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Structure of *N*-(2-Dimethylaminoethyl)dithiocarbamic Acid

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Abstract. $C_5H_{12}N_2S_2$, $M_r = 164.3$, monoclinic, $P2_1/n$, $a = 11.057$ (1), $b = 11.866$ (2), $c = 6.5885$ (7) Å, $\beta = 96.19$ (1)°, $V = 859.39$ Å³, $Z = 4$, $D_m = 1.262$, $D_x = 1.269$ Mg m⁻³, m.p. = 431 K, Mo $K\alpha$ X-rays, $\lambda = 0.71069$ Å, $\mu = 0.526$ mm⁻¹, $F(000) = 352$, $T = 295$ K, $R = 0.046$ for 1207 unique observed reflections. The molecule exists as a zwitterion $(CH_3)_2N^+H(CH_2)_2NHCS_2^-$. In the planar NCS_2 dithiocarbamate group the lengths of the partially double C–S bonds, 1.730 (4) and 1.682 (4) Å, differ significantly. The C–N bond, 1.340 (6) Å, also has strong double-bond character. A bifurcated N–H...S₂ and a normal N–H...S intermolecular hydrogen bond result in infinite interconnected zigzag chains of molecules parallel to the b axis.

Introduction. As part of a continuing study of the structure of dithiocarbamates, we recently reported the structures of three zwitterionic alkylaminoalkyldithiocarbamates (see below). These substances were chosen to help delineate the effects of the substituents R on the

structure of dithiocarbamate ligands, $-S_2CNR_2$ [$R = R'_2NH(CH_2)_n$], without the attendant effects of a complexing metal ion. The availability of one additional compound in this series, *N*-(2-dimethylaminoethyl)dithiocarbamic acid (DMAE hereafter) prompted us to extend this study to provide additional insights into the factors affecting the molecular and crystal structure of these substances.

Experimental. Colourless transparent crystals prepared by one of us (PK), $0.45 \times 0.34 \times 0.31$ mm, D_m by flotation in CCl_4/CH_3COCH_3 ; computer-controlled Philips PW1100 four-circle single-crystal diffractometer, graphite-monochromated Mo $K\alpha$, ω -scan mode; cell parameters and their e.s.d.'s by least-squares analysis of measured θ angles of the 42 strongest reflections; space group from systematic absences; three standard reflections per 90 min (120, 202, $\bar{1}31$) without significant intensity variation; no absorption correction, 2960 measured reflections, $\theta = 3$ –25°, max. hkl 13, 14, ± 7 , 1458 unique reflections, $R_{int} = 0.038$,

Table 1. Atomic coordinates and equivalent isotropic temperature factors ($\times 10^2$) for the non-hydrogen atoms in DMAE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
S(1)	0.3500 (1)	0.0768 (1)	0.7627 (2)	4.9
S(2)	0.1374 (1)	0.1147 (1)	0.4472 (2)	4.8
N(1)	0.1378 (4)	-0.0252 (3)	0.7530 (6)	3.9
N(2)	0.1267 (4)	-0.2495 (3)	1.1501 (6)	3.8
C(1)	0.2061 (4)	0.0500 (4)	0.6650 (7)	3.5
C(2)	0.1847 (5)	-0.0928 (4)	0.9294 (7)	4.5
C(3)	0.0799 (4)	-0.1624 (4)	0.9953 (7)	4.1
C(4)	0.0249 (5)	-0.3253 (5)	1.1978 (9)	5.6
C(5)	0.1916 (6)	-0.1986 (5)	1.3395 (8)	5.8

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i \cdot a_j U_{ij}$$

Table 2. Interatomic distances (Å) and selected bond angles (°) in DMAE

S(1)—C(1)	1.682 (4)	N(2)—C(3)	1.504 (6)
S(2)—C(1)	1.730 (4)	N(2)—C(4)	1.500 (7)
N(1)—C(1)	1.340 (6)	N(2)—C(5)	1.498 (6)
N(1)—C(2)	1.461 (6)	C(2)—C(3)	1.524 (7)
C(1)—N(1)—C(2)	122.7 (4)	S(1)—C(1)—N(1)	121.0 (3)
C(3)—N(2)—C(4)	110.0 (4)	S(2)—C(1)—N(1)	115.9 (3)
C(3)—N(2)—C(5)	112.8 (4)	N(1)—C(2)—C(3)	107.9 (4)
C(4)—N(2)—C(5)	111.7 (4)	N(2)—C(3)—C(2)	119.4 (4)
S(1)—C(1)—S(2)	123.1 (3)		
Hydrogen bonds			
S(2)⋯H(N1 ⁱⁱ)	2.314	S(2)⋯H(N1 ⁱ)—N(1 ⁱ)	161.2
S(2)⋯H(N2 ⁱⁱ)	2.168	S(2)⋯H(N2 ⁱⁱ)—N(2 ⁱⁱ)	155.6
S(1)⋯H(N2 ⁱⁱ)	2.663	S(1)⋯H(N2 ⁱⁱ)—N(2 ⁱⁱ)	128.3

Symmetry codes: (i) $\bar{x}, \bar{y}, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

1207 unique observed reflections with $I \geq 2\sigma(I)$. Structure solved with *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), all non-H atoms located on *E* map; full-matrix least-squares refinement using *F* with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), positional and anisotropic thermal parameters refined, atomic scattering factors from *International Tables for X-ray Crystallography* (1974); H atoms at calculated positions very close to those from a difference Fourier synthesis, with isotropic temperature factors assumed equal to those of bonded C or N atoms. $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\{1 + [(F-B)/A]^2\}$ with $A = 58$, $B = 32$; $R = 0.046$, $wR = 0.061$, $S = 1.024$, $(\Delta/\sigma)_{\max} = 0.00053$, $(\Delta\rho)_{\max} = 0.28$ and $(\Delta\rho)_{\min} = -0.33 \text{ e \AA}^{-3}$.

Discussion. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths involving H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51358 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and angles are given in Table 2. A clinographic projection of the DMAE molecule is shown in Fig. 1 while the molecular packing in the unit cell is illustrated in Fig. 2. The molecule exists as a zwitterion $(\text{CH}_3)_2\text{N}^+\text{H}(\text{CH}_2)_2\text{NHCS}_2^-$. The NCS_2 dithiocarbamate group is planar to within 0.004 (2) Å. The bond length $\text{C}(1)-\text{N}(1) = 1.340$ (6) Å is significantly shorter than the normal value of 1.426 Å for a C—N single bond (*International Tables for X-ray Crystallography*, 1968) implying strong double-bond character. Similarly the bond distances $\text{S}(1)-\text{C}(1) = 1.682$ (4), $\text{S}(2)-\text{C}(1) = 1.730$ (4) Å, with a difference $\Delta(\text{C}-\text{S}) = 0.048$ (6) Å (or 8.5σ), indicate that the two C—S bonds have partial double-bond character and also that they are not equivalent. This may explain why the IR spectrum of the compound exhibits two discrete bands at 955(s) and 1020(s) cm^{-1} . This feature of the molecular structure of DMAE is also observed in the structures of guanidinodithiocarbamic acid, in which $\Delta(\text{C}-\text{S}) = 0.028$ (7) Å (Gattow, Kiel & Eul, 1983). *N*-(3-Dimethylaminopropyl)dithiocarbamic acid, in which $\Delta(\text{C}-\text{S}) = 0.028$ (4) Å (Schramm, Kokkou &

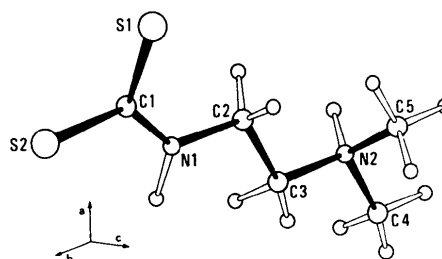


Fig. 1. Clinographic projection of an *N*-(2-dimethylaminoethyl)-dithiocarbamic acid molecule.

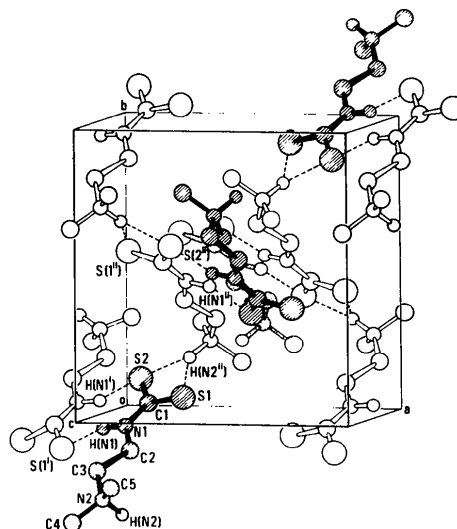


Fig. 2. Clinographic projection of the unit-cell contents.

Karagiannidis, 1984) and *N*-(2-diethylaminoethyl)-dithiocarbamic acid, in which $\Delta(\text{C}-\text{S}) = 0.032$ (7) Å (Kokkou, Cheer, Rentzeperis & Karagiannidis, 1988).

$\Delta(\text{C}-\text{S})$ values for dithiocarbamic acids are comparable with values for dithiocarbamate salts of strongly positive ions or groups which interact weakly with the S atoms of the S_2CN^- moiety. The most characteristic of these are: $(\text{N}_2\text{H}_5)(\text{H}_2\text{NNHCS}_2)$ with $\Delta(\text{C}-\text{S}) = 0.028$ (8) Å (Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969), $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2)_4] \cdot 2\text{H}_2\text{O}$ with $\Delta(\text{C}-\text{S}) = 0.023$ (3) Å (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980), $\text{Na}(\text{S}_2\text{CNMe}_2) \cdot 2\text{H}_2\text{O}$ with $\Delta(\text{C}-\text{S}) = 0.027$ (3) Å (Oskarsson & Ymén, 1983), $\text{K}(\text{S}_2\text{CNHCOH})$ with $\Delta(\text{C}-\text{S}) = 0.057$ (11), 0.028 (13), 0.063 (13), 0.044 (11) Å for the four molecules in the asymmetric unit (Gerner, Kiel & Gattow, 1985), although in this case the mesomeric effect also probably influences the molecular conformation, and $[\text{N}(n\text{-C}_4\text{H}_9)_4][\text{S}_2\text{CN}(\text{CH}_2)\text{CSH}]$ with $\Delta(\text{C}-\text{S}) = 0.032$ (3) Å (Gerner & Kiel, 1986).

The ammonium nitrogen N(2) is bonded to three C atoms and one H atom in an approximately tetrahedral coordination. The distance of N(2) from the plane of the C atoms is 0.447 (5) Å. H(N2) interacts with both S atoms of a neighbouring molecule (Table 2, Fig. 2). This results in bifurcated $\text{N}-\text{H}\cdots\text{S}_2$ hydrogen bonds interconnecting molecules to form infinite zigzag chains parallel to the *b* axis. In addition, the carbamate H(N1¹) is strongly hydrogen bonded to S(2) (Fig. 2). This normal $\text{N}-\text{H}\cdots\text{S}$ hydrogen bond and its inversion equivalent form centrosymmetric eight-membered rings interconnecting the chains of molecules described above. The IR spectrum of DMAE in KBr disk exhibits

two discrete bands $\bar{\nu}(\text{NH})$ and $\bar{\nu}(\text{N}^+\text{H})$ at 3160(s) and 2600(m) cm^{-1} correspondingly.

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Structure of 2-Hydroxy-5-methyl-5-nitro-2-oxo-1,3,2λ⁵-dioxaphosphorinane Monohydrate

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Abstract. $\text{C}_4\text{H}_8\text{NO}_6\text{P} \cdot \text{H}_2\text{O}$, $M_r = 215$, orthorhombic, $P2_12_1$ (No. 19), $a = 6.142$ (2), $b = 8.851$ (1), $c = 16.493$ (2) Å, $U = 896.7$ Å³, $Z = 4$, $D_m = 1.58$ (1) (carbon tetrachloride/hexane flotation), $D_x = 1.59$ Mg m^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.306$ mm^{-1} , $F(000) = 448$, $T = 298$ K, final $R = 0.037$ over 634 unique diffractometer data [$I_o > 3\sigma(I_o)$]. The 5-nitro and 2-hydroxyl groups are both

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axial with respect to the dioxaphosphorinane chair ring, which is more evenly puckered than in some 1,3,2-dioxaphosphorinanes: chair planes O(1)–P–O(3) and C(3)–C(2)–C(1) are inclined at angles 136 (1) and 134 (1)° to the central O(1)–C(1)–C(3)–O(3) ring plane. The water oxygen is an acceptor for a hydrogen bond to the 2-hydroxyl [O(4)⋯O(5) = 2.40 (1) Å with angle O(4)–H(401)⋯O(5) = 156 (2)°], while the

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