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The Crystal and Molecular Structure of 2-Mercaptobenzimidazole

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$C_7H_6N_2S$ is monoclinic, space group $P2_1/m$, with $a=4{\cdot}91(1)$, $b=8{\cdot}56(3)$, $c=8{\cdot}29(4)$ Å, $\beta=91{\cdot}6(1)^\circ$, $Z=2$. Crystal data were photographically recorded by the Weissenberg method with Cu $K\alpha$ radiation. Integrated intensities were obtained photometrically. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares calculations. A final $R=0{\cdot}102$ was obtained for 633 observed reflexions. The fused ring system is planar and aromatic. An exocyclic C–S distance of 1·671(8) Å indicates the thione to be the predominant tautomer in the solid. The molecules are linked by N–H···S bonds (3·366 Å) along **b** in the form of an extended chain. Each thione S makes contact with one N atom from two adjacent molecules.

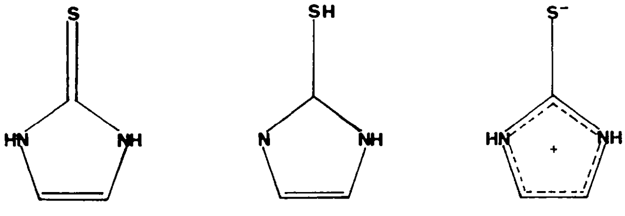
Introduction

Derivatives of benzimidazoles are useful inhibitors of the corrosion of metals and alloys in various aggressive media. The rate of dissolution of mild steel in 0·1 *M* H_2SO_4 is lowered in the presence of 2-mercaptobenzimidazole (Aronson & Belen'kii, 1965). Similarly the corrosion of brass in 0·2 *M* NaOH solution is inhibited by the same compound (Patel, Makwana & Patel, 1974).

A possible explanation of the inhibition involves coordination of the molecules at the metal surface and the resultant formation of a protective layer. Poling (1970) has shown this to be the case with benzotriazole and Cu in 0·1 *M* H_2SO_4 where the protective layer was a polymeric complex of benzotriazole and Cu(1).

2-Mercaptobenzimidazole is a potentially ambidentate ligand with either exocyclic S or heterocyclic N (Fig. 1) available for coordination. With the removal of the mercapto proton and the formation of the anion both atoms become available. It is most probably this anion which is involved in the inhibition of brass in NaOH solution.

The ligand forms complexes with transition metals in widely differing media and this contributes to its use as an inhibitor. This analysis has been undertaken as part of a programme in which the structural and coordination chemistry of inhibitors is being studied.



(I) (II) (III)

Fig. 1. Structural forms of the molecule: (I) thione, (II) thiol, (III) ionic.

Experimental

(i) *Crystal data*

White needle-shaped crystals were obtained by evaporation from ethanol. Cell parameters were obtained from precession photographs taken with Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation.

The systematic absences suggested the space groups $P2_1/m$ or $P2_1$. Intensity statistics (Howells, Phillips & Rogers, 1950) suggested $P2_1/m$. This was supported by an infrared spectrum which agreed with the assignment of Harrison & Ralph (1967) and indicated the compound to be thione rather than thiol in the solid. The thione possesses a mirror plane, the thiol does not; hence the compound was assigned to $P2_1/m$.

Table 1 contains the crystal and experimental data.

Table 1. *Crystal and experimental data*

$C_7H_6N_2S$
$M=150{\cdot}20$
a = 4·91 (1) Å
b = 8·56 (3)
c = 8·29 (4)
β = 91·6 (1)°
V = 348·20 Å^3

D_c = 1·43 g cm^{-3}
D_m = 1·42
Systematic absences $0k0$: $k=2n+1$
Space group $P2_1/m$,
$Z=2$
μ(Cu $K\alpha$) = 32·9 cm^{-1}
$F(000)=156$

(ii) *Data collection and reduction*

The crystals used to collect intensities were 0·20 × 0·40 × 0·60 and 0·20 × 0·30 × 0·40 mm. Multiple-film packs of Weissenberg photographs were recorded for $h=0$ to 3, for the first crystal, and $k=0$ to 5, for the second. Ni-filtered Cu $K\alpha$ radiation was used. Integrated intensities were measured on a Joyce–Loebl

Table 2. *Atomic coordinates and thermal parameters with their e.s.d.'s in parentheses*

(*a*) Non-hydrogen parameters ($\times 10^4$)

The values of b_{ij} are defined by: $\exp[-\frac{1}{4}(h^2a^{*2}b_{11}+2hka^*b^*b_{12}+\ldots)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
S(2)	−5629 (5)	2500 (0)	1139 (3)	444 (12)	64 (3)	136 (4)	0	76 (9)	0
C(2)	−3329 (10)	2500 (0)	−308 (10)	325 (37)	54 (9)	141 (12)	0	20 (34)	0
N(1)	−2179 (10)	1226 (5)	−999 (6)	353 (22)	48 (6)	166 (8)	−14 (10)	−3 (21)	24 (18)
C(5)	−393 (12)	1682 (6)	−2170 (7)	321 (25)	72 (8)	144 (9)	−7 (12)	−2 (25)	4 (20)
C(6)	1215 (14)	834 (8)	−3200 (9)	443 (32)	84 (8)	188 (11)	−33 (15)	50 (30)	31 (28)
C(7)	2789 (15)	1692 (9)	−4246 (9)	454 (34)	139 (11)	187 (12)	−22 (17)	127 (32)	26 (31)

(*b*) H atom coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$)

	x	y	z	β
H(1)	−2595	88	−593	6008
H(6)	1207	−5440	−2955	7646
H(7)	4061	1103	−5173	4383

microdensitometer. The data for each axis were separately processed for Lorentz and polarization factors. Interlayer scaling factors were obtained (Monahan, Schiffer & Schiffer, 1965) and used to place the structure amplitudes on a common scale. Of the 746 independent amplitudes recorded, 110 were considered too weak to be observed.

Structure determination and refinement

The coordinates of the non-hydrogen atoms were obtained by Patterson and Fourier methods and least-squares refinement. With $R=0\cdot127$ a difference map was calculated which revealed the three non-equivalent H atoms. The map also demonstrated that no H atom was bonded to S. Full-matrix refinement was commenced with isotropic temperature factors allocated to the H atoms.

The weighting scheme was:

$$w=1/[P_1+|F_o|+P_2|F_o|^2+P_3|F_o|^3]$$

with $P_1=2\cdot10$, $P_2=0\cdot034$ and $P_3=1\cdot0\times10^{-4}$. 001, 102 and 111 were omitted from the last two cycles as they appeared subject to extinction. At $R=0\cdot102$ no parameter shift was greater than one-third of the corresponding e.s.d., and refinement was stopped. A weighting analysis showed $\sum w\Delta^2/N$ to be independent of $|F_o|$ and $\sin^2\theta$.

Scattering factors for S, N and C were obtained from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965).

Final positional and thermal parameters are in Table 2.*

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(2)–C(2)	1·671 (8)	C(2)–N(1)–C(5)	110·4 (4)
N(1)–C(2)	1·362 (6)	C(2)–N(1)–H(1)	121 (5)
N(1)–C(9)	1·383 (8)	C(5)–N(1)–H(1)	128 (5)
N(1)–H(1)	1·05 (9)	S(2)–C(2)–N(1)	126·8 (5)
C(4)–C(9)	1·400 (7)	N(1)–C(2)–N(3)	106·4 (5)
C(6)–C(7)	1·384 (9)	C(6)–C(7)–C(8)	121·9 (6)
C(7)–C(8)	1·389 (9)	C(6)–C(7)–H(7)	117 (4)
C(7)–H(7)	1·12 (7)	C(7)–C(8)–C(9)	116·5 (5)
C(8)–H(8)	1·2 (1)	C(7)–C(8)–H(8)	114 (4)
C(9)–C(8)	1·383 (8)	N(1)–C(5)–C(4)	106·4 (4)
		N(1)–C(5)–C(6)	132·0 (5)
		C(4)–C(9)–C(8)	121·6 (5)

Table 4. *Equation of the plane through the molecule*

(X, Y and Z are in Å relative to the Cartesian axial system defined by a, b and c^*)

$$-0\cdot7204X+0\cdot0Y-0\cdot6935Z-1\cdot3526=0$$

Atomic displacements with their e.s.d.'s (Å)

S(2)	+0·005 (2)	H(1)	−0·104 (77)
N(1)	−0·025 (5)	H(7)	+0·094 (66)
C(2)	−0·003 (7)	H(8)	−0·133 (84)
C(7)	+0·028 (7)		
C(8)	−0·001 (6)		
C(9)	−0·004 (5)		

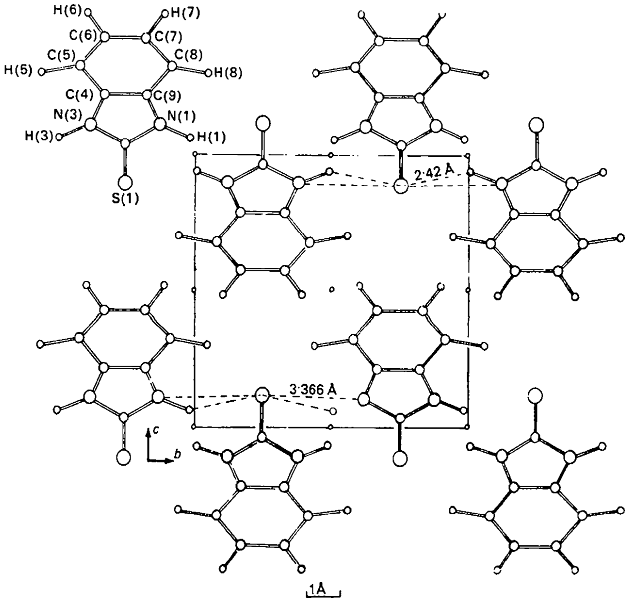


Fig. 2. Molecular packing in a^* projection.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31171 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Some imidazole ring dimensions* (Å)

Compound and reference	N(1)–C(2)	C(2)–N(3)	N(3)–C(4)	C(4)–C(9)	C(9)–N(1)
Imidazole at −150°C (Martínez-Carrera, 1966)	1·326	1·349	1·369	1·358	1·378
Imidazole at room temperature (Will, 1969)	1·311	1·337	1·372	1·311	1·381
6-Mercaptopurine monohydrate (Brown, 1969)	1·352	1·333	1·368	1·394	1·373
Hypoxanthine hydrochloride monohydrate (Sletten & Jensen, 1969)	1·333	1·318	1·376	1·368	1·375
1,3-Dimethyl-2(3*H*)-imidazolethione (Ansell, Forkey & Moore, 1970)	1·35	1·35	1·41	1·31	1·41
This investigation	1·362	1·362	1·383	1·400	1·383

Description and discussion of the structure

Bond lengths and angles are in Table 3.

(*a*) *Planarity in the molecule*

The best plane through the molecule, with atomic displacements, is given in Table 4. The molecule is planar, within experimental error, and in this respect is similar to other fused benzo-heterocyclic systems, *e.g.* 2-methylthiobenzothiazole (Wheatley, 1962) and 2-mercaptobenzothiazole (Chesick & Donohue, 1971).

(*b*) *Molecular dimensions*

In the thione form the molecules possess *mm* symmetry and occupy the mirror planes in the cell.

A mean C–C distance of 1·389 Å, with an r.m.s. deviation of 0·010 Å is within the expected range for benzene-ring dimensions both in the free molecule and in fused ring systems. The imidazole ring is characterized by three bond lengths, all of which show multiple character. There are no significant differences in the lengths of the two unique C–N bonds [1·362 (6) and 1·383 (7) Å] and because of the inherent symmetry of the molecule all four C–N bonds are similar. This strongly suggests that the π electrons are delocalized and aromatic character exists in the imidazole ring.

This situation appears to be common in fused benzimidazole rings (Table 5). The bond lengths in the imidazole component are generally longer than those in the free molecule at room temperature (Table 5). Bond angles show good agreement with those of Ansell, Forkey & Moore (1970) with the larger internal angles at the N atoms.

The C(2)–S(2) length of 1·671 Å possesses 80% double-bond character on Abraham's (1956) scale and is typical of exocyclic thiones (Downie, Harrison, Raper & Hepworth, 1972).

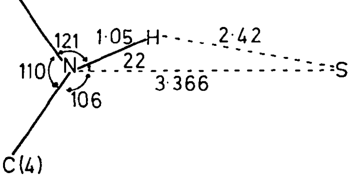

Fig. 3. Details of the N–H···S hydrogen-bonding scheme.

This confirms the thione nature of the compound in the solid (Fig. 1).

(*c*) *Molecular packing and hydrogen-bonding*

Table 6 lists all the shortest (<4·0 Å) intermolecular contacts. Fig. 2 shows the cell contents in a^* projection and the essential features of the H-bonding.

Table 6. *Shortest intermolecular contacts* (<4·0 Å)

Symmetry code

(*a*)	x, y, z	(*d*)	$1-x, 1-y, 1-z$
(*b*)	$1+x, y, 1+z$	(*e*)	$1-x, 1-y, \bar{z}$
(*c*)	$\bar{x}, 1-y, \bar{z}$	(*f*)	$\bar{x}, 1-y, 1-z$

*S(2)–N(1)^a	3·366 (4)	C(2)–C(7)^a	3·797 (9)
S(2)–C(9)^b	3·622 (6)	C(7)–C(8)^e	3·577 (9)
*S(2)–H(1)^c	2·42 (9)	C(7)–C(9)^a	3·722 (8)
N(1)–N(1)^d	3·395 (6)	C(7)–H(7)^c	2·89 (7)
N(1)–C(7)^a	3·624 (8)	C(8)–C(8)^e	3·492 (9)
N(1)–C(8)^a	3·691 (8)	H(1)–H(1)^f	2·6 (1)
N(1)–H(1)^d	2·89 (8)	H(7)–H(7)^c	2·1 (1)

* Hydrogen-bonded contact.

The molecules form an extended H-bonded chain along **b**. Each S atom is H-bonded to two imidazole N atoms, one from each of two adjacent molecules (Fig. 2). This supports the existence of some ionic thione contribution in the overall resonance scheme of the molecule (Fig.1). Details of the N–H···S bonds are shown in Fig. 3. The H···S contact (2·42 Å) is significantly shorter than the corresponding van der Waals radii sum (2·85 ± 0·2 Å) and the H–N···S angle (22°) shows slight deviation from linearity. The dimensions of the N–H···S bonds are similar to those reported by Chesick & Donohue (1971).

All calculations were performed on the IBM 360/67 computer at the University of Newcastle upon Tyne. The programs used were from the integrated set derived by Dr F. R. Ahmed and his group at N.R.C., Ottawa, Canada. The *SFLS* block-diagonal refinement program (NRC-10) has been adapted for full-matrix refinement by Dr H. M. M. Shearer of Durham University.

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Solid-State Phase Transition in Triethylenediamine, $N(CH_2CH_2)_3N$. I. The Crystal Structure of Phase II at 298 K

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At atmospheric pressure, triethylenediamine, $N(CH_2CH_2)_3N$, undergoes a solid-state structural transition at 351K; the so-called phase I is stable between 433K (m.p.) and 351 K, phase II below 351K. Single crystals of phase II have been grown by slow sublimation *in vacuo* and the crystal structure has been determined at 298K (room temperature) from three-dimensional neutron diffraction data. The hitherto ambiguous situation concerning the molecular conformation has been resolved by considering the agreement of the following structural models, in turn, with the experimental neutron data: (i) an ordered structure of non-twisted molecules, (ii) an ordered structure of twisted (in the same sense) molecules, (iii) a disordered structure of composite molecules (each consisting of two half-weighted molecules twisted in opposing senses). [The twists refer to the upper half relative to the lower half of the molecule about the NN direction.] A hexagonal cell with $a=6{\cdot}14$ (2), $c=9{\cdot}46$ (2) Å and $Z=2$ was employed for all models, but only the model with non-twisted molecules resulted in an acceptable structure. The space group was $P6_3/m$ and the molecular symmetry $\bar{6}m2$. Full-matrix least-squares refinements were used and all non-fixed positional and anisotropic thermal parameters were varied. Rigid-body motion is a reasonably good approximation for the thermal motion of the molecule. Intramolecular bond length and interbond angle magnitudes indicate good internal consistency and agree well with those values generally accepted for equivalent bonds in other compounds.

Introduction

Triethylenediamine, $N(CH_2CH_2)_3N$, formally known as 1,4-diazabicyclo[2,2,2]octane, is a globular molecule with a structural phase transition at 351 K (Chang & Westrum, 1960; Trowbridge & Westrum, 1963). In the room-temperature phase (phase II), X-ray diffraction studies have shown that the crystal system is hexagonal with two molecules per unit cell (Wada, Kishida, Tomiie, Suga, Seki & Nitta, 1960; Weiss, Parkes, Nixon & Hughes, 1964). Above 351 K, the compound structurally transforms to phase I for which a face-centred crystal system has been tentatively suggested (Brüesch, 1966; Brüesch & Günthard, 1966). [The structure of phase I has been studied by the authors and details are given in part II (Nimmo & Lucas, 1976).]

For the structurally similar compound bicyclo-[2,2,2]octane, Hendrickson (1961) has concluded from molecular orbital calculations that the molecule would be energetically most favourably arranged in a slightly twisted conformation. If the triethylenediamine (TEDA) molecule were also twisted and about the NN direction, the molecular symmetry would be 32 as compared with the more symmetric $\bar{6}m2$ of the non-twisted molecule. These molecular conformations are illustrated in Fig. 1.

Wada *et al.* (1960) have reported the phase II space group to be $P6_3/m$, which would preclude the twisted