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## Structures of *N*-(3-Diethylaminopropyl)dithiocarbamic Acid and *N*-(2-Diethylaminoethyl)dithiocarbamic Acid

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**Abstract.** C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>, *M<sub>r</sub>* = 206.4, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.187 (2), *b* = 11.558 (1), *c* = 7.3701 (9) Å, β = 99.62 (1)°, *V* = 1107.55 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.226, *D<sub>x</sub>* = 1.237 Mg m<sup>-3</sup>, m.p. = 417 K, λ(Mo Kα) = 0.71069 Å, μ = 0.418 mm<sup>-1</sup>, *F*(000) = 448, *T* = 295 K, *R* = 0.051 for 1525 unique observed reflections. C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>, *M<sub>r</sub>* = 192.4, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 11.916 (2), *b* = 13.351 (2), *c* = 6.487 (1) Å, β = 96.80 (2)°, *V* = 1024.73 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.233, *D<sub>x</sub>* = 1.246 Mg m<sup>-3</sup>, m.p. = 422 K, λ(Mo Kα) = 0.71069 Å, μ = 0.447 mm<sup>-1</sup>, *F*(000) = 416, *T* = 295 K, *R* = 0.056 for 1274 unique observed reflections. Both molecules exist as zwitterions, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N<sup>+</sup>H(CH<sub>2</sub>)<sub>3</sub>NHCS<sub>2</sub><sup>-</sup> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N<sup>+</sup>H(CH<sub>2</sub>)<sub>2</sub>NHCS<sub>2</sub><sup>-</sup>,

the bonding at the ammonium nitrogen being approximately tetrahedral. In the planar dithiocarbamate groups the C–S bond lengths in the first compound, 1.706 (5) and 1.712 (5) Å, are nearly equal while those in the second one, 1.685 (5) and 1.717 (5) Å with a difference of 4.5σ, are not equivalent. In both structures intermolecular N–H...S hydrogen bonds result in interconnected infinite zigzag chains of molecules extending along the *b* axis.

**Introduction.** The structure of *N*-(3-dimethylaminopropyl)dithiocarbamic acid (DMAP hereafter) was recently studied (Schramm, Kokkou & Karagiannidis, 1984) in an attempt to delineate the substituent effects on the structure of dithiocarbamates without the attendant effects of a complexing metal ion. The availability of a series of substances prompted us to extend our study to two more compounds, *N*-(3-

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Table 1. *Experimental data and structure refinement parameters*

	DEAP	DEAE
Crystal size (mm)	0.52 × 0.32 × 0.28	0.48 × 0.32 × 0.20
Range of <i>hkl</i>	±18, 16, 10	±16, 17, 8
$[(\sin\theta)/\lambda]_{\max}$ (Å <sup>-1</sup> )	0.7035	0.7035
Standard reflections	131; 122; 501	210; 060; 121
Number of reflections measured	6179	5508
Number of unique reflections	3355	2815
$R_{\text{int}}$	0.046	0.051
Number of unique observed reflections $I \geq 2\sigma(I)$	1525	1274
Number of parameters refined	181	164
Quantity minimized	$w( F_o  -  F_c )^2$	$w = 1/\sigma^2(F_o) + gF_o^2$
	$\sigma(F_o)$ from counting statistics	$g = 0.00055$
	$g = 0.00027$	
$R$	0.051	0.056
$wR$	0.042	0.050
$S$	1.184	1.111
$(\Delta/\sigma)_{\max}; (\Delta/\sigma)_{\text{mean}}$	0.071; 0.014	0.075; 0.014
$(\Delta\rho)_{\max}; (\Delta\rho)_{\text{min}}$ (e Å <sup>-3</sup> )	0.28; -0.31	0.39; -0.37

diethylaminopropyl)dithiocarbamic acid (DEAP hereafter) and *N*-(2-diethylaminoethyl)dithiocarbamic acid (DEAE hereafter) in order to provide additional insights into the structure of potential dithiocarbamate ligands.

**Experimental.** Colourless transparent crystals prepared by one of us (PK),  $D_m$  by flotation in KBr solution, computer-controlled Philips PW1100 four-circle single-crystal diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\omega$  scan, three reference reflections without significant intensity variation, space groups from systematic absences, cell parameters and their standard deviations by least-squares analysis of the 106 strongest reflections, no absorption correction. Experimental data and structure-solution parameters are summarized in Table 1. Both structures were solved with *SHELX76* (Sheldrick, 1976), full-matrix least-squares refinement using  $F$  at first with *SHELX76* and then with *SHELXTL* (Sheldrick, 1981); for DEAP, H atoms located on difference Fourier map, refined with isotropic temperature coefficients, starting from  $U = 0.05$  Å; for DEAE, H atoms included in the refinement starting from calculated positions with C—H = 0.96 Å and isotropic temperature factors 1.2 times the equivalent isotropic  $U$  of the C or N atoms to which they are bonded; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final positional parameters are given in Table 2.\* Interatomic distances and angles are given in Table 3. *ORTEPII* (Johnson, 1976) views of the DEAP and DEAE molecules are shown in Fig. 1. Both molecules exist as zwitterions,  $(C_2H_5)_2N^+H(CH_2)_3-$

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and associated parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51151 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for DEAP and DEAE*

Here and throughout this paper the e.s.d.'s are given in parentheses and refer to the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^*$
<b>DEAP</b>				
S(1)	0.18373 (6)	0.02771 (7)	0.8438 (1)	0.0426 (3)
S(2)	0.37277 (6)	0.09987 (7)	1.1070 (1)	0.0416 (3)
N(1)	0.3663 (2)	-0.0696 (2)	0.8692 (3)	0.0393 (9)
N(2)	0.3845 (2)	-0.2889 (2)	0.3724 (3)	0.0277 (8)
C(1)	0.3109 (2)	0.0137 (2)	0.9344 (4)	0.031 (1)
C(2)	0.3331 (3)	-0.1467 (3)	0.7150 (5)	0.039 (1)
C(3)	0.3610 (2)	-0.0991 (3)	0.5380 (4)	0.037 (1)
C(4)	0.3312 (2)	-0.1727 (3)	0.3690 (5)	0.037 (1)
C(5)	0.4978 (2)	-0.2853 (3)	0.4476 (4)	0.036 (1)
C(6)	0.5584 (3)	-0.2162 (3)	0.3313 (6)	0.061 (2)
C(7)	0.3597 (3)	-0.3441 (3)	0.1857 (4)	0.039 (1)
C(8)	0.3990 (3)	-0.4654 (4)	0.1796 (6)	0.049 (1)
<b>DEAE</b>				
S(1)	0.2682 (1)	-0.0723 (1)	0.6747 (2)	0.0525 (4)
S(2)	0.1375 (1)	-0.1025 (1)	1.0384 (2)	0.0437 (4)
N(1)	0.0948 (2)	0.0357 (2)	0.7588 (5)	0.031 (1)
N(2)	0.1534 (2)	0.2497 (2)	0.4045 (5)	0.030 (1)
C(1)	0.1634 (3)	-0.0415 (3)	0.8159 (6)	0.029 (1)
C(2)	0.0899 (3)	0.0906 (3)	0.5639 (6)	0.034 (1)
C(3)	0.1672 (3)	0.1811 (3)	0.5900 (6)	0.032 (1)
C(4)	0.1764 (4)	0.2000 (3)	0.2040 (6)	0.042 (1)
C(5)	0.2891 (4)	0.1485 (4)	0.2195 (8)	0.059 (2)
C(6)	0.0417 (3)	0.3029 (3)	0.3833 (7)	0.043 (1)
C(7)	0.0376 (5)	0.3914 (5)	0.2419 (12)	0.076 (3)

\*  $U_{\text{eq}}$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 3. *Interatomic distances (Å) and angles (°) in DEAP and DEAE*

DEAP		DEAE	
S(1)—C(1)	1.706 (5)	S(1)—C(1)	1.685 (5)
S(2)—C(1)	1.712 (4)	S(2)—C(1)	1.717 (5)
N(1)—C(1)	1.345 (5)	N(1)—C(1)	1.339 (5)
N(1)—C(2)	1.453 (5)	N(1)—C(2)	1.457 (6)
N(2)—C(4)	1.515 (5)	N(2)—C(3)	1.505 (6)
N(2)—C(5)	1.505 (5)	N(2)—C(4)	1.513 (6)
N(2)—C(7)	1.502 (5)	N(2)—C(6)	1.501 (6)
C(2)—C(3)	1.516 (6)	C(2)—C(3)	1.516 (6)
C(3)—C(4)	1.506 (5)	C(4)—C(5)	1.502 (7)
C(5)—C(6)	1.497 (6)	C(6)—C(7)	1.493 (9)
C(7)—C(8)	1.498 (6)		
<b>Hydrogen bonds</b>			
N(1)—H(N1)···S(2 <sup>ii</sup> )	2.64 (3)	N(1)—H(N1)···S(2 <sup>iii</sup> )	2.46 (3)
N(2)—H(N2)···S(1 <sup>ii</sup> )	2.29 (3)	N(2)—H(N2)···S(2 <sup>iv</sup> )	2.22 (3)
<b>Hydrogen-bond angles</b>			
C(1)—N(1)—C(2)	127.4 (3)	C(1)—N(1)—C(2)	126.0 (3)
C(4)—N(2)—C(5)	114.2 (3)	C(3)—N(2)—C(4)	114.0 (3)
C(4)—N(2)—C(7)	109.4 (2)	C(3)—N(2)—C(6)	111.9 (3)
C(5)—N(2)—C(7)	113.6 (3)	C(4)—N(2)—C(6)	112.2 (3)
S(1)—C(1)—S(2)	123.5 (2)	S(1)—C(1)—S(2)	124.0 (2)
S(1)—C(1)—N(1)	119.0 (2)	S(1)—C(1)—N(1)	120.3 (3)
S(2)—C(1)—N(1)	117.5 (2)	S(2)—C(1)—N(1)	115.6 (3)
N(1)—C(2)—C(3)	111.5 (3)	N(1)—C(2)—C(3)	110.1 (3)
C(2)—C(3)—C(4)	116.1 (3)	N(2)—C(3)—C(2)	112.8 (3)
C(3)—C(4)—N(2)	115.6 (3)	N(2)—C(4)—C(5)	113.2 (3)
N(2)—C(5)—C(6)	113.4 (3)	N(2)—C(6)—C(7)	113.3 (4)
N(2)—C(7)—C(8)	113.7 (3)		

Hydrogen-bond angles  
 N(1)—H(N1)···S(2) 155.9 (2.2) N(1)—H(N1)···S(2<sup>iii</sup>) 164.6 (2.5)  
 N(2)—H(N2)···S(1<sup>ii</sup>) 164.5 (2.3) N(2)—H(N2)···S(2<sup>iv</sup>) 164.6 (2.9)

Symmetry code: (i) 1—*x*, -*y*, 2—*z*; (ii)  $\frac{1}{2}$ -*x*,  $-\frac{1}{2}+y$ ,  $\frac{3}{2}$ -*z*; (iii) -*x*, -*y*, 2—*z*; (iv)  $\frac{1}{2}$ -*x*,  $\frac{1}{2}+y$ ,  $\frac{3}{2}$ -*z*.

$NHCS_2^-$  and  $(C_2H_5)_2N^+H(CH_2)_2NHCS_2^-$ . The dithiocarbamate groups  $-NCS_2$  are planar to within 0.003 (4) Å in DEAP and 0.005 (5) Å in DEAE. The C(1)–N(1) bond lengths, 1.345 (5) Å in DEAP and 1.339 (5) Å in DEAE, like the corresponding distance in DMAP, 1.338 (5) Å, indicate significant C–N double-bond character and compare well with the values 1.326 (3)–1.339 (4) Å found in some sodium dialkyldithiocarbamate hydrates (Colapietro, Domenicano & Vacigo, 1968; Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980; Ymén, 1982; Oskarsson & Ymén, 1983; Mereiter, Preisinger, Mikenda & Steidl, 1985) or the distance of 1.395 (2) Å in acetamidinium *N*-acetimidoyldithiocarbamate (Eul, Kiel & Gattow, 1986).

The C–S bonds in DEAP, C(1)–S(1) = 1.706 (5) and C(1)–S(2) = 1.712 (4) Å, appear practically equivalent. In DEAE, by contrast, a significant difference of  $4.5\sigma$  is observed between the bond lengths C(1)–S(1) = 1.685 (5) and C(1)–S(2) = 1.717 (5) Å. A comparable difference of  $6.6\sigma$  between the C–S bond distances was also found in the earlier study of DMAP in which C(1)–S(1) = 1.699 (3) and C(1)–S(2) = 1.727 (3) Å.

The coordination of the ammonium nitrogen N(2) is approximately tetrahedral and the C–N(2) bond lengths are slightly greater than the accepted C–N distance, 1.48 Å, for four-covalent nitrogen (*International Tables for X-ray Crystallography*, 1968). The distance of N(2) from the plane of the three C atoms to which it is bonded is  $-0.424$  (3) Å in DEAP and 0.416 (4) Å in DEAE.

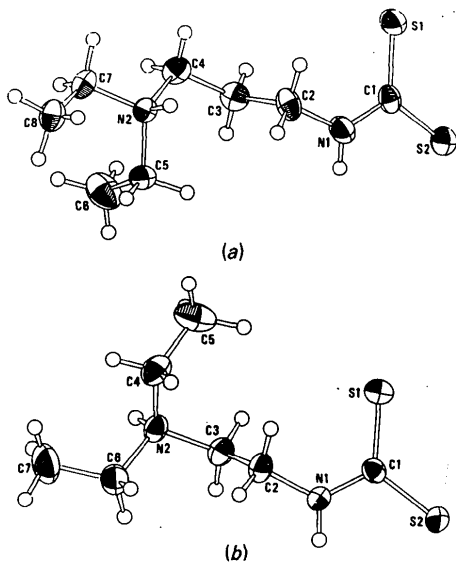


Fig. 1. ORTEP drawing of (a) the DEAP and (b) the DEAE molecules. Thermal ellipsoids are drawn at 50% probability level; isotropic H thermal parameters are represented by spheres of arbitrary size.

In both substances, S(2) is hydrogen-bonded to the carbamate NH of a translated enantiomeric molecule (Table 3 and Fig. 2). In DEAE, S(2) is further strongly hydrogen-bonded to H(N2), the proton attached to the quaternary ammonium N atom in an adjacent molecule. In sharp contrast to this, in DEAP, such a hydrogen atom H(N2) is strongly associated with S(1) and not S(2). IR spectra of the compounds in KBr disks exhibit two discrete bands  $\bar{\nu}(NH)$  and  $\bar{\nu}(N^+H)$  at 3180 (s), 2600 (m)  $cm^{-1}$  for DEAP and at 3170 (s), 2580 (m)  $cm^{-1}$  for DEAE correspondingly. The N–H...S hydrogen-bonding pattern in DMAP, in which

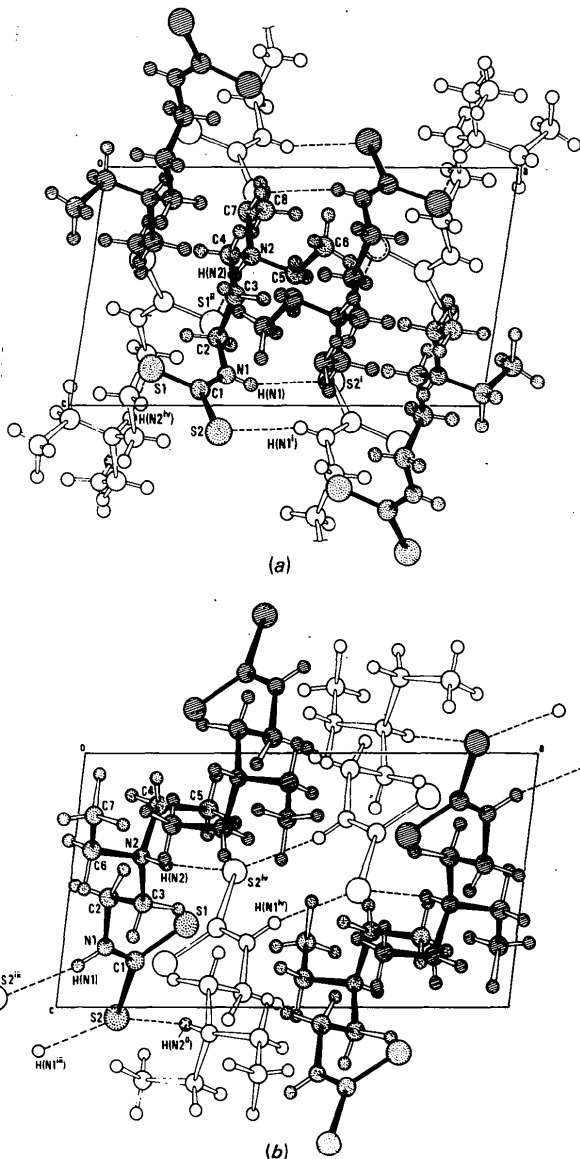


Fig. 2. Packing diagram viewed down the *b* axis for (a) DEAP and (b) DEAE. Hydrogen bonding is indicated by dashed lines. For clarity, only one of the two molecules with symmetry codes (ii) and (iv) is shown.

the C—S bonds are not equivalent (see above), is similar to that in DEAP, in which, however, the C—S bond lengths are nearly equal, and not to that in DEAE. As a result, the contribution of the N—H...S hydrogen bonds to the observed alteration in the relative C—S bond distances in going from DEAP to DEAE or DMAP is not easily discerned.

The molecular packing is shown in Fig. 2. The N—H...S hydrogen bonds result in interconnected infinite zigzag chains of molecules extending along the *b* axis.

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## Structure of Diethylmalonic Acid

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**Abstract.**  $C_7H_{12}O_4$ ,  $M_r = 160.17$ , monoclinic,  $P2_1$ ,  $a = 7.338$  (1),  $b = 10.626$  (1),  $c = 11.237$  (2) Å,  $\beta = 93.47$  (1)°,  $V = 874.6$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.22$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54180$  Å,  $\mu = 9.7$  cm<sup>-1</sup>,  $F(000) = 344$ ,  $T = 291$  K,  $R = 0.038$  for 1431 observed reflections. The asymmetric unit contains two independent molecules linked by two intermolecular hydrogen bonds. The two carboxylic groups are rotated by 79° and give extensive zigzag chains along the *c* axis.

**Introduction.** In a previous spectroscopic paper, Delarbre, Maury & Bardet (1985) have concluded that, in aqueous solution, the diethylmalonic acid molecule belongs to the point group  $C_2$  corresponding to a twisted conformation and that, in addition, the acid salt is intramolecularly hydrogen bonded while the acid is not. The dissociation constant ratio  $K_1/K_2$  (Ebersson, 1969) is very high in disubstituted malonic acids. Diethylmalonic acid was therefore presumed to exhibit an intramolecular hydrogen bond in the crystalline state