

unit cell makes an angle of 65° with c . This may be compared with the angle of 65° between R_{\max} and c (Gramaccioni & Simpson, 1972). Furthermore, the N(1)–N(2) vector for two molecules in the unit cell is calculated to make an angle of $+61.5^\circ$ with R_{\max} , while the angle for the other two glide-related molecules is -61.5° . As discussed above, Gramaccioni & Simpson (1972) predict about $\pm 55^\circ$ or $\pm 60^\circ$. The agreement between the optical and X-ray data is therefore excellent, and within the expected error of the spectroscopic analysis.

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References

- ANEX, B. G. & SIMPSON, W. T. (1960). *Rev. Mod. Phys.* **32**, 466–476.
 CLARK, L. B. & PHILPOTT, M. R. (1970). *J. Chem. Phys.* **53**, 3790–3801.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 915–924.
 CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, edited by J. S. ROLLETT, p. 112. Oxford: Pergamon Press.
 FANCONI, B. M., GERHOLD, G. A. & SIMPSON, W. T. (1969). *Molecular Crystals and Liquid Crystals*, **6**, 41–81.
 GRAMACCIONI, P. & SIMPSON, W. T. (1972). Private communication, unpublished.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
 PHILPOTT, M. R. (1970). *J. Chem. Phys.* **52**, 5842–5850.
 PHILPOTT, M. R. (1971). *J. Chem. Phys.* **54**, 2120–2129.
 PHILPOTT, M. R. (1972). Private communication.
 STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination, A Practical Guide*, p. 456. New York: Macmillan.
 WHEATLEY, P. J. (1953). *Acta Cryst.* **6**, 369–377.

Acta Cryst. (1973). **B29**, 454

The Crystal Structure of Methyl Orange Monohydrate Monoethanolate

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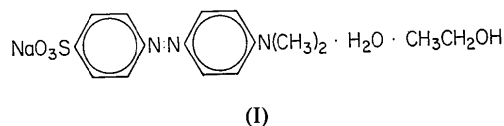
(Received 16 October 1972; accepted 18 October 1972)

Crystals of the title compound (sodium 4'-dimethylaminoazobenzene-4-sulphonate monohydrate monoethanolate, $C_{14}H_{14}NaN_3O_3S \cdot H_2O \cdot C_2H_6O$) are monoclinic, $P2_1/c$, with $a=22.11$ (2), $b=10.34$ (1), $c=8.30$ (1) Å, $\beta=91.58$ (5)°, $Z=4$. 2952 of a possible 3221 independent reflexions in the range $\sin\theta/\lambda \leq 0.59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures and refined by block-diagonal least-squares methods to a final R index of 0.049. The two phenyl rings of the azobenzene nucleus are inclined to each other at 10° . The coordination of the sodium ion is distorted octahedral; two water molecules lie at opposite corners, and the remaining positions are occupied by an oxygen atom from each of three different sulphonate groups and by an ethanol hydroxyl group. The water and ethanol molecules each donate one hydrogen bond, and the sulphonate group accepts two.

Introduction

Methyl orange has long been used as an acid-base indicator, and its protein-binding properties have been of interest for nearly as long. Recent spectroscopic work by Carey, Schneider & Bernstein (1972) suggests that, when bound to bovine serum albumin, the conformation of the organic moiety is such that the phenyl rings are effectively parallel. Similar indications are obtained for solid material, including the monohydrate monoethanolate (I). It was considered to be of interest to check the interpretation of the spectroscopic results by means of an X-ray analysis of I. It was found that the

rings were indeed nearly parallel, the angle between them being only 10° .



Experimental

Crystal data: F.W. 391.4, $V=1900$ Å³, $D_m=1.39$ (floatation in ether–chloroform), $D_x=1.37$ g cm⁻³,

$\mu = 24.0 \text{ cm}^{-1}$ (Cu $K\alpha$). (The wavelength assumed for Cu $K\alpha_1$ was 1.54050 \AA .)

The presence of molecules of solvation was indicated by a density anomaly. These molecules were identified as water and ethanol by chemical analysis, supplemented by the X-ray structure determination.

The space group was determined from single-crystal photographs.

The specimen material was crystallized from ethanol, yielding orange laths elongated along c , with prominent forms $\{100\}$ and $\{110\}$. A fragment of such a lath, of cross-section $0.2 \times 0.33 \text{ mm}$ and 0.5 mm long, was used for all measurements. This was mounted on a four-circle diffractometer with c parallel to the φ axis. The relative intensities were measured in the θ - 2θ scan mode (scans of 2° for $2\theta < 100^\circ$, 3° otherwise)

Table 1. *Final atomic parameters and their e.s.d.'s*

Quantities given are: fractional coordinates $\times 10^5$ for non-hydrogen, $\times 10^3$ for hydrogen atoms; $U_{ij} \times 10^4 \text{ \AA}^2$ for non-hydrogen atoms, where T.F. = $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$; r.m.s. displacements D_i along principal axes of vibration ellipsoids, in \AA ; isotropic Debye-Waller factors for hydrogen atoms, in \AA^2 . Quantities for which e.s.d.'s are not given were not refined.

	x	y	z	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
C(1)	83493 (9)	8580 (20)	14160 (25)	303 (10)	-6 (8)	9 (8)	338 (11)	44 (8)	335 (10)
C(2)	82046 (11)	18790 (25)	24116 (33)	368 (12)	-10 (10)	12 (11)	438 (13)	-134 (12)	618 (15)
C(3)	76101 (12)	20898 (28)	28123 (37)	429 (12)	46 (12)	78 (12)	530 (15)	-193 (13)	683 (17)
C(4)	71574 (11)	13025 (25)	22253 (29)	380 (12)	37 (10)	60 (9)	479 (14)	36 (10)	447 (12)
C(5)	73005 (11)	2929 (28)	12131 (33)	361 (12)	-156 (11)	-30 (10)	591 (16)	-13 (12)	539 (14)
C(6)	78989 (11)	624 (25)	8098 (30)	379 (12)	-69 (10)	30 (10)	478 (13)	-105 (11)	465 (13)
C(7)	55837 (10)	9983 (24)	27638 (28)	337 (10)	77 (10)	62 (9)	480 (13)	100 (10)	420 (12)
C(8)	54069 (11)	18418 (24)	39839 (31)	389 (12)	-17 (10)	1 (10)	443 (13)	29 (11)	511 (13)
C(9)	48173 (11)	18619 (24)	44671 (30)	398 (12)	35 (12)	58 (10)	442 (13)	-8 (13)	482 (13)
C(10)	43750 (10)	10544 (24)	37450 (28)	354 (10)	45 (9)	32 (9)	445 (12)	92 (10)	424 (12)
C(11)	45609 (11)	2182 (27)	25235 (32)	412 (12)	-29 (11)	1 (10)	565 (15)	-52 (12)	489 (14)
C(12)	51504 (12)	1962 (27)	20680 (30)	449 (12)	44 (11)	52 (10)	555 (15)	-42 (11)	438 (13)
C(13)	35994 (14)	19454 (35)	54776 (46)	501 (15)	92 (14)	270 (15)	701 (20)	-72 (17)	909 (22)
C(14)	33501 (13)	1656 (40)	35797 (45)	407 (15)	-145 (15)	39 (14)	965 (25)	-11 (18)	802 (21)
N(1)	65594 (10)	15726 (22)	27814 (27)	450 (10)	5 (9)	18 (9)	486 (11)	-50 (10)	547 (12)
N(2)	61707 (9)	8308 (22)	21880 (25)	427 (10)	9 (9)	11 (8)	525 (12)	52 (12)	472 (11)
N(3)	37901 (9)	10689 (25)	42291 (29)	354 (10)	0 (10)	90 (9)	680 (15)	-23 (11)	638 (14)
O(1)	94667 (7)	9025 (15)	23966 (19)	373 (7)	7 (6)	-67 (6)	378 (8)	-27 (6)	440 (8)
O(2)	92435 (7)	14507 (19)	-3852 (21)	372 (7)	1 (8)	55 (7)	625 (11)	225 (8)	492 (9)
O(3)	91653 (7)	-7630 (16)	4943 (20)	419 (7)	36 (7)	-13 (7)	390 (8)	-100 (7)	504 (9)
S	91194 (2)	5917 (5)	9436 (6)	268 (3)	-4 (2)	-2 (2)	286 (2)	20 (2)	301 (2)
Na	101225 (4)	24724 (8)	37387 (10)	454 (5)	13 (4)	15 (3)	347 (4)	-10 (3)	340 (4)
O(W)	99988 (8)	13324 (16)	62140 (19)	537 (10)	76 (7)	7 (7)	418 (9)	38 (7)	379 (8)
O(E1)	91098 (9)	-10038 (25)	-29847 (23)	526 (10)	193 (10)	-66 (8)	1014 (16)	-249 (10)	471 (10)
C(E2)	85129 (20)	-8665 (76)	-34903 (59)	678 (22)	518 (33)	-190 (21)	2208 (67)	-625 (37)	911 (28)
C(E3)	83736 (19)	-12161 (49)	-50602 (48)	771 (22)	119 (22)	-156 (18)	1144 (32)	47 (21)	735 (22)

	D_1	D_2	D_3	x	y	z	B	
C(1)	0.17	0.17	0.20	H(2)	851	242	283	5.0
C(2)	0.19	0.19	0.26	H(3)	751	277	348	5.0
C(3)	0.18	0.22	0.29	H(5)	699	-25	81	5.0
C(4)	0.19	0.21	0.23	H(6)	800	-63	13	5.0
C(5)	0.17	0.23	0.26	H(8)	569	239	448	5.0
C(6)	0.18	0.20	0.24	H(9)	470	243	527	5.0
C(7)	0.17	0.18	0.24	H(11)	427	-34	203	5.0
C(8)	0.20	0.21	0.23	H(12)	526	-36	125	5.0
C(9)	0.19	0.21	0.22	H(13A)	386 (2)	184 (5)	649 (6)	8.0 (1.1)
C(10)	0.18	0.19	0.23	H(13B)	320 (2)	186 (5)	566 (6)	7.7 (1.1)
C(11)	0.20	0.22	0.24	H(13C)	368 (2)	280 (4)	523 (5)	6.6 (0.9)
C(12)	0.20	0.22	0.24	H(14A)	329 (3)	31 (6)	236 (7)	10.3 (1.5)
C(13)	0.18	0.27	0.32	H(14B)	299 (3)	25 (6)	403 (7)	9.5 (1.3)
C(14)	0.19	0.28	0.32	H(14C)	352 (2)	-72 (5)	357 (6)	8.4 (1.2)
N(1)	0.21	0.21	0.24	H(WA)	1015 (2)	73 (4)	649 (4)	5.1 (0.7)
N(2)	0.21	0.21	0.24	H(WB)	969 (2)	121 (4)	624 (5)	6.6 (0.8)
N(3)	0.18	0.25	0.26	H(E1)	917 (2)	-85 (4)	-216 (4)	5.0 (0.7)
O(1)	0.18	0.19	0.22	H(E2A)	828	-134	-281	9.0
O(2)	0.17	0.20	0.28	H(E2B)	841	-3	-338	9.0
O(3)	0.18	0.20	0.24	H(E3A)	794	-113	-532	7.0
S	0.16	0.17	0.18	H(E3B)	846	-210	-518	7.0
Na	0.18	0.19	0.21	H(E3C)	859	-78	-575	7.0
O(W)	0.19	0.20	0.24					
O(E1)	0.19	0.21	0.34					
C(E2)	0.23	0.26	0.51					
C(E3)	0.24	0.30	0.34					

METHYL ORANGE MONOHYDRATE MONOETHANOLATE

Table 2. Observed and calculated structure amplitudes x 10³

An asterisk denotes an unobserved reflexion, for which the estimated threshold value is given. A minus sign preceding 10F_o means that the reflexion was assigned zero weight.

Table with multiple columns of numerical data representing structure amplitudes. The table is organized into several sections, each with a header row indicating the type of reflection (e.g., h k l, h k 0, etc.) and the corresponding observed (F_o) and calculated (F_c) values. The data is presented in a grid format with various sub-headers and numerical entries.

Table 2 (cont.)

Table with multiple columns of numerical data, likely representing crystallographic parameters or diffraction data.

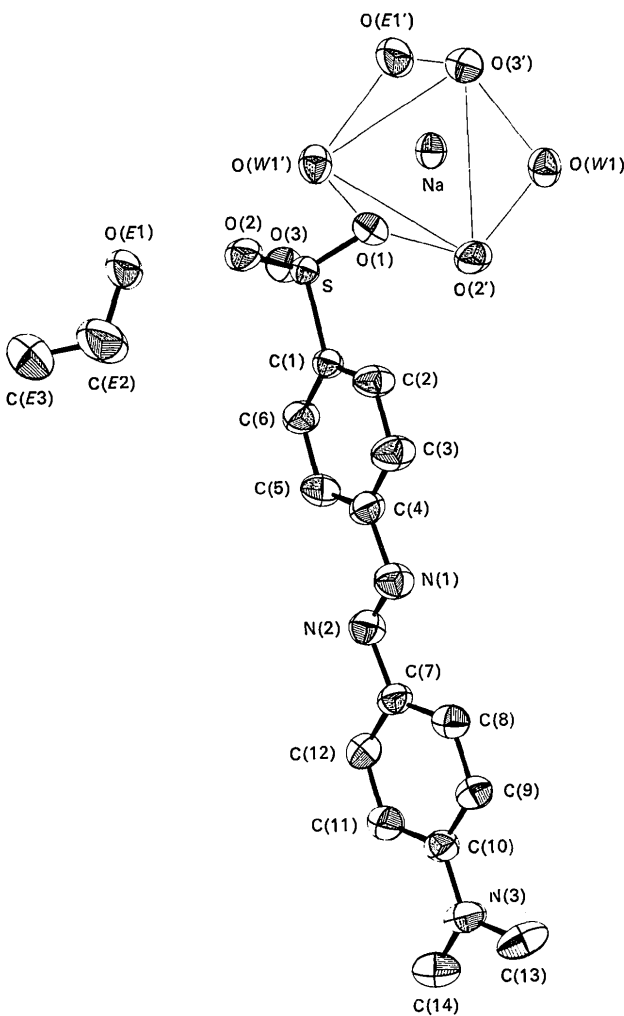


Fig. 1. The asymmetric unit, giving the arbitrary numbering scheme. The thermal ellipsoids correspond to 50% probability.

A C 29B - 6*

using nickel-filtered Cu Kα radiation with pulse-height discrimination. Background counts were measured at the beginning and end of each scan. The intensity of a standard reflexion was measured periodically, and subsequently used for scaling. No significant change was observed in the intensity of this reflexion during data collection. Reflexions were treated as unobserved if their net intensities were less than 7 (deca-) counts or 0.1 times the measured background count. In the range explored, 2952 of a possible 3221 reflexions were observed above background. Absorption corrections, ranging from 1.47 to 1.96, were applied to the measured intensities.

Structure determination

The approximate structure was readily deduced by symbolic addition procedures, and refined by block-diagonal least-squares methods. The quantity minimized was ΣwΔF². The weighting scheme, chosen to ensure reasonable constancy of wΔF² with respect to F₀ and sin² θ, was w = w₁w₂, where

Equations for w₁ and w₂ based on F₀ and sin² θ values.

(The nominal threshold value of F₀ is 2.5). The scattering factor curve of Stewart, Davidson & Simpson (1965) was used for hydrogen, and those of Hanson, Herman, Lea & Skillman (1964) for the others. (The sodium atom was assumed to be the neutral species.) The curves for sulphur and sodium were corrected for the real part of the anomalous scattering (International Tables for X-ray Crystallography, 1962). Where possible, reasonable parameters were assigned to the hydrogen atoms and were not refined. Hydrogen atoms whose positions were not readily predictable (those on

the water molecule, the ethanol hydroxyl group, and the amino methyl groups) were initially located on a difference map, and their parameters were refined in the usual way. During refinement it became obvious that the stronger reflexions were diminished by extinction and a correction term was derived in the manner of Pinnock, Taylor & Lipson (1956). The maximum value of this correction was 1.51. At a late stage in the refinement a number of weak reflexions were found to have calculated amplitudes which were unacceptably low. Some 62 such reflexions were arbitrarily assigned zero weight.

Refinement was terminated when the average and maximum coordinate shifts for non-hydrogen atoms were 0.2 and 0.8 times, respectively, the corresponding e.s.d.'s. The final parameters are given in Table 1.

Assessment of analysis

The agreement between observed and calculated structure amplitudes (Table 2) is satisfactory, and there can be no doubt of the essential correctness of the proposed structure. The final agreement index ($R_1 = \sum | \Delta F | / \sum | F_o |$)

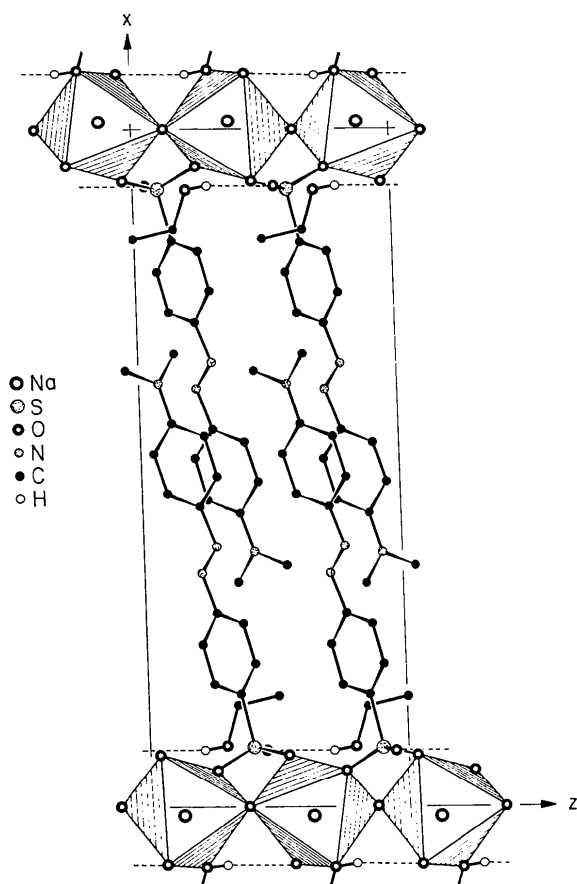


Fig. 2. The structure viewed along **b**. Only one layer of coordination octahedra is shown. The broken lines represent the hydrogen bonds $O(E1)-H(E1)\cdots O(3')$.

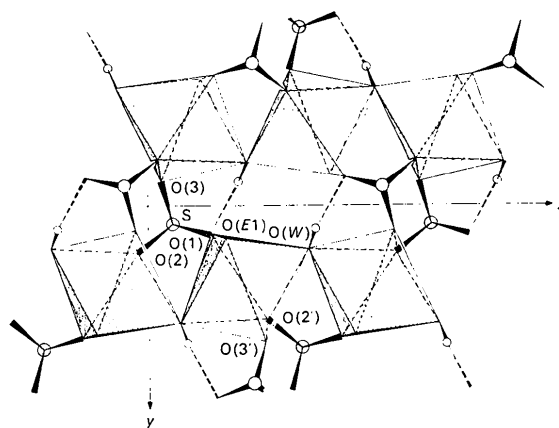


Fig. 3. A layer of coordination octahedra, with connective sulphate groups, viewed along **c**. The broken lines represent the hydrogen bonds $O(W)-H(WA)\cdots O(1')$.

is 0.049, for observed reflexions only, and the corresponding weighted index (R_2) is 0.047. The residual electron density stays within the limits $\pm 0.4 \text{ e}\text{\AA}^{-3}$, and does not suggest the presence of any atoms not considered in the analysis. The nominal e.s.d.'s of atomic coordinates are: Na, 0.0009; S, 0.0005; O, 0.0023; C, 0.0026; H, 0.05 Å. However, a comparison of chemically equivalent bond lengths (Table 3) suggests that these are optimistic. They ought probably to be doubled, and this has been done in Table 3 and elsewhere. Moreover, it is obvious from Table 1 and Fig. 1 that the thermal motion is appreciable, and this may of course be non-rigid in character, with systematic but indeterminate effects on the observed bond distances. The thermal motion is particularly severe for the central carbon atom of the ethanol molecule; the situation here might well be described as disorder. The observed geometry of the ethanol molecule is therefore unreliable, and is tabulated only as a matter of record.

Table 3. Distances and angles

(a) Distances. E.s.d.'s: S—O, 0.003; S—C, Na—O, 0.004; C—C, C—N, N—N, 0.006 to 0.009 Å

S—O(1)	1.449 Å	C(9)—C(10)	1.408 Å
S—O(2)	1.449	C(10)—C(11)	1.404
S—O(3)	1.454	C(10)—N(3)	1.365
S—C(1)	1.780	N(3)—C(13)	1.449
C(1)—C(2)	1.384	N(3)—C(14)	1.443
C(1)—C(6)	1.377	O(E1)—C(E2)	1.381
C(2)—C(3)	1.382	C(E2)—C(E3)	1.380
C(5)—C(6)	1.383	Na—O(1)	2.428
C(3)—C(4)	1.370	Na—O(2')	2.372
C(4)—C(5)	1.383	Na—O(3')	2.483
C(4)—N(1)	1.440	Na—O(W)	2.393
N(1)—N(2)	1.244	Na—O(W')	2.444
N(2)—C(7)	1.407	Na—O(E1')	2.375
C(7)—C(8)	1.401	O(1) \cdots O(W')	2.828
C(7)—C(12)	1.382	O(3) \cdots O(E1')	2.901
C(8)—C(9)	1.375	C(5) \cdots N(2)	2.705
C(11)—C(12)	1.368	C(8) \cdots N(1)	2.777

Table 3 (cont.)

(b) Angles. E.s.d.'s: C-S-O, 0.2; C-C-S, 0.3; C-C-C, C-C-N, C-N-C, C-N-N, 0.4 to 0.5; O-Na-O, 0.15°

O(1)—S—O(2)	113.0°	C(9)—C(10)—C(11)	117.4°
O(1)—S—O(3)	112.9	C(9)—C(10)—N(3)	121.4
O(2)—S—O(3)	112.3	C(11)—C(10)—N(3)	121.2
C(1)—S—O(1)	105.7	C(10)—N(3)—C(13)	121.0
C(1)—S—O(2)	106.0	C(10)—N(3)—C(14)	121.2
C(1)—S—O(3)	106.2	C(13)—N(3)—C(14)	117.8
S—C(1)—C(2)	119.2	O(E1)—C(E2)—C(E3)	116.6
S—C(1)—C(6)	120.9	O(1)—Na—O(2')	88.3
C(2)—C(1)—C(6)	119.9	O(1)—Na—O(3')	167.5
C(1)—C(2)—C(3)	120.1	O(1)—Na—O(W)	89.1
C(1)—C(6)—C(5)	119.4	O(1)—Na—O(W')	83.8
C(2)—C(3)—C(4)	120.7	O(1)—Na—O(E1')	82.7
C(4)—C(5)—C(6)	120.6	O(2')—Na—O(3')	95.5
C(3)—C(4)—C(5)	119.2	O(2')—Na—O(W)	81.6
C(3)—C(4)—N(1)	116.0	O(2')—Na—O(W')	87.3
C(5)—C(4)—N(1)	124.7	O(2')—Na—O(E1')	168.2
C(4)—N(1)—N(2)	112.6	O(3')—Na—O(W)	103.2
N(1)—N(2)—C(7)	115.0	O(3')—Na—O(W')	84.5
N(2)—C(7)—C(8)	127.0	O(3')—Na—O(E1')	94.9
N(2)—C(7)—C(12)	114.8	O(W)—Na—O(W')	167.0
C(8)—C(7)—C(12)	118.2	O(W)—Na—O(E1')	90.6
C(7)—C(8)—C(9)	120.4	O(W')—Na—O(E1')	99.3
C(7)—C(12)—C(11)	122.0	O(W)—H(WA)—O(1)	171
C(8)—C(9)—C(10)	121.3	O(E1)—H(E1)—O(3)	165
C(12)—C(11)—C(10)	120.7		

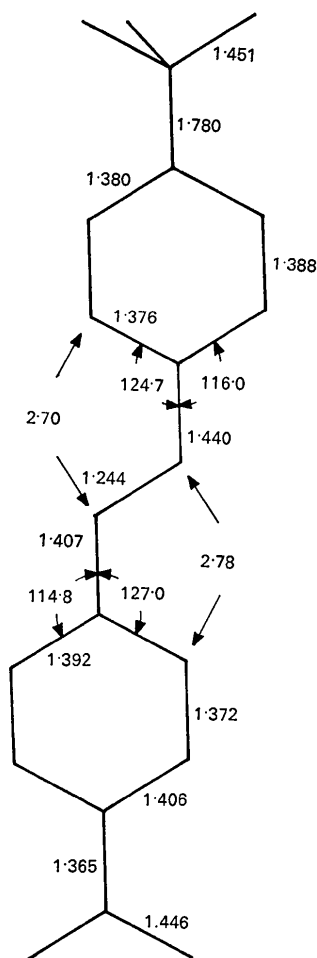


Fig. 4. Some distances and angles in the organic anion, averaged where appropriate. The orientation is as in Fig. 1.

Discussion

The geometry of the organic anion (summarized in Tables 3 and 4, and Figs. 1 to 4) is similar to that found for azobenzene (Brown, 1966). Although steric repulsion between C(5) and N(2), and between C(8) and N(1) is sufficient to distort the angles about the bridgehead atoms, the anion is nevertheless approximately planar, with all nitrogen and carbon atoms lying within 0.27 Å of their mean plane. The phenyl rings are inclined at about 10° to each other, a finding consistent with the spectroscopic indications for both the specimen material and the protein complex (Carey *et al.*, 1972).

Table 4. Distances (Å × 10²) of some atoms from certain mean planes

Atoms specified in bold type define the mean plane.						
Phenyl ring 1:	C(1)	0	C(2)	0	C(3)	0
	C(4)	0	C(5)	0	C(6)	0
	S	-2	N(1)	-7	N(2)	-6
Phenyl ring 2:	C(7)	0	C(8)	0	C(9)	0
	C(10)	0	C(11)	0	C(12)	0
	N(1)	0	N(2)	-4	N(3)	-1
	C(13)	0	C(14)	-12		
Organic anion:	C(1)	-11	C(2)	2	C(3)	13
	C(4)	11	C(5)	0	C(6)	-12
	C(7)	13	C(8)	2	C(9)	-6
	C(10)	-1	C(11)	10	C(12)	16
	C(13)	-19	C(14)	-15	N(1)	17
	N(2)	16	N(3)	-9	S	-27

The dihedral angle between the phenyl rings is 10.3°.

The distribution of bond lengths in the aniline end of the anion is consistent with observations of aniline

derivatives (Sakurai, Sundaralingam & Jeffrey, 1963; Trotter, Whitlow & Zobel, 1966). Thus C(10)–N(3) is much shorter than a single bond, and N(2)–C(7), while longer than C(10)–N(3), is significantly shorter than C(4)–N(1). C(9)–C(10) and C(10)–C(11) are the longest bonds in the ring, C(8)–C(9) and C(11)–C(12) are the shortest, and C(7)–C(8) and C(7)–C(12) have intermediate values. (These differences are, however, of marginal significance.) In contrast, bond distances in the other ring are equal.

The coordination of the sodium atom is distorted octahedral, with Na–O distances ranging from 2.37 to 2.48 Å. The octahedron is made up of two water molecules at opposite corners, three sulphonate oxygen atoms, each from a different group, and the oxygen atom of the ethanol molecule. Adjacent octahedra share water molecules, and are linked in endless chains parallel to *c*. The structure is stabilized by two sets of O–H...O bonds, linking the water molecule to O(1), and the ethanol molecule to O(3). The hydrogen-bonding potential of the structure is not fully realized, however, as one aqueous hydrogen atom [H(*WB*)] and one sulphonate oxygen atom [O(2)] do not participate.

The crystalline material and useful discussion were provided by Dr P. R. Carey. Computer programs used

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References

- AHMED, F. R. (1970). *Crystallographic Computing*, p. 279. Copenhagen: Munksgaard.
- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd Ed. Appendix p. 52.
- BROWN, C. J. (1966). *Acta Cryst.* **21**, 146–152.
- CAREY, P. R., SCHNEIDER, H. & BERNSTEIN, H. J. (1972). *Biochem. Biophys. Res. Commun.* **47**, 588–595.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173–178.
- SAKURAI, T., SUNDARALINGAM, M. & JEFFREY, G. A. (1963). *Acta Cryst.* **16**, 354–363.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TROTTER, J., WHITLOW, S. H. & ZOBEL, T. (1966). *J. Chem. Soc. (A)*, pp. 353–356.

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The Crystal Structure of Cesium Nonfluorodiuranate(IV), CsU₂F₉*

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Cesium nonfluorodiuranate(IV) is monoclinic, space group *C2/c*, with $a=15.649$ (3), $b=7.087$ (1), $c=8.689$ (2) Å, $\beta=118.11^\circ$ (2), and $Z=4$. The structure was refined by full-matrix least squares techniques, using data collected with a Picker four-circle diffractometer, to an R value of 4.8%. Uranium is coordinated to eight fluorines in polyhedra which share edges to form (U₄F₁₆) sheets parallel to (100). The full uranium coordination approximates a tri-capped trigonal prism, the ninth corner of the polyhedron being a half-filled eightfold set of fluorines so that the coordination number is effectively 8½. The U–F distances span the range from 2.28 to 2.42 Å, with an average value of 2.33 Å.

The compound CsU₂F₉ was obtained by L. B. Asprey from a 40% aqueous HF solution from which crystals of CsUF₆ had been previously obtained. On being allowed to stand in contact with air, disproportionation of the remaining U(V) slowly occurred, yielding U(VI) and U(IV). Deep green, tabular crystals of

CsU₂F₉ up to 2 × 1 × 0.2 mm crystallized from this solution together with a number of other phases. The measured density, by pycnometer, of this impure material was approximately 6.4 g cm⁻³. Optically the monoclinic crystals are biaxial negative, with $2V_x$ approximately 54°. The optical axes display marked symmetrical dispersion with $v > r$. The refractive indices, optical orientation and pleochroism, for white light are as follows:

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