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Statistical Analysis of Noncovalent Interactions of Anion Groups in Crystal Structures. II. Hydrogen Bonding of Thiocyanate Anions

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Abstract

The hydrogen-bond acceptor function of the thiocyanate anion is analyzed in 52 crystal structures retrieved from the Cambridge Crystallographic Database. All modes of hydrogen-bond coordination are represented: by the sulfur, by the nitrogen and by the π-system of the anion. The preferred areas for the H donors ($D = \text{OH}$ and NH groups) were determined: (*a*) around sulfur, as a torus centered at the S end, the axis of which is the linear anion, and with an average *D*SN angle of 99°, and (*b*) around nitrogen, on a spherical cap delimited by the solid angle, SN*D* (average = 145°), with the linear anion. The anion–acceptor function is characterized by multiple hydrogen bonding and, in most cases (80%), thiocyanate binds through both acceptor centers (S and N). Important backbonding of sulfur in the thiocyanate anion is structurally evidenced.

1. Introduction

Experimental data on the associations between macromolecules and anions being very rare and far from accurate (Chakrabarti, 1993; Pflugrath & Quiocho, 1988), it appeared to us that a good way to study the interactions with anions was to observe their hydrogen bonding through a survey of small-molecule crystal structures, with the aim of relating the results to biological systems. It has been reported that thiocyanate belongs to a family of powerful protein-solubilizing and structure-destabilizing agents (Bradbury & Jakoby, 1972; Arakawa & Timasheff, 1982*a*,*b*; Sousa, 1995). This property is related to their interaction with the protein. In the course of our studies of the hydrogen bonding of anions in the crystal state (Chertanova & Pascard, 1996), we undertook systematic studies on the thiocyanate (isothiocyanate) anion whose H-coordination function has not previously been the subject of such an analysis.

Thiocyanate is a linear triatomic system, wherein the negative charge can be localized on one of the terminal atoms or delocalized over the whole anion

$$^{-}\text{SCN} \longleftrightarrow \text{SCN}^{-} \longleftrightarrow (\text{SCN})^{-}.$$

Binding by both sulfur and nitrogen can occur, along with the possible interaction with the combined π-system of SC and CN bonds and the lone pairs of N and S, respectively. The first theoretical studies were reviewed by Hargittai & Paul (1977) and recently developed by *ab initio* molecular orbital (MO) calculations (Parrini & Morales, 1993). Experimental data, however, were obtained only by microwave, IR and photoelectron spectroscopy (Leung, Suffolk & Watts, 1986) in the gas phase.

Up to now, structural data from crystallographic studies were scattered throughout the literature and the accuracy of each structure was not sufficient to describe the real binding properties of $(\text{SCN})^{-}$. The availability of the Cambridge Crystallographic Database allows systematic studies of all the structures containing SCN stored in the database. As we were concerned primarily with the hydrogen bonding of the $(\text{SCN})^{-}$ anion, and with a comparison of the geometrical features of the hydrogen bonds (H-coordination function) around sulfur and nitrogen, we selected crystal structures in which the anion neither binds covalently nor coordinates to metal cations. From the search outputs, some representative examples have been selected and are discussed in detail.

2. Methods

A search of the X-ray and neutron crystal structures of small molecules was performed using the Cambridge Crystallographic Database (Version 5.8, 1994; Allen *et al.*, 1991). The selection of structures was made with the following criteria: only discrete thiocyanates (not coordinated to metal, not covalently bonded) in crystal structures solved with good precision ($R < 0.085$, no disorder) were considered. H-atom positions had to be reported. The substructure search was carried out using the program *QUEST3D* (Cambridge Structural Database, 1992).

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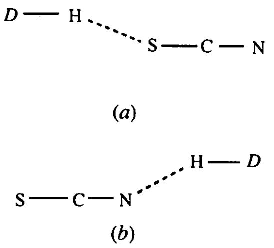
2.1. *Selection of the donor atoms (D)*

We considered only oxygen (O_D) and nitrogen (N_D) as H donors. The $A\cdots H—C_D$ hydrogen bond is now well accepted as a weak interaction (Sharma & Desiraju, 1994). However, a CH group of the molecular skeleton, neighboring an O(H) or N(H) donor, will, of necessity, be at a close distance from an acceptor atom (S_A or N_A). To accept a short $CH\cdots A$ distance as an effective CH bond requires the selection of only those CH groups which alone bind to $(SCN)^-$. Over 100 CH groups could be putative H donors out of 862 retrieved short contacts. The identification is necessarily made by checking each selected bond on the graphics screen. Consequently, we did not consider them in a first approach.

2.2. *Geometry of thiocyanate. Definition of the acceptor (A) type*

The constraints on the $S_A—C_A$ and $C_A—N_A$ bond lengths [$S_A—C_A$ 1.50–1.75 and $C_A—N_A$ 1.00–1.25 Å; angle $\angle(S_A—C_A—N_A)$ 170–180°] were chosen after a preliminary statistical survey of the thiocyanates. The hydrogen bonds are described by the distances $A\cdots D$, $A\cdots H$ and the angle at H. Geometrical calculations were performed on the retrieved data for $A\cdots H—D$ interactions separately for each acceptor center.

Thus, the evaluation with *GSTAT* was carried out on the probe fragments of Scheme I. We used an $A\cdots H$ cutoff of 3.0 Å and angle at H > 90° (Taylor & Kennard, 1982; Steiner & Saenger, 1993). The coordinates of the H atoms were normalized (Taylor & Kennard, 1984). Additionally, the hydrogen-bonding geometry was also examined individually using the graphics program *PLUTO* (Motherwell & Clegg, 1978). As far as possible an attempt was made to have this done automatically and accurately.



Criteria:

thiocyanate

S—C: 1.50–1.75 Å

C—N: 1.00–1.25 Å

<(SCN): 170–180°

Hydrogen bonding

$N\cdots D<3.5$, $S\cdots D<4.0$

$A(S,N)\cdots H<3.0$ Å

<(AH*D*): 90–180°

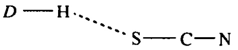
Scheme I.

3. Results

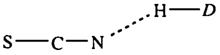
The resulting subfile contains 52 crystal structures with 78 observed anions. Relevant CSD reference codes are given in Table 1.

Table 1. *Statistical results for the geometry of the hydrogen bonding*

CSD refcodes: ABGTCU, BAYPIA, BINHOV, BIVNEZ, BMXCOE, BOCFEE, CAHLIG, COCREN01, COENTC, CRENTC01, CUPCEV, CUTATE10, EDCOPT, ENDACR, FAGYAN, FERBOT, FESTEC, FOWMEJ, FUJBER, GAMTUJ, GASRUN, GIFKUB, GIGXOJ, GLXCOB10, HACDUK, HALBOL, HMACNI, HXZTBA, JEKGEL, JOJHUL, JOSNIO, JUHDOF, JUJVIT, KEMRAV, KIJJIW, LEBCEA, MCYECO, MGLPCP, MXPENA, NATHOD, OXTREC, PAKJCT, SANKUN, SEANCO, STETCU, TAMGET, TEACOT, TPSETC, VIZZAF, VOBMOO, WANHUO, YAKLAX.



	$S\cdots D$		$H\cdots D$		<(SH*D*)	
	$D=N$	$D=O$	$D=N$	$D=O$	$D=N$	$D=O$
Minimum	3.30	3.22	2.33	2.26	105	144
Maximum	3.77	3.41	2.99	2.54	175	167
Mean	3.43	3.28	2.63	2.36	146	157
SD sample	0.11	0.07	0.17	0.09	15	9
No. of observations	106	7	106	7	106	7



	$N\cdots D$		$H\cdots D$		<(NH*D*)	
	$D=N$	$D=O$	$D=N$	$D=O$	$D=N$	$D=O$
Minimum	2.76	2.42	1.78	1.73	90	108
Maximum	3.47	3.09	2.98	2.16	178	169
Mean	3.05	2.79	2.17	1.93	150	152
SD sample	0.14	0.16	0.25	0.14	17	21
No. of observations	97	14	97	14	97	14

3.1. *Observed geometry of SCN and stoichiometry of the donors*

The average dimensions [with e.s.d.'s (sample) in parentheses] of the triatomic anion are: SC = 1.63 (2) and CN = 1.15 (3) Å, $\angle(SCN) = \beta = 178.0(2)°$. Considering the precision of the retrieved structures, we assumed the anion to be perfectly linear (β = 180°) and the specific point-group symmetry of the fragment S—C—N to be $C_{\infty V}$.

The stoichiometry of the potential donor groups in the dataset is 29 O—H and 203 N—H. In crystal structures containing a large number of H donors the hydrogen bonds form complex spatial networks around the thiocyanates, which led us to consider every mode of hydrogen-bond coordination separately.

3.2. *Numerical characterization of the hydrogen-bond parameters*

There are 224 thiocyanate–hydrogen bond interactions retrieved from 52 coordinate entries of the CSD that satisfy our structural criteria.

3.2.1. *$S_A\cdots H—D$ fragment.* We identified 113 $S_A\cdots H—D$ fragments: seven cases correspond to $D = O_D$, 106 to $D = N_D$. Although the number of observations is limited for $D = O_D$, it is clear that the $S_A\cdots H—O_D$ bond is short [mean values (m.v.) with e.s.d. (sample) $S_A\cdots O_D$ 3.28 (7) and $S_A\cdots H$ 2.36 (9) Å] and almost linear [m.v. of $\angle(S_AHO_D)$ 157(9)° (Table 1)]. Bonding with nitrogen donors, $S_A\cdots N_D$, occurs in the range 3.30–3.77 Å [m.v. 3.43(11) Å], $S_A\cdots H$ 2.33–3.0 Å [m.v. 2.63(17) Å]. Bond angles at H range from 105 to 175° [m.v. 146(15)°].

3.2.2. *$N_A\cdots H—D$ fragment.* We identified 111 $N_A\cdots H—D$ fragments: 14 cases correspond to O_D, 97 to N_D. Data for $D = O_D$ were sparse. Mean values for $N_A\cdots O_D$, $N_A\cdots H$ and $\angle(N_A—H—O_D)$ are 2.79(16) and 1.93(14) Å, and 152(21)°, respectively (Table 1). The hydrogen bonds to $D = N_D$ are characterized by the parameters $N_A\cdots N_D$, which range from 2.76 to 3.47, $N_A\cdots H$ from 1.78 to 2.98 Å and the angle at H from 90 to 178°. Most of these observations (70%) can be regarded as strong hydrogen bonds [with mean values for $N_A\cdots N_D$ 2.97(11), $N_A\cdots H$ 2.06(18) Å; $\angle(N_AHN_D)$ 154.15°].

3.3. *Bivariate analysis*

Bivariate correlations were calculated for all combinations of parameters. There is an empirical correlation between $A\cdots H$ and $A\cdots D$ with the coefficients $r = 0.76$ for $A = N$ (Fig. 1*a*) and $r = 0.75$ for $A = S$ (Fig. 1*b*). It is evident that both correlation functions are similar. Fig. 2 represents the scatterplot for discrete values $A\cdots D$ and $A\cdots H$ *versus* $\angle(AHD)$. For the two acceptor centers, a good correlation between the distance $A\cdots H$ and angle at H is observed [correlation coefficient $r = -0.76$ for $A = S$ (Fig. 2*a*) and $r = -0.77$ for $A = N$ (Fig. 2*b*)]. No obvious correlation for the $A\cdots D$ distance and angle at H is observed for either acceptor atom.

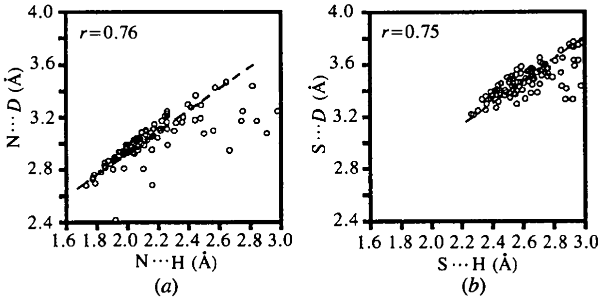


Fig. 1. Plot of the distances involved in $A\cdots H—D$ intermolecular contacts in the thiocyanate crystal structures. (*a*) N acceptor center; (*b*) S acceptor center. All donors merged. Curves of linear regression and coefficients (*r*) are also given.

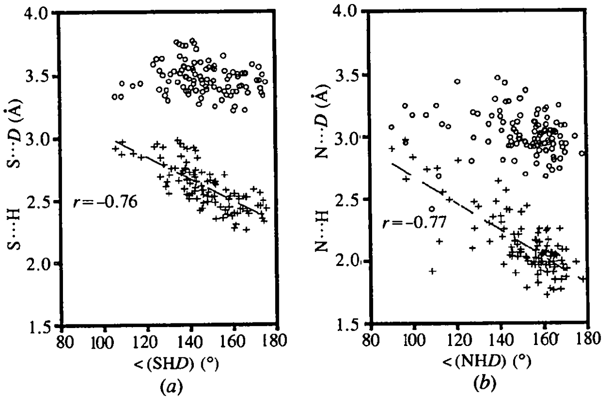
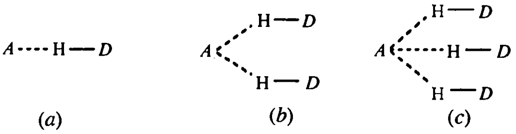


Fig. 2. Scatterplots for discrete values $A\cdots D$ and $A\cdots H$ *versus* angle at H. Linear regression lines correspond to: (*a*) $S_A\cdots H$ *versus* $\angle(SHD)$; (*b*) $N_A\cdots D$ *versus* $\angle(NHD)$. All donors merged.

3.4. *Directionality of the $A\cdots H—D$ interactions*

A much more comprehensive presentation of the results is provided when all fragments are superimposed to form a giant 'molecule'. Fig. 3 shows the localization of donor groups around thiocyanate: this is a cumulative distribution for $A\cdots H—D$ bonding in which an acceptor center forms a total of one, two or three hydrogen bonds (Scheme II). Although the distribution areas of donors around S_A and N_A overlap, we can distinguish the principal binding zone of every acceptor center: for a S acceptor, there is a cluster of donors in a direction that is almost perpendicular to the S—C—N line (Fig. 3*a*), whereas for a N acceptor, all donors gather mostly in the angular domain with $\angle(SND)$ from 120 to 160° (Fig. 3*b*). There is a common area to both domains, where a donor is at a hydrogen-bond distance from both acceptors S_A and N_A. This particular position will be discussed later.



Scheme II.

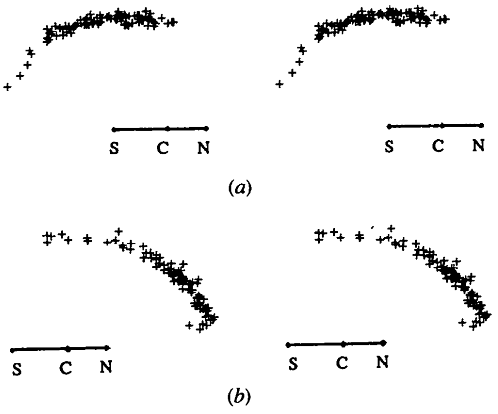


Fig. 3. Stereo representation of the preferred areas of H donors (*a*) around the S acceptor; (*b*) around the N acceptor. N—H and O—H donors merge together. Crosses represent the donor atoms.

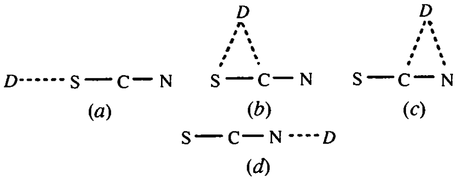
3.5. *Multiple coordination*

In most cases (80%) thiocyanate binds to donor groups through both acceptor centers (S_A and N_A). The H donors around nitrogen are scattered on the surface of a half sphere, with no apparent preference with respect to the average D—H···S direction (Fig. 4). If an acceptor forms more than one hydrogen bond, there may be steric hindrance between the proton donors. In fact, in most SCN anions observed, both acceptor atoms share two or three hydrogen bonds.

4. Thiocyanate coordination: discussion

Almost all potential oxygen H donors bind with thiocyanate: 21 O—H groups out of 29 are involved in hydrogen bonding (seven to S_A and 14 to N_A). Nitrogen H donors are amine cations as well as flat N—H and NH_2 groups, and *all* potential N donors participate in hydrogen bonding with thiocyanate (106 to S_A and 97 to N_A). The number of observed bonds to both acceptors, within our criteria, is almost identical.

These results indicate the extraordinarily active character of thiocyanate hydrogen bonding. The following geometries of interaction (Scheme III) are observed and every type of donor can be a partner in these interactions.



Scheme III.

The following detailed examples will illustrate these special cases:

Figs. 5, 6 and 7 show all the different modes of binding: mode (III*d*) is encountered in each example: N acceptor with oxygen and nitrogen H donors and an average (SN*D*) angle of 155°. Scheme III(*a*) is illustrated in Fig. 5 (structure ABGTCU) with $S2_A$···N3 and $S2_A$···N8 bonding, the *D*SN angles being 105° on average.

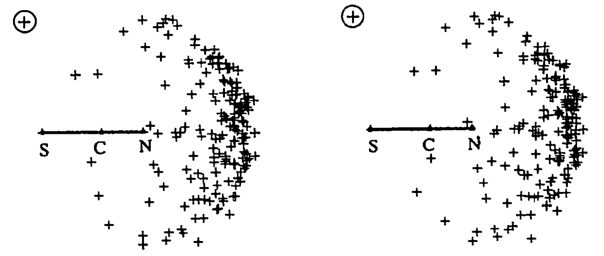


Fig. 4. Stereo representation of the distribution of the H donors around N_A, the cluster of H donors around S being represented by the small circle. Crosses represent the donor atoms.

Schemes III(*b*) and III(*c*) are indeed not rare. Bridging by a single donor can be realized either by a

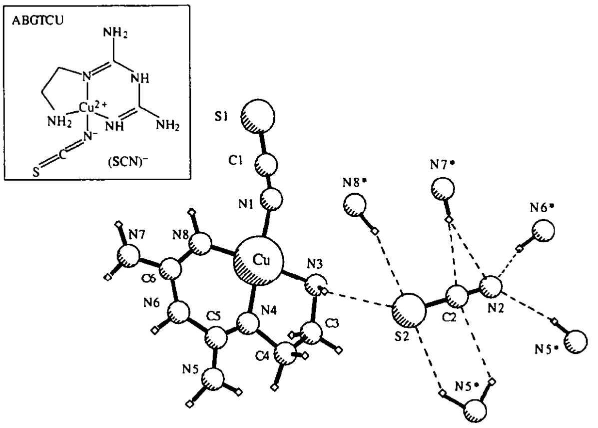


Fig. 5. *PLUTO* (Motherwell & Clegg, 1978) diagram illustrating the hydrogen bonding in the structure ABGTCU. Example for the thiocyanate anion accepting only N—H donors. Sulfur participates three times in the hydrogen bonds S···H—N_D [S···N5 3.39, S···H 2.69 Å, ∠(S—H—N5) 126, ∠(C2—S—N5) 77°; S···N3 3.51, S···H 2.76 Å, ∠(S—H—N3) 132°; S···N8 3.62, S···H 2.71 Å, ∠(S—H—N8) 149°]. Nitrogen accepts three hydrogen bonds, N_A···H—N_D [N2···N6 2.98, N2···H 2.03 Å, ∠(N2—H—N6) 156°; N2···N5 3.10, N2···H 2.56 Å, ∠(N2—H—N5) 114°; N2···N7 3.43, N2···H 2.57 Å, ∠(N2—H—N7) 143°; C2···N7 3.35, C2···H 2.43 Å, ∠(C2—H—N7) 152, ∠(C2—N2—N7) 77°]. The hydrogen bonds are shown by dashed lines.

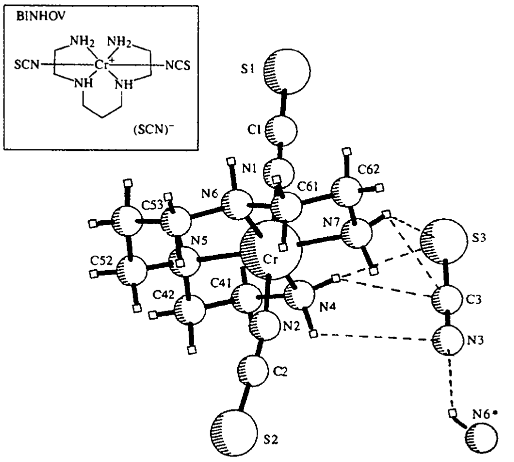


Fig. 6. *PLUTO* (Motherwell & Clegg, 1978) diagram illustrating the hydrogen bonding of SCN in the structure BINHOV: S3···N7 3.38, S3···H 2.45 Å, ∠(S3—H—N7) 154° and C3···N7 3.21, C3···H 2.57 Å, ∠(C3—H—N7) 121, ∠(C3—S3—N7) 64°; S3···N4 3.63, S3···H 2.81 Å, ∠(S3—H—N4) 138° and C3···N4 3.26, C3···H 2.76 Å, ∠(C3—H—N4) 111, ∠(C3—S3—N4) 70°; N3···N6 2.93, N3···H 2.05 Å, ∠(N3—H—N6) 144°; N3···N4 3.44, N3···H 2.81 Å, ∠(N3—H—N4) 122, ∠(C3—N3—N4) 65°. The hydrogen bonds are shown by dashed lines.

bifurcated hydrogen bond (N7 in ABGTCU between N and C, and N4 in BINHOV between S and C) or by two amino hydrogens (N5 in ABGTCU between S and C, N4 in BINHOV between N and C). Scheme III(*b*) is most frequent, as can be seen by the distribution of donors around S (Fig. 3*a*). The average ∠(SN*D*) and ∠(NS*D*) angles are less than 80° in these cases.

These hydrogen-bonding modes III(*b*) and III(*c*) illustrate the contribution of the electron cloud of the π-orbital of C_AN_A and S_AC_A bonds combined with the lone pair of S_A and N_A, respectively.

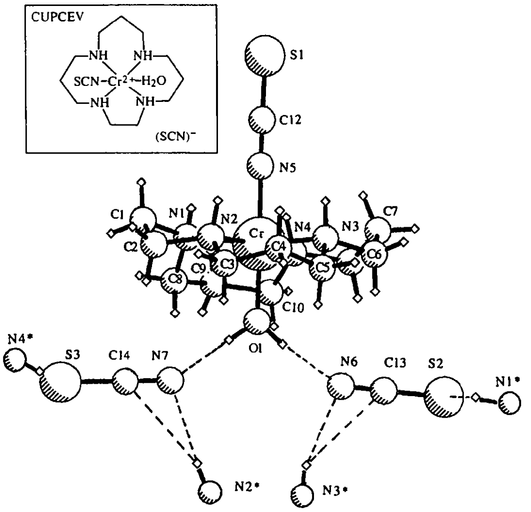


Fig. 7. *PLUTO* (Motherwell & Clegg, 1978) diagram illustrating the hydrogen bonding of SCN in the structure CUPCEV. There are two crystallographically independent anions in the unit cell. O—H donor: N6···H—O (2.73 and 1.77 Å, ∠164°), N7···H—O (2.68 and 1.73 Å, ∠161°); N—H donor: N6···H—N3 (3.05 and 2.16 Å, ∠147°), C13···H—N3 (3.41 and 2.72 Å, ∠126°), N7···H—N2 (3.12 and 2.21 Å, ∠148°) and C14···H—N2 (3.46 and 2.77 Å, ∠126°); S2···H—N1 (3.47 and 2.51 Å, ∠158°) and S3···H—N4 (3.51 and 2.65 Å, ∠143°). The hydrogen bonds are shown as dashed lines.

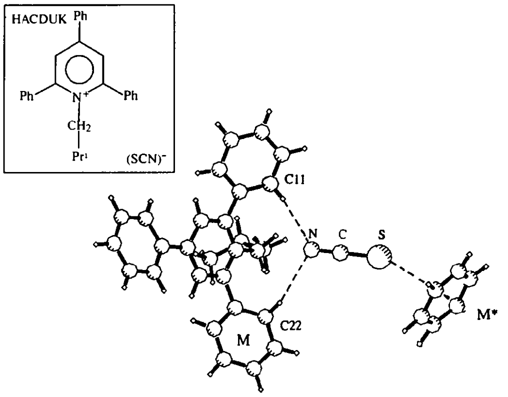
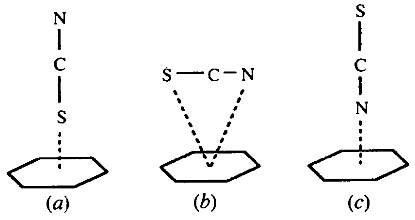


Fig. 8. *PLUTO* (Motherwell & Clegg, 1978) diagram illustrating the hydrogen bonding in the structure HACDUK, C11—H···N (3.44 and 2.5 Å, ∠166°), C22—H···N (3.59 and 2.68 Å, ∠155°). S···*M** (*M** is the centroid of a symmetry-related phenyl C22-C28): 4.13 Å, ∠NS*M*: 133°.

In the course of our study we came across unusual bonding modes. The structure HACDUK (Fig. 8) is a very interesting case as the H donor is uniquely carbon. In this structure thiocyanate interacts by its nitrogen terminal with two sp^2-hybridized carbons forming a symmetrical bridge between two phenyl rings. Moreover, the anionic cylinder is bonded through sulfur to the aromatic π-system of a nearly perpendicular phenyl ring (Scheme IV*a*). In this last example the ligand interacts quite differently with both sides of the anion. We have not as yet encountered examples of type (IV*b*) and (IV*c*) interactions, but the CSD offers six cases of type IV(*a*), where the $S_A\cdots$ phenyl distance is less than 4.2 Å and the angle at S_A lies between 120 and 180°.



Scheme IV.

5. Summary and conclusions

The most important observations resulting from this systematic analysis of the hydrogen-bond coordination of thiocyanate are the following.

(i) Thiocyanate is able to accept all types of hydrogen donors: O and N in all expected cases and also C donors in compounds with a limited number of functional groups able to form strong hydrogen bonding.

(ii) Thiocyanate exhibits all modes of hydrogen-bond coordination: by the S, N and by the π-system of the anion (contacts with two atoms of thiocyanate: S_A and C_A or N_A and C_A); the influence of the backbonding of sulfur (or nitrogen) cannot be detected in the S_AC_A and C_AN_A bond lengths, as the anion is usually bonded on both sides and to multiple donors.

(iii) The relative orientations of the donors are different around sulfur and nitrogen. The more favorable sulfur coordination is in an almost perpendicular direction to the anionic cylinder and that of the N acceptor forms a spherical cap.

Bonding by both acceptor centers in most cases, thiocyanate is seen to act as a powerful anionic bridge between the different molecular fragments.

In the course of this research, we came across many structures where SCN is covalently bonded to a metal at one end and is hydrogen-bonded through the other end. We did not include these values in our dataset as they might induce some biased conclusions. The behavior of this anion is, with respect to covalent bonding, extremely peculiar. Again, theoretical studies have been published (Musaiev & Charkin, 1991), but only the availability of a large amount of structural data will allow a good representation of the bonding criteria of SCN. Therefore, our next research program will consider the complete coordination properties of SCN.

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