

Hydrogen Bonding to Thiocyanate Anions: Statistical and Quantum-Chemical Analyses

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(Received 9 June 1997; accepted 27 October 1997)

Abstract

A statistical analysis of entries from the CSD (Cambridge Structural Database) showed that the average hydrogen-bond geometry to the nitrogen acceptor atom of the thiocyanate anion was not collinear with respect to the molecular axis of the anion and so not collinear with the nitrogen lone pair [Tchertanov & Pascard (1996). *Acta Cryst.* B52, 685–690]. This somewhat unexpected result has been investigated further using theoretical energy calculations applying Intermolecular Perturbation Theory in combination with a more detailed statistical analysis of an appropriate CSD dataset. The energy calculations pointed to the formation of the strongest hydrogen bonds in the nitrogen lone-pair direction. The statistical analysis showed that this directionality occurs in cases where the N atom accepts one hydrogen bond only. The non-linear average hydrogen-bond geometry observed in the earlier study can be attributed to multiple hydrogen bonding to the N atom. In such cases, there is a shift away from the optimum orientation.

1. Introduction

Recently, Tchertanov & Pascard (1996) (hereafter referred to as TP96) studied hydrogen bonding to thiocyanate anions, using crystallographic data retrieved from the Cambridge Structural Database (CSD: Allen *et al.*, 1991). It was found that the average hydrogen-bond geometry around the sulfur acceptor atom is approximately perpendicular to the SCN axis ($\theta_S = \angle D \cdots S-N \simeq 100^\circ$, $D = N$ or O), whereas the average geometry of hydrogen-bond formation to the N atom was found to be at an angle of $\theta_N = \angle D \cdots N-S \simeq 145^\circ$. Furthermore, it was observed that the thiocyanate anion usually accepts more than one hydrogen bond.

This non-linear hydrogen-bond geometry at nitrogen contrasts with an *ab initio* study of the hydrogen bonding of water molecules to the thiocyanate anion (Baranovskii *et al.*, 1985). Supermolecule calculations using a 4-31G basis set indicated that the preferred hydrogen-bond geometry is collinear with the C–N axis ($\theta_N = 180^\circ$), *i.e.* in the direction of the nitrogen lone pair. The lone-pair directionality of hydrogen bonds is

observed frequently (Legon & Millen, 1982; Taylor *et al.*, 1983) and can be ascribed, primarily, to optimization of the electrostatic attraction which is the largest energy contribution to hydrogen-bond formation. It is difficult to draw a general conclusion from the study by Baranovskii *et al.* (1985), however, as water molecules appear to have special donor features by comparison with other (aliphatic) hydroxyl donors (Tse *et al.*, 1980; Kroon-Bateburg & van Duijneveldt, 1986; Zheng & Merz, 1992). In theoretical calculations (Lommerse *et al.*, 1997) ether O atoms accept water hydroxyl donors in the direction of one of their lone pairs, but methanol hydroxyl donors between their lone pairs.

This paper presents a more detailed study of hydrogen bonding to thiocyanate anions. A further statistical survey of CSD information is presented which considers the effect of hydrogen-bond coordination on the mean hydrogen-bond geometry to thiocyanate anions. Theoretical energy calculations using Intermolecular Perturbation Theory (IMPT: Hayes & Stone, 1984) for a suitable model system are also presented.

2. Methods

Ab-initio-based intermolecular energy calculations were carried out using the CADPAC6.0 program package (Amos, 1996), using the hydroxyl group of methanol as the hydrogen-bond donor. All calculations were performed at the 6-31G** basis set level. Individual monomer geometries of the thiocyanate anion and the methanol molecule were optimized prior to calculation of intermolecular interaction energies by the IMPT methodology (Hayes & Stone, 1984). The total energy derived by IMPT (E_i) is given by adding two first-order and three second-order energy contributions. The first-order contributions are the electrostatic and exchange-repulsion interaction energies (E_{es} and E_{er}). The second-order contributions are the polarization (or induction), charge-transfer and dispersion interaction energies (E_{pol} , E_{ct} and E_{disp}). IMPT energies are calculated for fixed dimer geometries and are free of basis-set superposition errors (Stone, 1993). The separate calculation of individual systems provides valuable evidence concerning the nature of the interaction.

The model dimers were constructed as shown in Fig. 1(a) (for hydrogen bonding to N). The S—C—N···H—O system was kept planar with the methanol C—O—H plane perpendicular to it. This minimized the influence of the methanol methyl group. Both the orientation and the distance of the O—H group were varied with respect to the thiocyanate anion. Around the terminal nitrogen, the angle θ_N was varied between 90 and 180° in steps of 15°, at distances d_N between 1.7 and 2.6 Å. The same angular constraints and step size were used for θ_S about the terminal sulfur, but with distances d_S ranging from 2.1 to 3.0 Å. Interactions with the π -electron system were explored in steps of ≤ 0.3 Å (along x from carbon to sulfur for $d_\pi = 1.9$ –2.8 Å; the H—O bond was kept perpendicular to the S—C—N vectors). All distances were varied in step sizes of 0.1 Å.

Crystal structure data for intermolecular hydrogen bonds to thiocyanate anions were obtained from the Version 5.12 release of the CSD (Allen *et al.*, 1991), using similar selection criteria to those employed in the previous study (TP96).

3. Results

Fig. 1(b) shows an overview of the total IMPT interaction energy E_t for the various geometries of the methanol···thiocyanate system. As the primary attractive energy contribution to hydrogen bonds is from the electrostatic component, the negative charge of the anion will result in a strong interaction everywhere within reasonable O—H···S—C—N separations. Thus, E_t ranges from approximately -20 kJ mol⁻¹ at the S terminus up to -54 kJ mol⁻¹ at the N terminus of the anion. All energy contributions to the various minima are given in Table 1.

3.1. Sulfur acceptor atom

A local minimum energy orientation for hydrogen-bond formation with the sulfur is found at the distance $d_S = 2.5$ Å, with θ_S (the angle C—S···H) = 105°. This geometry corresponds well with the average values obtained in the previous study ($d_S = 2.4$ Å and $\theta_S = 100^\circ$ TP96) and with a further recent statistical survey of

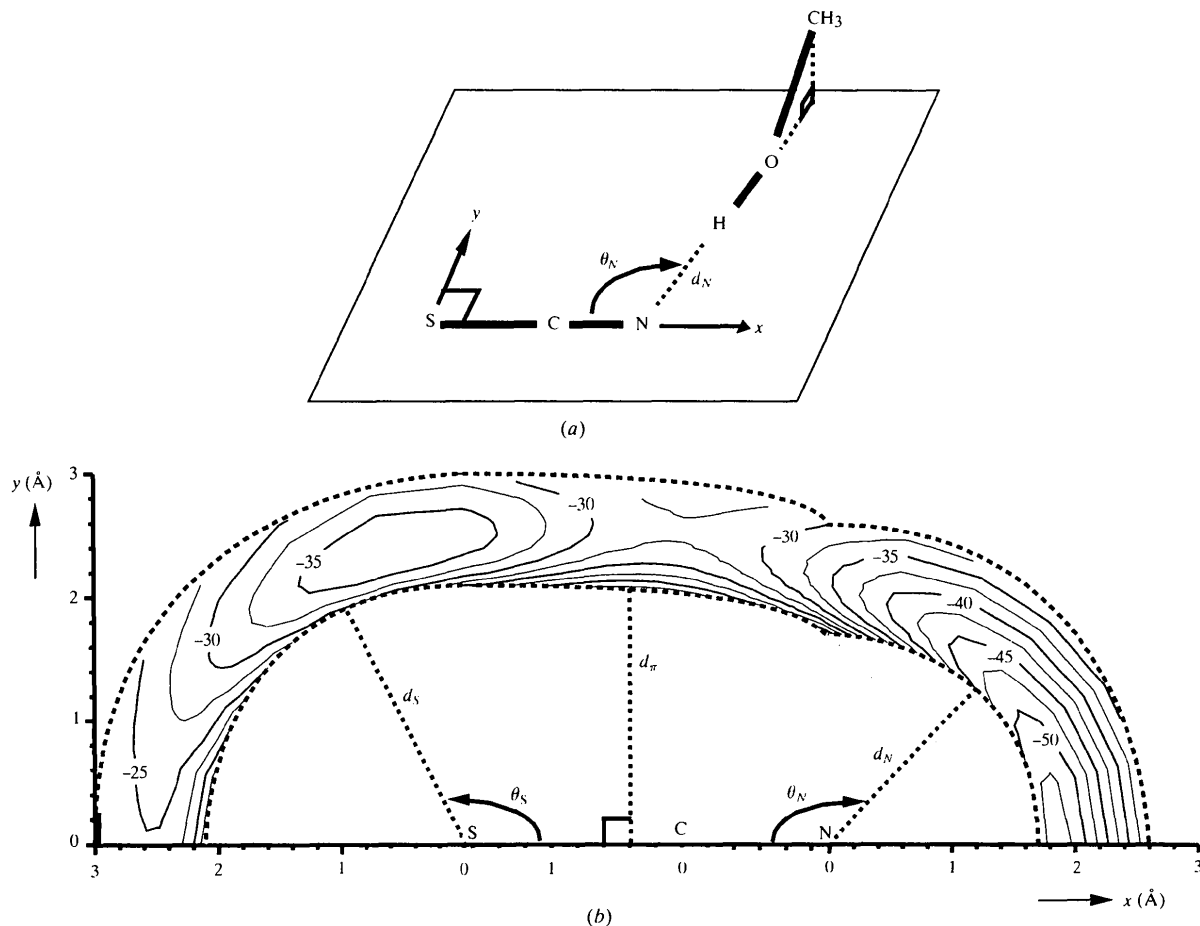


Fig. 1. (a) Definitions of geometrical parameters, describing the orientation of the methanol hydroxyl groups toward the thiocyanate anion. (b) IMPT total energy (E_t) contour plot summarizing the interaction of the methanol hydroxyl group with the thiocyanate anion. The contour levels are given in kJ mol⁻¹.

Table 1. *IMPT energy contributions (kJ mol⁻¹) to total energies for minima in the SCN–methanol model system*

| | E_{es} | E_{er} | E_{pol} | E_{ct} | E_{disp} | E_{total} |
|--|----------|----------|-----------|----------|------------|-------------|
| Sulfur acceptor | | | | | | |
| $d_S = 2.5 \text{ \AA}$, $\theta_S = 105^\circ$ | -43.5 | +22.4 | -6.0 | -5.6 | -4.7 | -37.3 |
| $d_S = 2.5 \text{ \AA}$, $\theta_S = 180^\circ$ | -23.4 | +8.9 | -3.7 | -2.2 | -4.3 | -24.8 |
| Thiocyanate π -electron system | | | | | | |
| $d_\pi = 2.5 \text{ \AA}$ | -24.0 | +7.4 | -4.3 | -2.5 | -4.3 | -27.7 |
| Nitrogen acceptor | | | | | | |
| $d_N = 1.9 \text{ \AA}$, $\theta_N = 180^\circ$ | -64.0 | +40.9 | -11.4 | -8.9 | -10.1 | -53.5 |

C=S··H–O hydrogen bonds in CSD entries which reported values of $\theta_S = 111 (3)^\circ$ and $d_S = 2.42 (3) \text{ \AA}$ (Allen *et al.*, 1997).

E_i in this minimum is $-37.3 \text{ kJ mol}^{-1}$, which is strong for a hydrogen bond to a sulfur acceptor (*cf.* $E_i \simeq -20 \text{ kJ mol}^{-1}$; Allen *et al.*, 1998). In comparison, E_i is only $-24.8 \text{ kJ mol}^{-1}$ for the hydrogen bond to the S atom at the same distance, but collinear with the S–C–N axis ($\theta_S = 180^\circ$). This is due mainly to a dramatic decrease in the electrostatic interaction (Table 1), which can be ascribed to a quadrupole moment at the S atom and the (related) anisotropic ‘shape’ of the atom. A previous CSD analysis has shown that sulfur has a shorter effective radius along the extension of the C–S axis in comparison with the radius perpendicular to this axis (Nyburg & Faerman, 1985). Furthermore, it has been shown from *ab initio* studies that, when taking the S–C–N anion on the x axis, delocalized p_y and p_z orbitals have a relatively high electron density, whereas the p_x orbital is less populated (Howell *et al.*, 1973). This anisotropic electron distribution results in a reduced electrostatic attraction as well as a reduced exchange repulsion at a fixed distance from the sulfur nucleus for a linear hydrogen bond in comparison with the perpendicular direction. The balance between these first-order energies is, however, dominated by the electrostatic interaction.

3.2. Thiocyanate π -electron system

No (local) minimum exists for hydrogen bonding to the π system around the S–C–N axis. Instead, a saddle point occurs 2.5 \AA from the C atom in a direction perpendicular to the S–C–N axis. The total interaction energy E_i for this saddle point is $-27.7 \text{ kJ mol}^{-1}$. This is less favourable than the strongest interaction to the S atom ($E_i = -37.3 \text{ kJ mol}^{-1}$), but is still strong enough to accept hydrogen bonds as is observed in the CSD (TP96).

3.3. Nitrogen acceptor

The global minimum energy orientation for the methanol··thiocyanate anion system is found on the SCN axis ($\theta_N = 180^\circ$) at the distance $d_N = 1.9 \text{ \AA}$. The total interaction energy, $E_i = -53.5 \text{ kJ mol}^{-1}$, is high. Individual contributions to the total interaction energy

are given in Table 1. Strong contributions by the $2p_y$ and $2p_z$ orbitals to the C–N bond in the thiocyanate anion demonstrate triple-bond character. Consequently, the N atom shows sp^1 hybridization properties, which is reflected in the relatively low-energy molecular orbital of the nitrogen lone pair. Thus, the position of the hydrogen-bond interaction energy minimum coincides with the nitrogen lone pair and, in comparison to the local minimum at the S atom, is located in a steeper energy well. These results are in agreement with those for the thiocyanate anion··water system (Baranovskii *et al.*, 1985).

The previous CSD analysis (TP96) seems to give contradictory results; the average hydrogen-bond geometry is located at $\theta_N = 145^\circ$. The fact that the thiocyanate anion usually accepts more than one hydrogen-bond donor provides a hypothesis: when two hydrogen bonds form to the N atom, the total interaction will be more favourable when both donor groups are non-collinear with the C–N bond vector rather than having one hydrogen bond in the global minimum (linear) energy orientation and the other far away from this position.

Currently, IMPT cannot be used to test this hypothesis since it is not yet possible to perform calculations on three body systems. As an alternative to calculation we have performed a new statistical analysis of a subset of the CSD to test the hypothesis.

3.4. CSD analysis

The CSD was searched for all hydrogen bonds to the thiocyanate N atom. The geometrical results were separated into three sets: in which the nitrogen accepts (a) one hydrogen bond only, (b) two hydrogen bonds and (c) three or more hydrogen bonds. The corresponding θ_N angles have been plotted in three histograms. (Figs. 2a–c), correcting for a conical distribution in each case (Stouten *et al.*, 1991). When the nitrogen accepts only one hydrogen bond (Fig. 2a), the preferred geometry is linear, in agreement with our global minimum geometry, found by the theoretical energy calculations. When the nitrogen accepts two hydrogen bonds, the maximum of the distribution clearly moves away from linearity with a preferred $\theta_N \simeq 150^\circ$ (Fig. 2b). There are just a few cases where nitrogen accepts

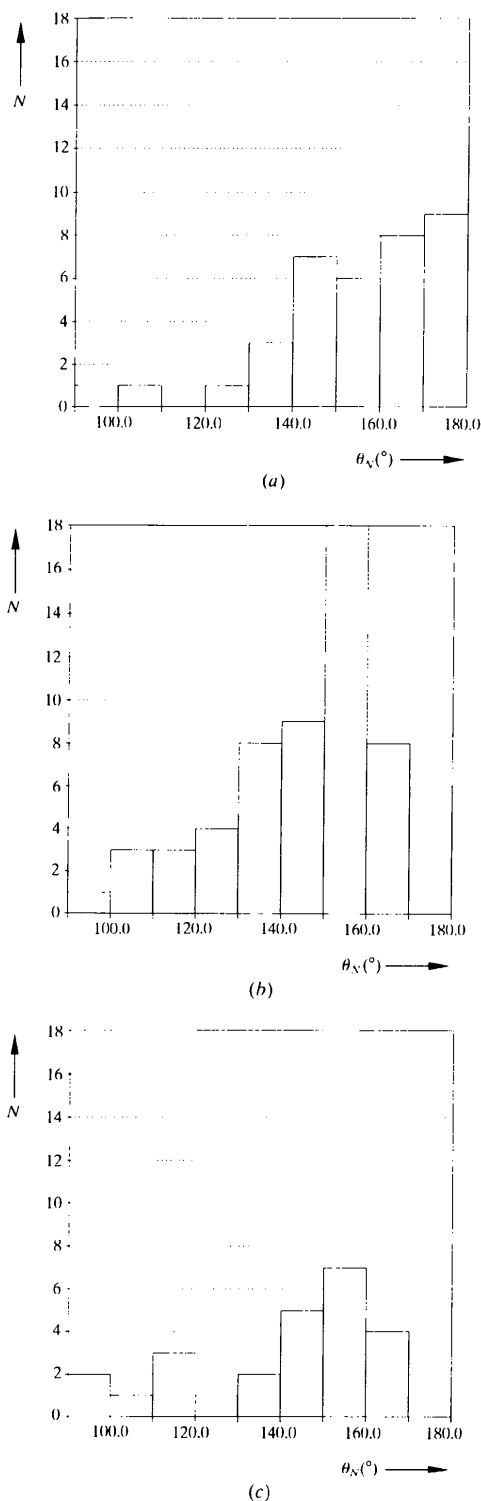


Fig. 2. Histograms summarizing hydrogen-bond geometries at the thiocyanate nitrogen acceptor atom. The number (N) of O—H...N and N—H...N hydrogen bonds has been plotted as a function of the angle θ_N . The histograms have been corrected for a conical distribution (Stouten, 1991). They are shown for those cases where nitrogen accepts (a) one hydrogen bond only, (b) two hydrogen bonds and (c) three or more hydrogen bonds.

three or more hydrogen bonds, but a further shift away from linearity can be detected.

4. Conclusions

Thiocyanate anions form strong hydrogen bonds. The minimum energy hydrogen-bond geometry at the S atom is at $\theta_S = 105^\circ$ and $d_S = 2.5 \text{ \AA}$ with an interaction energy of -37 kJ mol^{-1} . This geometry agrees well with the overall CSD analysis as performed by TP96. On the other hand, the minimum energy orientation at the N atom is linear with respect to the S—C—N axis ($\theta_N = 180^\circ$), with the short distance $d_N = 1.9 \text{ \AA}$ and interaction energy -54 kJ mol^{-1} . This result is in agreement with the observations found in the CSD, when the multiple hydrogen-bonding nature of thiocyanate N atoms is taken into account.

We would like to thank Dr Frank Allen for useful comments and discussions.

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