

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles involving non-H atoms (°)

O(1)—C(2)	1.363 (3)	C(8)—C(9)	1.376 (4)
O(1)—C(9)	1.384 (3)	C(9)—C(10)	1.389 (3)
C(2)—C(3)	1.457 (3)	C(13)—C(14)	1.509 (2)
C(2)—O(11)	1.211 (3)	C(14)—C(15)	1.389 (3)
C(3)—C(4)	1.348 (3)	C(14)—C(19)	1.403 (3)
C(3)—C(13)	1.512 (4)	C(15)—C(16)	1.385 (3)
C(4)—C(10)	1.428 (4)	C(16)—C(17)	1.402 (3)
C(5)—C(6)	1.372 (4)	C(16)—C(20)	1.497 (3)
C(5)—C(10)	1.403 (3)	C(17)—C(18)	1.373 (3)
C(6)—C(7)	1.394 (3)	C(18)—C(19)	1.391 (3)
C(6)—C(12)	1.511 (3)	C(19)—O(21)	1.365 (2)
C(7)—C(8)	1.382 (3)		
C(2)—O(1)—C(9)	122.1 (1)	C(5)—C(10)—C(9)	117.4 (2)
O(1)—C(2)—O(11)	116.4 (2)	C(4)—C(10)—C(9)	117.8 (2)
O(1)—C(2)—C(3)	118.4 (2)	C(4)—C(10)—C(5)	124.8 (2)
C(3)—C(2)—O(11)	125.1 (3)	C(3)—C(13)—C(14)	113.4 (2)
C(2)—C(3)—C(13)	117.4 (2)	C(13)—C(14)—C(19)	122.3 (2)
C(2)—C(3)—C(4)	118.9 (2)	C(13)—C(14)—C(15)	119.5 (2)
C(4)—C(3)—C(13)	123.7 (2)	C(15)—C(14)—C(19)	118.2 (2)
C(3)—C(4)—C(10)	122.2 (2)	C(14)—C(15)—C(16)	123.2 (2)
C(6)—C(5)—C(10)	121.7 (2)	C(15)—C(16)—C(20)	122.2 (2)
C(5)—C(6)—C(12)	122.1 (2)	C(15)—C(16)—C(17)	117.0 (2)
C(5)—C(6)—C(7)	118.9 (2)	C(17)—C(16)—C(20)	120.7 (2)
C(7)—C(6)—C(12)	118.9 (2)	C(16)—C(17)—C(18)	121.2 (2)
C(6)—C(7)—C(8)	120.8 (2)	C(17)—C(18)—C(19)	120.8 (2)
C(7)—C(8)—C(9)	119.1 (2)	C(14)—C(19)—C(18)	119.4 (2)
O(1)—C(9)—C(8)	117.5 (1)	C(18)—C(19)—O(21)	117.9 (2)
C(8)—C(9)—C(10)	122.0 (2)	C(14)—C(19)—O(21)	122.6 (2)
O(1)—C(9)—C(10)	120.5 (2)		
C(2)—C(3)—C(13)—C(14)	-78.3 (2)	C(3)—C(13)—C(14)—C(15)	-83.2 (3)
C(4)—C(3)—C(13)—C(14)	100.7 (3)	C(3)—C(13)—C(14)—C(19)	98.3 (3)

The packing of the molecules in the unit cell viewed down the *a* axis is shown in Fig. 1. The crystal structure is stabilized by van der Waals interactions; the shortest non-hydrogen contact [3.432 (3) Å] is between C(20) and O(21) transformed to *x* - 1, *y*, *z* - 1.

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References

- COLE, M. S., MINIFEE, P. K. & WOLMA, F. J. (1988). *Surgery*, **103**, 271-277.
- GOPAL, D. & RAJAGOPALAN, K. (1987). *Tetrahedron Lett.* **28**, 5327-5330.
- GREENFIELD, L. J. (1988). *Surgery*, **103**, 386-387.
- NARDELLI, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis*. Univ. of Parma, Italy.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- SHIMIZU, S., KASHINO, S. & HAISA, M. (1975). *Acta Cryst.* **B31**, 1287-1292.

Acta Cryst. (1991). **C47**, 332-337

Carbon Tetrachloride-Thiourea (1/3) Adduct at 170 K

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Abstract. $\text{CCl}_4 \cdot 3\text{CH}_4\text{N}_2\text{S}$, $M_r = 382.17$, trigonal, $R\bar{3}$, $a = 15.539$ (4), $c = 12.529$ (9) Å, $V = 2620.0$ (20) Å³, $Z = 18$, $D_m = 1.42$ (2) (298 K), $D_x = 1.433$ g cm⁻³ (170 K), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.17$ cm⁻¹, $F(000) = 1164$, $T = 170$ K, $R = 0.043$ for 640

observed ($F > 6.0\sigma_F$) reflections. The structure of the adduct has been solved and a model for the disordered carbon tetrachloride guest molecule has been developed. The adduct is isostructural with other non-aromatic adducts of this type. The carbon of the disordered carbon tetrachloride molecule is clearly co-planar with the three thiourea S atoms that point

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into the center of the thiourea channel. There appear to be Coulombic interactions between the partial negative charges on the three thiourea S atoms and the partial positive charge on the central C atom of the carbon tetrachloride guest molecule; these interactions seem to be the driving force involved in the formation of this adduct. A classification system for the various disorder types found in thiourea adducts has been developed and is introduced. Recognition of the disorder involved allowed the development of a reasonable model for the CCl_4 molecule in the adduct.

Introduction. Angla reported the discovery of crystalline thiourea adducts with a variety of compounds in 1947; the observation that carbon tetrachloride formed a crystalline adduct with thiourea was included in this initial report (Angla, 1947). The earliest crystal structure work on this class of compounds was concerned with the thiourea-cyclohexane adduct (Hermann & Lenné, 1952; Lenné, 1954). Smith briefly discussed incomplete X-ray results of work on thiourea adducts of cyclohexane, hexachloroethane and triptane (Smith, 1950). This early work established the honeycomb-type channel structure of the thiourea when an adduct molecule was involved. Lenné (1954) recognized that, for cyclohexane, the thiourea S atoms pointed into the channel, and that the cyclohexane molecule appeared to be centered in the plane of the three S atoms. Owing to the substantial disorder of the cyclohexane molecule neither its geometry or orientation could be clearly determined.

We have, as a result of studying several disordered thiourea adducts, developed a descriptive classification of disordered types. The disorder types are: (1) symmetry, (2) positional, (3) conformational, (4) orientation, (5) site, and (6) substitutional disorder. Disorder types 2, 3 and 4 have previously been described by Westrum & McCullough (1963). More complete descriptions of these will be introduced in the appropriate structural reports (papers in preparation).

The thiourea adducts crystallize into two space-group types: rhombohedral [$R\bar{3}2/c$, Lenné (1954); $R3c$, Schlenk (1951); $R\bar{3}$, this work] and monoclinic [$P2_1/a$, Nicholaides & Laves (1965); Clement, Jegoudez & Mazieres (1974), space groups not defined other than monoclinic; $P2_1/a$, Chatani & Nakatani (1976); $P2_1/a$, Wick, Fait, Coughlan, McCandless & Fitzgerald (1991)]. The monoclinic space groups, which are observed with planar or pseudoplanar adducts, have the advantageous characteristic of not containing a threefold axis and, therefore, no symmetry disorder of a threefold nature occurs; this is a substantial contrast to the disorder problem in the rhombohedral complexes.

The monoclinic space groups, except for the squalene/thiourea adducts (Nicholaides & Laves, 1965) and the aromatic/thiourea adducts (Wick *et al.*, 1991), occur only at reduced temperatures (Clement *et al.*, 1974).

We had hoped that carbon tetrachloride, with its molecular threefold axes might, at reduced temperature, become the first example of a non-disordered rhombohedral thiourea adduct. The possibility that the carbon tetrachloride, with its more negative Cl atoms (relative to cyclohexane), might be bonding with the thiourea N atoms rather than the thiourea S atoms was also a consideration. The solid-state NMR work of McKinnon & Wasylishen (1986) indicates that the equatorial conformation of methylcyclohexane is preferred in the thiourea adduct but that for chloro, bromo- and iodocyclohexanes the preference is for the axial conformation. Since the van der Waals volume for the methyl group is intermediate between those reported for chloro and iodo substituents (methyl $V_w = 13.67$; chloro, bromo and iodo $V_w = 11.62, 14.40$ and $19.18 \text{ cm}^3 \text{ mol}^{-1}$, respectively) one must consider interactions other than steric effects for stabilizing the observed conformers in the adducts (Bondi, 1964). If different types of bonding (interactions) are important when comparing methylcyclohexane to the halogenated cyclohexanes then one might well expect that carbon tetrachloride would display a different set of interactions in the thiourea adduct than would cyclohexane.

It was also hoped that, owing to the electron-rich Cl atoms, we would be able to observe a clearer 'picture' of the adducted carbon tetrachloride molecule than Lenné was able to see with the cyclohexane adduct. It was felt that additional information about this structure could be obtained by collecting intensity data at low temperature. The primary goal of this work was to obtain a basic understanding of the bonding interactions involved in this class of compounds.

Experimental. Reagent-grade thiourea, methanol and carbon tetrachloride were purchased from the J. T. Baker Chemical Company. Carbon tetrachloride was allowed to diffuse into a saturated solution of thiourea in methanol at room temperature ($\sim 298 \text{ K}$) and good-quality crystals appeared in $\sim 24 \text{ h}$. An experimental density was obtained by flotation in chloroform/heptane solutions. The adduct is unstable in air; the crystals decompose by loss of the carbon tetrachloride through evaporation. The crystal used for intensity data collected was mounted and sealed in a Lindemann capillary tube. Crystal dimensions were $\sim 0.5 \times 0.5 \times 1.0 \text{ mm}^3$.

Intensity data were collected on a Nicolet $R3mE$ four-circle diffractometer using the ω -scan technique and the Nicolet LT-1 liquid-nitrogen low-tem-

Table 1. *Experimental data for CCl₄·3SCN₂H₄*

$(\sin\theta)/\lambda_{\max}$ (\AA^{-1})	0.5944
Range of h	0 to ± 19
k	0 to 19
l	0 to ± 15
Total number of reflections	3531
Number of unique reflections	1017 ($R_{\text{merge}} = 0.033$)
Number of observed reflections	640 ($6\sigma_F$ cutoff)
Number of parameters refined	83
R	0.043
wR	0.033
S	1.997

perature system. Three standard reflections were measured periodically throughout the course of the data collection to monitor crystal alignment and/or deterioration. There was no decrease in the standards over the course of the data collection; the maximum variation from the average was less than 3%. Lattice parameters were obtained from the least-squares fit to 12 reflections for which $8.5 < 2\theta < 25.5^\circ$. Experimental details can be seen in Table 1.

The data were reduced in the usual manner with appropriate Lorentz and polarization corrections. Scattering factors for S, Cl, N, C and H, and anomalous-scattering terms for S, Cl, N and C were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 3); all atoms were assumed to be in the zero ionization state. No correction for absorption was made.

An initial model was obtained by direct methods; computational work was performed utilizing the Nicolet program package (Sheldrick, 1983), the *XTAL* system of programs (Stewart & Hall, 1983) and programs written locally. The S, N and C atoms of the thiourea lattice structure were refined with anisotropic thermal parameters by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with all parameters refined in each full-matrix block. Thiourea amino H-atom position coordinates, determined from a difference electron density map at an intermediate stage of refinement, were refined, as were isotropic thermal parameters for the H atoms. The weighting scheme used in the latter stages of refinement was $w = (\sigma_F)^{-2}$, where σ_F was based on counting statistics. A final difference Fourier electron density map showed maximum peak heights of $\sim 0.32 \text{ e \AA}^{-3}$ in the vicinity of the Cl atoms in the channel (the most negative peak was -0.21 e \AA^{-3}). The largest shift over e.s.d. value was < 0.1 at convergence. No corrections for secondary extinction were made or refined.

Fig. 1(a) illustrates the structure of the carbon tetrachloride/thiourea adduct and the substantial disordering of the CCl₄ molecule. Fig. 1(b) illustrates the difference electron density distribution as calculated from the final model with the adducted carbon tetrachloride removed from the computation. Initial attempts at fitting this electron density distribution

with many Cl-atom positions of varying occupancies yielded the model illustrated in Fig. 2(a). Because of the substantial disorder, obtaining a model for the CCl₄ that made chemical sense was not a trivial problem. The initial model suggested the three anisotropic Cl atoms used in the final refined model. The final model for the disordered carbon tetrachloride (shown in Fig. 2b) is represented by an approximately tetrahedral CCl₄ molecule with the C atom on the threefold axis. One of the molecular twofold axes of CCl₄ is perpendicular to the threefold axis in the plane of the three S atoms and approximately along the thiourea C—S vector. All atoms of the carbon tetrachloride were refined anisotropically; the C—Cl bond lengths ranged from 1.6 to 1.83 Å and the sum of the occupancies of the various Cl positions was 1.33 as each orientation could be occupied only one third of the time due to the threefold axis ($3 \times 1.33 = 4$ total Cl atoms). The occupancy of the Cl atom

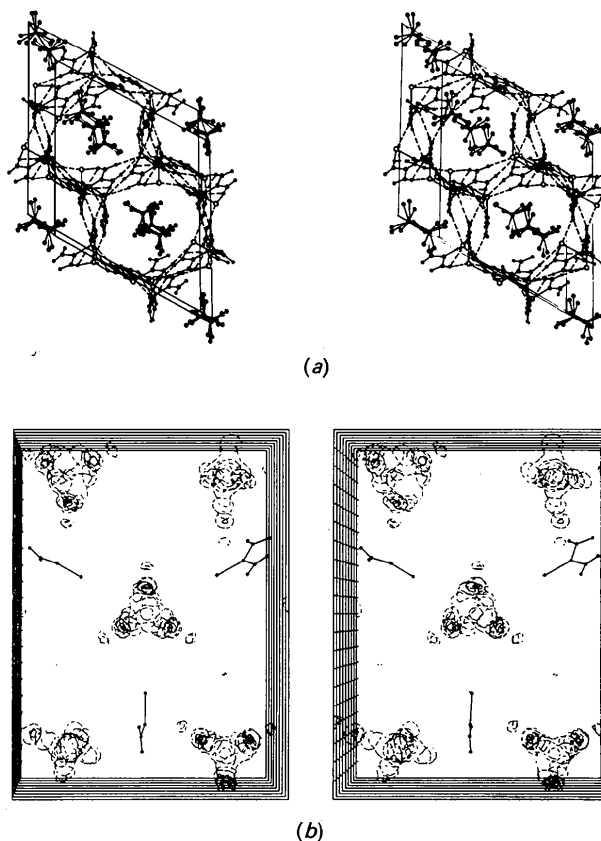


Fig. 1. (a) Stereopacking diagram tilted $\sim 20^\circ$ from the threefold axis of symmetry illustrating the hydrogen bonding in the channel walls and the threefold disorder of the adducted CCl₄ molecules. (b) Stereodifference electron density contour map calculated from the final refinement without the guest molecule. The view is approximately down the threefold axis with layers 0.5 \AA apart, solid contours at 3 e \AA^{-3} and dotted contours at 1 e \AA^{-3} .

[Cl(1)] in the plane of the thiourea S atoms was set at $\frac{1}{3}$, and the other two Cl-atom positions [Cl(2) and Cl(3)] were assigned occupancies of $\frac{1}{3}$ each, for a total occupancy of 1.333, *i.e.* [$1(\frac{2}{3} \times 3 = 2) + 2(\frac{1}{3} \times 3 = 1) = 4$ total Cl atoms]. Note that Cl(1*a*) and Cl(1*b*) are generated from Cl(1) by the action of the threefold axis. When we attempt to fit an idealized carbon tetrachloride molecule [all angles tetrahedral, C—Cl distances of 1.766 (3) Å (*Handbook of Chemistry and Physics*, 1980)] to the refined Cl coordinates the C atom moves off the threefold axis by 0.184 Å, the C—Cl bond distances refine to 1.717 Å and the bond angles range from 107.4 to 112.2°. The observed C—Cl bond lengths of 1.62 (3), 1.83 (3) and 1.83 (4) Å are a direct result of a slight disordering of the C atom relative to the threefold axis. The shortening of the C—Cl distance from the expected 1.766 Å to the refined idealized value of 1.717 Å is consistent with the large 'thermal' motion observed for the Cl atoms.

Discussion. Tables 2 and 3 contain the derived parameters for the carbon tetrachloride/thiourea adduct.* The bond lengths and angles for the thiourea molecule compare well with those previously observed for pure crystalline thiourea (Mullen, Heger & Treutmann, 1978; Elcombe & Taylor, 1968).

The hydrogen bonding in the walls of the thiourea honeycomb structure is shown in the stereopacking plot (Fig. 3). The N—H...S distances in pure

* Tables of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53179 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

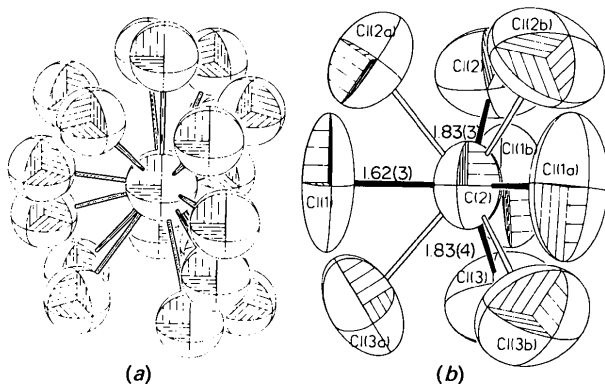


Fig. 2. (a) Initial and (b) final models for the CCl_4 molecule in the adduct. Bond distances (Å) have been included on the figure. The threefold symmetry forces a distortion of the tetrahedral angle between Cl(1) and Cl(1*a*) to 120°. The unique CCl_4 molecule is shown with solid bonds.

Table 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for $\text{CCl}_4 \cdot 3\text{SCN}_2\text{H}_4$

	x	y	z	U
C(2)	0	0	7508 (9)	81 (4)*
Cl(1)	1039 (2)	1045 (2)	7512 (4)	138 (2)*
Cl(2)	-57 (6)	-793 (5)	6399 (5)	151 (5)*
Cl(3)	53 (6)	-728 (5)	8626 (5)	157 (6)*
S(1)	2932 (1)	-2 (1)	7501 (1)	31 (1)*
C(1)	4043 (3)	-4 (3)	7499 (3)	30 (2)*
N(1)	4595 (3)	234 (3)	8371 (3)	39 (2)*
N(2)	4353 (3)	-238 (3)	6622 (3)	38 (2)*
H(1)	5137 (29)	106 (30)	8384 (38)	76 (17)
H(2)	4458 (25)	380 (25)	8885 (26)	22 (12)
H(3)	4909 (26)	-176 (27)	6588 (39)	59 (16)
H(4)	3979 (26)	-368 (26)	5947 (30)	62 (14)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond lengths (Å) and angles (°) for $\text{CCl}_4 \cdot 3\text{SCN}_2\text{H}_4$

C(2)—Cl(1)	1.620 (2)	C(2)—Cl(2)	1.830 (11)
C(2)—Cl(3)	1.827 (12)	S(1)—C(1)	1.727 (5)
C(1)—N(1)	1.322 (5)	C(1)—N(2)	1.322 (6)
N(1)—H(1)	0.959 (54)	N(1)—H(2)	0.748 (37)
N(2)—H(3)	0.822 (44)	N(2)—H(4)	0.987 (39)
Cl(1)—C(2)—Cl(2)	111.5 (5)	Cl(1)—C(2)—Cl(3)	106.7 (5)
Cl(2)—C(2)—Cl(3)	99.6 (3)	S(1)—C(1)—N(1)	120.5 (4)
S(1)—C(1)—N(2)	120.2 (3)	N(1)—C(1)—N(2)	119.3 (4)
C(1)—N(1)—H(1)	118.1 (28)	C(1)—N(1)—H(2)	123.6 (31)
H(1)—N(1)—H(2)	117.4 (43)	C(1)—N(2)—H(3)	121.2 (33)
C(1)—N(2)—H(4)	120.7 (26)	H(3)—N(2)—H(4)	117.2 (42)

thiourea are 3.397 (3), 3.522 (8) and 3.683 (6), and none are linear, the angles varying from 120 to 168°. In the CCl_4 adduct, the distances are 3.426 (5), 3.359 (5), 3.362 (5) and 3.409 (5) Å with the angles varying from 156 to 169°. Even though the average N—H...S distance is less in the adduct, there are six hydrogen bonds per thiourea in the pure thiourea [if we accept the hydrogen-bond scheme proposed by Mullen *et al.* (1978)]. This higher total number of hydrogen bonds in the pure thiourea (even though two of the H atoms per molecule are involved in bifurcated hydrogen bonds) apparently accounts for the lower energy of pure thiourea.

The structure as shown in Fig. 1(a) and careful consideration of the disordered CCl_4 molecule suggests, qualitatively, the nature of the interaction(s) between the adducted CCl_4 and the thiourea molecules forming the channels. There are three 'open' areas of approach to the central C atom of the CCl_4 molecule. These are 120° apart and the thiourea S atoms point directly into them. The distance between the CCl_4 C atom and the thiourea S atom is 4.47 Å. This appears to be the closest possible C...S approach and was calculated from the disordered central C-atom model (see above, coordinates are: S, $x = 0.29320$, $y = 0.00020$, $z = 0.75070$; C, $x = 0.00009$, $y = -0.01159$, $z = 0.75069$). The interaction(s) may be due to either Coulombic or exchange

forces. Since the 4.47 Å separation distance is substantially larger than the sum (3.50 Å) of the van der Waal radii (Bondi, 1964), the interactions of importance would appear to be Coulombic in nature. One might also express these interactions as a set of dipole-dipole and dipole-induced dipole interactions; this involves several approximations in the calculations.

A simple bond-moment calculation for thiourea predicted a dipole moment of 3.11 debye (1.04×10^{-29} C m) (Huhey, 1978). Dipole moments calculated for the free thiourea molecule and the thiourea found in this structure (*MNDO*; Dewar & Thiel, 1977) are 4.7211 debye (1.5748×10^{-29} C m) (exp. 4.89 debye; Kumler & Fohlen, 1942) and 6.9788 debye (2.3279×10^{-29} C m).

It appears that the simplest way to view the formation of the CCl_4 -thiourea adduct is as a set of interactions of partially charged atoms. The interaction of primary importance is that between the partially positively charged C atom in CCl_4 and the partially negatively charged S atom of the thiourea [even though their electronegativities (Pauling, 1960) are both 2.5]. Calculations (*MNDO*; Dewar & Thiel, 1977) predict a +0.28 partial charge on the CCl_4 C atom, -0.07 partial charges on each of the Cl atoms, -0.52 partial charge on the thiourea S atom and -0.33 charges on the two thiourea N atoms. When simple potential energy calculations are carried out for a C...S attractive interaction and Cl...S and Cl...N repulsive interactions the attractive interaction potential is about three times the total negative interaction potential (Berry, Rice & Ross, 1980). This qualitative approach strongly suggests that the contribution from the Coulombic interactions to the stability of the adduct is substantial.

We have developed a classification of disorder types to facilitate discussion of disorder in thiourea adducts. The intent is to help describe what is seen in the crystal structure rather than a more theoretical classification of what occurs in the disordering process [discussions of what occurs may be found in, for example, Welberry (1985) and Parsonage & Staveley (1978) and references therein]. Westrum & McCull-

ough (1963) and Parsonage & Staveley (1978) have both suggested some classifications of disorder. The types suggested by Westrum & McCullough (1963), 'overall orientational disorder,' 'conformational disorder,' and 'positional disorder' would appear to be included in our types 2, 3 and 4. The 'distribution of vacancies' and 'orientational disorder' used by Parsonage & Staveley (1978, p. 717) appear to be combinations of several of the types we describe. The 'head-tail' or 'end-for-end' disorder described by Parsonage & Staveley (1978, p. 774 for urea adducts) would fit under our type 4, orientation disorder. We are primarily concerned with what we have called symmetry disorder in the CCl_4 /thiourea adduct.

Symmetry disorder occurs when a molecular fragment in the crystal structure does not exhibit or conform to the site symmetry. Fig. 2(b) illustrates the effect of this disordering for the CCl_4 molecule. The first obvious disordering feature is clearly seen in the multiple Cl-atom positions. The second feature is related to the lack of agreement between the C-Cl bond distances. The explanation is, of course, that the central C atom was also disordered but in such a small way that the thermal parameters could easily accommodate the disorder. As was shown earlier, when we pick a particular tetrahedral set of Cl coordinates and then fit the C-atom position to this arrangement, the result is a much more acceptable model for the CCl_4 molecule.

The other disorder types will be covered more completely in subsequent papers describing various disordered adducts of thiourea.

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References

- ANGLA, B. (1947). *C. R. Acad. Sci.* **244**, 402-404.
 BERRY, R. S., RICE, S. A. & ROSS, J. (1980). *Physical Chemistry*, p. 282. New York: John Wiley.
 BONDI, A. (1964). *J. Phys. Chem.* **68**, 441-451.
 CHATANI, Y. & NAKATANI, S. (1976). *Z. Kristallogr.* **144**, 175-188.
 CLEMENT, R., JEGOUDEZ, J. & MAZIERES, C. (1974). *J. Solid State Chem.* **10**, 46-50.
 DEWAR, M. J. S. & THIEL, W. (1977). *J. Am. Chem. Soc.* **99**, 4899-4907.
 ELCOMBE, M. M. & TAYLOR, J. C. (1968). *Acta Cryst.* **A24**, 410-420.
Handbook of Chemistry and Physics (1980). Edited by R. C. WEAST, p. F.221. Cleveland: The Chemical Rubber Co.
 HERMANN, C. & LENNÉ, H.-U. (1952). *Naturwissenschaften*, **39**, 234-235.
 HUHEY, J. E. (1978). *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd ed. New York: Harper and Row.

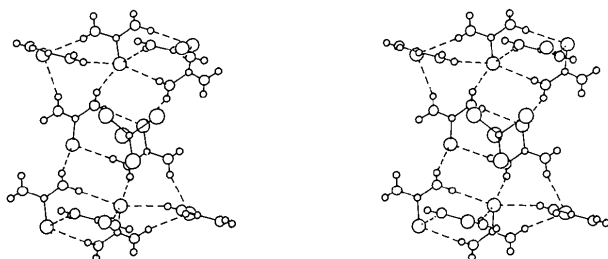


Fig. 3. Stereoplot illustrating the hydrogen bonding in a portion of the channel and one of the CCl_4 orientations in the binding site.

- KUMLER, W. D. & FOHLEN, G. M. (1942). *J. Am. Chem. Soc.* **64**, 1944–1948.
- LENNÉ, H.-U. (1954). *Acta Cryst.* **7**, 1–16.
- MCKINNON, M. S. & WASYLISHEN, R. E. (1986). *Chem. Phys. Lett.* **130**, 565–568.
- MULLEN, D., HEGER, G. & TREUTMANN, W. (1978). *Z. Kristallogr.* **48**, 95–100.
- NICHOLAIDES, N. & LAVES, F. (1965). *Z. Kristallogr.* **121**, 283–296.
- PARSONAGE, N. G. & STAVELEY, L. A. K. (1978). *Disorder in Crystals*. Oxford: Clarendon Press.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- SCHLENK, W. JR (1951). *Justus Liebigs Ann. Chem.* **573**, 142–162.
- SHELDRIK, G. M. (1983). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- SMITH, A. E. (1950). *J. Chem. Phys.* **18**, 150–151.
- STEWART, J. M. & HALL, S. R. (1983). Editors. *The XTAL System of Crystallographic Programs*. Tech. Rep. TR-1364. Computer Science Center, Univ. of Maryland, College Park, MD 20742, USA.
- WELBERRY, T. R. (1985). *Rep. Prog. Phys.* **48**, 1543–1593.
- WESTRUM, E. F. JR & McCULLOUGH, J. P. (1963). *Physics and Chemistry of the Organic Solid State*, edited by D. FOX, M. M. LABES & A. WEISSBERGER, pp. 1–178. New York: Interscience.
- WICK, T. A., FAIT, J., CAUGHLAN, C. N., McCANDLESS, F. P. & FITZGERALD, A. (1991). In preparation.

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Structure of 2-Amino-4,5-dicyanoimidazole

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Abstract. 2-Aminoimidazole-4,5-dicarbonitrile, $C_5H_3N_5$, $M_r = 133.14$, monoclinic, $C2/m$, $a = 11.764$ (4), $b = 9.855$ (10), $c = 11.656$ (4) Å, $\beta = 116.54$ (3)°, $V = 1209$ (1) Å³, $Z = 8$, $D_m = 1.41$ (2), $D_x = 1.46$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.66$ cm⁻¹, $F(000) = 544$, $T = 183$ K, $R(F) = 0.064$ for 1425 independent reflections. There are two independent half molecules in the asymmetric unit, each of which lies perpendicular to a mirror plane. Each molecule forms six hydrogen bonds with neighboring molecules which may explain the unusually high decomposition temperature of 543 K. The molecules form hydrogen-bonded zigzag sheets about the $(\bar{2}02)$ planes.

Introduction. Cyanoimidazoles are important as intermediates in the formation of pyrimidine bases from hydrogen cyanide. They are also used in the preparation of ligands for stacked metal complexes as described by Rasmussen, Bailey & Bayón (1984) and Rasmussen, Bailey, Bayón & Butler (1984). The sample was prepared (Rasmussen, 1984) using the method of Sheppard & Webster (1973) who report a very high decomposition temperature of 543 K which is to be contrasted with a melting point of 363–364 K for imidazole (*The Merck Index*, 1976). This investigation is part of a continuing study of the properties of other imidazoles and their acid salts.

Experimental. Powder was supplied by P. G. Rasmussen, recrystallized from ethanol–water mixture, a crystal $0.80 \times 0.25 \times 0.10$ mm was mounted on a glass fiber, 25 reflections were scanned to obtain the unit-cell parameters, intensities of 1425 independent reflections were measured with a CAD-4 diffractometer in the ranges $0 \leq \theta \leq 28^\circ$, $-15 \leq h \leq 15$, $0 \leq k \leq 13$, $0 \leq l \leq 15$. Density measured by flotation. No absorption corrections made. Three standard reflections measured periodically showed no significant deviations. 171 reflections with $F_o < 3\sigma$ were considered unobserved.

Structure solution using *MULTAN* (Germain, Main & Woolfson, 1971), full-matrix least-squares refinements on I_{obs} in *SHELX76* (Sheldrick, 1976), amino hydrogens found from an $F_o - F_c$ synthesis and refined isotropically, C and N atoms refined anisotropically, and the half H atoms between N(3) atoms were fixed at $\frac{1}{3}$ and $\frac{2}{3}$ the distance between the ring N atoms of adjacent molecules. $R(F) = 0.064$, $wR = 0.081$, $S = 1.07$, $w = 1.000/[\sigma^2(F) + 0.0070F^2]$, $\Delta/\sigma_{max} = 0.07$, $\Delta\rho_{max} = 0.45$, $\Delta\rho_{min} = -0.31$ e Å⁻³. Atomic scattering factors for non-H atoms were from *International Tables for X-ray Crystallography* (1968, Vol. III) and for hydrogens from Stewart, Davidson & Simpson (1965).‡

‡ An attempt was made to refine this structure in space group $C2$. The resulting parameters gave a structure with exceptionally large deviations between bond distances on opposite sides of the imidazole ring and thermal parameters for N(3') which led to a non-positive-definite thermal ellipsoid.

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