

The Structure of Pyrrolidinium 1-Pyrrolidinecarbodithioate

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Abstract. $[C_4H_{10}N]^+[C_5H_8NS_2]^-$, monoclinic, $P2_1$, $a = 8.565$ (2), $b = 6.882$ (1), $c = 10.886$ (2) Å, $\beta = 113.17$ (2)°, $Z = 2$, $V = 589.9$ Å³, $D_m = 1.228$, $D_x = 1.229$ Mg m⁻³. The structure has been refined to $R(F^2) = 0.051$ for 1845 reflexions and 189 parameters. The structure is built up of helical chains along b . Each ion participates in three intermolecular hydrogen bonds involving the ammonium H and the dithiocarbamate S atoms with $H \cdots S = 2.51$ (4), 2.51 (4) and 2.84 (4) Å.

Introduction. This investigation is related to three recent studies: dimethylammonium dimethyldithiocarbamate (M) (Wahlberg, 1978*a*), diisopropylammonium diisopropylthiocarbamate (iP) (Wahlberg, 1978*b*), and diethylammonium diethyldithiocarbamate (E) (Wahlberg, 1978*c*).

The compound was synthesized in benzene from pyrrolidine and CS₂ and was recrystallized from CS₂. The colourless crystals were generally elongated along [010]. On heating they sublimed and decomposed. Systematically absent reflexions among $0k0$ for odd k indicated the space groups $P2_1$ or $P2_1/m$. The statistical distribution of normalized structure factors supported non-centrosymmetry. $P2_1/m$ is inconsistent with the final structure. The cell parameters were based on 15 lines from a Guinier–Hägg powder photograph. The internal standard was CoP₃ ($a = 7.70778$ Å) and the radiation was Cr $K\alpha_1$.

A crystal was sealed in a thin-walled glass capillary. Approximate dimensions were: 0.09 mm along [101], 0.16 mm along [001] and 0.32 mm along [010]. A Stoe–Philips four-circle PDP 8/I computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation was used for the intensity collection. The count rate was reduced by a factor 2^n , $0 \leq n \leq 5$. The reflexions in one quadrant of reciprocal space were measured, $4.5 < 2\theta < 60^\circ$. The longest scan time, in the ω – 2θ mode, was 192 s. The background was measured on each side of the reflexion for 30 s. The intensities of three standard reflexions $\bar{3}05$, $0\bar{4}0$ and 500 decreased by *ca* 3%. They were measured at intervals of 40 reflexions. The decrease could be satisfactorily described by a least-squares line. This line was used to scale the data to the mean level. The data were corrected for background and for Lorentz, polarization and absorption effects [$\mu(\text{Mo } K\alpha) = 0.390$ mm⁻¹]. The

transmission factor varied from 0.91 to 0.97. 2673 intensities were reduced to 1845 structure factors with $F_m^2 \geq -2.02\sigma(F^2)$ and $0.060 < (\sin \theta)/\lambda < 0.704$ Å⁻¹.

The positions of the S atoms were obtained from the Patterson function, and those of the remaining atoms from subsequent difference syntheses. All the structure factors were included and 189 independent parameters were varied in the last cycle of full-matrix least-squares refinement. The thermal parameters were anisotropic for the non-hydrogen atoms and isotropic for H. The coordinates are presented in Table 1.* The largest parametric $| \Delta I / \sigma |$ were 0.5 for H(8), 0.4 for H(5) and H(6), 0.3 for C(7); the average value was 0.08. The expression minimized was $\sum w\delta^2$, where $\delta = F_m^2 - F_c^2$ and $w^{-1} = \sigma^2(F^2) = \sigma_{\text{count}}^2(F^2) + (0.03 F_m^2)^2$. The refinement converged at $R(F^2) = \sum |\delta_i| / \sum F_m^2 = 0.051$ and $R_w(F^2) = (\sum w\delta^2 / \sum wF_m^4)^{1/2} = 0.078$. The strongest reflexion 202 appeared to be slightly affected by extinction, but no measures were adopted. The quantity $|\delta_i| / \sigma(F^2)$ was >2.0 for 227 reflexions; the largest value was 7.6 for the reflexion 122. A normal ΔR probability plot (Abrahams & Keve, 1971) had a slope of 0.80 and

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33996 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

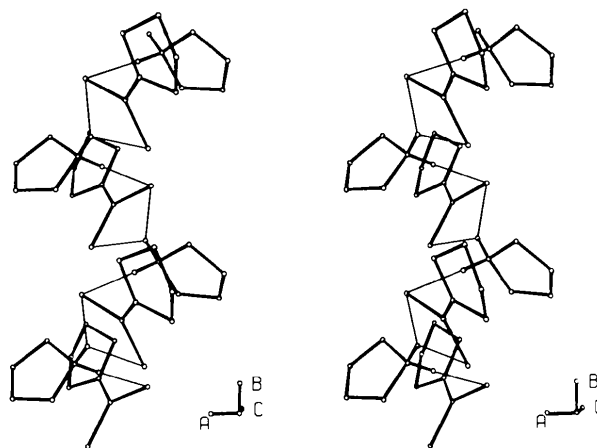


Fig. 1. Part of the helical chain. Only the ammonium H atoms have been drawn, the other H atoms are omitted for clarity.

Table 1. Fractional coordinates (for S $\times 10^5$, for N and C $\times 10^4$ and for H $\times 10^3$)

	x	y	z		x	y	z
S(1)	40093 (7)	10000	16890 (5)	H(4)	655 (6)	34 (8)	-73 (5)
S(2)	66207 (10)	-21643 (14)	26960 (7)	H(5)	956 (9)	156 (12)	3 (7)
N(1)	6512 (2)	953 (4)	4064 (2)	H(6)	977 (7)	-18 (10)	73 (5)
N(2)	6683 (3)	2417 (4)	365 (3)	H(7)	45 (6)	273 (9)	218 (5)
C(1)	5786 (3)	-11 (4)	2925 (2)	H(8)	897 (13)	138 (19)	249 (9)
C(2)	5938 (4)	2834 (5)	4377 (3)	H(9)	854 (6)	435 (9)	106 (5)
C(3)	7424 (5)	3529 (6)	5604 (4)	H(10)	770 (5)	337 (7)	204 (4)
C(4)	8208 (6)	1687 (6)	6296 (3)	H(11)	573 (4)	375 (6)	374 (3)
C(5)	8043 (4)	278 (6)	5194 (3)	H(12)	490 (4)	258 (6)	456 (3)
C(6)	7430 (7)	807 (7)	-110 (4)	H(13)	844 (4)	420 (5)	521 (3)
C(7)	9197 (6)	708 (10)	748 (6)	H(14)	706 (6)	445 (8)	610 (5)
C(8)	9516 (5)	2000 (9)	1871 (5)	H(15)	925 (6)	183 (7)	684 (4)
C(9)	8069 (5)	3333 (5)	1495 (3)	H(16)	727 (7)	149 (8)	661 (4)
H(1)	618 (5)	314 (7)	-20 (4)	H(17)	908 (4)	56 (5)	492 (3)
H(2)	599 (4)	205 (6)	62 (3)	H(18)	787 (4)	-84 (5)	543 (3)
H(3)	741 (7)	103 (12)	-80 (6)				

an intercept of -0.10 . A difference synthesis showed some spurious peaks of density $<0.08 \text{ e } \text{Å}^{-3}$. Scattering factors for S, N, C and H, and the f' anomalous-dispersion corrections for S, N and C were taken from *International Tables for X-ray Crystallography* (1974). An attempt to determine the absolute configuration by introducing the f'' values was not successful. Lundgren (1976) has described the computer programs. The calculations were performed on the IBM 370/155 and IBM 1800 computers in Uppsala.

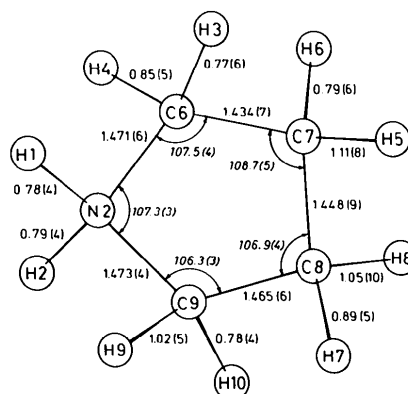
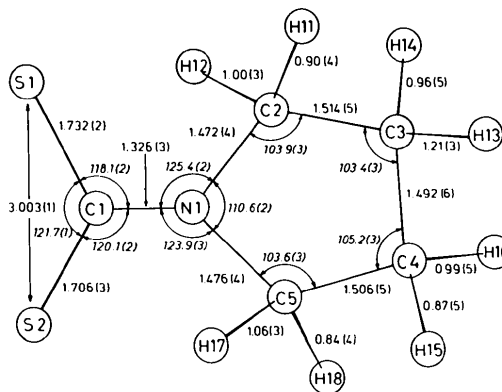
Discussion. *The chain:* the ions are linked by hydrogen bonds to form helical chains extending along b . Part of a chain is shown in Fig. 1. The chains are packed at approximately the van der Waals distances (Bondi, 1964).

A 2_1 screw axis is situated at the centre of the chain. One of the ammonium H atoms forms intermolecular bonds with both S atoms in one anion. The H...S distances (corresponding N...S distances are given in square brackets) are H(1)...S(1) 2.51 (4) [3.223 (3)] and H(1)...S(2) 2.84 (4) [3.432 (3)] Å. The other H atom bonds to just one of the S atoms in a 2_1 -related anion at H(2)...S(1ⁱ) 2.51 (4) [3.297 (3)]; H(2)...S(2ⁱ) is 3.58 (4) [4.060 (3)] Å. S(1) is involved in the two shortest H...S distances. The coordination number per ion is 3.

Intermolecular ammonium H...H distances <4.0 Å are intrachain H(1)...H(2ⁱ) = 3.20 (6) and H(2)...H(2ⁱ) = 3.84 (3) Å. The shortest intermolecular S...S distance is intrachain S(1)...S(2ⁱ) = 4.759 (2) Å.

The pyrrolidinium cation (Fig. 2): the cation resembles that in pyrrolidinium *p*-chlorobenzoate (PYC) and in pyrrolidinium *p*-toluate (PYT) (Kashino, Kataoka & Haisa, 1978).

C(7) and C(8), having ring positions 3 and 4, are 0.058 (7) and 0.312 (5) Å, respectively, from the plane through N(2), C(6) and C(9). In (PYC) and (PYT) the

Fig. 2. Distances (Å) and angles ($^\circ$) in the pyrrolidinium cation.Fig. 3. Distances (Å) and angles ($^\circ$) in the 1-pyrrolidinecarbodithioate anion.

largest deviations from planarity occur at the ring positions 2 and 1, respectively. The C-N bonds are comparable to those in (M), but are *ca* 0.02 Å shorter than those in (PYT) and the mean value in (PYC).

The 1-pyrrolidinecarbodithioate anion (Fig. 3): the non-hydrogen atom arrangement is similar to that in tris(1-pyrrolidinecarbodithioato)iron(III) (Mitra, Raston & White, 1978), (FePy₃).

The mean C–S length is 1.719 Å. C(1)–S(2) is *ca* 10σ shorter than C(1)–S(1). The probable explanation of this discrepancy is, as in (E) and (iP), unsymmetrical intermolecular hydrogen bonding. C(1)–N(1) is *ca* 0.02 Å shorter than that in (M), (E) and (iP), and 0.014 Å longer than the mean value in (FePy₃). The bonds between the alkyl C atoms and the N atoms agree with those in the present cation and those in (FePy₃), and are intermediate between those in (E) and (iP).

Distances of some atoms from the least-squares plane through S(1), S(2), C(1), N(1), C(2) and C(5) are: S(1) 0.000 (1), S(2) 0.001 (1), C(1) –0.010 (3), N(1) –0.005 (2), C(2) 0.010 (3), C(5) 0.005 (4), C(3) 0.378 (4), and C(4) –0.196 (5) Å. The dithiocarbamate plane is a little bent, in agreement with observations in (M) and (E).

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Structure of 1,4-Difluoro-1,1,4,4-tetranitro-2,3-butanediol

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Abstract. C₄H₄F₂N₄O₁₀, monoclinic, *P*2₁/*c*, *a* = 5.5984 (5), *b* = 10.802 (1), *c* = 8.9371 (9) Å, β = 104.9 (4)°. *D_m* = 1.925 (measured by neutral buoyancy), *D_c* = 1.947 Mg m⁻³, *Z* = 2. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to an *R* value of 0.03, observed reflections only. The F atom and hydroxyl group are *gauche* to one another and no intramolecular hydrogen bond is formed. A weak intermolecular hydrogen bond does exist between the hydroxyl group and a nitro group.

Introduction. The material was synthesized at these laboratories and provided to us as clear, colorless crystals. Preliminary cell dimensions were obtained from oscillation, Weissenberg and precession films, and the systematic absences observed (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) indicated the space group to be *P*2₁/*c*. A crystal was mounted on a Picker FACS-I diffractometer (λ = 0.71069 Å) and cell-dimension and intensity data were collected. Cell-dimension data were gathered from 16 reflections measured at both positive and

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negative values of 2θ, and the intensity data were collected using an ω–2θ scan to 2θ_{max} = 55°. Of the 1879 intensity data collected, 1268 were crystallographically independent. The structure was solved by direct methods.* Full-matrix least-squares refinement using unit weights reduced the *R* value to 0.03 with anisotropic temperature factors for the non-hydrogen atoms. H atoms were given arbitrarily assigned isotropic values. Of the independent reflections, 888 had *I* ≥ 3σ(*I*). These were included in the refinement as were those of the remainder whose calculated structure factor was greater than the observed value, a total of 1010 reflections in the last cycle.† The *R* value for all reflections (1196 total) was 0.05. The scattering factors

* All calculations were performed using one or more versions of the XRAY calculational system (Stewart, 1972).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33973 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.