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Structure of Diammonium 2-Oxo-1,3-propanedisulphonate, $2NH_4^+.C_3H_4O_7S_2^{2-}$

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Abstract. $M_r = 252{\cdot}3$, orthorhombic, *Pbcn*, $a = 7{\cdot}483\ (1)$, $b = 7{\cdot}633\ (2)$, $c = 17{\cdot}120\ (3)$ Å, $V = 977{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}71$, $D_m = 1{\cdot}70$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, μ(Mo $K\bar{\alpha}$) = 5·47 cm^{-1}, $F(000) = 528$, $T = 295$ (3) K, final $R = 0{\cdot}0561$ for 1022 significant $[I > 3\sigma(I)]$ reflections. The structure contains alternate polar regions containing sulphonyl groups and ammonium ions and non-polar regions centred on (004) containing carbonyl groups. The ammonium ion is four-coordinate and has two short contacts with O atoms of sulphonyl groups, N—H···O being 2·850 (3) Å, indicating the presence of hydrogen bonding. Significant bond lengths: S—C, 1·784 (3); mean S—O, 1·450 (3); C=O, 1·205 (5) Å.

Introduction. The title compound (AADS) has been prepared by reaction of propanone and a sulphur trioxide–sulphuric acid mixture, followed by neutralization with ammonia (Grot, 1965). Industrially it is an unwanted by-product from the methyl methacrylate process, in which waste liquors containing dilute sulphuric acid are neutralized by aqueous ammonia to afford ammonium sulphate which is usable as a fertilizer (Giles, 1975). The presence of AADS alters the operation of the crystallizer, but it can be removed from the crystallizer purge by cooling as an anhydrous, almost pure compound (Giles, 1975). Brief reports in the patent literature mention AADS as a flame-proof additive to paper, cotton and fibres, as a pesticide-dispersing medium and in the formation of a copolymer with formaldehyde and phenol which is used as a cation-exchange resin.

The crystals were supplied by ICI Agricultural Division, and were those used for thermal-analysis studies (Giles, 1975). A brief preliminary account of the crystal structure exists in an industrial report (Wilford, 1976).

Experimental. Colourless crystals obtained from water had m.p. 473 K (decomp). Analysis: found C, 14·19; H, 4·75; N, 11·25; S, 25·19%. $C_3H_{12}N_2O_7S_2$ requires C, 14·3; H, 4·8; N, 11·1; S, 25·4%. Initial survey by Weissenberg and oscillation photographs (Shevels, 1976). The density, measured by both flotation (CCl_4/-C_6H_5I mixture) and xylene displacement, consistent with $Z = 4$, required that the anion lie across a twofold axis, since it cannot possess a centre of symmetry. Many-sided crystal roughly cubic in shape, all dimensions less than 1 mm, Picker four-circle diffractometer equipped with a scintillation counter and pulse-height analyser. Crystal mounting and data collection after Davies, Jarvis, Kilbourn, Mais & Owston (1970), θ–2θ scan technique, 1119 unique reflections with $4° < 2\theta < 55°$ $(0 \le h \le 9,\ 0 \le k \le 9,\ 0 \le l \le 21)$, 14 unobserved, 1026 with $I \ge 3\sigma(I)$, absorption correction omitted; standard reflections 600 and 0,0,14 did not change significantly. Lattice parameters by least-squares refinement of 20 reflections, widely placed in reciprocal space with $50° < 2\theta < 55°$. Structure solved by heavy-atom method. Full-matrix least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$ using the *COSMOS* suite of programs (Davies, Jarvis, Kilbourn, Mais & Owston, 1970) with isotropic temperature factors gave R 0·114. As the calculated structure factors were considerably larger than the observed when both values were relatively large, an extinction correction (Stout & Jensen, 1968) was applied, after which R was 0·080. Four of the six H atoms from a difference map but bond distance and angle calculations showed some positions to be unsatisfactory. A hydrogen-placing

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program (Wilford, 1983) set H atoms near to peaks in the difference map, but with all N—H distances 1·03 Å and both C—H distances 1·09 Å; all angles involving H atoms fixed to 109·47°. Further least-squares refinement, with anisotropic U for all non-hydrogen atoms, initially with the *COSMOS* programs but completed using the *LUX* suite (Goodacre & Lee, 1971), reduced R to 0·0561 ($R_w = 0{\cdot}065$). $w^{-1} = 1{\cdot}917 - 0{\cdot}163\,F_o + 0{\cdot}00719\,F_o^2$, parameters calculated by least squares (Goodacre, 1970); $(\Delta/\sigma)_{\max} = 0{\cdot}71$, $(\Delta/\sigma)_{\rm mean} = 0{\cdot}17$, maximum $\Delta\rho$ excursion $= |0{\cdot}6|\,e\,Å^{-3}$; four reflections with very small F_c omitted from final R value; Cromer's (1965) scattering factors used.

Discussion. Atom parameters are in Table 1.* The structure of the molecule is shown in Fig. 1 which also gives the atom-numbering system. The anion contains the non-linear S—C—C(O)—C—S chain which lies parallel to **c**. The symmetrical halves of the anion are related by a twofold axis parallel to **b**, with the carbonyl-group atoms lying on the axis, and the S···S distance of one molecule being 4·564 Å.

The structure consists of polar regions, centred on (001) and (002), which contain the sulphonyl groups and ammonium ions, and non-polar regions centred on the (004) planes, which contain the carbonyl groups. Each ammonium ion is surrounded by four sulphonyl groups belonging to different anions, with a short contact between each H and an O atom of a sulphonyl group. Two of these contacts are definitely hydrogen bonds, as discussed below. Likewise each sulphonyl group has contacts with four different ammonium ions (Fig. 2).

Evidence for hydrogen bonds is stronger when based on distances between the relatively heavier N and O atoms, than on distances involving H atoms, whose positions are less well determined from X-ray diffraction data. Formation of a hydrogen bond leads to a significant contraction in the distance between the two heavy atoms N and O, when compared to the sum of the N—H covalent bond distance and the van der Waals radii of H and of O (Vinogradov & Linnell, 1971).

More recent studies of hydrogen bonds using neutron diffraction data (Rahim & Barman, 1978), including many recent structure determinations, strongly justify the earlier claim. Using Bondi's (1964) covalent radii and standard bond lengths (Ondik & Smith, 1962), a contraction of the N···O distance between 0·1 and 0·3 Å from the sum of the covalent radii (3·07 Å) is expected when hydrogen bonds are formed. Two N···O distances in this structure (2·854 and 2·850 Å),* implying a contraction of 0·2 Å, clearly indicate the presence of hydrogen bonds between N(1)—H(1)···O(2) and N(1)—H(2)···O(1). Moreover, the N···O distances are in agreement with Pimentel & McClellan's (1960) value of 2·88 ± 0·13 Å for N^+—H···O distances. The H(1)···O(2) and

Table 1. *Fractional atomic coordinates* (×10⁵) *with their estimated standard deviations in parentheses and* $B_{\rm eq}$ *values* (×10⁴)

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	y	z	$B_{\rm eq}$(Å²)
S(1)	44834 (8)	37340 (8)	11864 (4)	56
C(1)	50000	17501 (44)	25000	58
C(2)	36019 (34)	27662 (34)	20533 (16)	59
O(1)	54000 (28)	23189 (28)	7847 (13)	88
O(2)	57361 (31)	50776 (27)	14374 (14)	93
O(3)	29657 (28)	44170 (32)	7665 (14)	103
O(4)	50000	1720 (37)	25000	88
N(1)	91642 (34)	34784 (31)	7517 (16)	78

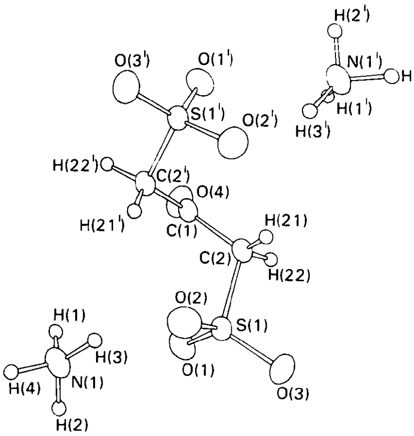

Fig. 1. Molecular structure of one molecule of the title compound showing the atomic numbering system used in the analysis.

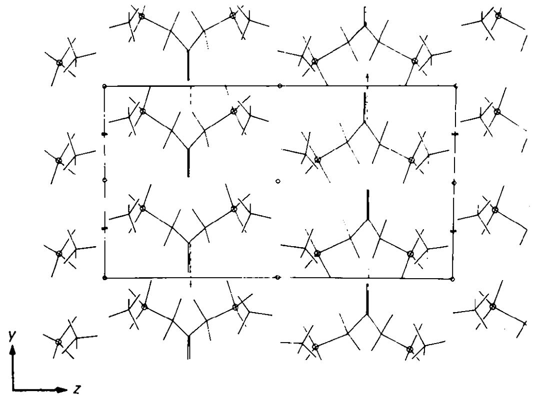

Fig. 2. The molecular packing viewed along the x axis. Circles represent S atoms and representative symmetry elements only are shown in the interests of clarity.

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* Lists of structure factors, H-atom parameters, non-bonded distances and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38826 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

S–O(1)	1·453 (2)	S–C(2)	1·784 (3)
S–O(2)	1·454 (2)	C(2)–C(1)	1·510 (3)
S–O(3)	1·442 (2)	C(1)–O(4)	1·205 (5)
O(1)–S–O(2)	111·1 (1)	O(3)–S–C(2)	105·9 (1)
O(1)–S–O(3)	113·9 (1)	S–C(2)–C(1)	112·2 (2)
O(2)–S–O(3)	113·6 (1)	C(2)–C(1)–O(4)	120·9 (2)
O(1)–S–C(2)	105·1 (1)	C(2)–C(1)–C(2^{i})	118·2 (2)
O(2)–S–C(2)	106·5 (1)		

H(2)···O(1) distances are also much shorter than other H···O distances in this crystal structure.*

A related structure is $(H_3O)_2(O_3SCH_2CH_2SO_3)$ (Mootz & Wunderlich, 1970) which has extensive O–H···O hydrogen bonds. The S–C bond length and the S–O bond lengths agree with the values for AADS (Table 2). The bond lengths and angles (Table 2) of the sulphonate groups also correspond closely to recently published (Wei & Hingerty, 1981) data for sodium methanesulphonate. Close correspondence is also found for corresponding bond lengths and angles for dipotassium methanedisulphonate (Truter, 1962) and disilver methanedisulphonate (Charbonnier, Faure & Loiseleur, 1979).

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* See deposition footnote.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Charbonnier, F., Faure, R. & Loiseleur, H. (1979). *Acta Cryst.* B**35**, 1773–1775.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 104–109.

Davies, G. R., Jarvis, J. A. J., Kilbourn, B. T., Mais, R. H. B. & Owston, P. G. (1970). *J. Chem. Soc. A*, pp. 1275–1283.

Giles, A. (1975). MSc Project Thesis, Teesside Polytechnic.

Goodacre, G. W. (1970). PhD Thesis, Loughborough Univ., pp. 255–265.

Goodacre, G. W. & Lee, J. D. (1971). *Acta Cryst.* B**27**, 1055–1061.

Grot, W. G. (1965). *J. Org. Chem.* **30**, 515–517.

Mootz, D. & Wunderlich, H. (1970). *Acta Cryst.* B**26**, 1820–1825.

Ondik, H. & Smith, D. (1962). *International Tables for X-ray Crystallography*, Vol. III, p. 258. Birmingham: Kynoch Press.

Pimentel, G. C. & McClellan, A. L. (1960). *The Hydrogen Bond*, p. 289. San Francisco: Freeman.

Rahim, Z. & Barman, B. N. (1978). *Acta Cryst.* A**34**, 761–764.

Shevels, J. S. (1976). MSc Project Report, Teesside Polytechnic.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*, pp. 410–412. London: Macmillan.

Truter, M. R. (1962). *J. Chem. Soc. A*, pp. 3393–3399.

Vinogradov, S. N. & Linnell, R. H. (1971). *Hydrogen Bonding*, pp. 176–197. New York: Van Nostrand Reinhold.

Wei, C. H. & Hingerty, B. E. (1981). *Acta Cryst.* B**37**, 1993–1997.

Wilford, J. B. (1976). Industrial Experience Scheme for Polytechnic and Technical College Teachers Research Report, ICI Ltd, Agricultural Division, Billingham, England.

Wilford, J. B. (1983). *Hydrogen Placing Program,* Teesside Polytechnic.