Table 3. *Comparison of some molecular parameters for compounds containing 3H-1,2-dithiole-3-thione or 3H-1,2-dithiol-3-one*

	S–S	C–S (thione)	C–C (central)	Angle between plane normals for six- and five-membered rings
4-Methyl-3H-1,2-dithiole-3-thione*	2·047 Å	1·627 Å	–	–
4-Methyl-5-(2-pyrazinyl)-3H-1,2-dithiole-3-thione†	2·049 (1)	1·655 (2)	1·480 (3) Å	3·71 (8)°
	2·041 (1)	1·670 (2)	1·480 (3)	8·92 (9)
5-(p-Methoxyphenyl)-3H-1,2-dithiole-3-thione‡	2·047 (1)	1·666 (3)	1·461 (3)	7·7 (1)
4-Methyl-5-(2-pyrazinyl)-3H-1,2-dithiol-3-one§	2·035 (1)	–	1·476 (4)	4·6 (1)
	2·038 (1)		1·477 (4)	9·6 (1)
3H-1,2-Dithiole-3-thione¶	2·050 (3)	1·688 (3)	–	–
This work: 4-PDT	2·050 (1)	1·668 (2)	1·482 (2)	67·40 (9)
This work: 5-PDT	2·047 (1)	1·659 (2)	1·474 (3)	29·36 (8)

*Jeffrey & Shiono (1959). †Wei (1983). ‡Wang, Lin & Wei (1985). §Wei (1985a). ¶Wei (1985b).

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Structure of Ammonium Methanesulfonate*

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Abstract. $CH_3O_3S^-.NH_4^+$, $M_r = 113\cdot138$, monoclinic, $C2/m$, $a = 7\cdot4993$ (6), $b = 7\cdot2882$ (6), $c = 9\cdot2342$ (8) Å, $\beta = 93\cdot341$ (7)°, $V = 503\cdot85$ (7) Å³, $Z = 4$, $D_m = 1\cdot50$ (2) by flotation, $D_x = 1\cdot491$ g cm^{-3}, $\lambda(Cu\,K\alpha_1) = 1\cdot54056$ Å, $\mu = 47\cdot07$ cm^{-1}, $F(000) = 240$, $T = 296$ (1) K. Final $R(F) = 0\cdot045$ for 476 counter data with $F_o^2 \geq \sigma(F_o^2)$. Seven particularly strong reflections significantly affected by isotropic extinction also omitted from refinements. The methanesulfonate anion as well as tetrahedral ammonium cation are located in the unit cell so as to possess crystallographic C_s symmetry in each case. All molecular parameters are similar to those obtained for other related compounds. Each of three O atoms for the anion is hydrogen-bonded to a neighboring H atom of the cation and forms an infinite H-bonding chain around the crystallographic twofold screw axis at $x = \frac{1}{4}$ (or $\frac{3}{4}$) and $z = 0$.

Introduction. Further attempts to crystallize the methanesulfonate salt of an antischistosomal drug, IA-4 N-oxide (Hulbert, Bueding & Hartman, 1974), containing a chlorobenzothiopyranoindazole fragment (Patterson, Capell & Walker, 1960), have led to an accidental preparation of yellowish thin-plate crystals which were subsequently characterized by X-ray analysis as the

ammonium salt of methanesulfonic acid. This is further confirmed by the complete coincidence of the diffraction patterns for the unknown with those taken from crystals of ammonium methanesulfonate that was prepared by diffusing ammonia vapor into a droplet of methanesulfonic acid. Although the crystal structures for metal salts of methanesulfonic acid have previously been reported (for example, see Wei & Hingerty, 1981), to date only two ammonium salts of analogous methanethiosulfonic acid (Cooper, Bloxham & Webster, 1982) and trifluorosulfonic acid (Gänswein & Brauer, 1975) have appeared in the literature. Results of the present study provide additional information concerning molecular parameters of the $CH_3O_3S^-$ anion and the hydrogen-bonding scheme involving the tetrahedral NH_4^+ cation and the $CH_3O_3S^-$ anion.

Experimental. After attempts to crystallize IA-4 N-oxide (30 mg) by use of several solvents including ethanol, 2-propanol, chloroform, pyridine and others all failed, the sample was recovered by dissolving in 1 ml of pyridine to result in a dark yellow solution as supernatant. To 100 µl of this solution, 40 µl ethanol containing 2% of methanesulfonic acid was added, and the droplet placed in a glass vessel containing 65%-saturated ammonium sulfate solution for a few days. Yellow-tinted, thin-plate crystals were obtained by exposing the droplet to air.

A crystal with approximate dimensions $0.65 \times 0.30 \times 0.13$ mm was mounted on a Picker four-circle diffractometer with a approximately parallel to the φ axis of the diffractometer; lattice parameters were refined by the least-squares method from angle measurements of 12 strong reflections in 2θ range 75–89° (Busing, Ellison, Levy, King & Roseberry, 1968); systematic absences hkl, $h + k = 2n + 1$, suggested space groups $C2/m$, $C2$ or Cm. Intensity data collected by θ–2θ step scans in the 2θ range 1–135° ($0 \leq h \leq 8$; $0 \leq k \leq 8$; $-10 \leq l \leq 11$). Of the 491 unique nonzero reflections, 476 with $F_o^2 \geq \sigma(F_o^2)$ were used for the structural analysis. Seven particularly strong reflections significantly affected by isotropic extinction (see below) were not included in the final least-squares refinements. Absorption corrections were applied by the method of Busing & Levy (1957), transmission range 0.263 to 0.574. Maximum mosaic spread of the crystal used was estimated to be 0.6°.

Interpretation of a Patterson map resulted in the positions of the methanesulfonate anion for which the crystallographic mirror plane in b passes through atoms S, C and one of the three O atoms (the other two O atoms are related to each other by the mirror plane). In addition, there was an unmistakeable peak corresponding to an atom of atomic number 7 which was subsequently assigned as an N atom. By iterated least-squares refinements [by the program ORXFLS4 which is an updated version of ORFLS (Busing, Martin

& Levy, 1962)] and difference-Fourier syntheses [by the program ORFFP3 (Levy, 1977)], all H atoms were eventually located. Scattering factors were those of Cromer & Waber (1974); anomalous-scattering corrections for S ($f' = 0.319$, $f'' = 0.557$) from Cromer (1974).

Since there was an ambiguity in choosing the correct space group, least-squares refinements were carried out for the three different space groups: $C2/m$, $C2$ and Cm. All refinements were carried out on F^2, the function minimized being $\sum w |F_o^2 - ys^2F_c^2|^2$, where the weights w are reciprocals of $\sigma^2(F_o^2) + (0.06F_o^2)^2$ and s stands for the scale factor on the intensity. Isotropic extinction corrections y were applied in the refinements using the expression of Zachariasen (1967) as described by Coppens & Hamilton (1970) and are incorporated in the program ORXFLS4 used. The measures obtained for the three cases are shown below.

	$C2/m$	$C2$	Cm
$R(F)$	0.045	0.042	0.041
$R(F^2)$	0.085	0.083	0.082
$wR(F^2)$	0.116	0.109	0.101
S	1.823	1.784	1.704
Number of atoms varied	10	13	20
Parameters varied	53	84	101

Although the R-factor ratio test (Hamilton, 1965) showed that the centrosymmetric space group is much less probable than the noncentrosymmetric ones, it should be pointed out that the refinements with each of the noncentrosymmetric space groups led to poor convergence even after 14 least-squares cycles, i.e. it gave unusually high Δ/σ and high e.s.d.'s for the resulting molecular parameters, and for space group $C2$ the refinements even diverged. Hence the results obtained from the centrosymmetric space group $C2/m$ are presented in this paper (see Baur & Tillmanns, 1986).* The refinement based on the higher symmetry was carried out until all Δ/σ became negligible; the isotropic extinction parameter obtained was $9(1) \times 10^2$;

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* Another reason for questioning the centrosymmetric space group is that program NORMAL [part of the program MULTAN (Germain, Main & Woolfson, 1971)] calculated statistical averages of 0.801 and 0.862 for $|E^2 - 1|$ and $|E|$, respectively, from our experimental data set. These are intermediate between the theoretical values of 0.968, 0.798 for centrosymmetric and 0.736, 0.886 for noncentrosymmetric structures (Karle, Dragonette & Brenner, 1965). After the structure was solved, statistical averages were computed again for a set of F^2 data calculated from the centrosymmetric $C2/m$ structure. The results were 0.802 and 0.861, almost identical with the experimental averages. Thus, for reasons not fully understood, a model known to be centrosymmetric yields averages intermediate between the theoretical values for centrosymmetric and noncentrosymmetric structures. Therefore the centrosymmetric space group was chosen without regard for the statistical averages. It was pointed out by the referee that the presence of S atoms in the unit cell perhaps caused the statistics to be warped towards a noncentrosymmetric indication according to the reasons given by Hargreaves (1955).

the final difference-Fourier map showed a maximum $\Delta\rho$ of 0.73 e Å^{-3}.

Discussion. Positional parameters and isotropic temperature factors (or their equivalents) are listed in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters and some molecular parameters involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43224 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters*

The e.s.d.'s are given in parentheses in all tables and in the text. The digits in parentheses correspond to the least-significant digits of the parameters. The equivalent isotropic temperature factors for non-H atoms were calculated from the corresponding anisotropic thermal parameters and unit-cell parameters by the relation $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$ (Hamilton, 1959).

	x	y	z	B_{eq} or $B(Å^2)$
S	0.33806 (8)	0	0.26734 (7)	2.93 (4)
C	0.2201 (5)	0	0.4254 (4)	3.94 (9)
O(1)	0.2043 (3)	0	0.1489 (2)	5.27 (10)
O(2)	0.4489 (3)	0.1619 (3)	0.2716 (3)	5.40 (7)
N	0.3006 (4)	0.5	0.1542 (3)	3.77 (9)
H(1)	0.291 (8)	0	0.494 (7)	7.8 (15)
H(2)	0.152 (5)	0.107 (5)	0.423 (4)	5.5 (7)
H(3)	0.301 (5)	0.5	0.058 (5)	4.2 (8)
H(4)	0.203 (10)	0.5	0.185 (7)	7.2 (13)
H(5)	0.373 (5)	0.408 (6)	0.183 (4)	6.5 (9)

Table 2. *Selected molecular parameters*

O(2') and H(2') are related to O(2) and H(2) by mirror plane at $y = 0$; H(5') is related to H(5) by mirror plane at $y = \frac{1}{2}$.

Interatomic distances (Å) and angles (°)

S–O(1)	1.440 (2)	O(1)–S–O(2)	113.3 (1)
S–O(2)	1.443 (2)	O(2)–S–O(2')	109.8 (1)
S–C	1.750 (3)	C–S–O(1)	105.7 (2)
		C–S–O(2)	107.2 (1)

Hydrogen bonds
Symmetry code: (i) x, y, z; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (iii) $x, 1 - y, z$.

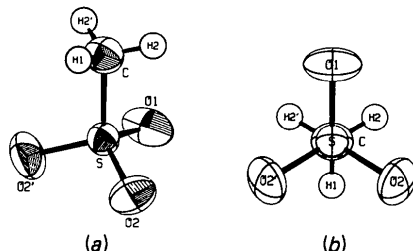| A	H	B	$A\cdots B$	$H\cdots B$	$A–H\cdots B$
N^i	H(3^i)	O(1^{ii})	2.797 (4) Å	1.91 (5) Å	179 (4)°
N^i	H(5^i)	O(2^i)	2.889 (3)	2.04 (4)	159 (3)
N^i	H(5^{iii})	O(2^{iii})	2.889 (3)	2.04 (4)	159 (3)

Fig. 1. Two different views of the CH$_3$O$_3$S$^-$ anion. Here and in Fig. 2, thermal ellipsoids enclose 50% probability.

The structure consists of CH$_3$O$_3$S$^-$ anions linked to NH$_4^+$ ions in a one-dimensional network (see below). The configuration of the anion is shown in Fig. 1(a) and another view down the S–C bond direction is given in Fig. 1(b). Some selected molecular parameters calculated from the program ORFFE4 (Busing, Martin & Levy, 1964) are listed in Table 2. All figures were prepared with the program ORTEPII (Johnson, 1976). The closest intermolecular contact between non-H atoms in this structure is 3.031 (4) Å for O(1)···N; the closest such contact between non-H and H atoms is 2.61 (4) Å for O(1)···H(5).

Both anion and cation are located in special positions in such a way as to result in C_s (m) symmetry in each case. The crystallographic mirror plane in b passes through S, C, O(1), H(1) and the midpoint of O(2) and O(2') (primed atoms are related to the corresponding non-primed atoms by the m_b plane) and of H(2) and H(2') in the anion (Fig. 1), and N, H(3), H(4) and the midpoint of H(5) and H(5') in the NH$_4^+$ ion. The bond distances and angles agree with those given in earlier studies of ammonium methanethiosulfonate (Cooper, Bloxham & Webster, 1982) and in sodium methanesulfonate (Wei & Hingerty, 1981, and references cited therein). Bond angles around S and N atoms are within a few degrees (in most cases, 2 e.s.d.'s) of the tetrahedral value. As can be seen in Table 2, the C–S–O angles are smaller and O–S–O angles larger than a regular tetrahedral angle because of mutual repulsion of charged O atoms (cited by Brandon & Brown, 1967; summarized by Arora & Sundaralingam, 1971; Cody & Hazel, 1977). Two planes, each formed by three O and three H atoms of the anion, are nearly
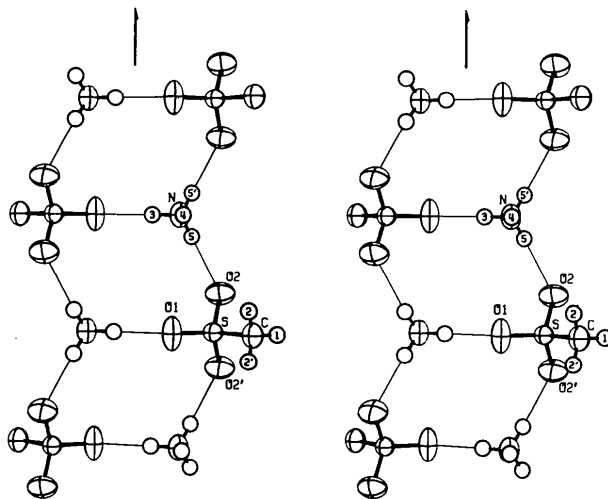

Fig. 2. Stereoscopic view of interionic hydrogen-bonding scheme around the twofold screw axis ($x = \frac{1}{4}$, $z = 0$) in the b direction. Labeled atoms are those of the asymmetric unit. The viewing direction is perpendicular to the b axis. The direction of the screw diad is shown at the top of the figure.

parallel, with the angle between the two plane normals being O(3)°.

The O atoms of the $CH_3O_3S^-$ anion form O···HN-type hydrogen bonds. The O(1) atom in this structure is unmistakably hydrogen-bonded to H(3) with an H(3)···O(1) distance of 1·91 (5) Å (Table 2). In addition, O(1) has close contacts with two mirror-related H(5) atoms with a distance of 2·61 (4) Å. This distance is much longer than the usual hydrogen-bond value of 2·0 Å given by Hamilton & Ibers (1968) for the NH···O-type bond. A value of 1·92 (2) Å was reported in the structure of hycanthone methanesulfonate (Wei & Einstein, 1978) and another value of 2·04 (4) Å was found in the structure of IA-4 methanesulfonate (Wei, 1981). According to these criteria, N—H(5)···O(1) is probably not a hydrogen bond. In summary, each O atom of the anion is hydrogen-bonded to a neighboring H atom while three of the four H atoms of the NH_4^+ ion participate in the bonding scheme, resulting in an infinite chain around the crystallographic twofold screw axis ($x = \frac{1}{4}$ or $\frac{3}{4}$, $z = 0$) in the **b** direction, as shown in Fig. 2.

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Structure of a Novel 3+2 Enone Cyclodimer

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Abstract. 3a-Hydroxytrispiro[octahydropentalene-1,1':2,1'':3,1'''-triscyclopentane]-2'''-one, $C_{20}H_{30}O_2$, $M_r = 302·46$, monoclinic, $P2_1/c$, $a = 11·626$ (3), $b = 10·761$ (2), $c = 12·989$ (3) Å, $\beta = 92·10$ (2)°, $V = 1623·93$ Å³, $Z = 4$, $D_x = 1·237$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·7093$ Å, $\mu(\text{Mo } K\alpha) = 0·72$ cm⁻¹, $F(000) = 664$, $T = 298$ K, $R = 0·048$ for 1030 observed reflections. The structure reveals the bicyclo[3.3.0]octan-7-ol skeleton

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