The absence of a C-H bond excludes it from the compilation. This structure has been determined from neutron and from high-angle, low-temperature X-ray diffraction intensities [4]. The structure is thus very well determined and the deformation densities for the thiocyanate ion are available. The structure contains two N-H...N interactions with H...N distances of 1.936(1) and 1.964(1)Å and two N-H...S interactions with H...S distances of 2.350(1) and 2.358(1)Å. These distances are derived from neutron diffraction data where the position of the atom nucleus is determined. X-ray diffraction locates the centre of gravity of the electron cloud and for N-H distances, those determined from X-ray diffraction experiments are typically 0.05-0.1Å shorter than the true (neutron determined) inter-nuclear separation. Even when this X-ray to neutron bond distance correction is taken into account, the H...N distances still represent very strong N-H...N hydrogen bonds. It can be

argued for this structure that again the dominant hydrogen bonding interaction is the N-H...N interaction and that the logic of crystal packing coupled with the very simple shapes of the two packed species makes N-H...S interactions inevitable.

The ammonium thiocyanate structure should be added to the list extracted from the CSD, to give 47 structures containing isolated SCN<sup>-</sup> ions with X-H...N interactions of which 13 also have X-H...S interactions. These 13 are mostly a mixture of metal coordination complex cations and large organic cations and it is difficult to avoid the impression that the thiocyanate ion was simply used in these cases as a convenient, structurally well-behaved, counter anion to provide a crystalline sample for X-ray diffraction. Certainly an examination of this diverse sample yields little useful information about the competing preferences of X-H...NCS and X-H...SCN hydrogen bonding.

It was decided therefore to prepare a series of thiocyanate salts where the cation was an organo-ammonium salt. This series was designed to provide a graded ratio of N-H bonds to thiocyanate ion. It was also designed to provide a gradual change in cation geometry. It was hoped that this series would show some of the influences of both the availability of N-H bonds and the gradually changing packing problems that decided the selection of N-H...NCS and N-H...SCN interactions in the formation of the crystal.

Attempts were made to prepare the whole series of ethylenediamine salts:



However, even after 15 months some of the salts had not crystallised and the saturated solutions were still oils. Those salts that did crystallise were the ethylenediammonium ( $m,n=0$ ; **en2T**) salt itself, the *unsymmetrical* N,N-dimethylethylenediammonium ( $m=2, n=0$ ; **u2Men2T**)<sup>3</sup>, the N,N,N'-trimethyl ethylenediammonium ( $m=2, n=1$ ; **3Men2T**) and the N,N,N',N'-tetramethyl-ethylenediammonium ( $m,n=2$ ; **4Men2T**). The monomethylated and *symmetric* N,N' dimethylated ethylenediamine salts were prepared but so far have only produced oils. In addition to the ethylenediamine salts the N,N,N',N'-tetramethyl- propylenediammonium and butylenediammonium salts (**4Mpn2T**, **4Mbn2T**) were also prepared in crystalline form.

The next three salts are just structural variations on **4Men2T**. These are the N,N' -dimethylpiperazine (**s2Mpiz2T**), Dabco (diaza-bicyclo[2.2.2]octane (**Da2Tw**) and quinuclidine (**QT**) salts with thiocyanic acid. In these, the flexibility of the  $-(\text{CH}_2)_2-$  skeleton is progressively reduced.

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<sup>3</sup> The N,N-dimethylethylenediamine salt recrystallised after standing for 13 months and came from a preparation which had originally used N,N'-dimethyl-ethylenediamine as the starting material. The probable explanation of this is discussed in the experimental section in the next chapter, but it is thought that the presence of the  $(\text{SCN})^-$  in the mixture makes the methyl groups mobile. If the methyl groups are mobile, this will make the crystallisation of the mono-methylated ethylenediamine very difficult.

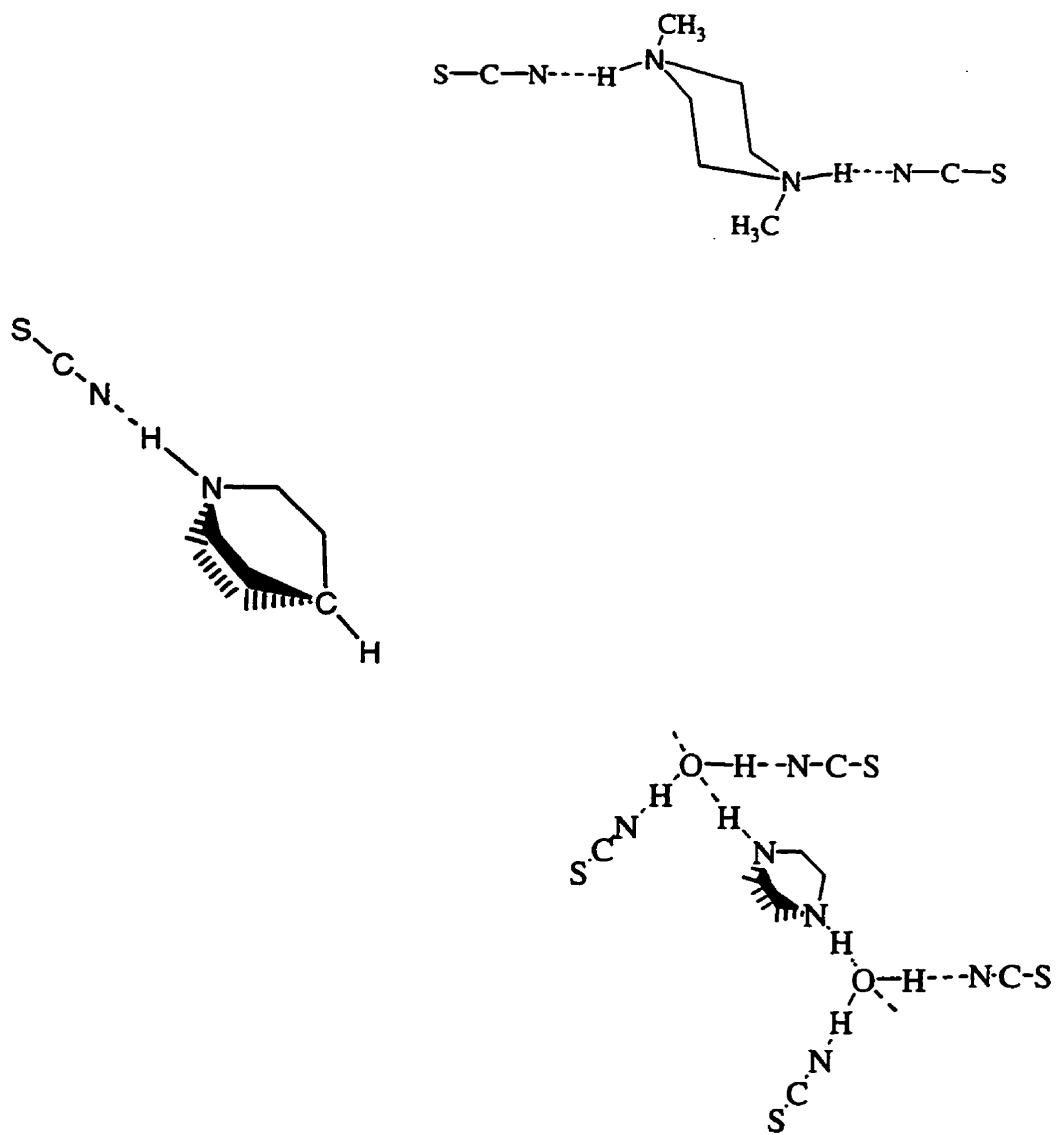


Figure 24.  $\text{N},\text{N}'$  dimethylpiperazine , Dabco (diaza-bicyclo[2,2,2]octane) and quinuclidine thiocyanates

The N,N'-dimethylethylenediammonium salt of  $[\text{Zn}(\text{NCS})_4]^{2-}$  (**s2MenZ4T**), the corresponding ethylenediammino salt (**enZ4T**) and the *tris*-ethylenediamine-zinc(2+) ( $\text{SCN}^-$ )<sub>2</sub> (**3enZ2T**) salts were also prepared. The (**s2MenZ4T**) and (**enZ4T**) salts strictly speaking do not belong in this series since in each case the four ( $\text{SCN}^-$ ) ions are coordinated to the zinc atom. However these two salts do throw some light onto the hierarchy of the  $\text{SCN}^-$  hydrogen bonding and therefore they are retained here.

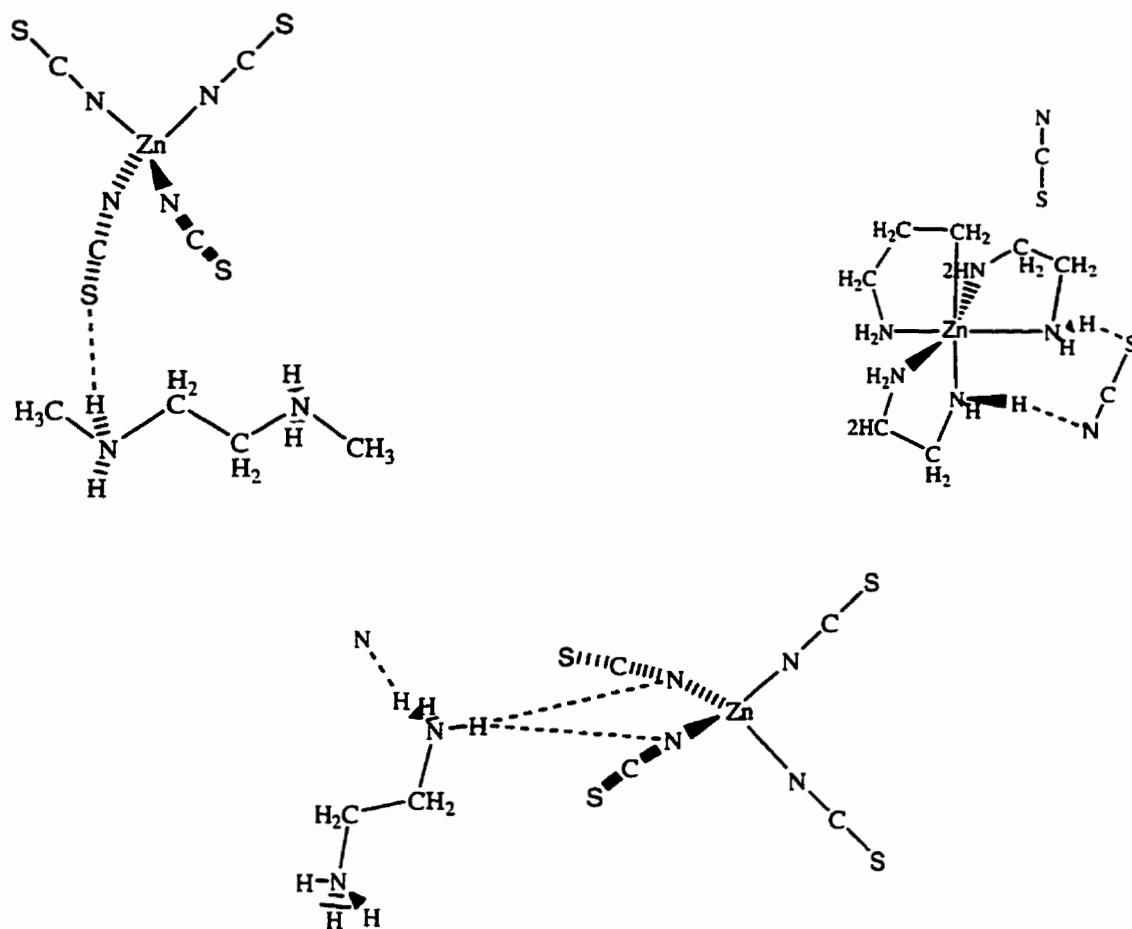


Figure 25 The N,N'-dimethylethylenediammonium , ethylenediammonium salt and the triethylenediamine zinc(2+) ( $\text{SCN}^-$ )<sub>2</sub>

Other structural arrangements of the cation were examined with the salts of terpyridine (**Tp3T**), betaine (**BeT**) and 2-aminoethanethiol (cysteamine), which formed cystamine ( $\text{NH}_2(\text{CH}_2)_2\text{S}_2$ ) with an S-S bond (through air oxidation) before crystallising as the thiocyanate salt (**Cy2T**). Finally the ( $\text{SCN}^-$ ) salt of the proton sponge (**spgT**) was prepared and the crystals examined by X-ray diffraction.

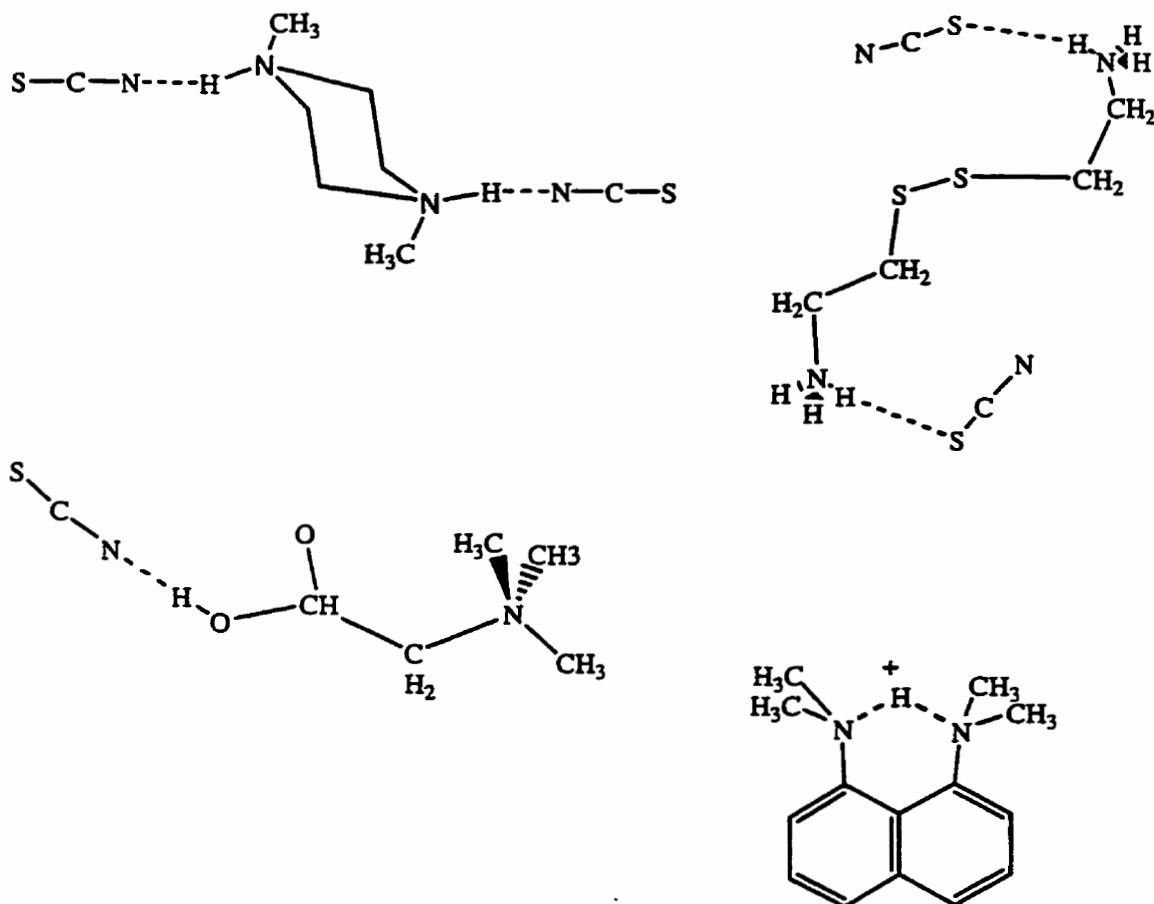


Figure 26 Terpyridinium, betaine, cystamine and the classical proton sponge thiocyanates

These 16 salts produce quite a range of environments for the SCN<sup>-</sup> ion. To introduce some order into this variety, the salts in the series are classified according to the ratio of N-H bonds in the cation to the number of SCN<sup>-</sup> anions.

Table 9 Ratio of N-H bonds in the cation to the number of SCN<sup>-</sup> anions

Ratio	Codename	Full name of thiocyanate complex
1:1	QT 4Men2T 4Mbn2T BeT	Quinuclidinium Tetramethylethylenediammonium Tetramethylbutylenediammonium Betaine
2:2	4Mpn2T Da2Tw s2Mpiz2T	Tetramethylpropylenediammonium Dabco Dimethylpiperazinium
3:3	Tp3T 3spg3T	Terpyridinium 1,8-bis(dimethylamine)naphthalene
4:4	s2MenZ4T	<i>sym</i> -dimethylethylenediammonium zinc(SCN) <sub>4</sub>
3:2	3Men2T	Trimethylethylenediammonium
2:1	U2Men2T	<i>unsym</i> -dimethylethylenediammonium
3:1	Cy2T en2T	Cystamine Ethylenediammonium
6:4	enZ4T	Ethylenediammonium zinc(SCN) <sub>4</sub>
12:2	3enZ2T	Tris(ethylenediamine)zinc(2+)

**Quinuclidinium thiocyanate (QT).** There is a single strong linear hydrogen bond between the quinuclidinium fragment N-H and the nitrogen atom of the  $(SCN^-)$  anion. These isolated units pack together in the unit cell as shown in the packing diagram.

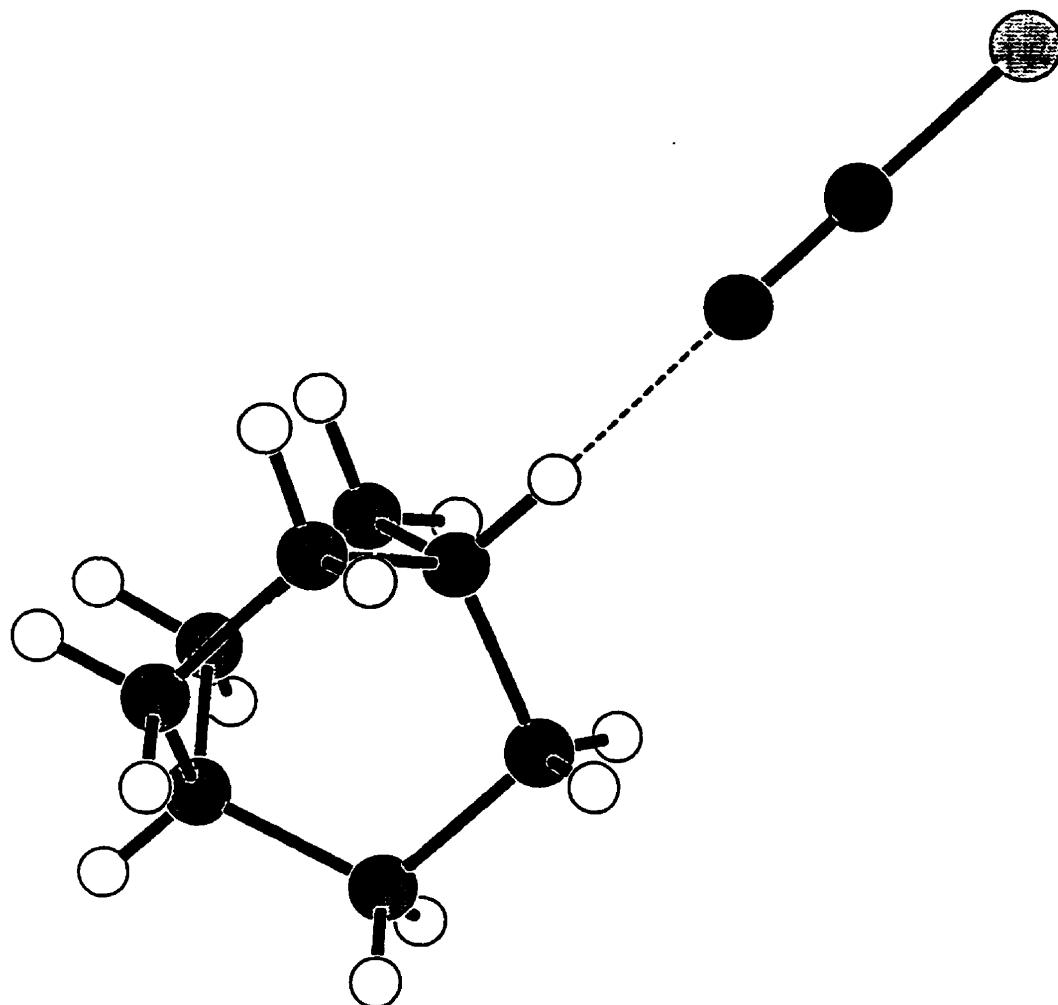


Figure 27. QT, quinuclidinium thiocyanate

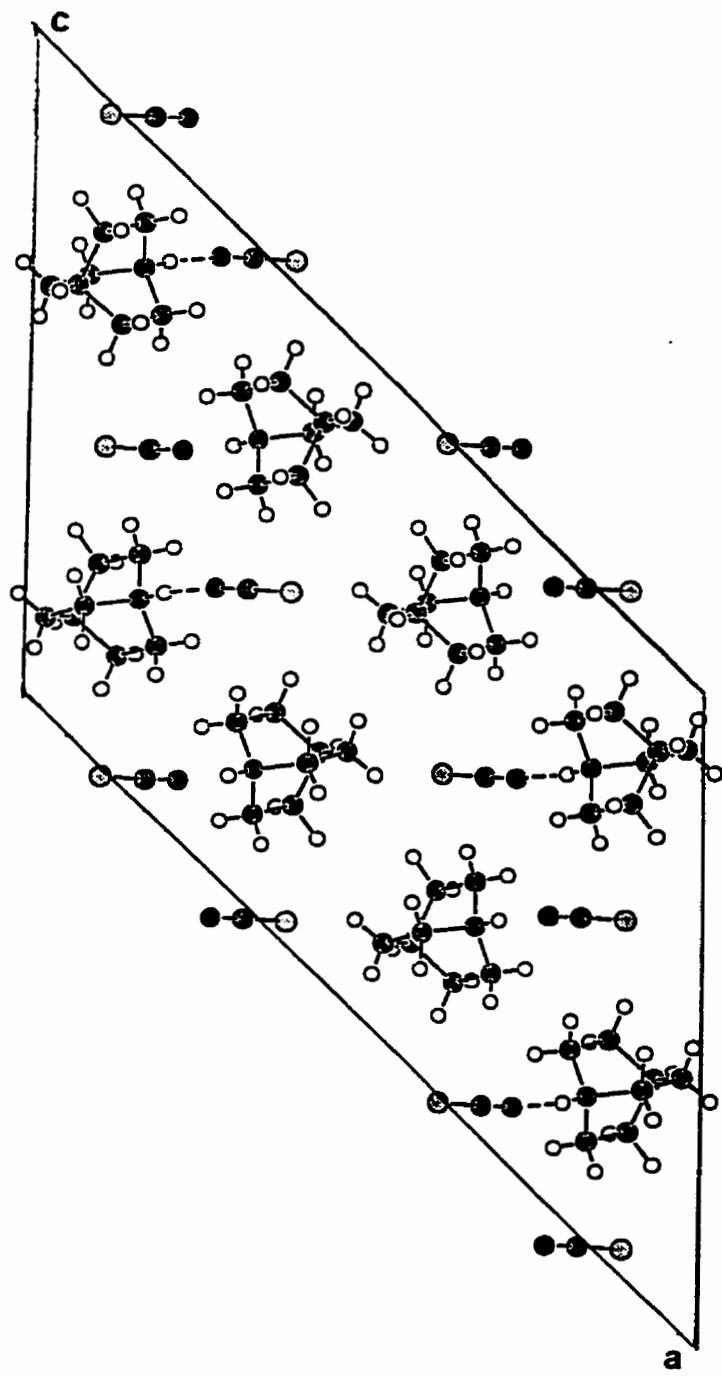


Figure 28. Packing of quinuclidinium thiocyanate

**4Men2T**

There is a single hydrogen available for hydrogen bonding on each of the two nitrogens. These nitrogens are related by a center of symmetry. There is one thiocyanate ion per nitrogen, and the single unbranched hydrogen bond is formed with nitrogen of the thiocyanate. The centro-symmetric structure packs together in the unit cell as shown in the following packing diagram.

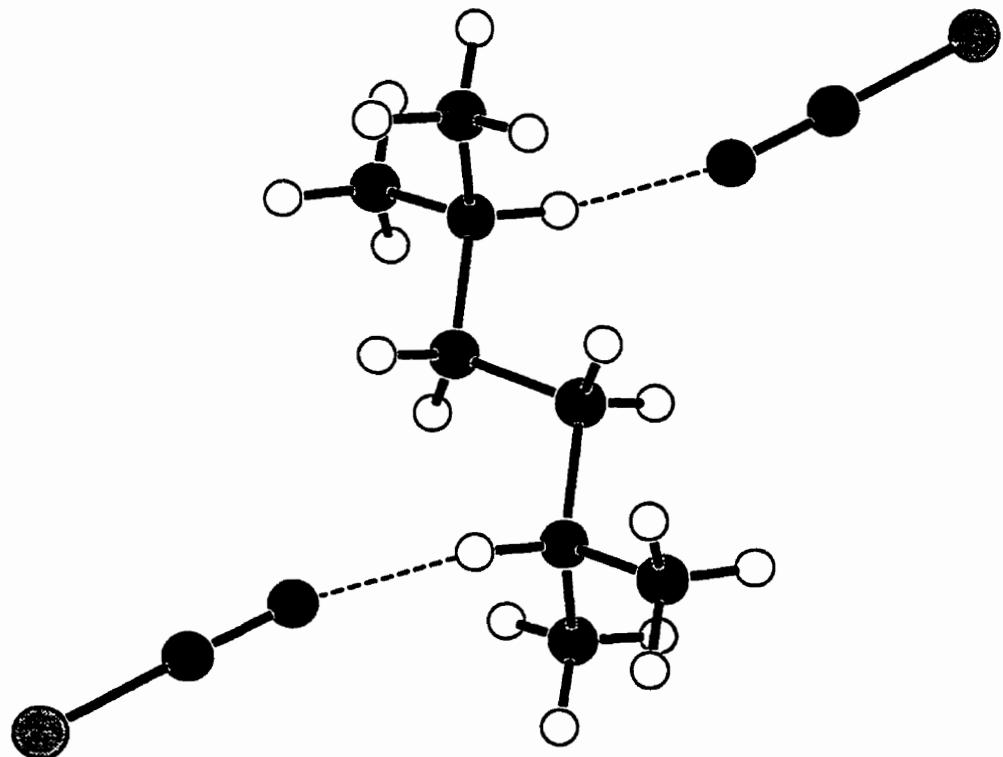


Figure 29. 4Men2T, Tetramethylethylenediammonium thiocyanate

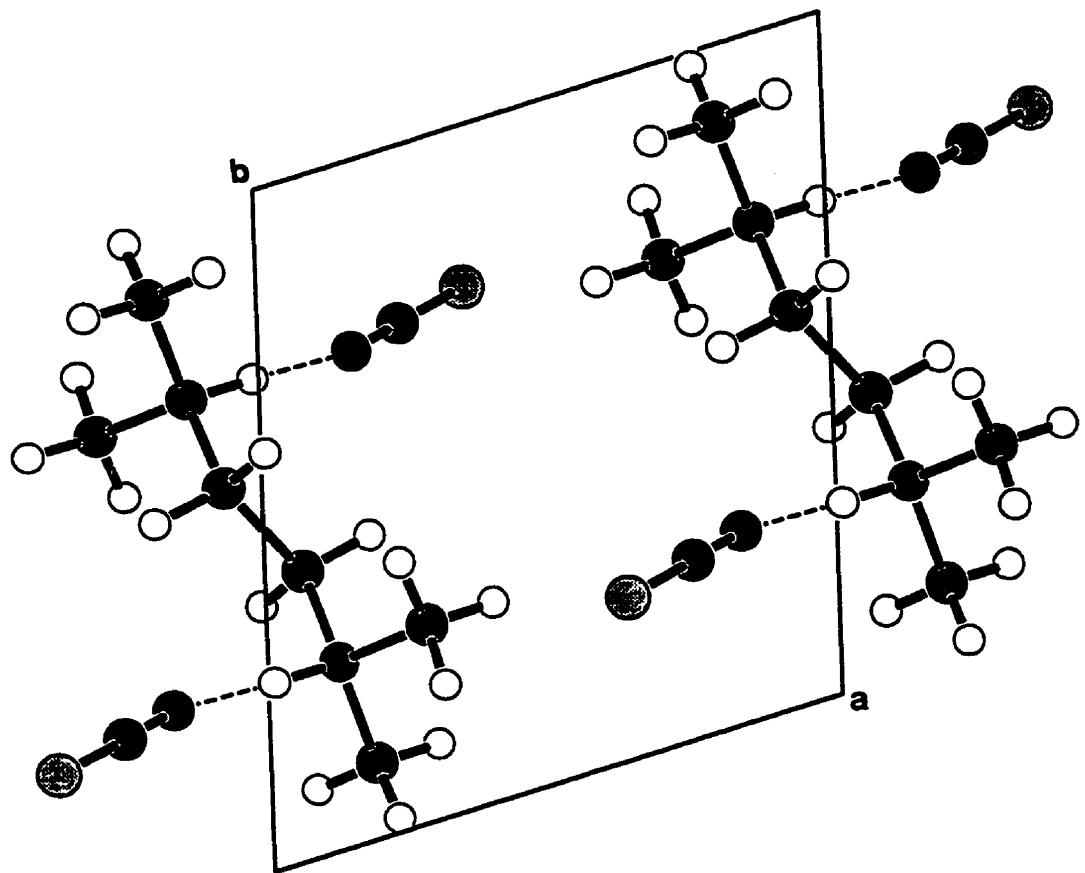


Figure 30. Packing of 4Men2T

**4Mbn2T**

This is a longer-chain version of the previous structure, and again has a center of symmetry. Again, there is a single H(N) per nitrogen atom available for hydrogen bonding, and it strongly hydrogen bonds with the nitrogen of the thiocyanate ion.

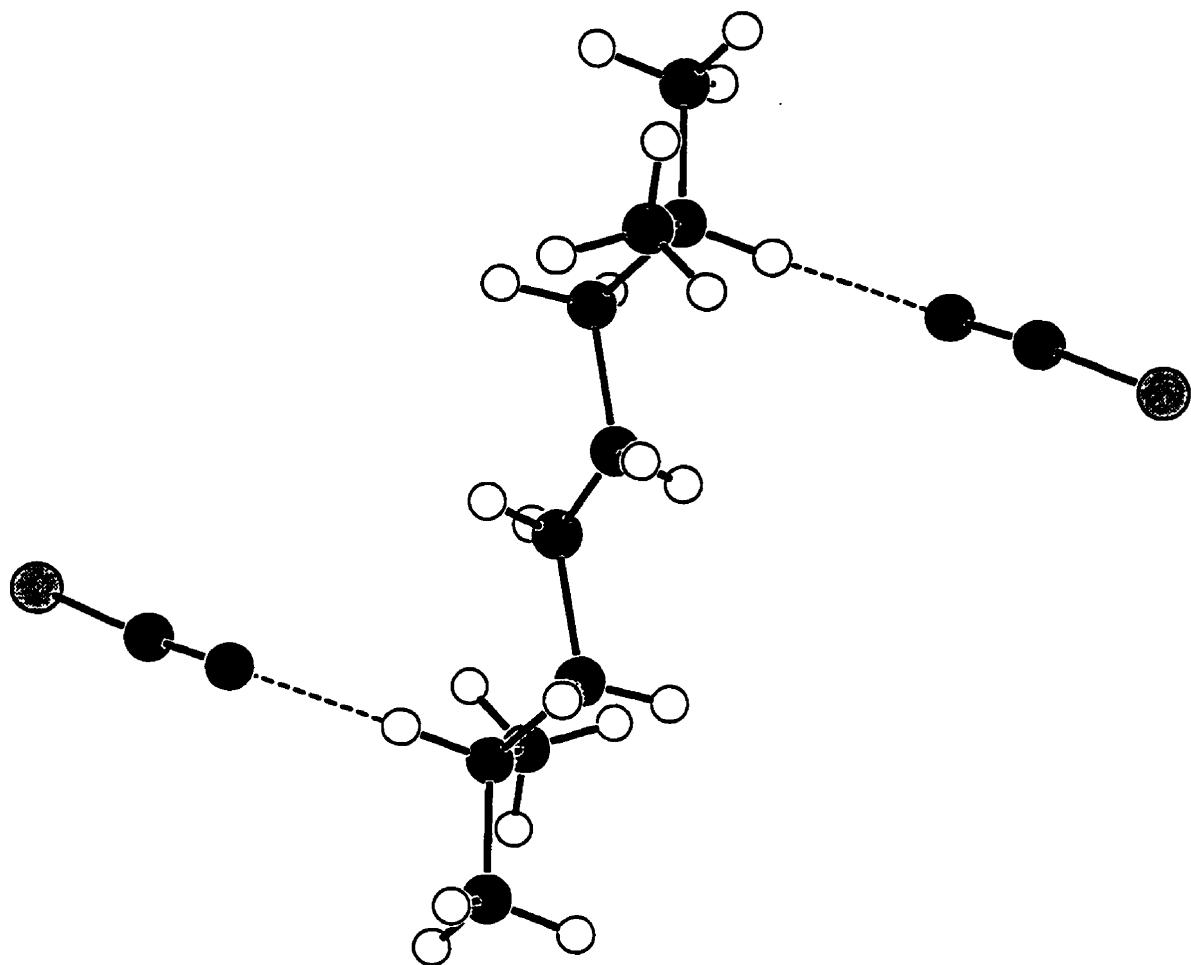


Figure 31. 4Mbn2T, tetramethylbutylenediammonium thiocyanate

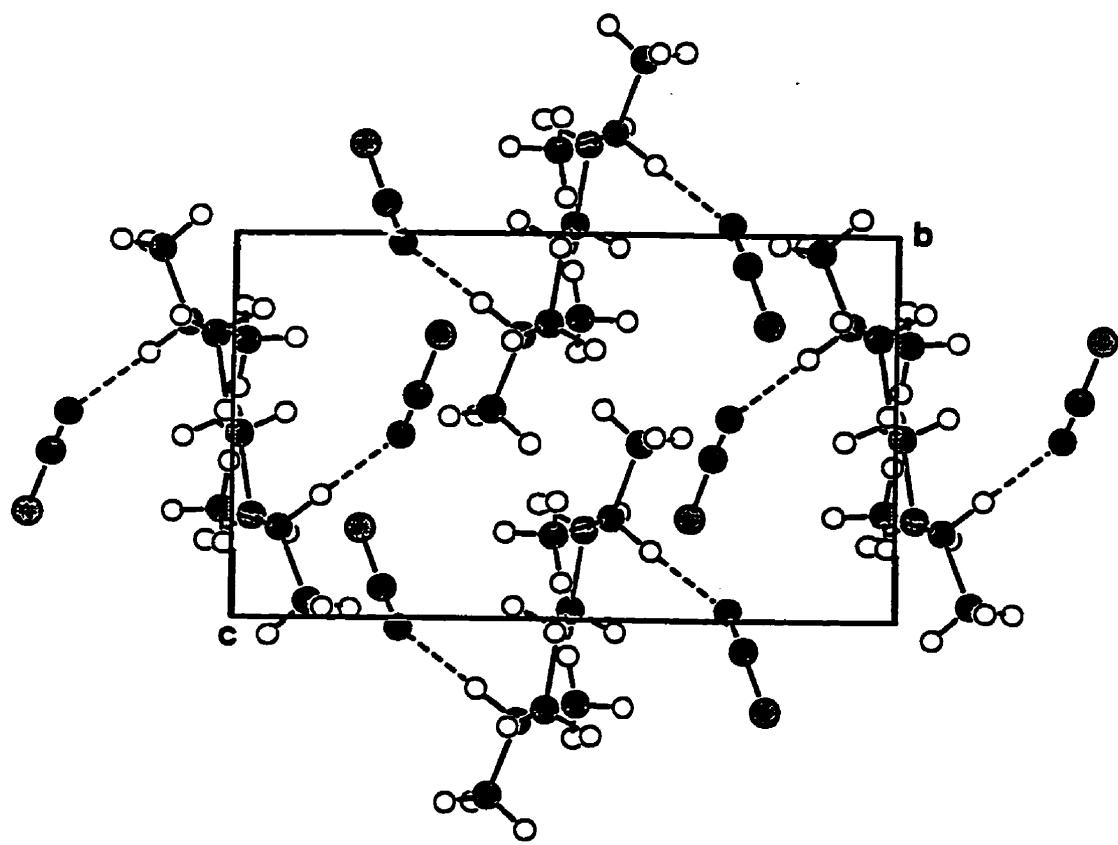


Figure 32. Packing of 4Mbn2T

**BeT**

In the structure of betaine, the hydrogen bond occurs with an H(O) atom instead of with an H(N) atom. Each nitrogen of the thiocyanate ion is hydrogen-bonded to the H(O) atom of the betaine molecule.

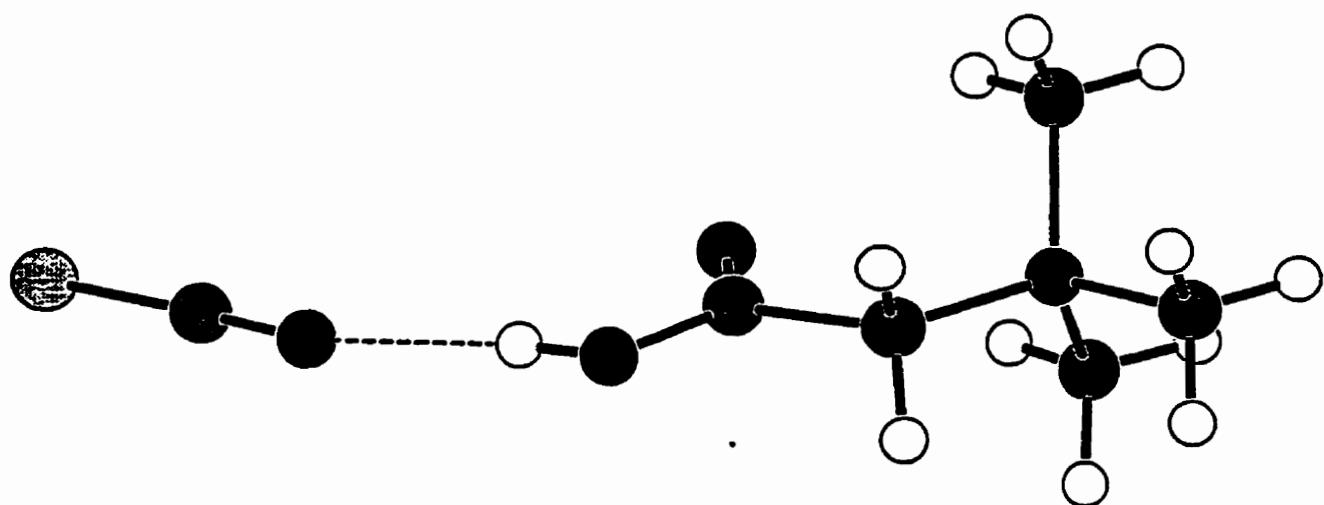


Figure 33. BeT, betaine thiocyanate

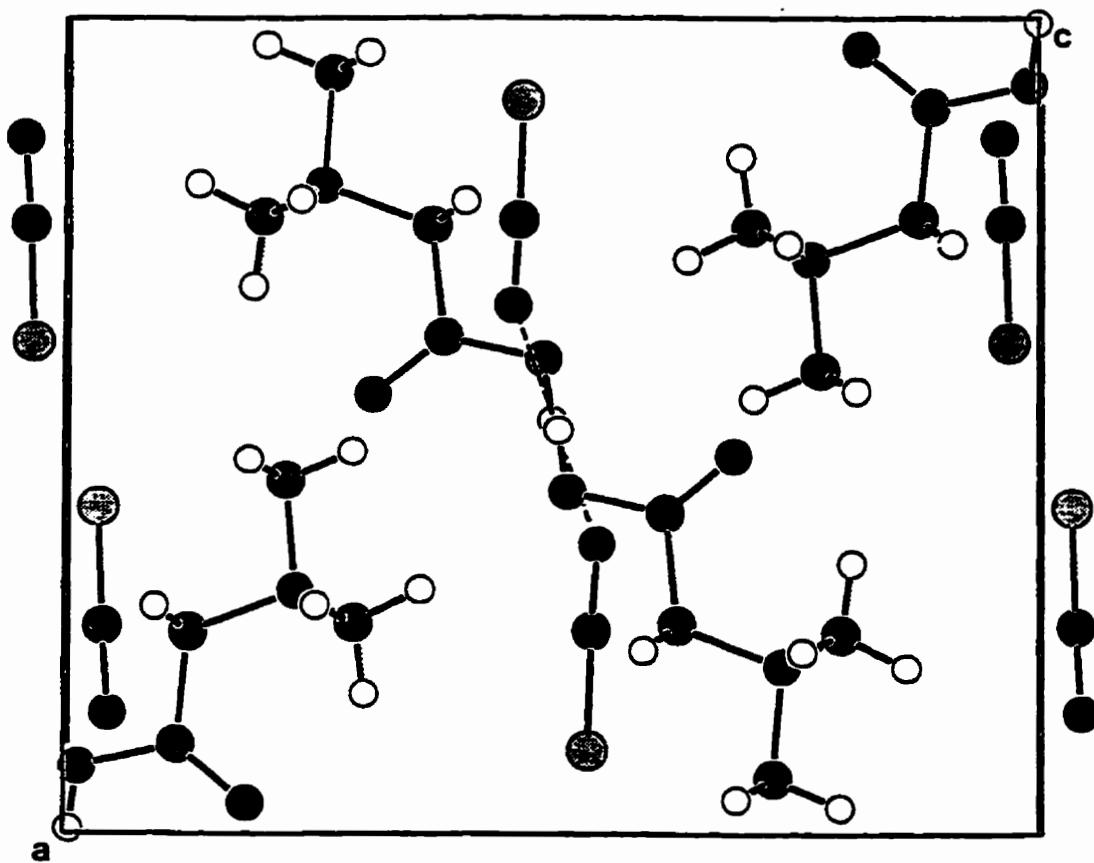


Figure 34. Packing of BeT

**4Mpn2T**

There is again only one hydrogen available for hydrogen bonding on each nitrogen. There are now two thiocyanate anions, and each nitrogen of the thiocyanate strongly hydrogen-bonds with one H(N) of the tetramethyl-propylenediammonium cation. There are no branched bonds, each nitrogen is singly coordinated. The packing shows no further interactions.

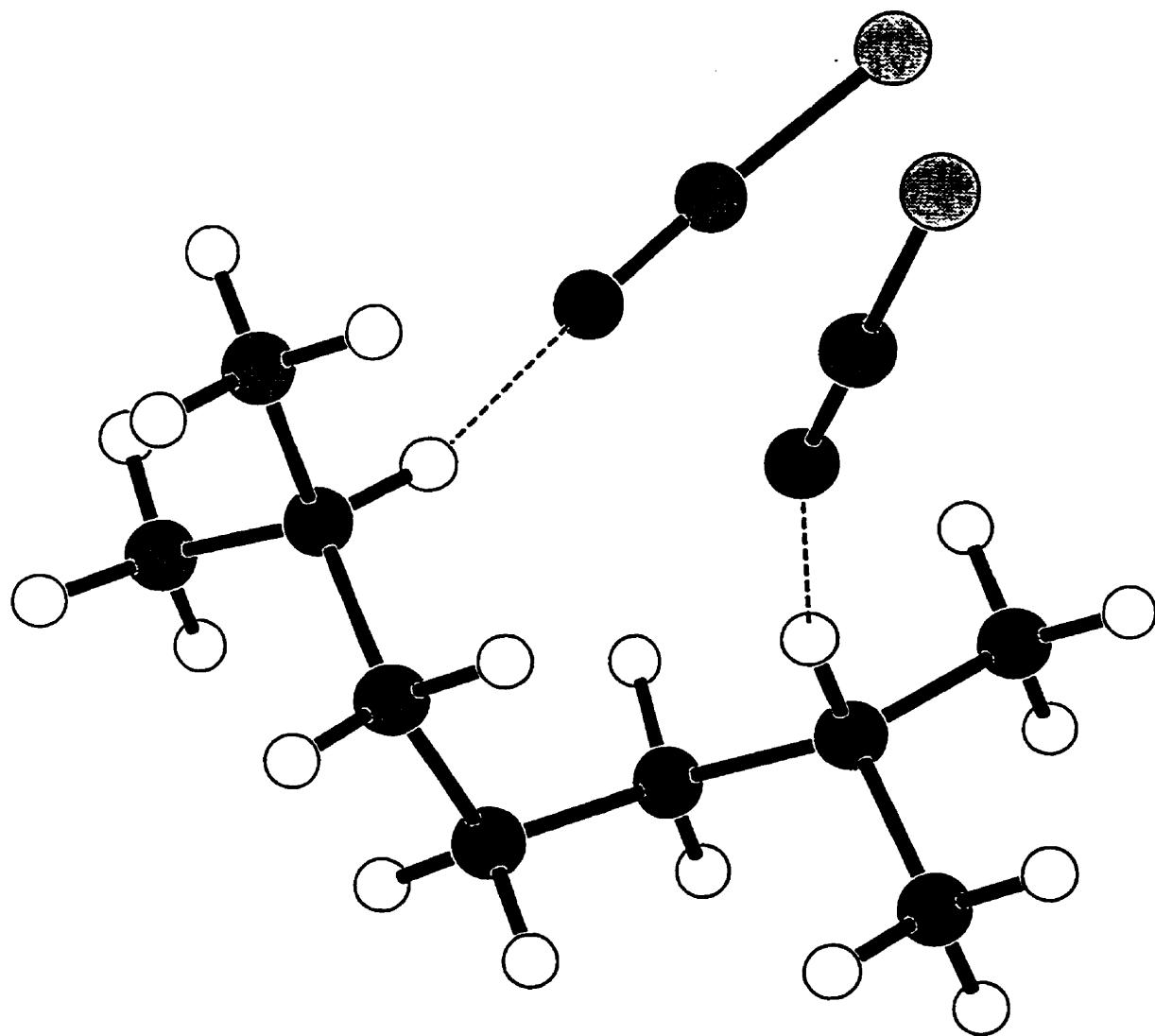


Figure 35. 4Mpn2T, tetramethylpropylenediammonium thiocyanate

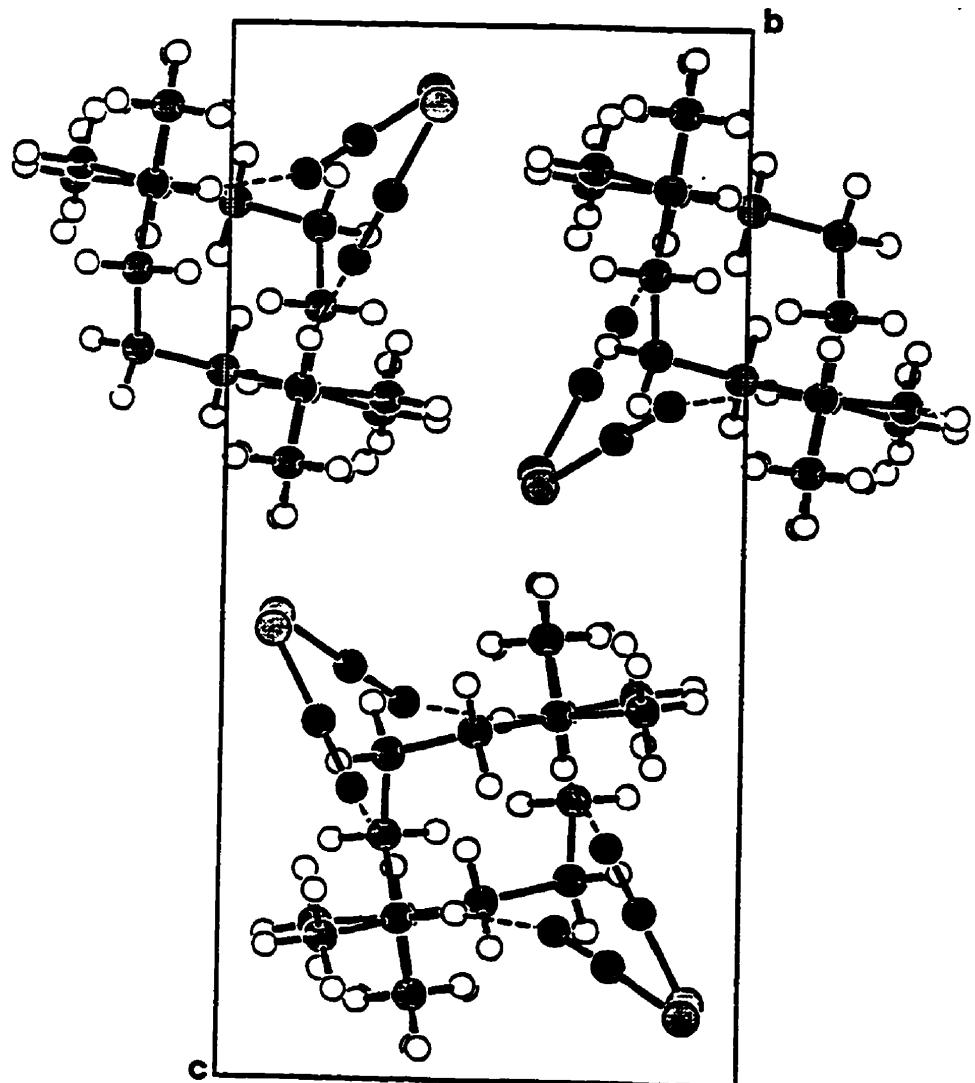


Figure 36. Packing of 4Mpn2T

**Da2Tw**

Both H(N) atoms of the dabco cation are available for hydrogen bonding.

This occurs not with the thiocyanates, but with the water molecule. The water molecule is then hydrogen bonded to the nitrogen atoms of the thiocyanate anions. Only unbranched hydrogen bonds exist. The molecules pack in columns, with the water molecules between each dabco cation, and the thiocyanates branching off each column.

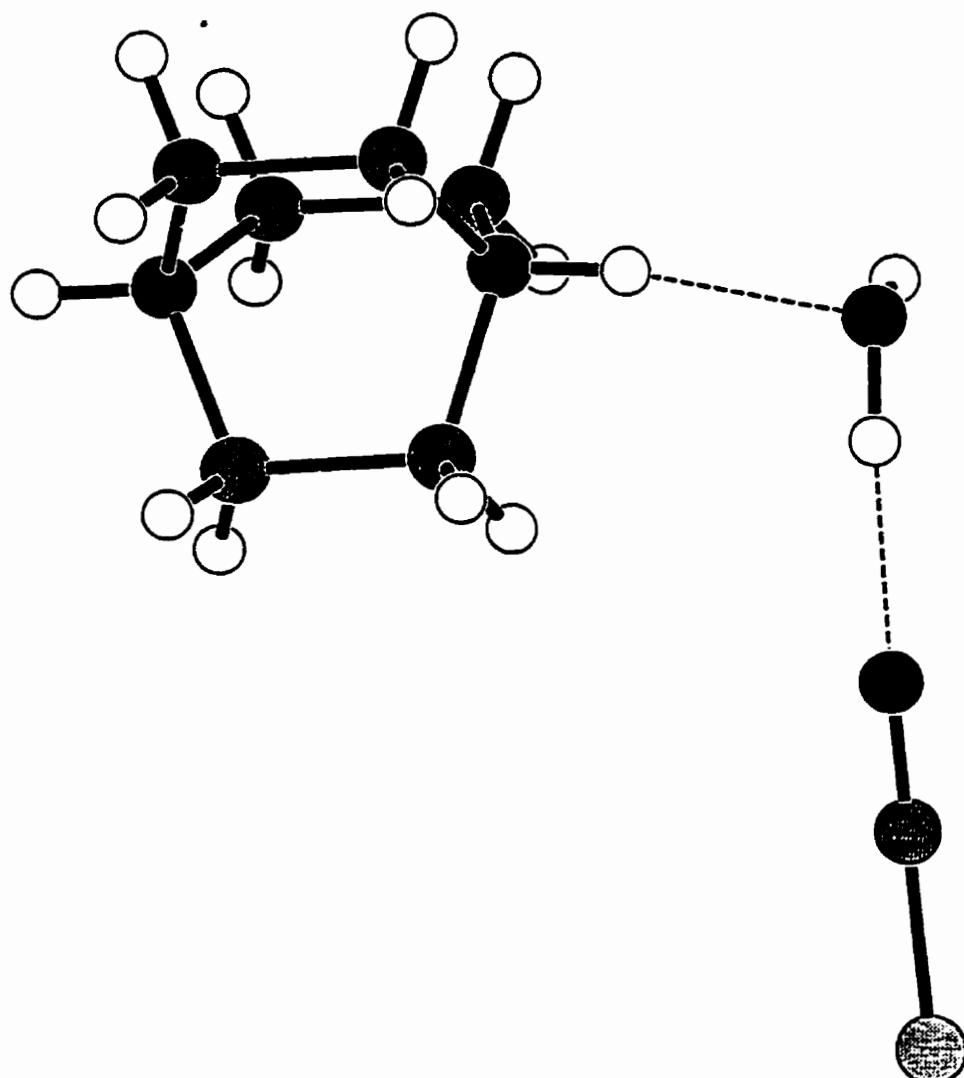


Figure 37. Da2Tw, dabco thiocyanate

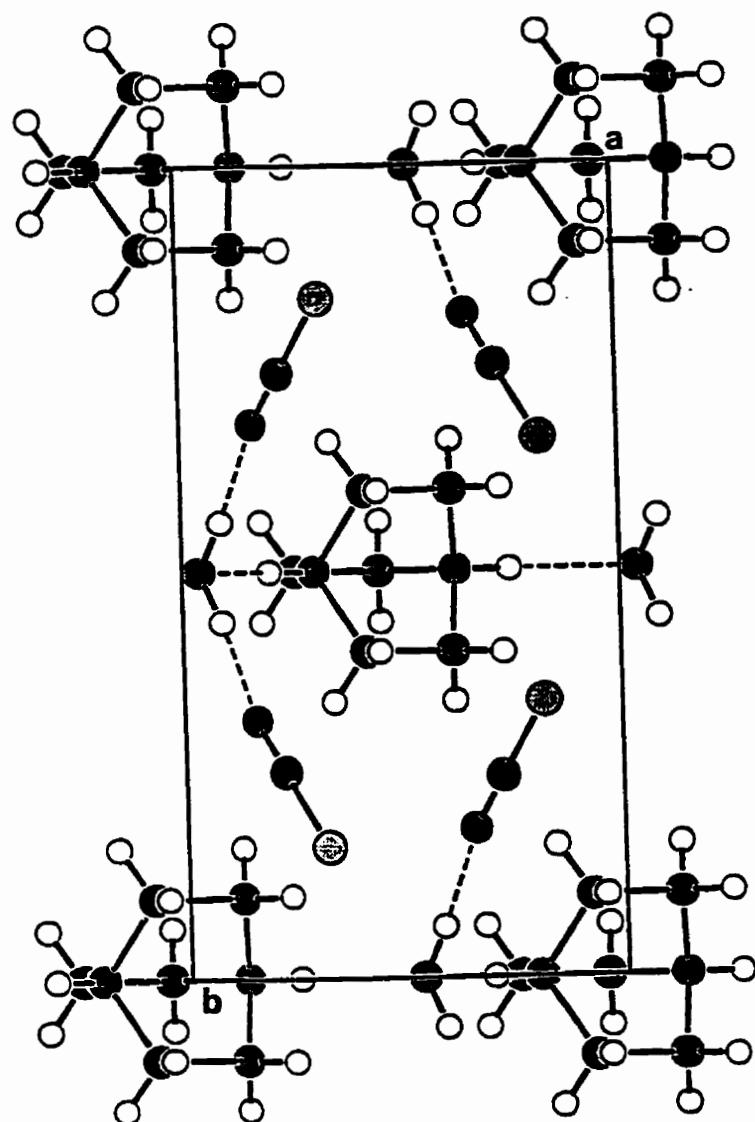


Figure 38. Packing of dabco thiocyanate

**s2Mpiz2T**

There are two N-hydrogens available for hydrogen bonding, and two thiocyanate ions. Each H(N) atom is then bonded to the nitrogen atom of a single SCN<sup>-</sup> anion. The crystal is badly twinned. The best R value obtained was 11%, and so no suitable packing diagram is available.

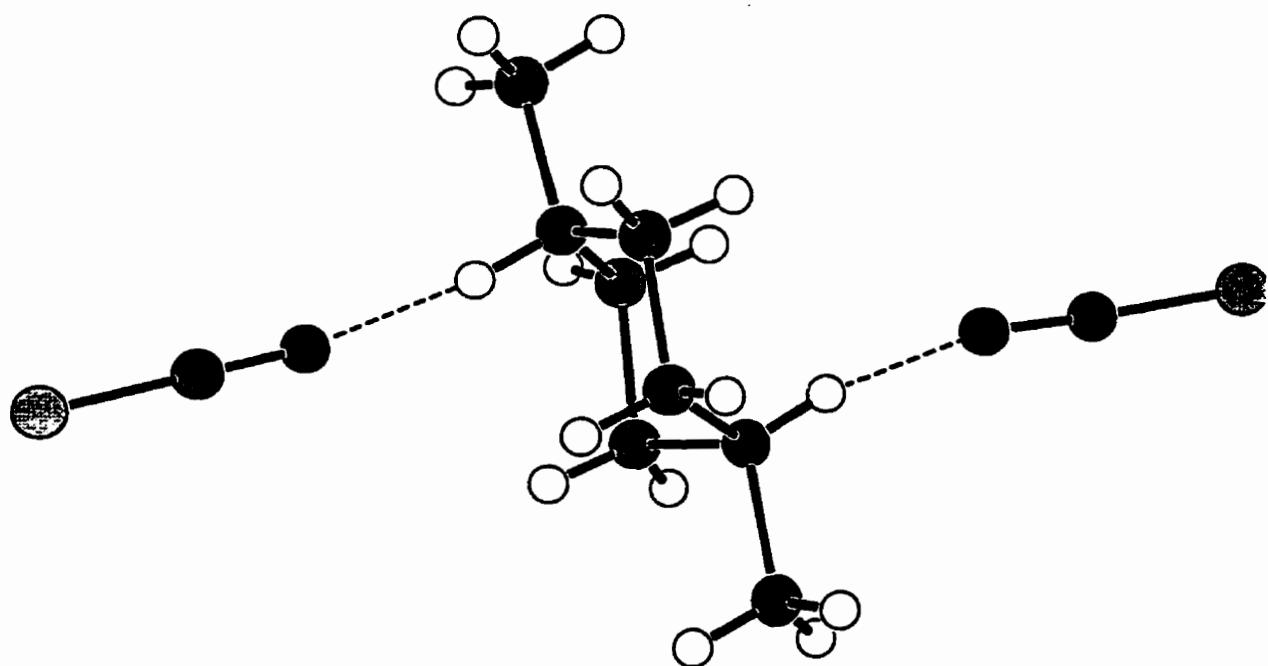


Figure 39. s2Mpiz2T, dimethylpiperazinium thiocyanate

### Tp3T

There are three thiocyanate anions for each terpyridinium  $^{3+}$  cation, however only one of the anions is involved in the hydrogen bonding. The one nitrogen of the thiocyanate is coordinated to the three hydrogens available for hydrogen bonding. These hydrogen bonds are not as strong as in the previously described structures (~1.85-2.4 Å as compared to 1.75-1.95 Å).

The torsion angles for each N-C-C-N interaction are  $5(3)^\circ$ ,  $-7(3)^\circ$ ,  $2(3)^\circ$ ,  $-4(3)^\circ$ . This shows that the molecule is essentially planar. In order to determine if this planarity is typical of the terpyridine structure, another CSD search was done to look at the torsion angles of other similar structures.

The results give torsion angles that center about  $0^\circ$ , but have a very large range, with values of  $20^\circ$ ,  $40^\circ$  and even  $80^\circ$  not uncommon. The planarity of this structure is therefore thought to be a result of the hydrogen bonding that occurs.

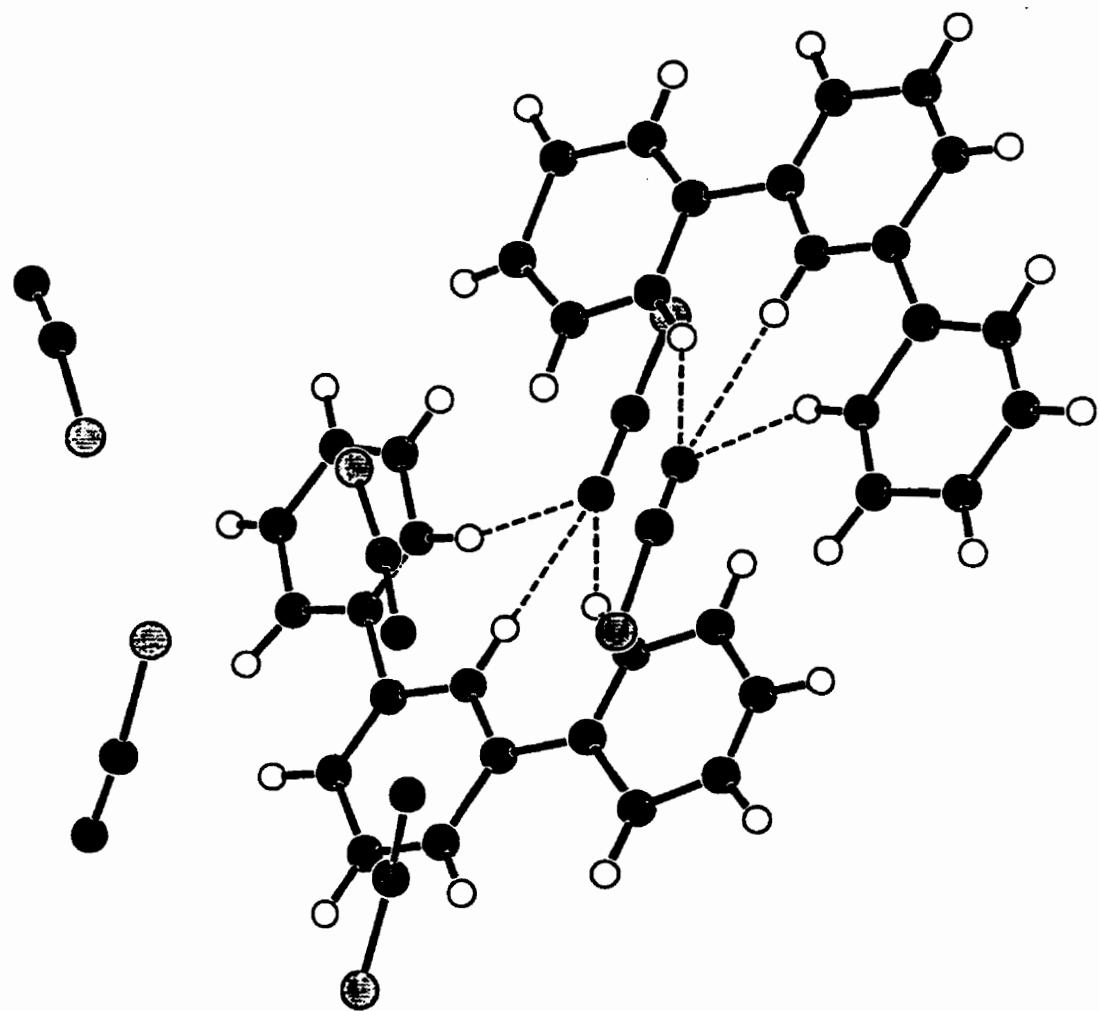


Figure 40. Tp3T, terpyridine thiocyanate

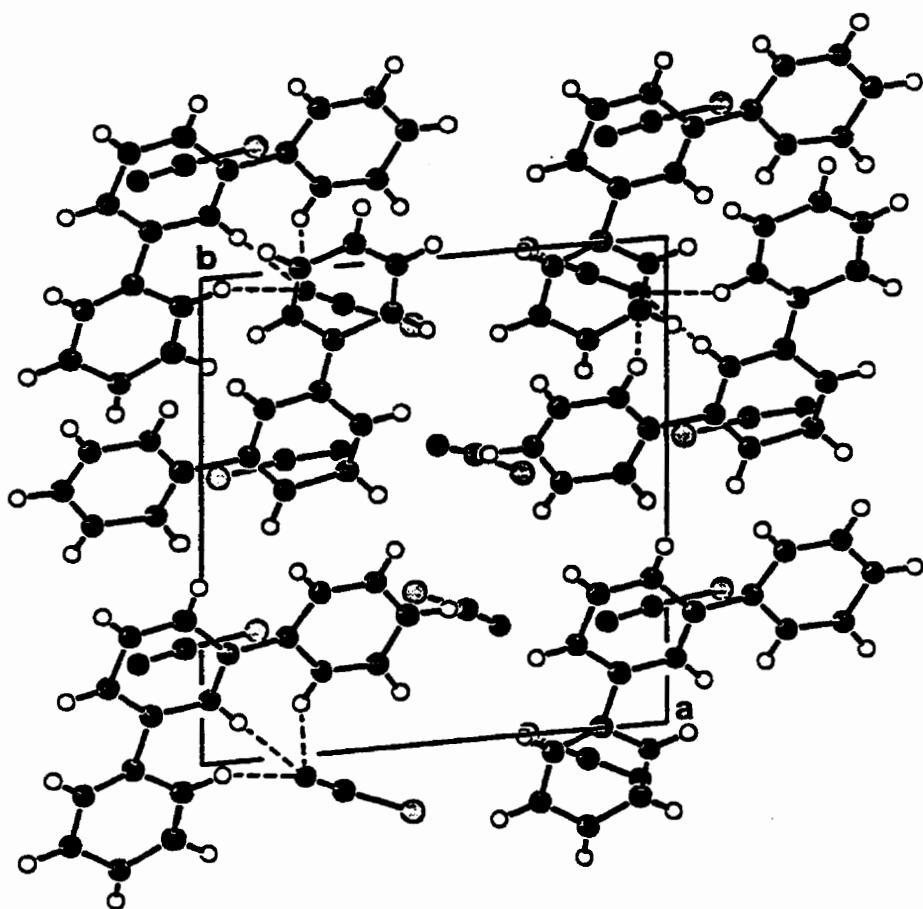


Figure 41. Packing of Tp3T

**3spg3T**

In the classical proton sponge cation, the H(N) atom is so strongly shielded that no interaction with the thiocyanate is possible. The angle between N-H-N is 175.6°. This close to linear arrangement and the effects of the two methyl groups on each nitrogen atom, make it difficult for the thiocyanate to reach the H(N). The thiocyanate itself is disordered about the two fold axis.

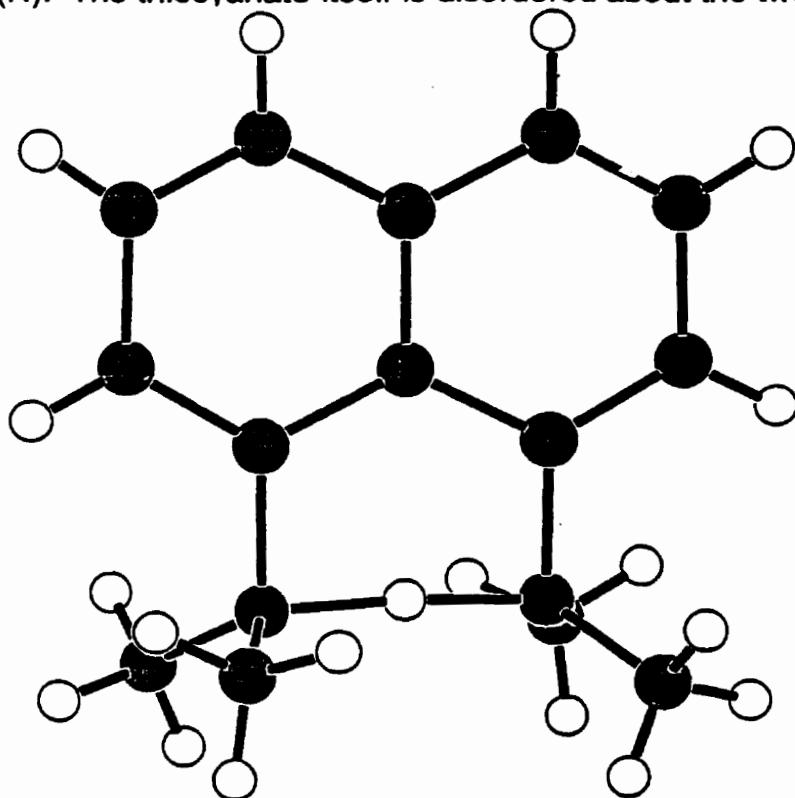


Figure 42. 3spg3T, Classical proton sponge

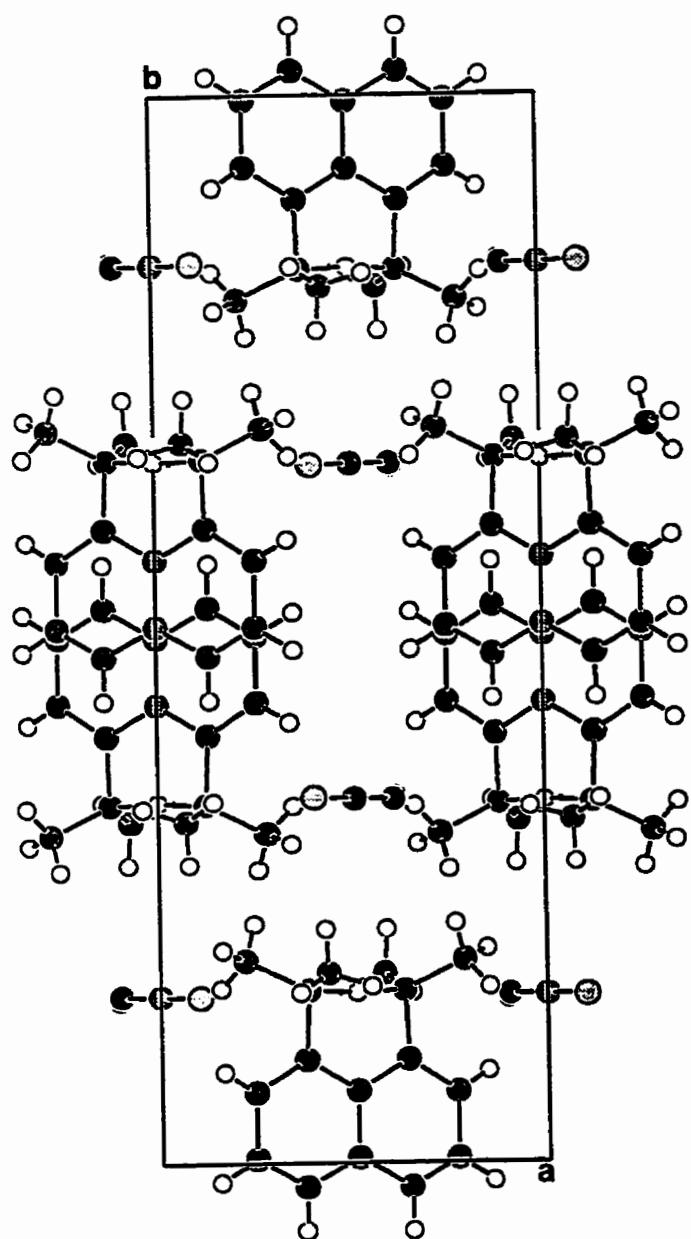


Figure 43. Packing of the classical proton sponge

**s2MenZ4T**

The H(N) atom of the methylated ethylenediammonium cation cannot get sufficiently close to the thiocyanate anions and so H(N)...S bonds are possible. Two sulphur atoms form single unbranched bonds to H(N). A third sulphur atom is two-coordinated to hydrogens of separate cations. The molecule packs as follows:

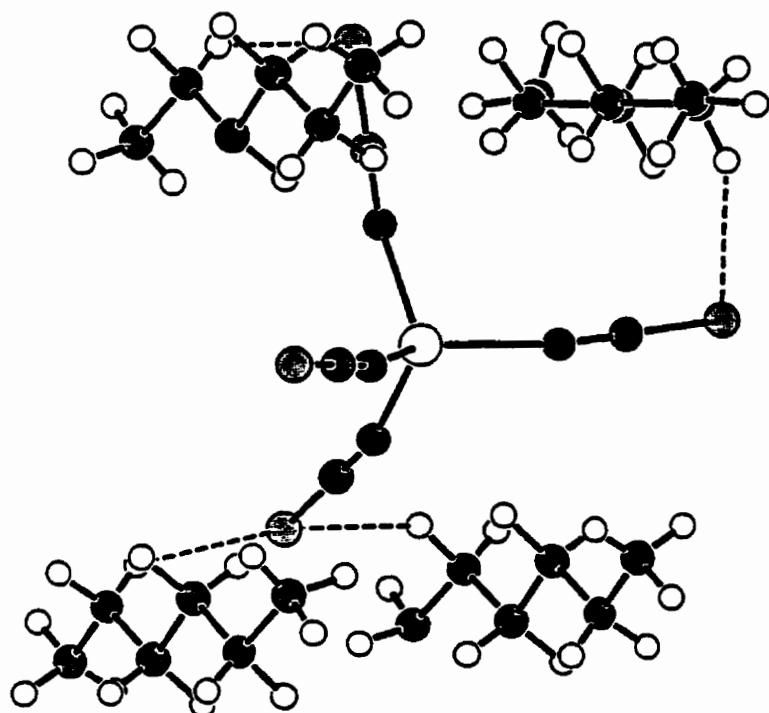


Figure 44. s2MenZ4T, sym-Dimethylethylenediammonium zinc(SCN)<sub>4</sub>

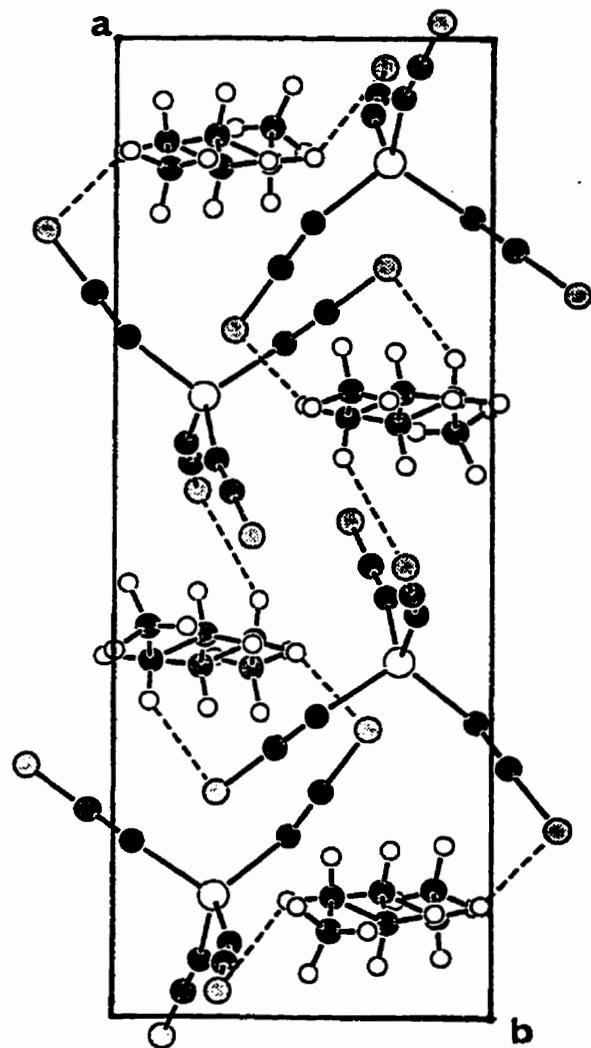


Figure 45. Packing of s2MenZ4T

**3Men2T**

This structure contains a disordered ethylenediammonium cation with three methyl groups attached. The carbon atoms of the chain are not in a stable position, seen by the large thermal parameters. They are positionally disordered. The locations of the atoms are resolved by splitting the original positions into two separate locations. This disorder may be static-where the different positions occur within the crystal itself, or dynamic, where the positions of the molecule are actually changing. The doubly methylated nitrogen on this ion has one H(N) atom available, and the other has two. There are three thiocyanates for each of these ions, but only two are involved in the hydrogen bonding. One nitrogen is two-coordinated to the H(N) atom, and the other is involved in a very strong single unbranched coordination.

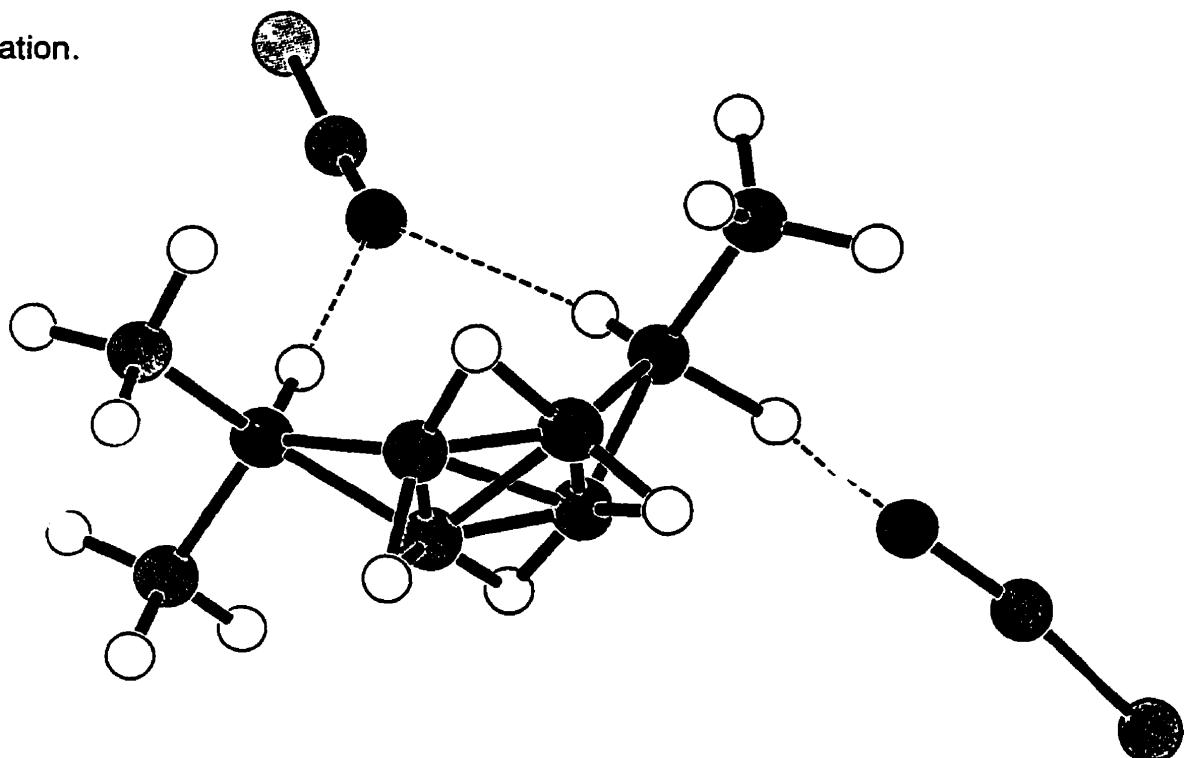


Figure 46. 3Men2T, Trimethylethylenediammonium thiocyanate

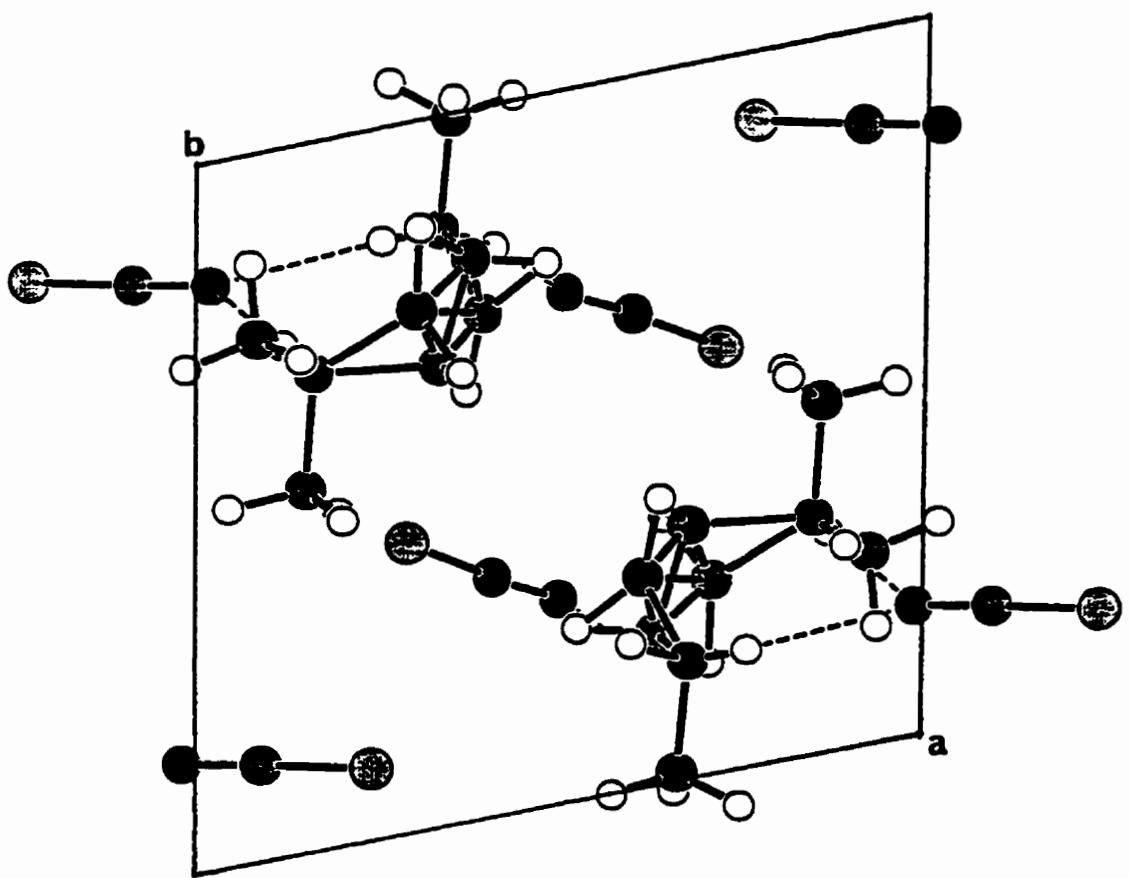


Figure 47. Packing of 3Men2T

**u2Men2T**

There is just one interaction with a sulphur of a thiocyanate. The length of this H...S bond is  $>2.4\text{\AA}$  and so the bond cannot be considered as strong.

The nitrogen of the thiocyanate anion that points into the structure (N2), forms strong bonds to two hydrogens. The second thiocyanate forms a single strong hydrogen bond between N1 and an H(N) atom.

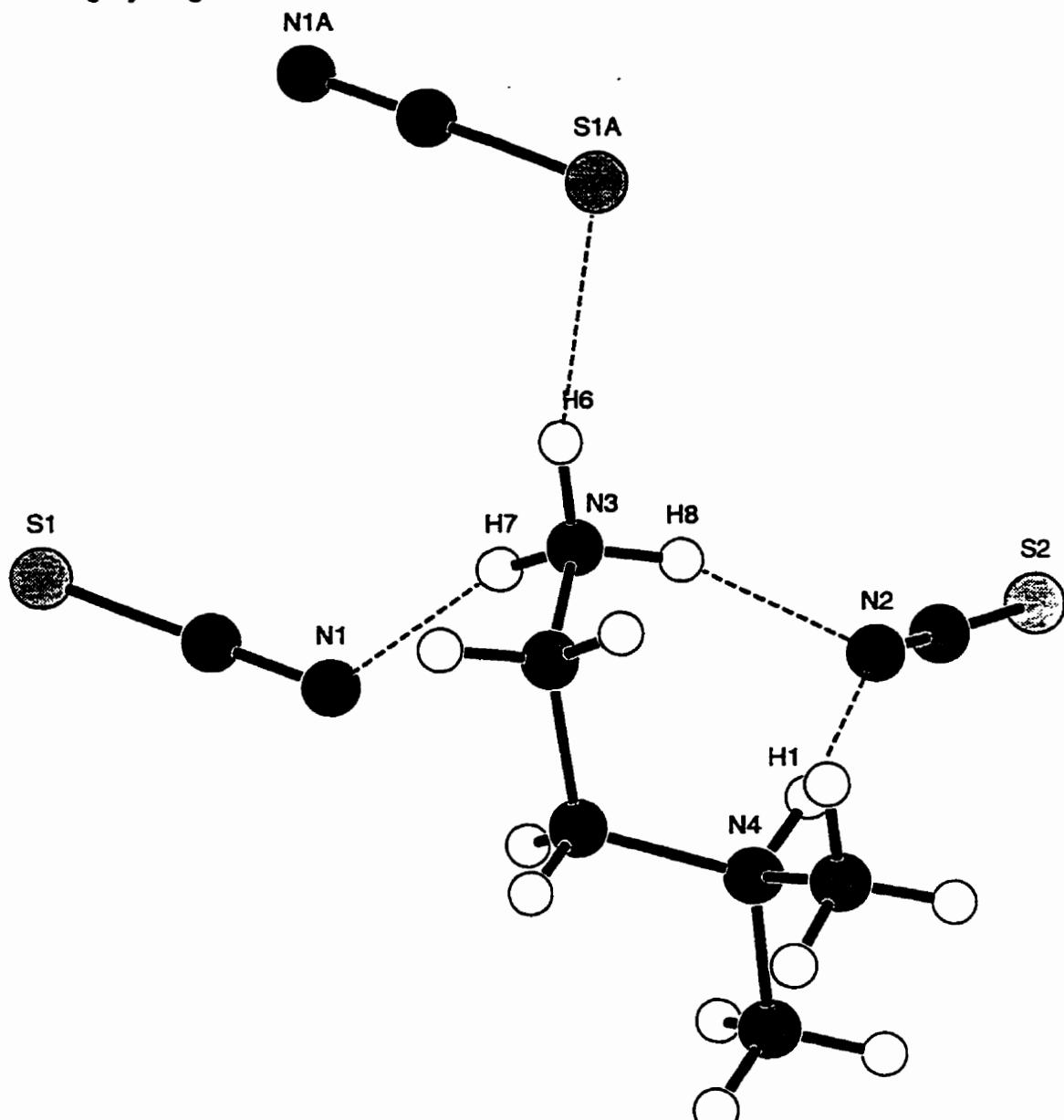


Figure 48. u2Men2T, unsym-Dimethylethylenediammonium thiocyanate

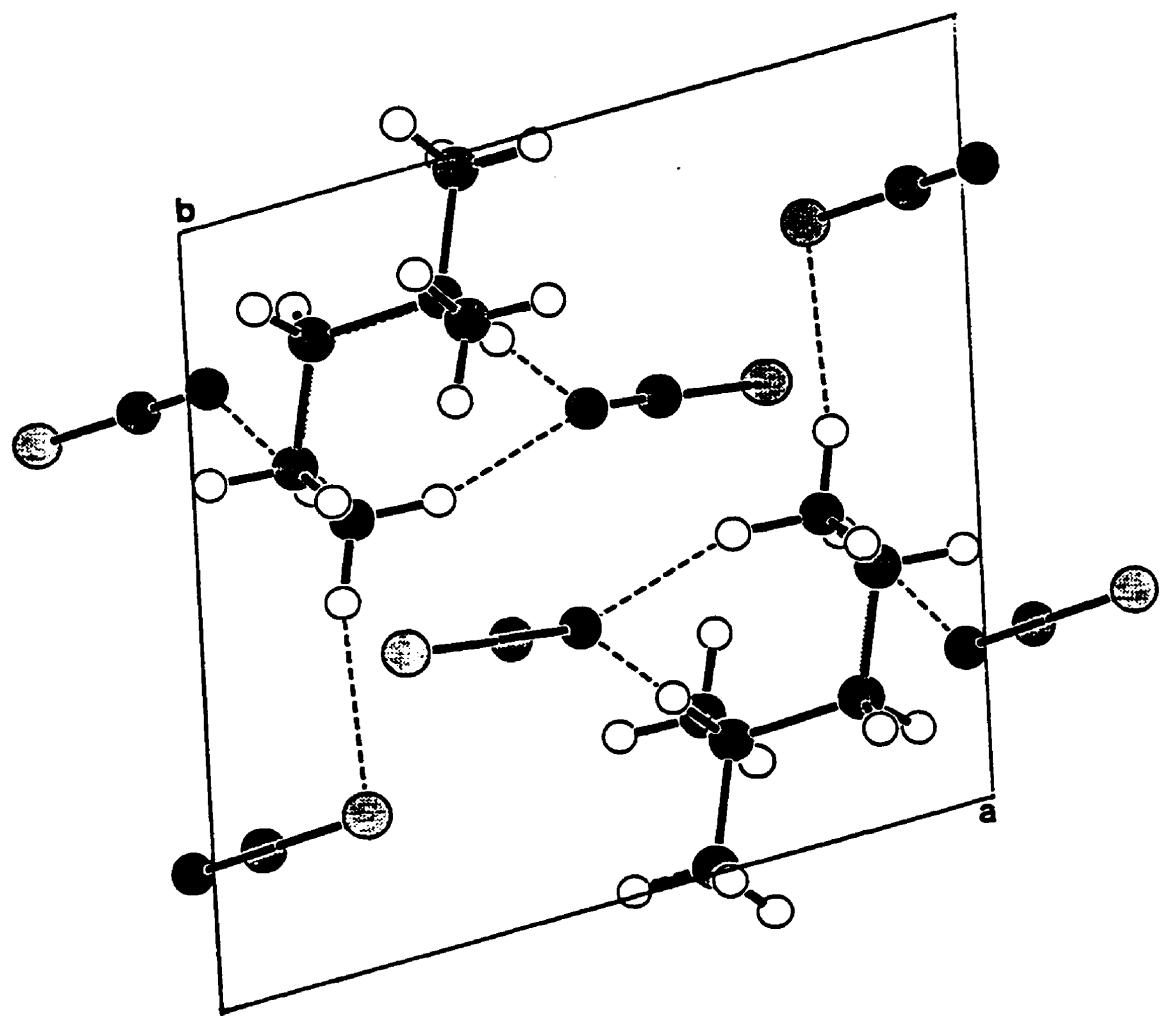


Figure 49. Packing of u2Men2T

## Cy2T

All six available N-hydrogens of the centrosymmetric cation form bonds with the sulphur or nitrogen of the thiocyanates. Each hydrogen forms just one bond. The nitrogens are each two-coordinated to the hydrogens, the sulphur atoms have a single coordination. These bonds are not as strong as the bonds in previously described structures.

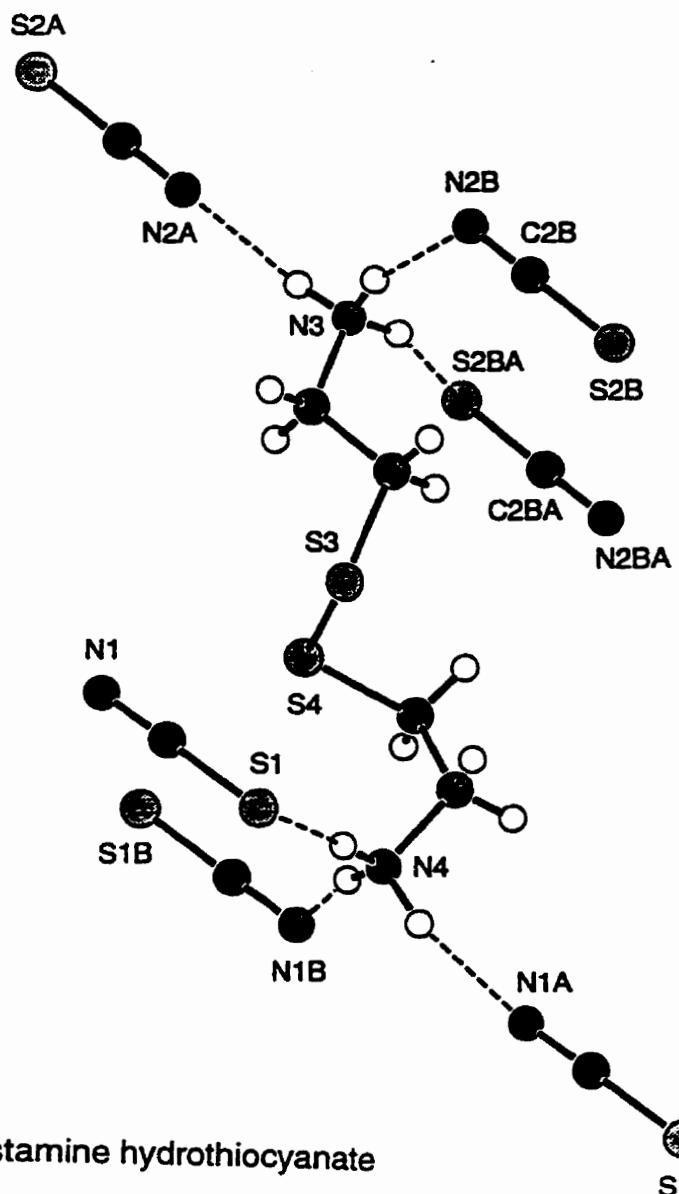


Figure 50. Cy2T, cystamine hydrothiocyanate

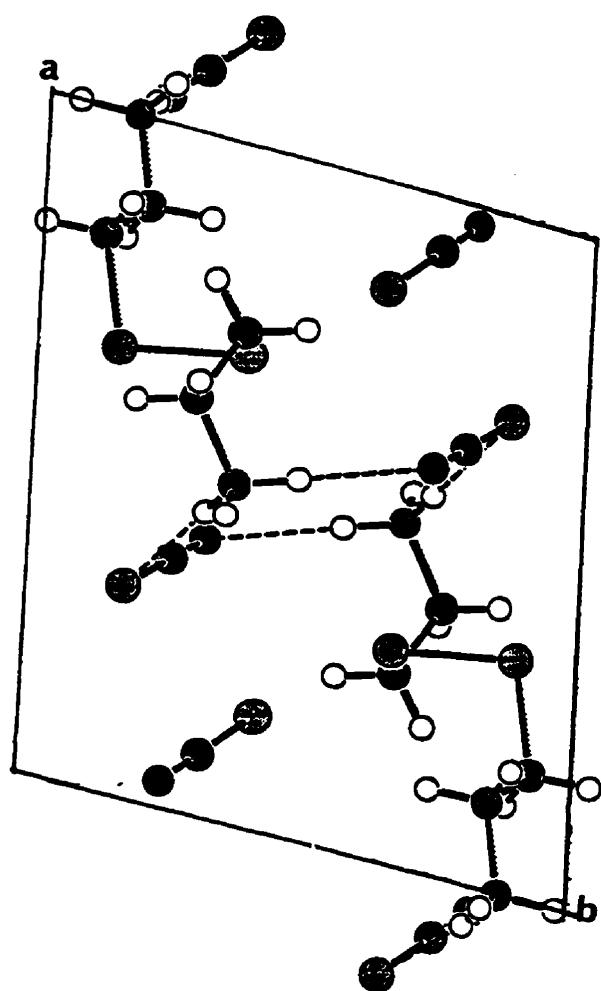


Figure 51. Packing of Cy2T

**en2T**

Although chemically, this is the simplest structure of the third chapter, it contains some of the more complicated bonding. Both thiocyanate anions (and both the nitrogen and sulphur ends) are involved in the hydrogen bonding. All six available hydrogens are involved in the hydrogen bonded packed structure. Two form single weak bonds to the sulphur atoms, the others form four stronger bonds to the nitrogen atoms, which are therefore 2-coordinated.

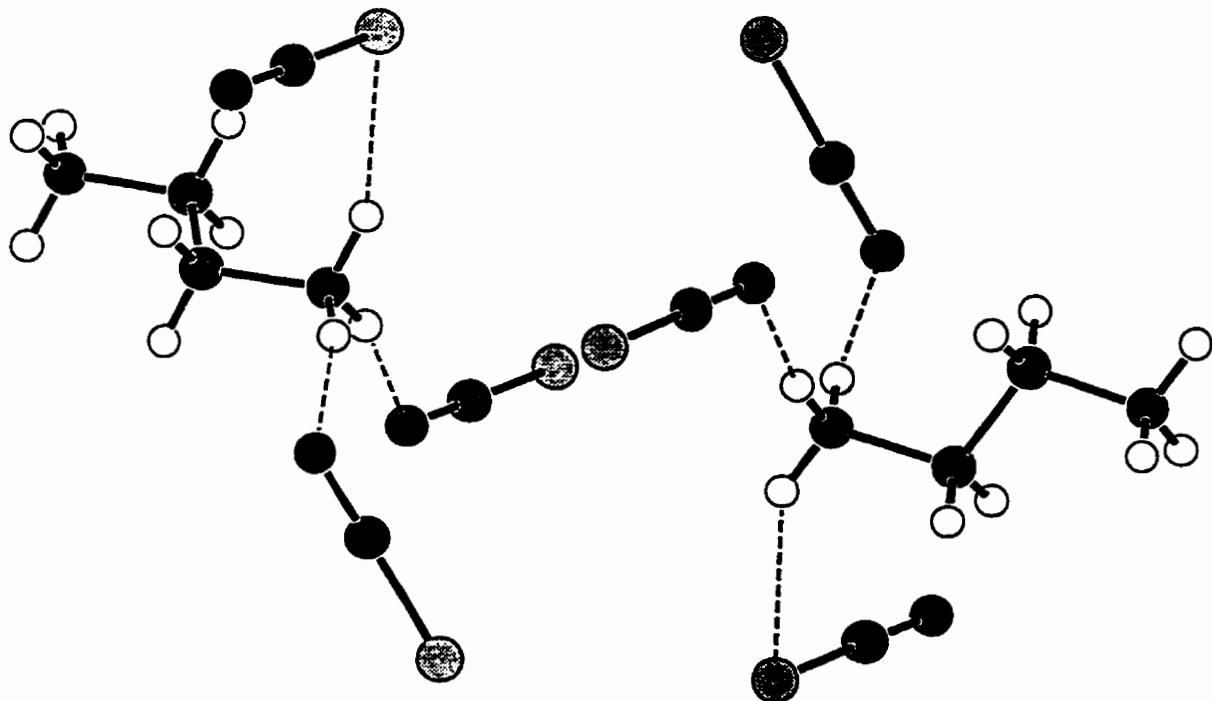


Figure 52. en2T, ethylenediammonium thiocyanate

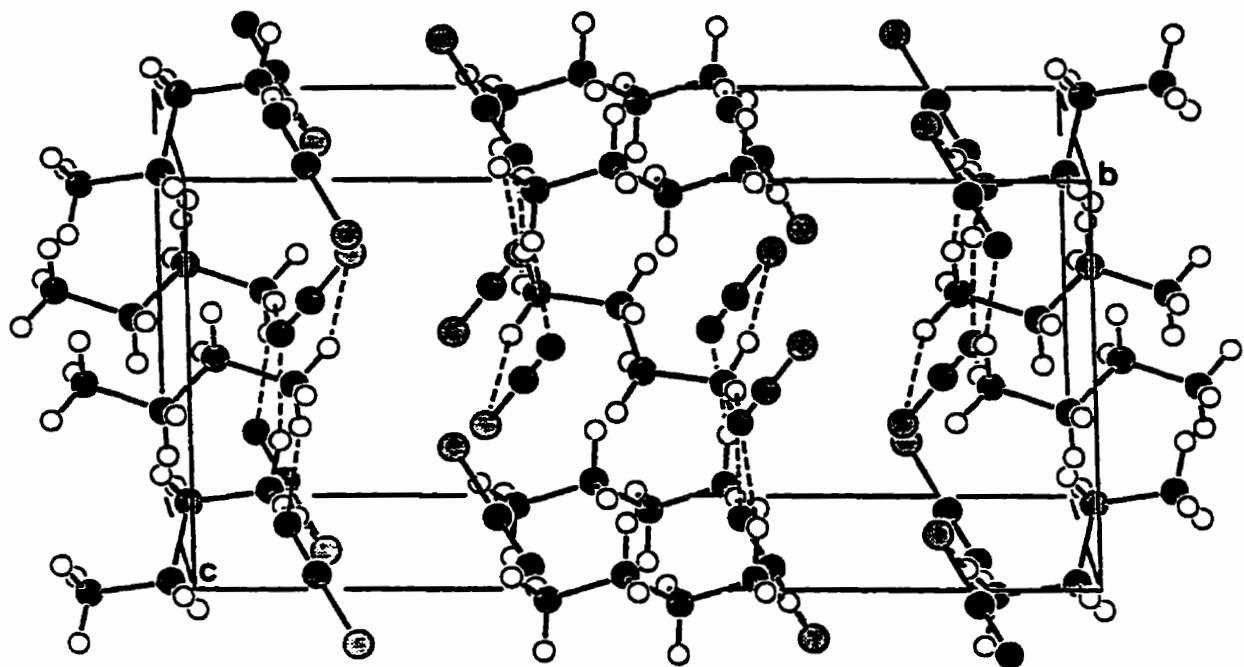


Figure 53. Packing of en2T

**enZ4Tw**

Each H(N) of the ethylenediammonium cation is coordinated to the closest two nitrogens of the thiocyanate. Since the Zn bonds with the nitrogen end of the thiocyanate, the H(N) atoms must reach towards the centroid of the Zn(SCN<sub>4</sub>) structure, displaying an obvious preference for the nitrogen over the sulphur. The bond lengths are 2.62Å and 2.59Å, with an N...H(N) angles of 138.95° and 140.91° respectively. The distance to each of the sulphur atoms is over 4Å. The molecules pack in zig-zag chains parallel to *a*.

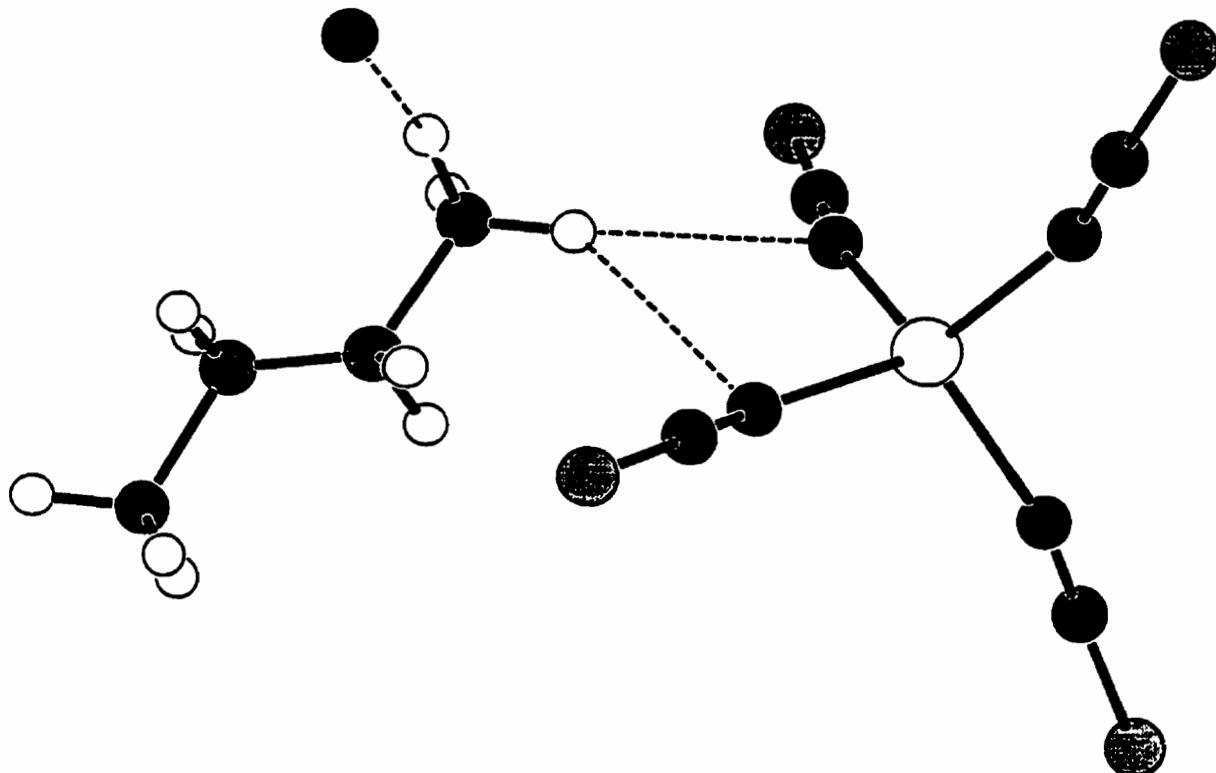


Figure 54. enZ4Tw, Ethylenediammonium zinc(SCN)<sub>4</sub>

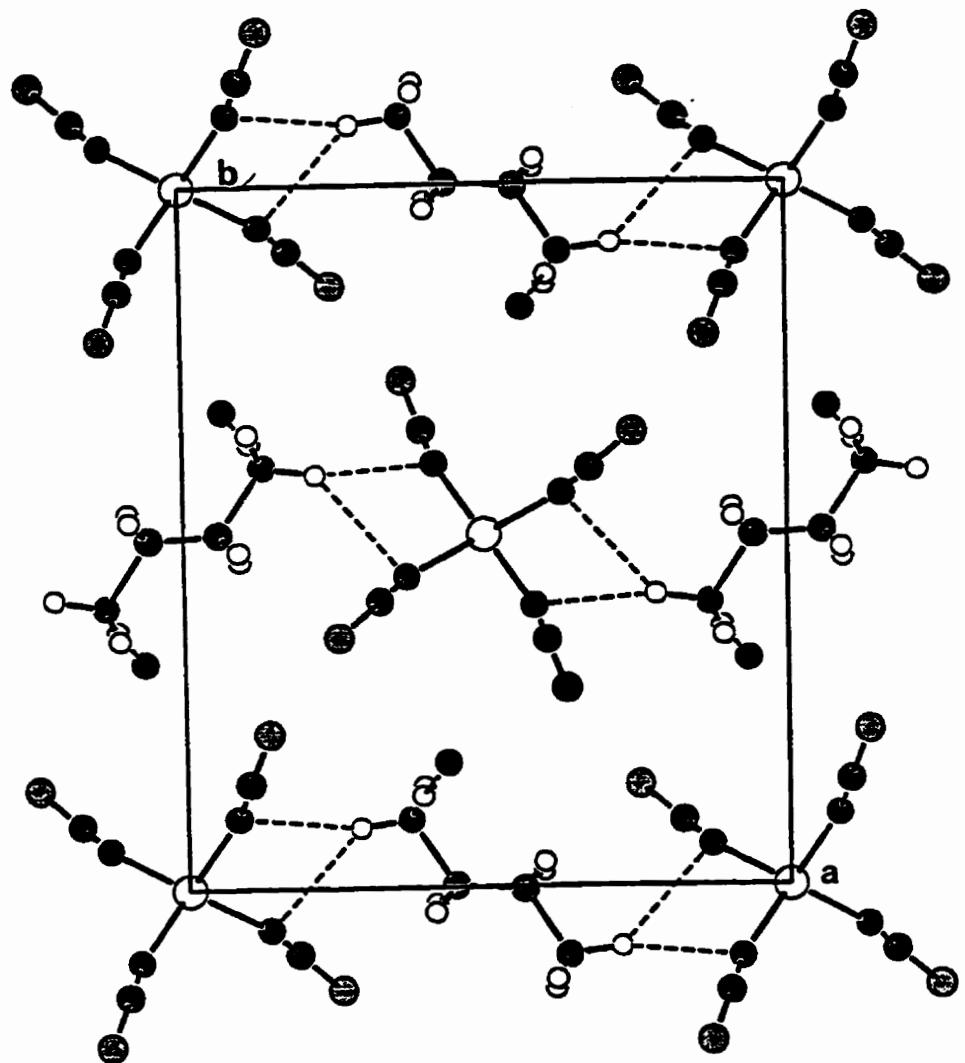


Figure 55. Packing of enZ4Tw

**3enZ2T**

There are many hydrogen bonds in this structure. Within the packing diagram, it is difficult to show all the possible hydrogen bonds. There are four N...H(N) bonds. Each nitrogen of the thiocyanate anion is 2-coordinated to the H(N) atoms. These bonds are not strong hydrogen bonds. Each sulphur atom is also bonded to the N-hydrogens. The S1 atoms is involved in three hydrogen bonds, but again these bonds are not strong. The S2 atom participates in two hydrogen bonds, of stronger character. The packing diagram shows the cross linking that creates a three-dimensionally hydrogen bonded crystal.

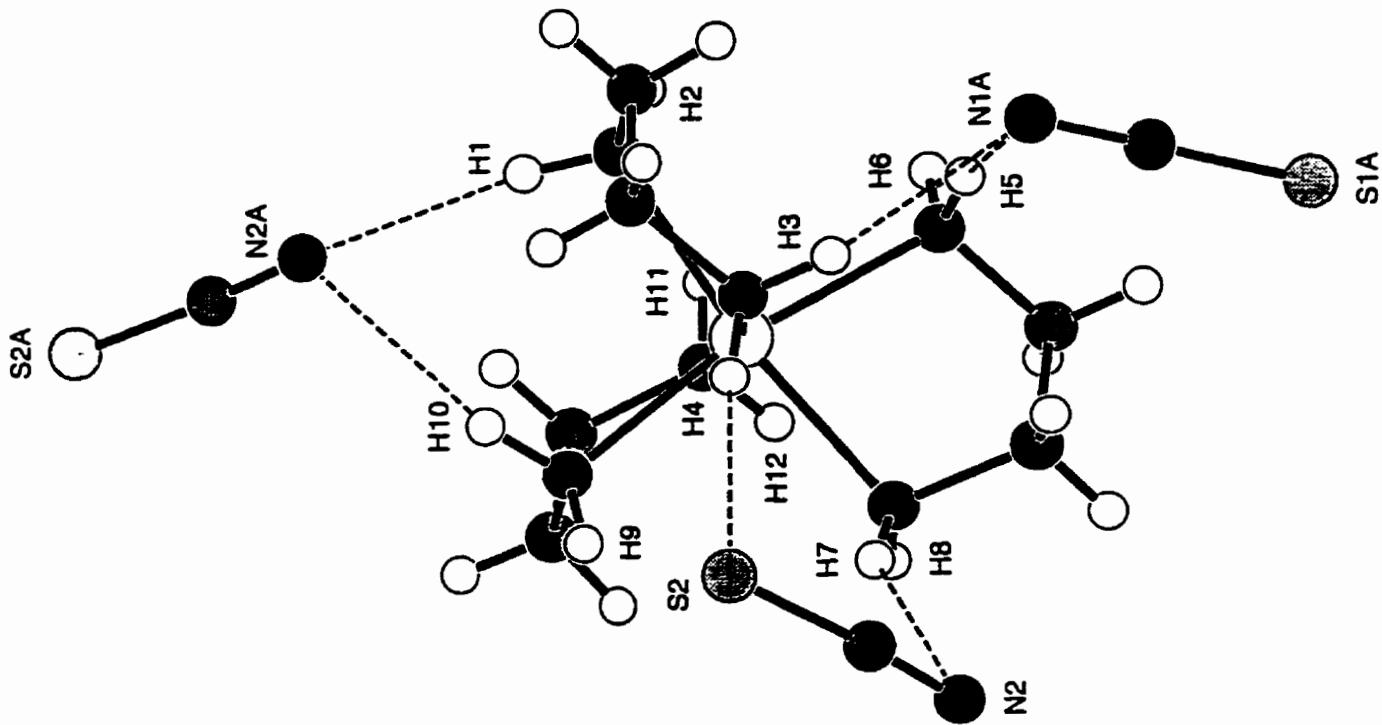


Figure 56. 3enZ2t, Trisethylenediamine zinc(2+)(SCN)<sup>-</sup><sub>2</sub>

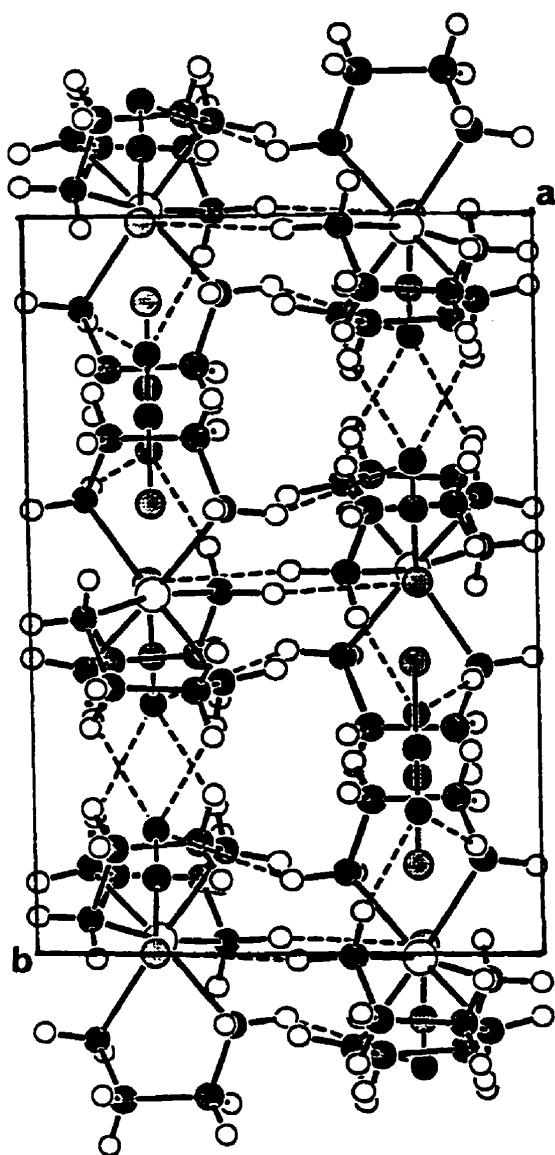


Figure 57. Packing of 3enZ2T

## Hierarchy of Hydrogen Bonding in N-H...SCN<sup>-</sup> systems

There are many factors that may influence the selection of the nitrogen and/or sulphur atom for the formation of hydrogen bonds. These factors include the nature of the X-H bond donor, the presence of a metal that can be either a hard or soft acid and thus interact with the (SCN<sup>-</sup>) nitrogen atom or sulphur atom respectively. The aim of chapter 3 is to provide a benchmark for the simplest case, that of an N-H interaction with the SCN<sup>-</sup> anion. The N-H bonds will belong to a quaternary nitrogen so that a (+1) charge is held at that fragment of the structure and there can then be one, two, three or four N-H bonds available for hydrogen bonding.

In this chapter, the hydrogen bonding preference of the thiocyanate anion (within the chemical possibilities of the quaternary nitrogen system) will be determined according to the ratio of the number of H(N) atoms to the number of thiocyanate anions.

### The 1:1 and n:n systems

The three true 1:1 systems QT, 4Men2T and 4Mbn2T<sup>4</sup> each show a single strong N-H...NCS interaction and the sulphur atoms take no part in any hydrogen bonding interaction. The betaine structure (BeT) also contains

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<sup>4</sup> 4Men2T and 4Mbn2T have a symmetry centre between the central two (CH<sub>2</sub>) groups.

interactions to the nitrogen atom of the (SCN<sup>-</sup>) anion. In this case it is an O-H...NCS bond which is formed.

Table 10 Hydrogen bond distances and angles for the 1:1 systems

QT	H14...N1	1.8304 Å	N1...H14-N2	173.5°
4Men2T	H9...N1	1.8324	N2...H9-N1	163.89
4Mbn2T	H11...N3	1.7516	N3...H11-N2	177.9
BeT	(O1)H1...N1	1.7799	N1...H1-O1	169.03

The n:n systems 4Mpn2T, s2Mpiz2T, Da2Tw, and Tp3T repeat this pattern with strong N-H...NCS interactions and no sulphur interaction. These hydrogen bonds are less strong than those in 1:1 structures. An interesting case is that of Dabco, where the two N-H bonds do not form a hydrogen bond with the SCN<sup>-</sup> ion; rather they each form hydrogen bonds with a water molecule and that water molecule then forms an O-H...NCS hydrogen bond. Presumably the problem of packing a DabcoH<sub>2</sub><sup>2+</sup> with two SCN<sup>-</sup> ions hydrogen-bonded one at each end of the cation precludes a repeat with Dabco of the arrangement seen with quinuclidine.

The proton sponge system (3spg3T) has the very strong interaction of N-H...N so securely shielded that no interaction with the thiocyanate is possible. In this structure there are at least three solvent molecules (water

and EtOH) which provide O-H bonds for an extended hydrogen-bonding network. The whole network involves only bonding to the nitrogen atom of the SCN<sup>-</sup> anion.

Table 11 Hydrogen bond distances and angles for 2:2 systems

4Mpn2T	N2...H1 N1...H2	1.8627 Å 1.8140	N2...H1-N3 N1...H2-N4	161.57 166.24
Da2Tw	O1...H7 O1...H8 N1...H9	1.9594 1.9678 1.8655	N2-H7...O1 N3-H8...O1 N1...H9-O1	141.96 141.86 141.1

Table 12 Hydrogen bond distances and angles for 3:3 systems

Tp3T	N4...H1 N4...H6 N4...H7 N6...H4 N6...H28 N6...H5	1.8359 Å 2.2310 2.0045 2.0125 2.4363 1.9913		
3spg3T	No H(N)...	SCN	interaction is	possible.

From this it would seem that when there is only one N-H bond to one (SCN<sup>-</sup>) ion, where only one hydrogen bond can be formed, *the overwhelming preference of the (SCN) ion is to form a single N-H...NCS bond.*

### The 3:2 and 4:2 systems

In the 3:2 ( $3\text{MeN}_2\text{T}$ ) and 4:2 ( $2\text{MeN}_2\text{T}$ ) systems there is now a surplus of N-H bonds for the number of  $\text{SCN}^-$  ions. The question is where will these additional N-H form hydrogen bonding attachments. In the 3:2 case the anion forms a strong hydrogen bond with each available N-H. The *geminal* end of the cation and one of the two N-H bonds from the other nitrogen atom both share a single  $\text{SCN}^-$  ion with a bifurcated bond at the  $\text{SCN}^-$  nitrogen atom. This produces a five-membered ring (seven-membered if the hydrogen atoms are counted) and is a well-known stable conformation for the ethylenediamine ligand. The remaining N-H forms a single hydrogen bond with the second  $\text{SCN}^-$  ion.

In the 4:2 system, the same five-membered ring is formed with a bifurcated bond between the N-H bond of the *geminal* nitrogen at and one of the *three* N-H bonds of the other nitrogen atom in the molecule. This has now exhausted the possibility of 'ring' formation. A second of the three N-H bonds forms a single N-H...NCS bond and the third N-H bond now forms an N-H...SCN bond to the same second, but now a symmetry related,  $\text{SCN}^-$  ion.

Table 13 Hydrogen bond distances and angles for the 3:2 and 4:2 systems

3Men2T	N2...H1 N1...H14 N1...H16	1.5281Å 1.9082 2.1310	N2...H1-N4 N1...H14-N3 N1...H16-N4	166.99° 178.89 167.92
u2Men2T	S1...H6 N1...H7 N2...H1 N2...H8	2.4471 1.9772 1.8711 1.9657	S1...H6-N3 N1...H7-N3 N2...H1-N4 N2...H8-N3	164.36 157.4 166.5 160.2

These two compounds are too small a group to allow a sure generalisation. However, it does appear that in the hierarchy of hydrogen bonding to the SCN<sup>-</sup>, *the ion will first form two separate bonds to the nitrogen atom of the SCN rather than form an N-H...SCN bond. Thus somewhat weaker (N-H)<sub>2</sub>...NCS bonds are preferred to a single N-H...SCN.*

### The 6:2 systems

There are two 6:2 systems (en2T) and (Cy2T). The ethylene-diammonium salt has a symmetry centre between the two (-CH<sub>2</sub>-) groups. The conformation of the ion is thus *trans* and a hydrogen-bonded ring is not possible. However the symmetry centre makes this salt a true 3:1 system. The bonding to the SCN<sup>-</sup> ion is a (N-H)<sub>2</sub>...NSC set of interactions and an N-H...SCN bond. Thus all the available N-H bonds are used. The cation in the second 6:2 system (Cy2T) does not contain a symmetry centre; however, at both cation nitrogen atoms it repeats the pattern of the previous

3:1 system – namely one set of bifurcated (N-H)<sub>2</sub>...NCS bonds with the third N-H forming an N-H...SCN interaction.

Table 14 Hydrogen bond distances and angles for the 3:1 systems

Cy2T	S1...H11	2.4125Å	S1...H11-N4	169.97°
	S2...H12	2.4503Å	S2...H12-N3	155.04
	N2...H14	2.0532Å	N2...H14-N3	161.09
	N2...H13	2.1026Å	N2...H13-N3	137.55
	N1...H10	2.0251Å	N1...H10-N4	166.76
	N1...H9	1.9932Å	N1...H9-N4	157.25
En2T	S1...H6	2.4543Å	S1...H6-N1	151.22
	S2...H9	2.5165Å	S2...H9-N2	144.46
	N3...H10	2.0139Å	N3...H10-N2	169.9
	N3...H7	1.9657Å	N3...H7-N1	166.4
	N4...H5	1.9542Å	N4...H5-N1	165.4
	N4...H8	1.9784Å	N4...H8-N2	162.6

### The Z4T Salts

As was explained earlier in this chapter, the two salts of  $[\text{Zn}(\text{NCS})_4]^{2-}$  do not really belong in this series since both have the nitrogen atoms of the SCN<sup>-</sup> ions coordinated to the zinc atom. However, the two cations are derived from ethylenediamine and *sym*-N,N'-dimethyl-ethylenediamine.

The s2MenZ4T salt with the two N,N' methyl groups contains only two significant N-H...SCN interactions. The less space-filling  $\text{-NH}_3^+$  group in the enZ4Tw salt allows for the formation of weak N-H...(NCS)<sub>2</sub> bonds with the  $\text{-NH}_3^+$  group slipping into the coordination system of the  $[\text{Zn}(\text{NCS})_4]^{2-}$  ion and bonding to the nitrogen atoms of the (NCS<sup>-</sup>) ions. The symmetry of this crystal is such that there is only one unique  $\text{-NH}_3^+$  group and only two unique NCS<sup>-</sup> ligands. Thus all the nitrogen atoms of the ligands form hydrogen bonds. In addition the structure contains a water molecule which forms further hydrogen bonds to the remaining N-H bonds of the  $\text{-NH}_3^+$  group.

The 12:2 system (3enZ2T) has a superabundance of N-H bonds and clearly not all of these can hydrogen bond to the SCN<sup>-</sup> ion. Both nitrogen atoms of the SCN<sup>-</sup> ion achieve a bifurcated bond and one nitrogen (N2) manages a third longer bond. There is one N-H...SCN bond to (S2...H4) but the other sulphur atom does not manage any *significant* N-H...SCN interaction.

Table 15 Hydrogen bond distances and angles for the Zinc systems

enZ4Tw	N1...H1 N2...H2	2.6219 Å 2.5927	N2...H1-N3 N1...H1-N3	138.95° 140.91
s2MenZ4T	S3...H4	2.4057	S3...H4-N5	151.10
	S4...H10	2.6268(wk)	S4...H10-N6	137.40
	S1...H12	2.6152(wk)	S1...H12-N6	138.13
	S1...H5	2.4841	S1...H5-N5	154.10
3enZ2T	S1...H12	2.6200	Too weak	
	S1...H8	2.6570		
	S1...H9	2.7192		
	S2...H4	2.4590	S2...H4-N4	170.46
	S2...H6	2.6929		
	N1...H3	2.3046	N1...H3-N4	164.83
	N1...H5	2.3132	N1...H5-N5	161.21
	N2...H1	2.3069	N2...H1-N3	156.37
	N2...H10	2.4332	N2...H10-N7	162.51
	N2...N7	2.5643	N2...H7-N6	151.09

These compounds underscore the observation that the N-H...NCS bonding system is the pre-eminent among the bonds formed to the NCS<sup>-</sup> ion. In the 6:2 and 12:2 systems the NCS<sup>-</sup> nitrogen atoms always form a bifurcated bond. In the 6:2 systems there is also an N-H...SCN bond formed to each (NCS<sup>-</sup>) ion. However in the 12:2 system, only one sulphur is involved in an N-H...SCN bond.

*This is further confirmation that an (N-H)<sub>2</sub>...NCS bonding system takes precedence over an N-H...SCN system.*

Table 16 Bond angles and distances for the chapter 3 complexes

Bond	H...N(CS) distance	N-H...N angle	N...N(H) distance	H...C distance	H...N-C angle
QT N1...H14-N2	1.8304 Å	173.5°	2.776(3)	3.150	174.45
4Men2T N2...H9-N1	1.8324	163.89	2.758(4)	2.963	107.21
4Mbn2T <sup>a</sup> N3...H11-N2	1.7516	177.9	2.76(2)	2.744	136.32
BeT <sup>b</sup> N1...H1-O1	1.7799	169.03	3.433(2)	2.88(7)	158(2)
4Mpn2T N2...H1-N3 N1...H2-N4	1.8627 1.8140	161.57 166.24	2.82(1) 2.76(1)	2.965 2.876	160.37 153.00
Da2Tw <sup>b</sup> N2-H7...O1 N3-H8...O1 N1...H9-O1	1.9594 1.9678 1.8655	141.96 141.86 141.1	2.750(6) 2.756(6) 2.736(5)	NA NA 2.97	NA NA 162.20
Tp3T N11-H1...N4 N12-H6...N4 N13-H7...N4 N8-H4...N6 N9-H28...N6 N10-H5...N6	1.8359 2.2310 2.0045 2.0125 2.4363 1.9913		2.72(3) 3.17(3) 2.90(3) 2.87(3) 3.40(3) 2.85(3)	3.086 3.450 2.787 2.635 3.369 2.938	157.60 153.22 112.88 118.97 157.85 160.50
3Men2T <sup>a</sup> N2...H1-N4 N1...H14-N3 N1...H16-N4	1.5281 1.9082 2.1310	166.99 178.89 167.92	2.74(1) 2.788(8) 2.856(9)	2.73(4) 2.93(8) 3.12(6)	169(2) 145(3) 143(2)
U2Men2T <sup>b</sup> S1...H6-N3 N1...H7-N3 N2...H1-N4 N2...H8-N3	2.4471 1.9772 1.8711 1.9657	164.36 157.4 166.5 160.2	3.376(3) 2.881(5) 2.803(4) 2.884(5)	2.972 2.847 2.910 2.894	91.05 129.21 147.41 134.55

Cy2T <sup>b</sup>					
S1...H11-N4	2.4125	196.97	3.342(8)	3.202	102.74
S2...H12-N3	2.4503	155.04	3.333(9)	3.089	96.05
N2...H14-N3	2.0532	161.09	2.88(1)	2.831	160.59
N2...H13-N3	2.1026	137.55	2.88(1)	3.082	140.26
N1...H10-N4	2.0251	166.76	2.95(1)	2.669	177.74
N1...H9-N4	1.9932	157.25	2.95(1)	3.093	130.97
En2T <sup>b</sup>					
S1...H6-N1	2.4543	151.22	3.318(5)	3.115	97.17
S2...H9-N2	2.5165	144.46	3.336(5)	3.130	95.37
N3...H10-N2	2.0139	169.9	2.954(7)	2.835	124.27
N3...H7-N1	1.9657	166.4	2.898(7)	2.766	122.32
N4...H5-N1	1.9542	165.4	2.883(7)	2.797	125.49
N4...H8-N2	1.9784	162.6	2.899(7)	2.763	120.78

Zinc complexes					
EnZ4Tw					
N2...H1-N3	2.6219	138.95	3.40(2)	3.823	110.79
N1...H1-N3	2.5927	140.91	3.38(1)	3.088	105.60
S2MenZ4T <sup>a,b</sup>					
S3...H4-N5	2.4057	151.10	3.287(4)	3.00(4)	94(1)
S4...H10-N6	2.6268	137.40	3.286(4)	3.28(4)	98(1)
S1...H12-N6	2.6152	138.13	3.44(7)	3.29(4)	98.6(9)
S1...H5-N5	2.4841	154.10	3.364(4)	3.23(5)	94(1)
3enZ2T <sup>b</sup>					
S2...H4-N4	2.4590	170.46	3.400(4)	3.076	94.97
N1...H3-N4	2.3046	164.83	3.231(7)	3.177	130.20
N1...H5-N5	2.3132	161.21	3.224(6)	2.658	94.04
N2...H1-N3	2.3069	156.37	3.200(7)	3.221	138.48
N2...H10-N7	2.4332	162.51	3.350(8)	2.951	106.84
N2...H7-N6	2.5643	151.09	3.418(7)	2.637	81.38

<sup>a</sup> The hydrogens were found, not placed, and so esd values for the hydrogens exist.

<sup>b</sup> The bonds do not only occur through, N, but also S or O, and so bond distances and angles are therefore to the appropriate atom.

Table 17 Crystal Data

<b>Code</b>	<b>en2t</b>	<b>3Men2T</b>	<b>4Men2T</b>	<b>4Mpn2T</b>	<b>4Mbn2T</b>
<b>Formula</b>	$C_4H_{10}N_4S_2$	$C_7H_{13}N_4S_2$	$C_8H_{16}N_4S_2$	$C_9H_{20}N_4S_2$	$C_{10}H_{22}N_4S_2$
<b>Crystal size</b>	0.04 0.2 0.25	0.06 0.15 0.35	0.05 0.10 0.12	0.10 0.15 0.20	0.04 0.20 0.25
$\mu, \text{cm}^{-1}$	49.8	37.1	34.9	32.5	30.1
<b>Max/min</b>	1.00-0.57	1.00-0.73	1.00-0.32	1.00-0.57	1.00-0.78
<b><math>\theta</math> range</b>	3.8-60.1 /25	4.9-63.5 /25	3.8-60.0 /25	4.7-60.1 /25	5.0-63.6/25
<b>a</b>	7.203(1)	9.356(1)	6.971(1)	11.529(1)	9.182(1)
<b>b</b>	7.780(1)	9.453(1)	8.315(1)	16.118(2)	7.115(1)
<b>c</b>	16.046(1)	7.286(1)	5.958(1)	7.592(1)	12.260(2)
<b><math>\alpha</math></b>	90	101.50(1)	100.35(1)	90	90
<b><math>\beta</math></b>	100.90(1)	99.80(1)	92.89(1)	90	106.69(1)
<b><math>\gamma</math></b>	90	75.90(1)	73.69(1)	90	90
<b>v</b>	883.0(2)	607.4(1)	326.0(1)	1410.7(4)	767.3(2)
<b>Z</b>	4	2	1	4	2
<b><math>\rho_c</math></b>	1.341	1.205	1.184	1.170	1.136
<b>F(000)</b>	376	236	124	536	284
<b>Space group</b>	$P2_1/c$	$P-1$	$P-1$	$P2_12_12_1$	$P2_1/c$

<b>Code</b>	<b>En2t</b>	<b>3Men2T</b>	<b>4Men2T</b>	<b>4Mpn2T</b>	<b>4Mbn2T</b>
<b>Formula</b>	$C_4H_{10}N_4S_2$	$C_7H_{13}N_4S_2$	$C_8H_{16}N_4S_2$	$C_9H_{20}N_4S_2$	$C_{10}H_{22}N_4S_2$
<b>Reflections:</b>					
<b>h, k, l</b>	0/8, 0/8, -18/17	0/10, -10 /10, -8/8	0/7, -8/9, -6/6	0/12, 0/18, 0/8	0/10, -8/8, -14/13
<b>Total measured</b>	1306	2115	971	1233	1262
<b>Unique total</b>	1306	1975	971	1233	1262
<b>Unique used</b>					
<b>100R<sub>merge</sub></b>					
<b>Program</b>	SHELXL	SHELXL	SHELXL	SHELXL	SHELXL
<b>Weighting scheme</b>	SHELXL	SHELXL	SHELXL	SHELXL	SHELXL
<b>Data/parameters</b>	14.2	14.41	14.9	17.1	7.3
<b>100R;100R<sub>w</sub></b>					
<b>100R1: 100<sub>w</sub>R2 (2σ)</b>	4.4; 11.7	7.87, 23.23	4.6; 12.4	5.9; 15.2	3.9; 10.3
<b>100R1:100<sub>w</sub>R2 (all data)</b>	5.0; 12.3	11.69, 27.6	6.6; 13.8	24.6; 21.9	4.0; 10.4
<b>GOF</b>	1.08 (on F <sup>2</sup> )	1.01 (on F <sup>2</sup> )	1.05 (on F <sup>2</sup> )	0.81 (on F <sup>2</sup> )	0.95 (on F <sup>2</sup> )
<b>ACP</b>					-0.11(8)
<b>Residual e.d.</b>	-0.46/0.51	-0.46/0.95	-0.22/0.55	-0.21/0.20	-0.60/0.31

<b>Code</b>	<b>Cy2T</b>	<b>Tp3T</b>	<b>BeT</b>	<b>QT</b>	<b>Da2Tw</b>
<b>Formula</b>	<chem>C6H14N4S4</chem>	<chem>C18H14N6S3</chem>	<chem>C6H12N2O2S</chem>	<chem>C8H14N2S</chem>	<chem>C4H8N2O1/2S2</chem>
<b>Crystal size</b>	0.07 0.40 0.45	0.15 1.15 0.20	0.08 0.20 0.25	0.05 0.15 0.25	0.15 0.20 0.25
$\mu, \text{cm}^{-1}$	64.9	35.9	28.1	25.6	39.4
<b>Max/min</b>	1.00-0.12	1.00-0.60	1.00-0.91	1.00-0.82	1.00-0.88
<b><math>\theta</math> range</b>	4.25-63.5 /25	3.9-60.1 / 25	5.0-63.4 /25	5.0-63.6 /25	7.13-60.0 /25
<b>a</b>	8.701(1)	11.091(1)	12.596(2)	24.039(2)	7.699(1)
<b>b</b>	11.133(2)	11.349(1)	6.677(2)	6.410(2)	12.427(1)
<b>c</b>	7.510(1)	8.201(1)	10.966(1)	17.220(2)	7.285(1)
<b><math>\alpha</math></b>	104.60(1)	94.31(1)	90	90	90
<b><math>\beta</math></b>	106.88(1)	107.29(1)	90	134.71(1)	121.89(1)
<b><math>\gamma</math></b>	99.73(1)	83.42(1)	90	90	90
<b>V</b>	650.2(2)	978.20(14)	922.3(2)	1885.6(5)	591.81(8)
<b>Z</b>	2	2	4	8	4
<b><math>\rho_c</math></b>	1.381	1.384	1.269	1.199	1.394
<b>F(000)</b>	282	418	376	736	264
<b>Space group</b>	<i>P</i> -1	<i>P</i> 1	<i>Pnma</i>	<i>C2/C</i>	<i>Cm</i>

Code	Cy2T	Tp3T	BeT	QT	Da2Tw
<b>Formula</b>	<chem>C6H14N4S4</chem>	<chem>C18H14N6S3</chem>	<chem>C6H12N2O2S</chem>	<chem>C8H14N2S</chem>	<chem>C4H8N2O½S2</chem>
<b>Reflections:</b>					
<b>h, k, l</b>	0/10, -12 /12, -8/8	0/12, -2/12, -9/8	0/14, 0/7, 0/12	0/27, 0/7, -20/14	0/8, 0/13, -8/6
<b>Total measured</b>	2271	2902	906	1737	501
<b>Unique total</b>	2113	2902		1691	501
<b>Unique used</b>			509 (3σ)	1143 (3σ)	
<b>100R<sub>merge</sub></b>				2.2	
<b>Program</b>	SHELXL	SHELXL	TeXsan	TeXsan	SHELXL
<b>Weighting scheme</b>	SHELXL	SHELXL	Unit	Unit	SHELXL
<b>Data/parameters</b>	16.5	6.0	5.6	9.9	6.5
<b>100R;100R<sub>w</sub></b>			4.3; 4.5	3.8; 3.5	
<b>100R1: 100<sub>w</sub>R2 (2σ)</b>	6.64;17.70	4.5; 12.3			3.33; 9.09
<b>100R1:100<sub>w</sub> R2 (all data)</b>	12.63; 20.05	5.6; 13.5			3.36; 9.23
<b>GOF</b>	1.30 (on $F^2$ )	1.05 (on $F^2$ )	2.01	2.03	0.96 (on $F^2$ )
<b>ACP</b>		-0.05(5)			
<b>Residual e.d.</b>	-0.55/0.88	-0.43/0.35	-0.19/0.16	-0.16/0.17	-0.19/0.26

<b>Code</b>	<b>s2Mpz</b>	<b>UMen2t</b>	<b>3Spg3T</b>
<b>Formula</b>	$C_{16}H_{28}N_8S_4$	$C_6H_{14}N_4S_2$	$C_{15}H_{19}SN_3$
<b>Crystal size</b>	0.15, 0.2, 0.2	0.15, 0.2, 0.2	0.07, 0.15, 0.20
$\mu, \text{ cm}^{-1}$	38.58	40.9	2.0
<b>Max/Min</b>	1.00-0.69	1.00-0.89	1.00-0.86
<b><math>\theta</math> range</b>	6.0-60.03/24	5.0-63.5 /25	5.0-50.1/25
<b>a</b>	16.526(9)	8.9559(8)	8.052(3)
<b>b</b>	8.295(5)	9.325(1)	22.921(3)
<b>c</b>	17.722(5)	7.2095(7)	8.257(3)
<b><math>\alpha</math></b>	90	106.113(9)	90
<b><math>\beta</math></b>	91.30(4)	102.112(7)	90
<b><math>\gamma</math></b>	90	72.736(9)	90
<b>V</b>	2429(2)	547.0(1)	1523.9(6)
<b>Z</b>	8	2	4
<b><math>\rho_c</math></b>	1.522	1.25	1.187
<b>F(000)</b>	1168	220	580
<b>Space group</b>	$P2_1/c$	$P-1$	$Pbca$

<b>Code</b>	<b>s2Mpz</b>	<b>uMen2t</b>	<b>3Spg3T</b>
<b>Formula</b>	<chem>C16H28N8S4</chem>	<chem>C6H14N4S2</chem>	<chem>C15H19SN3</chem>
<b>Reflections:</b> <b>h, k, l</b>	0/18, 0/9, -19/19	0/10, -10/10, -8/8	0/9, 0/27, -9/0
<b>Total measured</b>	4058	1907	1578
<b>Unique total</b>	4058	1777	1578
<b>Unique used</b>		1509	217
<b>100R<sub>merge</sub></b>		0.051	0.0
<b>Program</b>	SHELXL	TeXsan	TeXsan
<b>Weighting scheme</b>	SHELXL	Unit	Unit
<b>Data/ parameters</b>	14.21	13.68	4.0
<b>100R;100R<sub>w</sub></b>	11; 42	4.4; 5.4	6.6;7.3
<b>100R1: 100<sub>w</sub>R2 (2σ)</b>			
<b>100R1:100<sub>w</sub>R2 (all data)</b>			
<b>GOF</b>	2.310	3.15	2.18
<b>ACP</b>			
<b>Residual e.d.</b>	-0.61/2.86	-0.26/0.28	-0.19/0.27

<b>Code</b>	<b>enZ4Tw</b>	<b>3enZ2T</b>	<b>s2MenZ4T</b>
<b>Formula</b>	C <sub>6</sub> H <sub>14</sub> N <sub>6</sub> O <sub>2</sub> S <sub>4</sub> Zn	C <sub>8</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> Zn	C <sub>8</sub> H <sub>14</sub> N <sub>6</sub> S <sub>4</sub> Zn
<b>Crystal size</b>	0.06, 0.10, 0.45	0.17, 0.20, 0.40	0.05, 0.08, 0.30
<b>U, cm<sup>-1</sup></b>	72.9	44.1	66.9
<b>Max/Min</b>	1.00-0.57	1.00-0.56	1.00-0.73
<b>θ range</b>	2.7-60.0/25	5.0-63.5/25	5.0-63.5/24
<b>a</b>	10.680(1)	8.946(2)	307.897(1)
<b>b</b>	13.054(1)	13.262(1)	20.476(2)
<b>c</b>	5.579(1)	14.180(1)	11.046(2)
<b>α</b>	90	90	90
<b>β</b>	90	98.38(1)	110.88(1)
<b>γ</b>	90	90	90
<b>V</b>	777.8(2)	1664.4(3)	1668.9(4)
<b>Z</b>	2	4	4
<b>ρ</b>	1.1690	1.444	1.544
<b>F(000)</b>	404	760	792
<b>Space group</b>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> /c	<i>P</i> 2 <sub>1</sub> /n

<b>Code</b>	<b>EnZ4Tw</b>	<b>3enZ2T</b>	<b>s2MenZ4T</b>
<b>Formula</b>	C <sub>6</sub> H <sub>14</sub> N <sub>6</sub> O <sub>2</sub> S <sub>4</sub> Zn	C <sub>8</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> Zn	C <sub>8</sub> H <sub>14</sub> N <sub>6</sub> S <sub>4</sub> Zn
<b>Reflections:</b> <b>h, k, l</b>	0/12 0/14 0/6	-/10, 0/15, -16/6	0/9, 0/23, -12/11
<b>Total measured</b>	708	3045	3000
<b>Unique total</b>	708	2847	2786
<b>Unique used</b>		1946 (3σ)	3039 (3σ)
<b>100R<sub>merge</sub></b>		1.6	1.7
<b>Program</b>	SHELXL	TeXsan	TeXsan
<b>Weighting scheme</b>	SHELXL	Unit	Unit
<b>Data/parameters</b>	7.3	11.3	8.9
<b>100R;100R<sub>w</sub></b>		3.9; 4.0	2.8; 3.2
<b>100R1: 100<sub>w</sub>R2 (2σ)</b>	3.9; 10.3		
<b>100R1:100<sub>w</sub>R2 (all data)</b>	4.0; 10.4		
<b>GOF</b>	0.95 (on F <sup>2</sup> )	2.63	1.55
<b>ACP</b>	-0.11(8)		
<b>Residual e.d.</b>	-0.60/0.31	-0.50/0.31	-0.33/0.27

**Table 18 Positional and thermal parameters of Chapter 3 complexes  
Non-hydrogen and H(N) atoms only.**

QT	x	y	z	U
S(1)	0.1131(1)	0.5841(3)	0.4757(1)	0.083(1)
N(1)	0.2245(3)	0.9004(8)	0.5797(4)	0.085(2)
N(2)	0.3347(2)	0.2140(7)	0.7049(3)	0.066(1)
C(1)	0.1773(3)	0.7693(9)	0.5348(4)	0.064(1)
C(2)	0.4310(3)	0.5020(9)	0.8256(4)	0.067(2)
C(3)	0.3939(3)	0.5308(10)	0.7095(5)	0.079(2)
C(4)	0.3347(4)	0.3609(10)	0.6369(5)	0.072(2)
C(5)	0.4717(4)	0.2979(12)	0.8677(6)	0.100(2)
C(6)	0.4143(4)	0.1207(9)	0.7936(6)	0.091(2)
C(7)	0.3659(4)	0.5055(11)	0.8213(5)	0.082(2)
C(8)	0.3093(3)	0.3305(11)	0.7510(5)	0.078(2)
H(14)	0.2986	0.1047	0.6598	0.064

**4Men2T**

	x	y	z	U
S(1)	0.3651(1)	0.7635(1)	0.2847(2)	0.087(1)
N(1)	0.1652(4)	0.7208(3)	0.6487(4)	0.070(1)
N(2)	0.1259(3)	1.2761(2)	0.522(3)	0.044(1)
C(1)	0.2506(3)	0.7400(3)	0.5010(5)	0.048(1)
C(2)	0.2835(4)	1.2899(4)	0.2257(5)	0.062(1)
C(3)	0.0662(3)	1.4225(3)	-0.0736(4)	0.046(1)
C(4)	0.1879(4)	1.1123(3)	-1.095(5)	0.056(1)
H(9)	0.0109	1.2752	0.1301	0.066

**4Mbn2T**

	x	y	z	U(eq)
S(1)	0.8848(2)	0.7350(3)	0.6902(2)	0.099(1)
N(2)	0.7168(6)	0.2336(9)	0.9274(4)	0.080(2)
N(3)	0.6989(9)	0.4756(13)	0.7471(6)	0.117(3)
C(4)	0.7771(10)	0.5825(12)	0.7251(6)	0.078(2)
C(5)	0.5832(8)	0.2636(11)	0.9696(6)	0.085(2)
C(6)	0.7175(10)	0.0406(12)	0.8833(6)	0.099(3)
C(7)	0.8621(8)	0.2788(11)	1.0169(7)	0.100(3)
C(8)	0.5669(9)	0.4743(15)	0.9898(10)	0.151(4)
H(11)	0.7080	0.3181	0.8668	0.095

## BeT

	x	y	z	B
S(1)	0.4684(1)	0.7500	0.1021(1)	7.09(4)
O(1)	0.4869(2)	0.2500	0.4177(3)	5.24(8)
O(2)	0.3143(3)	0.2500	0.4623(3)	7.1(1)
N(1)	0.4584(4)	0.7500	0.3525(4)	6.8(1)
N(2)	0.2635(2)	0.2500	0.2046(3)	4.05(8)
C(1)	0.4641(3)	0.7500	0.2475(4)	4.5(1)
C(2)	0.3856(3)	0.2500	0.3908(4)	4.5(1)
C(3)	0.3735(3)	0.2500	0.2542(4)	4.0(1)
C(4)	0.2024(3)	0.4333(6)	0.2434(5)	6.2(1)
C(5)	0.2731(4)	0.2500	0.0681(4)	6.0(1)
H(1)	0.496(4)	0.2500	0.494(5)	7(1)

## 4Mpn2T

	x	y	z	B
S(1)	0.5459(3)	0.0757(2)	0.0991(5)	6.38(9)
S(2)	1.0473(3)	0.0629(2)	0.1063(4)	5.53(8)
N(1)	0.6069(8)	0.2229(6)	0.257(1)	7.3(3)
N(2)	0.9125(8)	0.1428(6)	0.353(1)	6.8(3)
N(3)	0.7671(7)	0.1525(5)	0.652(1)	4.5(2)
N(4)	0.7596(7)	0.3462(5)	0.356(1)	4.5(2)
C(1)	0.5834(8)	0.1618(7)	0.190(1)	4.5(3)
C(2)	0.9682(8)	0.1101(6)	0.250(1)	4.4(3)
C(3)	0.7022(8)	0.2323(6)	0.679(1)	4.6(2)
C(4)	0.7767(8)	0.3088(6)	0.675(1)	4.7(3)
C(5)	0.8378(8)	0.3306(6)	0.509(1)	4.6(2)
C(6)	0.8484(9)	0.1340(7)	0.799(2)	5.5(3)
C(7)	0.6874(9)	0.0801(7)	0.625(2)	5.9(3)
C(8)	0.824(1)	0.3533(8)	0.189(2)	6.7(4)
C(9)	0.6808(9)	0.4182(7)	0.378(2)	5.7(3)
H(1)	0.8115	0.1585	0.5421	5.5606
H(2)	0.7095	0.2985	0.3402&	5.5878

## Da2Tw

	x	y	z	U(eq)
S(1)	0.6023(1)	0.6628(1)	0.2739(1)	0.054(1)
O(1)	0.8144(4)	0.5000	0.6991(4)	0.030(1)
N(1)	0.4401(6)	0.8172(2)	-0.0512(5)	0.056(1)
N(2)	0.9047(5)	0	0.5597(6)	0.030(1)

N(3)	0.5831(6)	0	0.5587(6)	0.029(1)
C(1)	0.5060(6)	0.7539(3)	0.0819(5)	0.038(1)
C(2)	0.7316(8)	0	0.3338(8)	0.047(1)
C(3)	0.5318(8)	0	0.3308(8)	0.045(1)
C(4)	0.8990(6)	0.0983(3)	0.6693(8)	0.058(1)
C(5)	0.6999(6)	0.0987(3)	0.6690(8)	0.056(1)
H(7)	1.0294	0	0.5597	0.034
H(8)	0.4583	0	0.5570	0.032

## S2Mpz2T

	x	y	z	B
S(1)	0.3322	0.9772	0.8751	3.029
S(2)	0.4188	0.0330	0.3715	4.782
S(3)	0.0822	0.5015	0.6237	5.512
S(4)	0.1743	-0.4983	0.1269	8.520
N(1)	0.3661	0.7783	0.7504	3.053
N(2)	0.3772	0.2008	0.5009	4.343
N(3)	0.1221	0.2911	0.4835	12.596
N(4)	0.1174	-0.2930	0.3043	15.059
N(5)	0.3761	0.6574	0.6123	2.721
N(6)	0.3775	0.3287	0.6426	1.825
N(7)	0.1244	0.1884	0.3919	3.282
N(8)	0.1255	-0.1888	0.3970	4.952
C(1)	0.3481	0.8619	0.8017	1.123
C(2)	0.3961	0.1303	0.4465	1.646
C(3)	0.0986	0.3527	0.5435	14.510
C(4)	0.1442	-0.3871	0.2195	10.306
C(5)	0.4483	0.5557	0.5892	0.913
C(6)	0.4457	0.4159	0.6504	1.718
C(7)	0.3089	0.4109	0.6589	3.909
C(8)	0.2979	0.5498	0.5927	2.709
C(9)	0.3698	0.8019	0.5559	2.937
C(10)	0.3769	0.1800	0.6949	2.182
C(11)	0.2015	0.0704	0.3557	7.356
C(12)	0.1925	-0.0829	0.3681	13.212
C(13)	0.0507	-0.0667	0.3634	4.469
C(14)	0.0473	0.0590	0.3790	10.008
C(15)	0.1101	0.2829	0.3164	19.457
C(16)	0.1155	-0.2922	0.4858	5.699

## 3spg3T

x	y	z	B(eq)
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S(1)	0.594(1)	0.3439(4)	0.365(1)	11.6(3)
N(1)	0.617(2)	0.1625(5)	0.346(2)	1.9(3)
C(1)	0.5000	0.331(3)	0.2500	17(2)
C(2)	0.621(2)	0.0973(7)	0.336(2)	3.7(4)
C(4)	0.756(2)	0.004(1)	0.394(2)	5.1(4)
C(5)	0.627(2)	-0.0226(7)	0.320(2)	3.7(5)
C(6)	0.5000	0.007(1)	0.2500	1.9(5)
C(7)	0.5000	0.0683(9)	0.2500	1.4(5)
C(8)	0.564(2)	0.1788(7)	0.509(2)	2.3(4)
C(9)	0.779(2)	0.1894(7)	0.299(2)	4.3(5)
C(10)	0.759(3)	0.0673(9)	0.398(2)	4.9(5)

## s2MenZ4T

	x	y	z	B <sub>eq</sub>
Zn(1)	0.76925(6)	0.36786(2)	0.65237(4)	3.87(1)
S(1)	0.7839(1)	0.46243(4)	1.04397(8)	4.00(2)
S(2)	0.6345(1)	0.50783(5)	0.29516(9)	5.69(2)
S(3)	1.1876(1)	0.19961(4)	0.78076(9)	4.94(2)
S(4)	0.2741(1)	0.23639(5)	0.4431(1)	5.74(3)
N(1)	0.8146(4)	0.4149(1)	0.8164(3)	4.36(7)
N(2)	0.7332(4)	0.4316(1)	0.5152(3)	5.22(8)
N(3)	0.9744(4)	0.3077(1)	0.6740(3)	4.63(7)
N(4)	0.5493(4)	0.3133(2)	0.6050(3)	5.31(8)
N(5)	0.8755(4)	0.1120(1)	0.5645(3)	3.88(7)
N(6)	0.5952(4)	0.1319(2)	0.7766(3)	4.46(7)
C(1)	0.8020(4)	0.4349(1)	0.9098(3)	3.41(7)
C(2)	0.6902(4)	0.4635(2)	0.4234(3)	3.86(7)
C(3)	1.0623(4)	0.2629(2)	0.7164(3)	3.77(7)
C(4)	0.4354(5)	0.2817(2)	0.5375(3)	4.03(8)
C(5)	0.8673(6)	0.1390(2)	0.4383(4)	5.0(1)
C(6)	0.7289(4)	0.1373(2)	0.6079(4)	4.22(8)
C(7)	0.7407(5)	0.1063(2)	0.7342(4)	4.53(9)
C(8)	0.5871(6)	0.0979(2)	0.8931(5)	5.6(1)
H(4)	0.991(5)	0.124(2)	0.629(3)	5.6(8)
H(5)	0.887(5)	0.071(2)	0.564(3)	5.5(8)
H(10)	0.592(5)	0.172(2)	0.783(3)	4.7(8)
H(12)	0.473(5)	0.128(2)	0.702(3)	5.3(7)

## 3Men2T

	x	y	z	U(eq)
S(1)	1.2301(2)	0.1144(2)	-0.3057(2)	0.086(1)

S(2)	0.2798(2)	0.4132(3)	-0.7379(3)	0.114(1)
N(1)	0.9787(5)	0.1749(6)	-0.1297(7)	0.087(2)
N(2)	0.4924(8)	0.2908(9)	-0.4697(12)	0.135(3)
N(3)	0.8424(5)	0.3265(5)	0.1864(6)	0.067(1)
N(4)	0.6708(5)	0.1656(6)	-0.1795(7)	0.080(1)
C(1)	1.0830(5)	0.1497(5)	-0.2031(7)	0.058(1)
C(2)	0.4007(8)	0.3410(8)	-0.5872(11)	0.093(2)
C(3)	0.6723(13)	0.3535(15)	0.1080(2)	0.069(3)
C(4)	0.7018(12)	0.2715(15)	0.1604(16)	0.061(3)
C(5)	0.6278(13)	0.2136(15)	0.0272(18)	0.067(3)
C(6)	0.6119(12)	0.2962(15)	-0.0348(16)	0.063(3)
C(7)	0.8541(8)	0.4843(7)	0.2185(9)	0.092(2)
C(8)	0.9167(10)	0.2625(7)	0.3560(9)	0.105(2)
C(9)	0.6536(9)	0.0181(11)	-0.2037(11)	0.115(3)
H(1)	0.5900	0.2112	-0.3216	0.006
H(14)	0.8784	0.2957	0.0946	0.109
H(16)	0.7522	0.1665	-0.1852	0.060

## U2Men2T

	x	y	z	B(eq)
S(1)	1.20458(7)	0.20812(7)	0.74960(8)	4.11(1)
S(2)	0.26033(7)	0.39464(7)	0.34229(8)	4.20(1)
N(1)	0.9802(3)	0.1974(3)	0.4158(3)	5.21(6)
N(2)	0.4908(2)	0.3627(3)	0.1194(3)	5.49(5)
N(3)	0.8000(2)	0.4184(2)	0.1894(3)	3.60(4)
N(4)	0.6786(2)	0.1683(2)	-0.1637(2)	2.94(3)
C(1)	1.0722(3)	0.2021(2)	0.5535(3)	3.34(5)
C(2)	0.3972(2)	0.3735(2)	0.2140(3)	3.33(4)
C(3)	0.8692(2)	0.3319(3)	0.0075(3)	3.42(5)
C(4)	0.8424(2)	0.1748(2)	-0.0643(3)	3.39(4)
C(5)	0.6437(3)	0.2087(3)	-0.3575(3)	4.24(5)
C(6)	0.6525(3)	0.0150(3)	-0.1832(4)	4.90(6)
H(1)	0.6063	0.2423	-0.0832	3.534
H(6)	0.8158	0.5194	0.2258	4.317
H(7)	0.8500	0.3661	0.2907	4.317
H(8)	0.6901	0.4248	0.1677	4.317

## Cy2T

	x	y	z	U(eq)
S(1)	0.6383(2)	-0.1981(2)	0.2943(3)	0.058(1)
S(2)	0.8816(2)	0.6619(2)	0.7045(2)	0.059(1)

S(3)	0.6233(2)	0.1490(2)	0.3366(2)	0.055(1)
S(4)	0.8652(2)	0.1872(2)	0.5074(2)	0.054(1)
N(1)	0.7904(7)	-0.0973(6)	0.0660(9)	0.062(2)
N(2)	0.7091(7)	0.5326(6)	0.8932(9)	0.062(2)
N(3)	0.6538(6)	0.4961(5)	0.2374(7)	0.052(1)
N(4)	0.8452(6)	-0.0035(5)	0.7558(7)	0.050(1)
C(1)	0.7260(7)	-0.1394(6)	0.1587(9)	0.046(1)
C(2)	0.7816(7)	0.5861(6)	0.8144(8)	0.046(1)
C(3)	0.8595(8)	0.2200(7)	0.7539(9)	0.056(2)
C(4)	0.7722(8)	0.1062(7)	0.7925(9)	0.057(2)
C(5)	0.5946(7)	0.3091(6)	0.3487(9)	0.047(1)
C(6)	0.6755(8)	0.3653(7)	0.2269(9)	0.051(2)
H(9)	0.8196	-0.0563	0.8315	0.062
H(10)	0.9605	0.0264	0.7920	0.062
H(11)	0.7963	-0.0522	0.6206	0.062
H(12)	0.6853	0.5462	0.3704	0.062
H(13)	0.7223	0.5346	0.1776	0.062
H(14)	0.5410	0.4890	0.1694	0.062
H(15)	0.9706	0.2503	0.8456	0.069

## en2T

S(1)	1.0785(1)	-0.1168(1)	0.8240(1)	0.047(1)
S(2)	0.4435(1)	0.2197(1)	0.6959(1)	0.042(1)
N(1)	0.4590(3)	0.1187(3)	0.8963(1)	0.039(1)
N(2)	1.0599(3)	-0.0127(3)	0.6190(1)	0.041(1)
N(3)	0.6511(4)	-0.0237(3)	0.6238(2)	0.052(1)
N(4)	0.8581(4)	0.1251(3)	0.8904(2)	0.054(1)
C(1)	0.4620(4)	0.0879(4)	0.9875(2)	0.040(1)
C(4)	1.0681(4)	0.0504(4)	0.5325(2)	0.043(1)
C(5)	0.5657(4)	0.0768(4)	0.6542(2)	0.036(1)
C(6)	0.9487(4)	0.0244(4)	0.8628(2)	0.040(1)
H(5)	0.5845	0.1094	0.8857	0.091
H(6)	0.3813	0.0350	0.8637	0.114
H(7)	0.4114	0.2300	0.8814	0.003
H(8)	1.1069	-0.1260	0.6255	0.021
H(9)	1.1344	0.0608	0.6595	0.050
H(10)	0.9324	-0.0100	0.6270	0.048

## enZ4Tw

	x	y	z	U
Zn(1)	0	0	1.2477(2)	0.029(1)

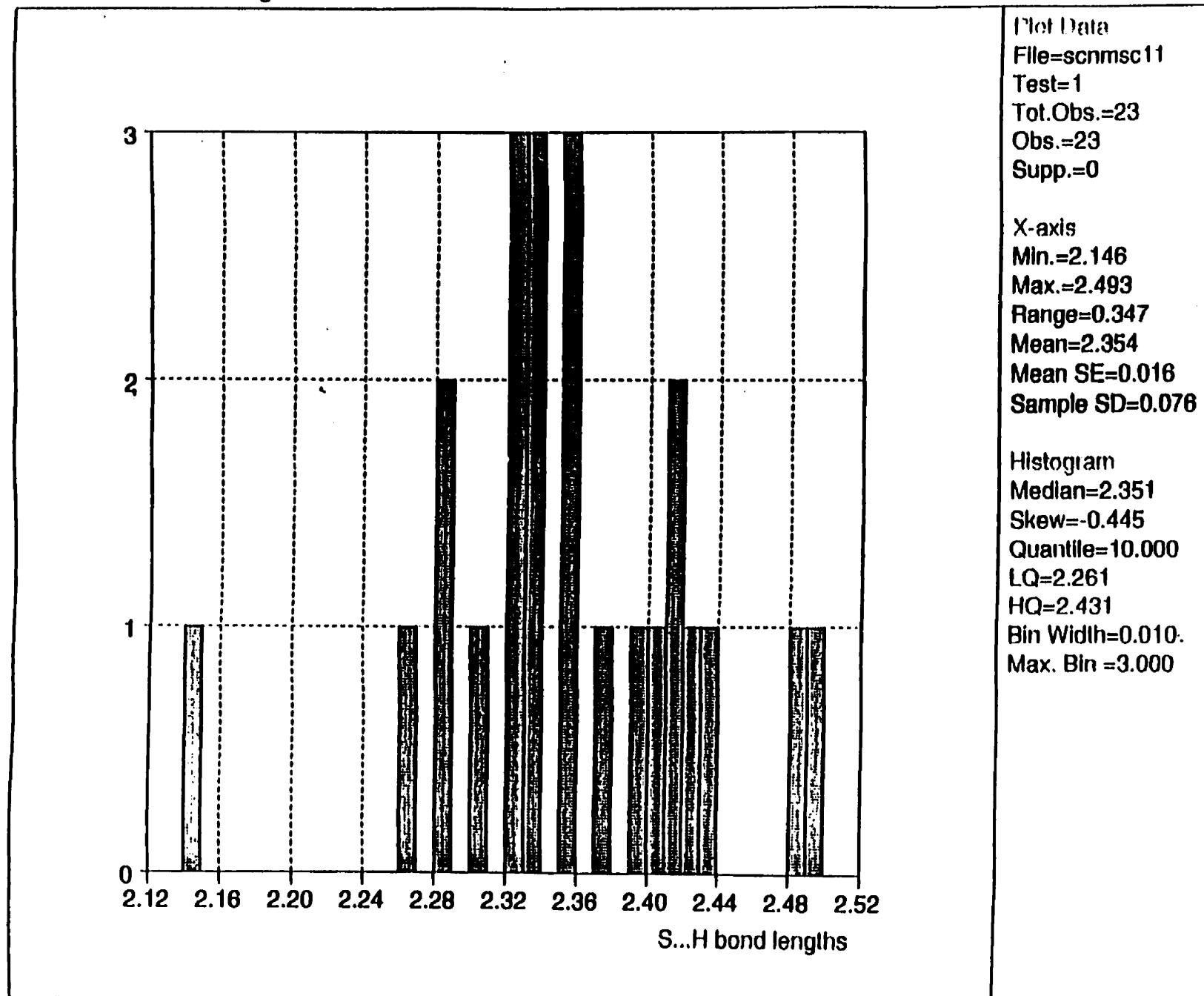
S(1)	0.2473(2)	-0.1438(2)	0.6420(4)	0.046(1)
S(2)	0.1343(2)	0.2190(2)	1.8602(4)	0.044(1)
O(1)	0.4325(7)	0.1771(6)	0.6929(18)	0.071(2)
N(1)	0.1306(7)	-0.0572(5)	1.0395(14)	0.039(2)
N(2)	0.0815(7)	0.1016(5)	1.4573(14)	0.039(2)
N(3)	0.3702(8)	0.0968(6)	1.2010(2)	0.062(3)
C(1)	0.1779(7)	-0.0930(6)	0.8743(18)	0.034(2)
C(2)	0.1034(7)	0.1493(6)	1.6236(16)	0.032(2)
C(3)	0.4390(14)	0.0042(11)	1.1940(4)	0.121(7)
H(1)	0.2830	0.0827	1.1919	0.077
H(2)	0.3874	0.1318	1.3473	0.077

## 3enZ2T

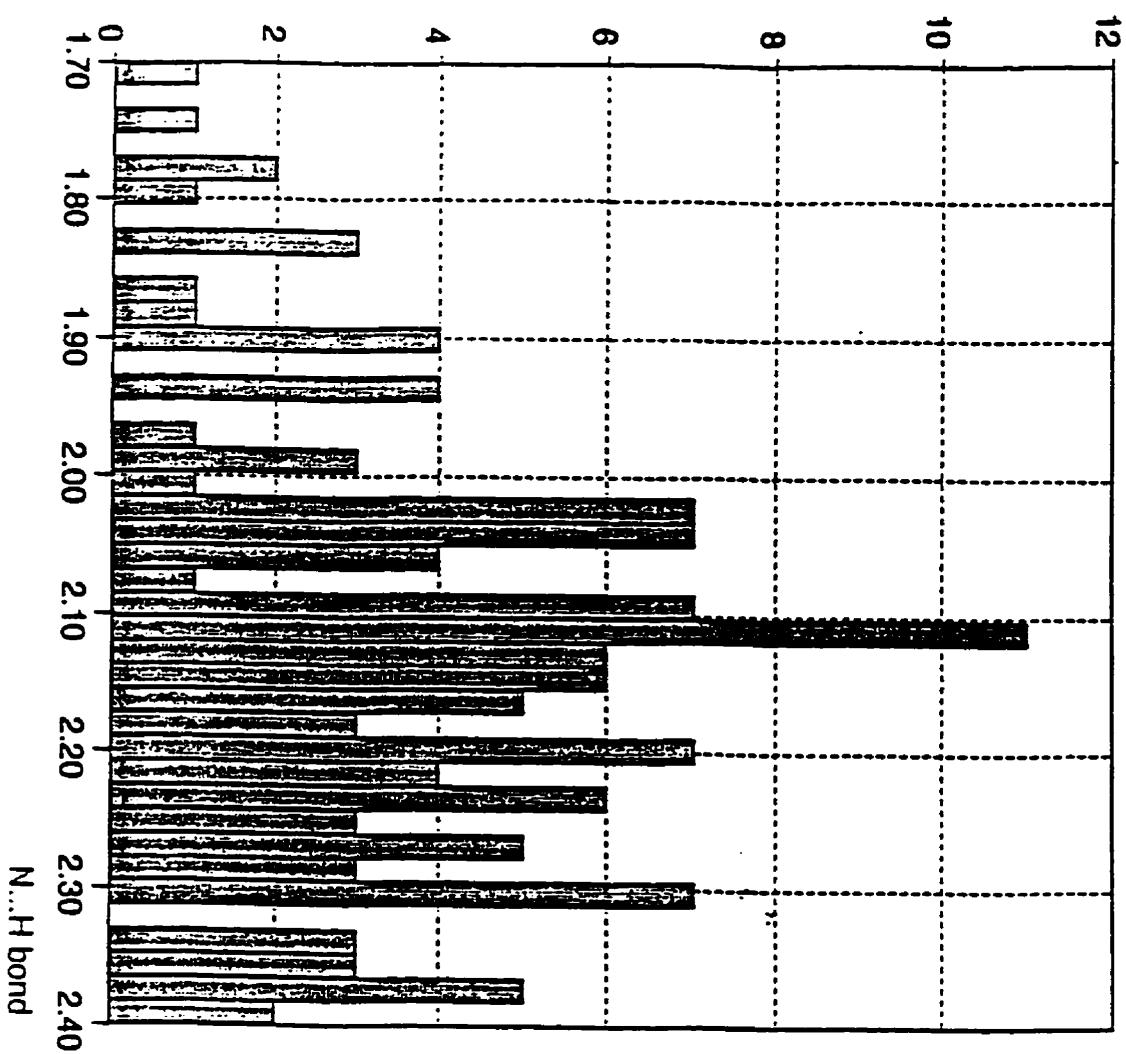
	x	y	z	B <sub>eq</sub>
Zn(1)	0.24905(4)	0.01436(2)	0.24442(2)	3.752(8)
S(1)	0.7514(1)	0.11171(9)	0.44920(7)	7.24(3)
S(2)	0.7600(1)	0.00279(9)	0.19290(8)	7.40(3)
N(1)	0.7528(5)	0.3154(3)	0.4941(2)	8.7(1)
N(2)	0.7546(4)	-0.1639(3)	0.3082(3)	8.2(1)
N(3)	0.1113(3)	0.1155(2)	0.1430(2)	4.66(6)
N(4)	0.3795(3)	0.0111(2)	0.1258(2)	4.76(6)
N(5)	0.1176(3)	-0.1198(2)	0.1976(2)	4.01(6)
N(6)	0.3890(3)	-0.1027(2)	0.3268(2)	4.35(6)
N(7)	0.3810(3)	0.1357(2)	0.3206(2)	5.05(7)
N(8)	0.1107(3)	0.0448(2)	0.3576(2)	4.38(6)
C(1)	0.7520(5)	0.2305(4)	0.4752(2)	6.8(1)
C(2)	0.7545(4)	-0.0988(3)	0.2592(3)	6.4(1)
C(3)	0.1633(4)	0.1046(3)	0.0493(2)	5.43(8)
C(4)	0.3332(4)	0.0979(3)	0.0637(2)	5.35(8)
C(5)	0.1691(4)	-0.2030(2)	0.2618(2)	4.83(8)
C(6)	0.3393(4)	-0.2009(2)	0.2852(2)	5.12(8)
C(7)	0.3294(4)	0.1468(3)	0.4145(3)	6.7(1)
C(8)	0.1624(4)	0.1400(3)	0.4046(3)	6.3(1)
H(1)	0.1236	0.1833	0.1641	5.5878
H(3)	0.3599	-0.0499	0.0910	5.7056
H(4)	0.4843	0.0154	0.1494	5.7056
H(5)	0.1319	-0.1371	0.1348	4.8911
H(7)	0.4921	-0.0934	0.3230	5.3107
H(10)	0.3653	0.1967	0.2856	6.0128

NCS...H-AA bond lengths for S...H<2.5A

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## SCN...II-AA where N...H bond is &lt;2.4 Å scnmisc6



Histogram  
 Median=2.126  
 Skew=-0.454  
 Quantile=10.000  
 LQ=1.909  
 HQ=2.331  
 Bin Width=0.018  
 Max. Bin = 11.000

## Chapter 4 Experimental

### a) Preparation of the compounds

The preparation of all the compounds described in this thesis starts with barium thiocyanate. Since  $\text{Ba}(\text{SCN})_2$  is very soluble in water and  $\text{BaSO}_4$  is very insoluble (0.0002 g/100 ml of water at 25°C) [14], the required thiocyanate salts can easily be prepared by removing the barium as the sulphate.

#### i) Barium thiocyanate

$\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$  was prepared according to the method of Herstein [15]. 7.6 g (0.1 mol) of ammonium thiocyanate was mixed with 15.8 g (0.05 mol) of barium hydroxide ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ). The mixture was shaken, until it liquefied, in a round bottom flask and was then boiled under reduced pressure until there was no longer a smell of ammonia (8 hours). Water lost during the boiling was replaced at intervals. After the eight-hour period the resulting solution was tested and found to be alkaline to phenolphthalein<sup>1</sup>. The solution was filtered and 3M  $\text{H}_2\text{SO}_4$  was added to the filtrate until the filtrate was just colourless to phenolphthalein.  $\text{CO}_2$  was bubbled through the solution to remove any residual  $\text{Ba}(\text{OH})_2$  and the solution was then boiled to remove any  $\text{Ba}(\text{HCO}_3)_2$ . The solution was filtered, and the filtrate concentrated by boiling until its boiling point reached 125°C (but no

---

<sup>1</sup> If the solution is not alkaline to phenolphthalein, more  $\text{Ba}(\text{OH})_2$  should be added and the boiling continued until no more ammonia is evolved.

higher). The solution was then allowed to cool and long clear white needles of  $\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$  separated out. The yield of the pure material was 9.7 g (63%). When the supernatant liquid was drained from the crystals and the liquid left to stand, a further 2.8g (18%) of smaller (slightly yellow) needles were collected.

### ii) Zinc complexes

The zinc complexes were prepared from zinc thiocyanate. A small quantity<sup>2</sup> of  $\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$  was dissolved in water.  $\text{ZnSO}_4$  solution was added until no further precipitate of  $\text{BaSO}_4$  formed<sup>3</sup>. The resultant solution contained the pure  $\text{Zn}(\text{SCN})_2$ .

The ethylenediamine complexes were prepared from this solution by the addition of an equi-molar quantity of the appropriate aqueous ethylenediamine or methylated ethylenediamine. The complex separated out overnight as a white powder. This was filtered and recrystallised from acetone.

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<sup>2</sup> The molecular weight of  $\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$  is 289.5. Usually 0.965 g (.0033 mol) was used as the starting material

<sup>3</sup> Initially a strong solution of  $\text{ZnSO}_4$  was added but more and more dilute  $\text{ZnSO}_4$  solutions were used as the concentration of  $\text{Ba}^{2+}$  ions in solution began to fall. When nearly all the  $\text{Ba}^{2+}$  ions had been precipitated, 0. 01 mol  $\text{ZnSO}_4$  was added, drop by drop, until no new turbidity was seen as the new drop was added.

### iii) Organoammonium thiocyanate salts

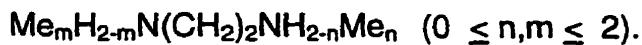
All the thiocyanate salts were prepared by adding thiocyanic acid to the amine until the acid was present in excess ( a drop of solution gave a red colour to universal indicator paper).

Thiocyanic acid was prepared from Ba(SCN)<sub>2</sub>.2H<sub>2</sub>O. A small quantity (1.0 g) was dissolved in water and treated with roughly 3 ml of 1M H<sub>2</sub>SO<sub>4</sub>. The solution was filtered and 0.01M H<sub>2</sub>SO<sub>4</sub> was added, drop by drop, until a drop produced no new turbidity. The solution was filtered again and the resultant thiocyanic acid was securely stoppered in a brown-glass bottle and stored in the refrigerator. Experience showed that under these conditions it remained stable for several months.

The amines were commercially available materials from Aldrich. The organoammonium thiocyanate salts were prepared by adding the thiocyanic acid to 0.01 mol of the amine in water. As the acid was added, the amine dissolved. Once the solution had excess acid it was put aside to recrystallise. By this method, many of the salts produced crystals suitable for X-ray diffraction study. Some produced only fine powders and these were successfully recrystallised from either acetone/water mixtures or from acetonitrile. Yields were not recorded since the purpose was the preparation of crystalline samples that contained at least one crystal suitable for X-ray diffraction studies.

(iiia) The thiocyanate salts of ethylenediamine and methylated ethylenediamines.

Attempts were made to prepare the whole series of thiocyanate salts derived from ethylenediamine and the methylated ethylenediamines:



Originally the *unsymmetric*  $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NH}_2$  amine was not available and had to be purchased from Aldrich. This took some three months to arrive so the preparation of the *unsymmetric* salt was delayed. Two batches of each preparation were done, the batches were separated by about 10 days and fresh thiocyanic acid was prepared for each batch. The salts derived from ethylenediamine ( $m=n=0$ ), and from the tetramethyl-ethylenediamine ( $m=n=2$ ) crystallised within a week of their preparation, the salt derived from the mono-methylated ethylenediamine ( $m=1, n=0$ ) is still an oil after 15 months. After 14 months, crystals appeared in one of the solutions where the salt was originally derived from the *symmetric*-  $\text{MeHN}(\text{CH}_2)_2\text{NHMe}$ . When the crystal structure of this salt was determined it was found to be the salt of the *unsymmetric* -  $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NH}_2$  amine. The flask was clearly labeled and dated. The date corresponded to a time when the *unsymmetric* - $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NH}_2$  amine was not available. It would appear therefore that the N-methyl group is labile when in solution as the thiocyanate salt.

A possible mechanism for this lability is shown below. If the methyl groups are labile, then, according to the scheme given below, they would tend to transform the *symmetric* to the *unsymmetric* amine. This lability of the methyl groups will, in some instances, produce a mixture of products and this mixture

may explain why the salt derived from monomethylethylenediamine has never crystallised [16].

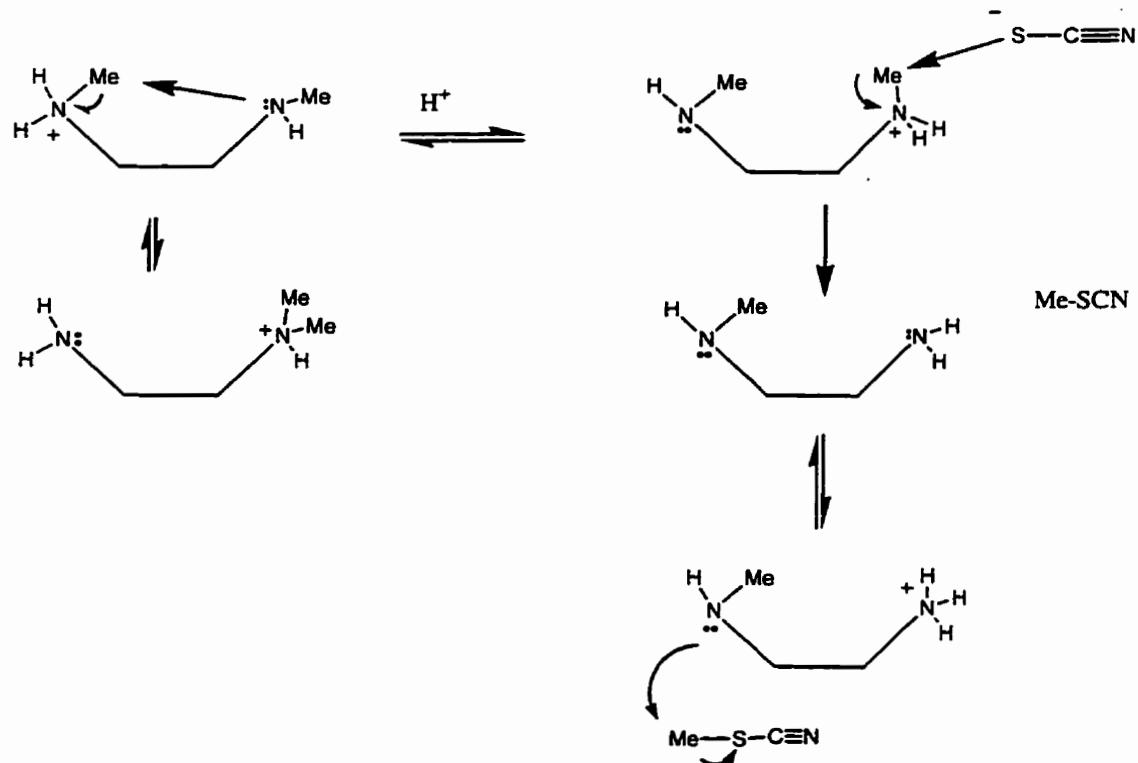


Figure 60. Methyl migration mechanism

### b) X-ray data collection

For the single-crystal X-ray diffraction, the crystals were mounted on glass fibres in the usual manner. All measurements were made on a Rigaku AFC5R

diffractometer with graphite monochromated Cu-K $\alpha$  radiation and a rotating anode generator. The individual details for each structure are given in the section on Crystal data on Table 7 (Chapter 2) and Table 17 (Chapter 3).

The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered high-angle reflections.

The data were collected at a temperature of  $23 \pm .1^\circ\text{C}$  using the  $\omega$ -2 $\theta$  scan technique to a maximum 2 $\theta$  value of  $127.1^\circ$ . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of  $0.28^\circ$  with a take-off angle of  $6.0^\circ$ . Scans of  $(1.10 + 0.35 \tan \theta)^\circ$  were made at a speed of  $8.0^\circ/\text{min}$  (in  $\omega$ ). The weak reflections ( $I < 15.0\sigma(I)$ ) were rescanned (maximum of 6 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 285 mm, and the detector aperture was 9.0 x 13.0 mm (horizontal x vertical).

Azimuthal scans (psi scans) were done with several reflections to determine an empirical absorption correction. The data were corrected for Lorentz and polarization effects and, if necessary, an empirical absorption or secondary extinction correction was applied.

### Structure Solution and Refinement

The structures were solved by direct methods[17] and expanded using Fourier techniques[18]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Neutral atom scattering factors were taken from Cromer and Waber [19]. Anomalous dispersion effects were included in  $F_{\text{calc}}$ [20]; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley[21]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[22]. All calculations were performed using the TeXsan [23] crystallographic software package of Molecular Structure Corporation.

### Conclusions

In Chapter 2, complexes of tetrahedral four-coordinate zinc were used to study the hydrogen bonding that occurs at the sulphur end of the thiocyanate ion. Two coordination sites of the zinc were occupied by the thiocyanate anion (with the nitrogen atom of the thiocyanate bonded to zinc) and the remaining two by the bidentate ligand ethylenediamine, or its methylated derivative. All hydrogen atoms were involved in hydrogen bonds, and branching occurred when not required. From the regressions that were done on the hydrogen bond distances and angles, it was shown that the N-H...S angles should be 180° for distances below 2.3 Å. Also, H(N)...S interactions were no longer effective at distances greater than 3.5 Å and H(N)...S distances greater than 2.7 Å occurred as the longer branch of a bifurcated bond.

The study of Chapter 3 was the preference of the thiocyanate system towards N-H...NCS or N-H...SCN bonding. In these systems, the thiocyanate ion had both ends free to form hydrogen bonds. A series of organoammonium thiocyanates were prepared, varying the ratio of available H(N) atoms to thiocyanate ions. In the group of cations that form an n:n ratio with the thiocyanate ions, the overwhelming preference of the thiocyanate ion is to form a single N-H...NCS bond. In the cases where the number of H(N) atoms were larger than the number of thiocyanate ions, the ion will first form two separate bonds to the nitrogen atom of the thiocyanate ion before forming an N-H...SCN bond. Thus the somewhat weaker (N-H)<sub>2</sub>...NCS bonds were preferred to a single N-H...SCN bond.

## References

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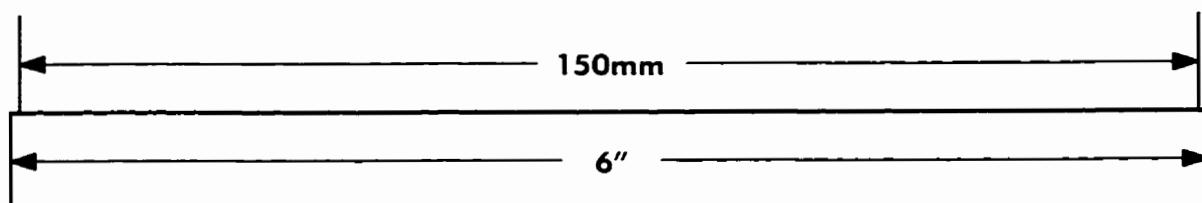
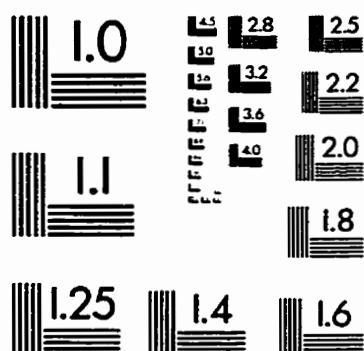
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