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The Structure of Diisopropylammonium Diisopropyldithiocarbamate

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Abstract. $\{[(CH_3)_2CH]_2NH_2\}^+\{[(CH_3)_2CH]_2NCS_2\}^-$, monoclinic, $P2_1/c$, $a = 9{\cdot}032\,(1)$, $b = 11{\cdot}525\,(1)$, $c = 16{\cdot}638\,(1)$ Å, $\beta = 98{\cdot}53\,(1)°$, $Z = 4$, $V = 1712{\cdot}6$ Å^3, $D_m = 1{\cdot}078$, $D_x = 1{\cdot}080$ g cm^{-3}, m.p. 96–97°C. The structure has been refined to $R(F^2) = 0{\cdot}065$ for 2683 reflexions and 274 parameters. Two cations and two anions are linked to form a centrosymmetric dimer. Each molecular ion participates in three intermolecular H···S hydrogen bonds between the ammonium protons and the dithiocarbamate S atoms, at 2·41 (3), 2·52 (3) and 2·85 (3) Å.

Introduction. This investigation closely follows the structural study of dimethylammonium dimethyldithiocarbamate (Wahlberg, 1978), (*M*).

The compound was synthesized in benzene from diisopropylamine and CS_2 and was recrystallized from CS_2. The plate-shaped transparent crystals were pale yellow. They sublimed markedly from *ca* 20°C below the melting point. The space-group assumption was made from systematically absent reflexions among *h*0*l* for odd *l* and 0*k*0 for odd *k*. The unit-cell parameters were based on 50 lines from a Guinier–Hägg powder photograph. The internal standard was CoP_3 ($a = 7{\cdot}70778$ Å) and the radiation used was Cr $K\alpha_1$.

A crystal was sealed in a thin-walled glass capillary. Approximate distances between pairs of surfaces were: (100) 0·04 mm, (001) 0·27 mm, (011) 0·22 mm and $(0\bar{1}1)$ 0·22 mm. A Stoe–Philips four-circle PDP 8/I computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation was used for data collection. A unique set of intensities was measured in one quadrant of reciprocal space, $4{\cdot}5 < 2\theta < 48°$. The count rate was reduced by a factor 2^n, $0 \leq n \leq 5$. The reflexions were scanned in the ω–2θ mode. The longest scan time was 160 s. The background was measured on each side of the reflexion for 25 s. Three standard reflexions showed stability of the crystal and the diffractometer system. Corrections were applied for background and for Lorentz, polarization and absorption effects [μ(Mo $K\alpha$) = 2·84 cm^{-1}]. The transmission factor varied from 0·94 to 0·99. 3458 intensities were reduced to 2683 structure factors with $F_m^2 > -2{\cdot}40\sigma(F^2)$ and $0{\cdot}060 < (\sin\theta)/\lambda < 0{\cdot}573$ Å^{-1}.

The structure was solved by direct methods (Long, 1965). The positions of the H atoms were obtained from a difference synthesis. In the last cycle of full-matrix least-squares refinement, 274 independent parameters were varied and all the structure factors were included. The thermal parameters were aniso-

Table 1. *Left-adjusted decimal parts of the fractional coordinates*

	x	*y*	*z*
S(1)	53176 (9)	30854 (7)	05467 (5)
S(2)	76652 (11)	32342 (8)	19703 (5)
N(1)	7894 (2)	1898 (2)	0682 (1)
N(2)	4451 (3)	0779 (2)	3693 (2)
C(1)	7068 (3)	2669 (2)	1034 (2)
C(2)	7314 (4)	1326 (3)	−0102 (2)
C(3)	7116 (6)	0028 (4)	0011 (3)
C(4)	8250 (6)	1616 (5)	−0756 (2)
C(5)	9441 (3)	1534 (3)	1030 (2)
C(6)	9516 (5)	0818 (4)	1803 (2)
C(7)	0566 (5)	2512 (5)	1086 (3)
C(8)	5666 (4)	0924 (3)	3170 (2)
C(9)	7008 (5)	0272 (5)	3559 (3)
C(10)	5110 (7)	0531 (6)	2300 (3)
C(11)	2963 (4)	1335 (3)	3424 (2)
C(12)	1981 (6)	1072 (7)	4060 (4)
C(13)	3157 (10)	2621 (4)	3262 (5)
H(1)	482 (3)	110 (3)	420 (2)
H(2)	426 (3)	002 (3)	375 (2)
H(3)	631 (3)	163 (2)	−024 (1)
H(4)	965 (3)	102 (2)	062 (2)
H(5)	587 (3)	174 (2)	315 (2)
H(6)	254 (3)	095 (2)	294 (2)
H(7)	814 (4)	−037 (3)	019 (2)
H(8)	652 (4)	−010 (3)	046 (2)
H(9)	666 (4)	−028 (3)	−049 (2)
H(10)	777 (4)	127 (3)	−123 (2)
H(11)	924 (4)	122 (3)	−062 (2)
H(12)	850 (4)	245 (3)	−077 (2)
H(13)	879 (4)	019 (3)	174 (2)
H(14)	050 (4)	043 (3)	194 (2)
H(15)	934 (3)	127 (3)	224 (2)
H(16)	153 (5)	221 (3)	116 (2)
H(17)	053 (4)	301 (3)	150 (2)
H(18)	037 (4)	306 (3)	060 (2)
H(19)	682 (5)	−056 (4)	355 (3)
H(20)	787 (4)	040 (3)	327 (2)
H(21)	735 (3)	051 (3)	413 (2)
H(22)	425 (4)	101 (3)	212 (2)
H(23)	596 (4)	052 (3)	202 (2)
H(24)	473 (4)	−025 (3)	230 (2)
H(25)	223 (5)	145 (4)	449 (2)
H(26)	181 (5)	028 (4)	418 (3)
H(27)	102 (5)	131 (4)	384 (3)
H(28)	370 (7)	282 (5)	286 (4)
H(29)	207 (4)	282 (4)	316 (2)
H(30)	359 (5)	297 (4)	374 (3)

tropic for the non-hydrogen atoms and isotropic for H. The fractional coordinates are given in Table 1.* The average $|\Delta|/\sigma$ was 0·06; the largest value was 0·5 for H(3). The expression minimized was $\sum w\delta^2$, where $\delta = F_m^2 - F_c^2$ and $w^{-1} = \sigma_{\text{count}}^2(F^2) + (0{\cdot}03\ F_m^2)^2 = \sigma^2(F^2)$. The refinement converged at $R(F^2) = \sum|\delta|/\sum F_m^2 = 0{\cdot}065$ and $R_w(F^2) = (\sum w\delta^2/\sum wF_m^4)^{1/2} = 0{\cdot}092$. $|\delta|/\sigma(F^2)$ was greater than 2·0 for 202 reflexions. The largest value was 4·7 for 051. A normal ΔR probability plot (Abrahams & Keve, 1971) had a slope of 0·91 and an intercept of −0·05. Some spurious peaks of density < 0·12 e Å^{-3} were observed in a difference synthesis. Values for the scattering factors, and the f' and f'' anomalous-dispersion corrections for S, N and C were taken from *International Tables for X-ray Crystallography* (1974). Lundgren (1976) has described the computer programs. The calculations were performed on the IBM 370/155 and IBM 1800 computers in Uppsala.

Discussion. The dimer: Two cations and two anions are linked to form a centrosymmetric dimer, Fig. 1. The dimers are packed at approximately the van der Waals distances (Bondi, 1964).

The dimer is connected by six intermolecular H···S hydrogen bonds. The corresponding N···S distances are given in brackets below. The ammonium proton H(2) bonds to both S atoms in one of the anions at H(2)···S(1) 2·52 (3) [3·348 (3)] and H(2)···S(2) 2·85 (3) [3·585 (3) Å]. The ammonium proton H(1) bonds to the centrosymmetrically-related anion at H(1)···S(1^{i}) 2·41 (3) [3·335 (3) Å]. The coordination number per molecular ion is 3.

Intermolecular ammonium H···H distances <4·0 Å are intradimeric H(1)···H(2^{i}) 3·63 (4) and H(1)···H(1^{i}) 3·66 (6) Å. The shortest intermolecular S···S distance is intradimeric S(1)···S(1^{i}) 4·775 (2) Å.

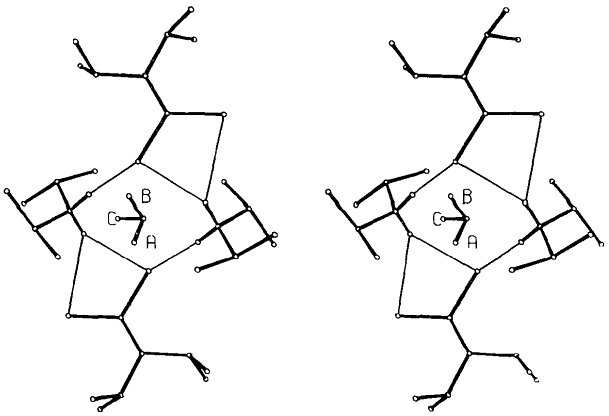

Fig. 1. The dimer. Only the ammonium protons have been drawn. The centre of symmetry in the dimer is at ½,½,0. This point coincides with the origin of the parallel translated and drawn crystal coordinate system.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33795 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

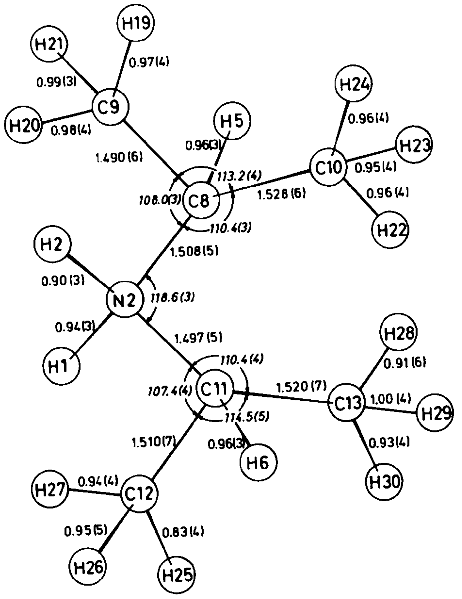

Fig. 2. Distances (Å) and angles (°) in the diisopropylammonium cation.

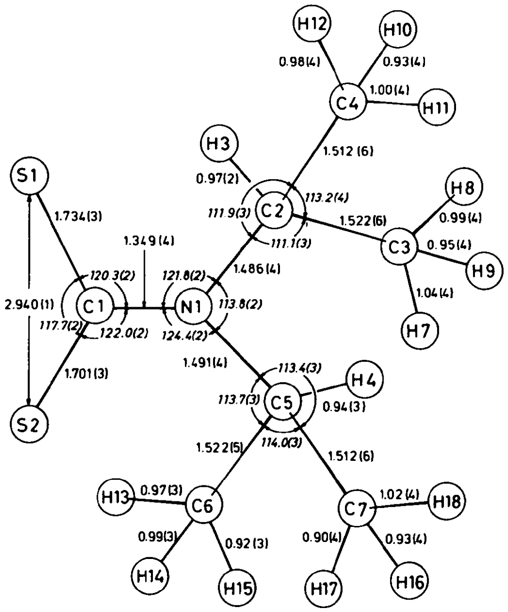

Fig. 3. Distances (Å) and angles (°) in the diisopropyldithiocarbamate anion.

The diisopropylammonium cation (Fig. 2): The cation possesses a pseudo twofold symmetry axis along the bisector to N(2)–C(8) and N(2)–C(11). Relative distances from some atoms to the plane through N(2), C(8) and C(11) are: C(9) 0·031 (5), C(12) –0·025 (8), C(10) 1·166 (6), C(13) –1·147 (6), H(5) –0·81 (3), and H(6) 0·84 (3) Å. The bonds between the alkyl C atoms and the N atoms are *ca* 0·03 Å longer in this cation than in the cation in (*M*).

The diisopropyldithiocarbamate anion (Fig. 3): The non-hydrogen atom arrangement is similar to that in thallium(I) diisopropyldithiocarbamate (Jennische, Olin & Hesse, 1972).

The mean value of the C–S distances is 1·718 Å. However, C(1)–S(2) is 11σ shorter than C(1)–S(1). This discrepancy is reasonably correlated to the intermolecular H···S hydrogen-bonding in which S(2) and S(1) participate with one and two bonds, respectively. The molecular and intermolecular bonding patterns are more symmetric in (*M*), and are *mm* symmetric in caesium dimethyldithiocarbamate (Wahlberg, 1976). Thus, the present bulky alkyl groups prevent a more effective intermolecular H···S hydrogen-bonding, and the asymmetric bonding obtained induces the asymmetry among the C–S bonds.

The dithiocarbamate plane is notably distorted; some distances from the least-squares plane through S(1), S(2), C(1), N(1), C(2) and C(5) are: S(1) 0·004 (1), S(2) –0·006 (1), C(1) 0·015 (3), N(1) 0·003 (2), C(2) –0·103 (4), C(5) 0·084 (3), C(3) –1·416 (5), C(7) 1·390 (6), C(4) 1·110 (5), C(6) –1·150 (5), H(3) –0·16 (2), and H(4) 0·07 (3) Å.

The bonds between the alkyl C atoms and the N atoms are *ca* three e.s.d.'s shorter in the anion than in the cation (Figs. 2 and 3), and are *ca* 0·03 Å longer in this anion than in the one in (*M*).

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