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The Crystal and Molecular Structure of Dithiobiurea, N,N'-Bis(thiocarbamoyl)hydrazine, (NH₂.CS.NH)₂

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The crystal and molecular structure of dithiobiurea, $(NH_2.CS.NH)_2$, has been solved by direct methods and refined by the least-squares method using counter data (1604 reflexions) including anisotropic temperature factors for non-hydrogen and positional parameters for hydrogen atoms, to a final $R = 0.060$. All hydrogen atoms were well defined in the difference Fourier syntheses. The crystals are monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), $a = 20.825$ (10), $b = 4.536$ (7), $c = 14.368$ (4) Å, $\beta = 109.33$ (4)°, $Z = 8$. One molecule corresponds to the asymmetric unit. The structure consists of four layers of molecules per unit cell, approximately parallel to the bc plane linked together by $S \cdots H(N)$ intermolecular hydrogen bonds (2·4–2·8 Å). The molecule is twisted around the central N–N bond. Each of the central nitrogen atoms has three intramolecular $N \cdots H(N)$ hydrogen bonds (2·0–2·5 Å) which may be responsible for the molecule twisting. The three bonds of each carbon atom have almost regular planar trigonal sp^2 symmetry. The S–C distances (1·691–1·701 Å) and the C–N distances (1·31–1·34 Å) indicate a high double-bond character of these bonds.

Introduction

N,N'-Bis(thiocarbamoyl)hydrazine, dithiobiurea, $(NH_2.CS.NH)_2$, has been studied (Mashima, 1964) in comparison with other hydrazine derivatives, both in their hydrogen and deuterated forms, by infrared spectroscopy in the solid state with KBr disks in the rock-salt region, but the crystal structure of this compound has until now been unknown. We have therefore determined its crystal structure by X-ray diffraction analysis.

Experimental

Dithiobiurea may be easily recrystallized from water or ethanol but almost all the crystals are twinned; only very few suitable crystals were found. The single crystal used was prismatic (dimensions: $0.11 \times 0.25 \times 1.5$ mm), elongated along the b axis; the angles between the normals to the faces of the prism, measured with an optical goniometer, were 69°42' and 110°18'.

The a, c and β cell parameters were determined by measuring to within 0·02° the ω and 2θ positions of the $h00$ and $00l$ reflexions with a Weissenberg two-circle counter diffractometer and Mo $K\alpha$ radiation

($\lambda = 0.71069$ Å). Plots of the $d(100)$ and $d(001)$ values *versus* the function $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)/2$ gave straight lines which were calculated and extrapolated to 90° by the least-squares method (Pignedoli & Peyronel, 1972). The b parameter was carefully determined with a precision precession camera and Mo $K\alpha$ radiation. The systematic absences were observed on Weissenberg and precession photographs by using both Cu $K\alpha$ and Mo $K\alpha$ radiation.

Crystal data

$(NH_2.CS.NH)_2$, $S_2N_4C_2H_6$. Monoclinic prismatic. Space group $C2/c$ (C_{2h}^6, No. 15) from the observed reflexions which obey the conditions: $0k0$ ($k = 2n$), $h0l$ ($l = 2n$), hkl ($h+k = 2n$); $a = 20.825$ (10), $b = 4.536$ (7), $c = 14.368$ (4) Å, $\beta = 109.33$ (4)° at 24°C. $V = 1280.7$ Å³, F.W. 150·23, $Z = 8$, $F(000) = 512$, $D_c = 1.56$ g cm⁻³.

The X-ray intensities ($h0l \rightarrow h3l$) were recorded on the same crystal as described above with the equi-inclination ω–2θ method and monochromatized Mo $K\alpha$ radiation by using a two-circle Weissenberg automatic counter diffractometer. The intensities were corrected for Lorentz and polarization factors. The

Table 1. *Fractional coordinates and thermal parameters*

Coordinates are $\times 10^5$ for non-hydrogen and $\times 10^4$ for hydrogen atoms. Thermal parameters for non-hydrogen atoms are defined by $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl) \times 10^{-3}]$. Assumed thermal parameters, $B(\text{Å}^2)$, for the hydrogen atoms are defined by $\exp[-B(\sin\theta/\lambda)^2]$. Standard deviations are in parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	20904 (3)	25321 (19)	35116 (4)	1680 (19)	12805 (61)	1962 (18)	292 (23)	91 (15)	−86 (24)
S(2)	4449 (3)	16608 (25)	−10922 (4)	1777 (19)	13349 (63)	1962 (18)	−644 (24)	−78 (15)	190 (24)
N(1)	8741 (10)	38728 (67)	22440 (15)	2197 (73)	13943 (195)	2649 (77)	1274 (95)	150 (60)	195 (100)
N(2)	16415 (10)	33914 (72)	1457 (15)	2407 (84)	15365 (208)	2208 (72)	−1700 (107)	69 (61)	246 (102)
N(3)	15084 (9)	5826 (66)	17160 (14)	1932 (67)	12855 (162)	2072 (61)	542 (83)	91 (51)	−275 (82)
N(4)	10131 (9)	3883 (71)	7872 (14)	1974 (66)	13909 (174)	1854 (59)	−633 (89)	59 (51)	3 (87)
C(1)	14435 (11)	23305 (74)	24256 (15)	1568 (67)	11747 (169)	2118 (69)	−36 (82)	446 (56)	628 (88)
C(2)	10816 (11)	18700 (70)	143 (15)	1623 (69)	12085 (167)	1861 (64)	−132 (84)	313 (53)	−329 (85)

Table 1 (*cont.*)

	x	y	z	B
H(3)	1895 (17)	−1139 (66)	1827 (25)	4·78
H(4)	630 (17)	−1049 (64)	827 (25)	4·60
H(11)	799 (16)	5348 (75)	2786 (25)	4·71
H(12)	576 (17)	4040 (71)	1688 (24)	4·71
H(21)	1662 (17)	4777 (82)	−221 (24)	4·97
H(22)	1851 (18)	3953 (63)	639 (25)	4·97

$\sigma(F_o)$'s were calculated by a statistical method previously described (Pignedoli, Peyronel & Antolini, 1974). Only the values of $F_o > 3\sigma(F_o)$ were used for the calculations (1604 reflexions).

The crystal structure was solved by direct methods using the *LSAM* program (Germain, Main & Woolfson, 1971) which allowed the assignment of sign to 206 reflexions. All the S, N and C atoms of the molecule were very well defined in three-dimensional Fourier sections.

The refinement was carried out by the block-diagonal least-squares method using the *MIQUAD* program of Immirzi (1967) on a CDC 6600 computer. The atomic scattering factors of Hanson, Herman, Lea & Skillman (1964) were used. Firstly the positional, isotropic and anisotropic thermal parameters were refined for the non-hydrogen atoms. The hydrogen atoms were then introduced in positions calculated for an almost trigonal symmetry of the nitrogen atoms, with the last isotropic temperature factor of the nitrogen atom to which they are bonded. Finally the positional parameters of all atoms and the anisotropic thermal parameters of the non-hydrogen atoms were refined until a final constant value of $R = \sum|F_o - F_c|/\sum|F_o| = 0·060$ was reached, and the variations of the positional parameters were of the same order as their standard deviations. Weights were calculated with the formula $1/w = \sigma^2 + 0·004F_o^2$ (Gilmore & Woodward, 1971). The final positional and thermal parameters are given in Table 1.

A projection of the cell on the ac plane is shown in Fig. 1. Interatomic distances and angles (Table 2 and Fig. 2) and their e.s.d.'s were calculated with the *MIQUAD* and *IMPACC* programs of Immirzi (1967) and the thermal ellipsoids (Fig. 3) were plotted with the *ORTEP* program of Johnson (1965). Three-dimensional difference Fourier syntheses (Fig. 4) show

well defined hydrogen atoms. The more relevant least-squares planes were calculated with the *PIAMED* program of Immirzi (1967).*
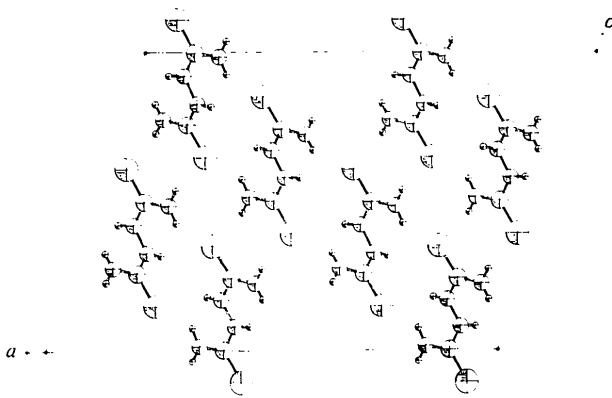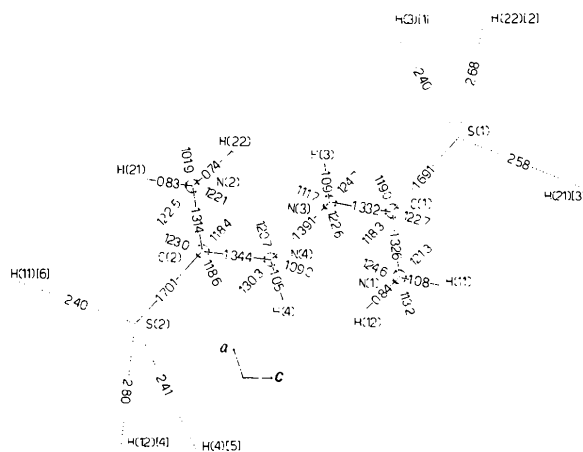

Fig. 1. Orthographic projection of the unit cel lon the xz plane (*ORTEP* plot).

Fig. 2. Interatomic distances (Å) and angles (°). Intermolecular S···H contacts are quoted; intramolecular N···H contacts are only indicated.

Table 2. *Interatomic distances (Å) and angles (°) and their e.s.d.'s*

Asymmetric units

[1]	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	[4]	$-x$ $1-y$ $-z$	
[2]	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$	[5]	$-x$ $-y$ $-z$	
[3]	x	$1-y$	$\frac{1}{2}+z$	[6]	x $1-y$ $z-\frac{1}{2}$	

Bond distances

S(1)–C(1)	1·691 (5)		S(2)–C(2)	1·701 (5)
C(1)–N(1)	1·326 (5)		C(2)–N(2)	1·314 (3)
C(1)–N(3)	1·332 (3)		C(2)–N(4)	1·344 (8)
N(3)–N(4)	1·391 (7)			
N(3)–H(3)	1·09 (4)		N(4)–H(4)	1·05 (3)
N(1)–H(11)	1·08 (3)		N(2)–H(21)	0·83 (7)
N(1)–H(12)	0·84 (7)		N(2)–H(22)	0·74 (6)

Other distances

S(1)····H(11)	2·84 (5)		S(2)····H(21)	2·81 (4)
S(1)····H(3)	2·85 (4)		S(2)····H(4)	2·92 (6)
C(1)···H(11)	2·10 (3)		C(2)···H(21)	1·89 (5)
C(1)···H(12)	1·93 (6)		C(2)···H(22)	1·82 (4)
C(1)···H(3)	2·15 (2)		C(2)···H(4)	2·17 (5)
N(3)···H(12)	2·49 (3)		N(4)···H(22)	2·44 (3)
N(3)···H(22)	2·44 (5)		N(4)···H(12)	2·45 (2)
N(3)···H(4)	1·99 (4)		N(4)···H(3)	2·06 (6)
S(1)····N(2) [2]	3·29		S(2)····N(1) [4]	3·37
S(1)····H(22) [2]	2·68		S(2)····H(12) [4]	2·80
S(1)····N(3) [1]	3·34		S(2)····N(4) [5]	3·34
S(1)····H(3) [1]	2·40		S(2)····H(4) [5]	2·41
S(1)····N(2) [3]	3·36		S(2)····N(1) [6]	3·47
S(1)····H(21) [3]	2·58		S(2)····H(11) [6]	2·40

Bond angles

S(1)—C(1)-N(1)	122·7 (2)		S(2)—C(2)-N(2)	123·0 (2)
S(1)—C(1)-N(3)	119·0 (2)		S(2)—C(2)-N(4)	118·6 (3)
N(1)—C(1)-N(3)	118·3 (2)		N(2)—C(2)-N(4)	118·4 (2)
C(1)—N(1)-H(11)	121·3 (16)		C(2)—N(2)-H(21)	122·5 (34)
C(1)—N(1)-H(12)	124·6 (60)		C(2)—N(2)-H(22)	122·1 (33)
H(11)-N(1)-H(12)	113·2 (41)		H(21)-N(2)-H(22)	101·9 (34)
C(1)—N(3)-N(4)	122·6 (2)		C(2)—N(4)-N(3)	120·7 (3)
C(1)—N(3)-H(3)	124·7 (16)		C(2)—N(4)-H(4)	130·3 (24)
N(4)—N(3)-H(3)	111·7 (25)		N(3)—N(4)-H(4)	109·0 (18)

Results and discussion

The structure of dithiobiurea (Fig. 1) consists of four layers of molecules per unit cell, approximately parallel to the bc plane and linked together by intermolecular hydrogen bonds. Each molecule, corresponding to the asymmetric unit, is twisted around the central N(3)–N(4) bond, forming the angles C(1)N(3)N(4)∧C(2)N(4)N(3) = 99·8° and S(1)C(1)N(1)N(3)∧S(2)C(2)-N(2)N(4) = 102·5° (Table 3), so that the molecule seems to have a *trans* configuration in projection on the $a \sin\beta, c$ plane and a *cis* configuration in the projection on the bc plane (Fig. 3).

The homologous bond distances of the two halves of the molecule have very close values differing by about 0·01 Å for the S–C and the C–N distances. The bonds of the carbon atoms have an almost regularly planar trigonal sp^2 symmetry; the SCN and NCN angles are close to 120° (Table 2) and the atoms SC(N)N are coplanar within an r.m.s. atom deviation of 0·005 Å. The central N(3) and N(4) atoms have CNN angles close to 120°; their CNH and NNH angles are respectively similar in the two halves of the molecule but are very different from each other (CNH = 125–130°; NNH = 109–112°) (Table 2). The three bonds of each central and each terminal nitrogen atom are less coplanar (Table 3) than those of the carbon atom because some of them involve hydrogen atoms.

Three intermolecular S···H short contacts are observed with distances of 2·40–2·58–2·68 Å for S(1) and 2·40–2·41–2·80 Å for S(2) (Table 2 and Fig. 2). All are lower than the S···H van der Waals distance of 3·05 Å assuming the radii given by Pauling (1960).

Table 3. *Least-squares planes and angles between planes (°)*

Equations of the form $Ax+By+Cz-D=0$ referred to the crystallographic axes a, b and c; plane coefficients A, B, C, D ($\times 10^4$). Deviations of the atoms from the planes and their r.m.s. deviation in Å ($\times 10^3$); the deviations of the atoms not included in the mean plane are indicated with an asterisk.

A	−5534	−5457	−5918	−6545	−6680	−5936	−5949	−6102
B	−7534	8018	−7554	7206	−6785	7750	−7197	7568
C	5183	4104	4612	4327	5095	4011	5347	4231
D	−6581	−5444	−9588	−8917	−9680	−6690	−6672	−6805
Central atom	C(1)	C(2)	N(1)	N(2)	N(3)	N(4)		
S(1)	−1		−158*				−51	
S(2)		−1		149*				21
N(1)	−2		41		203*		44	
N(2)		−2		−146				−153
N(3)	−2		37*	93*	−54	−2	−73	
N(4)		−1	99*	127*	15	7		5
C(1)	4		−12		18		−18	
C(2)		4		38		−2		−43
H(3)	224*		225*		20		96	
H(4)		−66*		203*		−3		22
H(11)	−16*		−13		250*		72	
H(12)	−129*		−17		159*		−69	
H(21)		263*		51		167*		74
H(22)		255*		58		138*		73
R.m.s. deviation	5	5	48	170	62	8	85	96

H(11)N(1)H(12) / S(1)C(1)N(3)	169·7		H(22)N(2)H(21) / S(2)C(2)N(4)	148·5
S(1)C(1)N(1) / H(3)N(3)N(4)	168·2		S(2)C(2)N(2) / H(4)N(4)N(3)	176·0
C(1)N(3)H(3) / C(2)N(4)H(4)	92·0		C(1)N(3)N(4) / C(2)N(4)N(3)	99·8
S(1)C(1)N(1)N(3) / S(2)C(2)N(2)N(4)	102·5			

No N···H(N) intermolecular hydrogen bond is observed in this structure, so that the S···H(N) bonds alone are responsible for the high stability of the crystal lattice shown by the very low solubility of the compound, which grows in the order ethanol < water < formamide depending on the increasing ability of these solvents to break the intermolecular hydrogen bonds of the solid.

Several intramolecular hydrogen contacts are observed in this structure: all homologous contacts in the two halves of the molecules have very similar distances (Table 2). Each of the central N(3) and N(4) atoms shows three N···H(N) similar intramolecular bonds (2·0–2·4–2·5 Å) which are definitely shorter than the Pauling's (1960) N···H van der Waals distance (2·70 Å). These intramolecular hydrogen bonds may be considered as principally responsible for the twisting of the molecule around the central N(3)–N(4) bond, both these nitrogen atoms being involved in the internal and symmetric hydrogen bond system. Among these intramolecular hydrogen bonds the N(3)···H(4) (1·99 Å) and N(4)···H(3) (2·06 Å) are the strongest ones.

It is remarkable that in the ac projection the thermal ellipsoids have an almost isodiametric shape while in the bc projection (Fig. 3) they are all much more elongated along the b direction, with nearly the same dimensions and orientation. This effect may be only partially due to the fact that the thermal parameter along the b axis is less well defined because of the few k values (0 → 3) involved in the refinement. However, it is very likely that this preferential orientation of the highest thermal motion is due to the fact that the intermolecular hydrogen bonds are almost parallel to the ac plane and consequently the molecules are more free to vibrate as a whole in the b direction.

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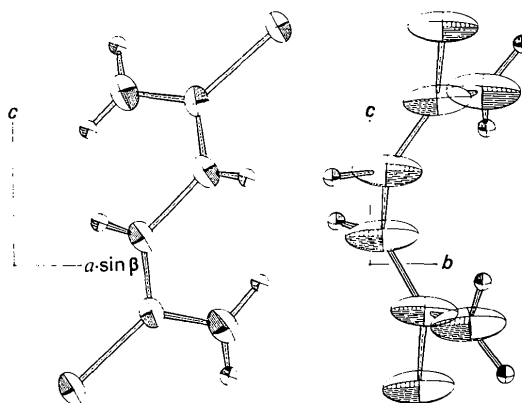GILMORE, C. J. & WOODWARD, P. (1971). J. Chem. Soc. (A), pp. 3453–3458.

Fig. 3. ORTEP plot of thermal ellipsoids scaled to include 60 % probability for non-hydrogen atoms. The hydrogen atoms are represented by spheres of 0·1 Å radius. Orthographic projections: (left) on the a sin β,c plane; (right) on the bc plane.
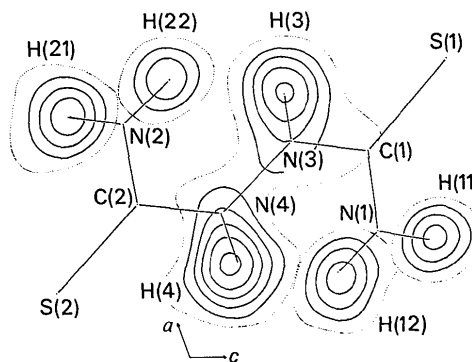

Fig. 4. Sections of the difference electron-density map, projected on the xz plane, corresponding to the y refined positions for hydrogen atoms. Contours are at 0·1 e Å^{-3} intervals beginning with the 0·5 e Å^{-3} contour (dotted line).

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