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Structure of a Psoralen Derivative of a Monosubstituted 18-Crown-6 Ether

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(Received 10 August 1990; accepted 11 December 1990)

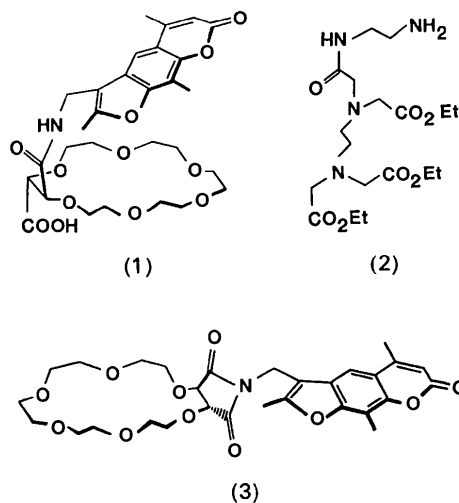
Abstract. *N*-[(2,5,9-Trimethyl-7-oxo-7*H*-furo[3,2-*g*]-[1]benzopyran-3-yl)methyl]-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboximide, C₂₉H₃₅NO₁₁, *M_r* = 573.60, monoclinic, *P*2₁, *a* = 18.877 (9), *b* = 6.888 (6), *c* = 24.488 (10) Å, β = 119.90 (4)°, *V* = 2760.2 Å³, *Z* = 4, *D_x* = 1.380 Mg m⁻³, λ(Cu Kα) = 1.54178 Å, μ = 0.85 mm⁻¹, *F*(000) = 1216, *T* = 170 K, *R* = 0.065, *wR* = 0.057 for 3720 observed reflections. There are two molecules (I and II) in the asymmetric unit and the 18-crown-6 part of molecule II is disordered. The psoralen moieties of the two molecules are nearly centrosymmetrically related.

Introduction. The utilization of psoralens in medicine started more than 3000 years ago for the treatment of vitiligo and psoriasis, two skin diseases, and has been practised ever since (Parrish, Fitzpatrick, Tanenbaum & Pathak, 1974; Scott, Pathak & Mohn, 1976). In recent years, psoralen derivatives have been applied to the treatment of certain forms of skin cancer (Edelson, 1986, 1987). The successful use of psoralens in medicine has been linked to their ability to cross-link adjacent pyrimidine bases on two strands of the DNA double helix upon irradiation (Scott *et al.*, 1976; Haran & Crothers, 1978). In this context, psoralen molecules and derivatives have been used for a number of years as aromatic intercalants to probe nucleic acid structure, damage and repair, and more importantly, recombination through their involvement in photocross-linking to DNA upon irradiation by ultraviolet light (Saffran, Goldenberg & Cantor, 1982; Goldenberg, Welsh, Haas, Rideout & Cantor, 1988).

Owing to the growing interest in the design of photochemical DNA cleaving molecules we have developed the synthesis of a series of mono- and

bis-intercalant crown ethers having either a methidium or a psoralen function covalently attached to the macrocyclic ring with well defined stereochemistry (Basak & Dugas, 1986). More recently, an iron complex substituted psoralen has been prepared by Nakamura as a new photochemical DNA cleaver (Nakamura, 1989). It behaves as a model for bleomycin, one of the most potent antitumor antibiotic agents known.

In our own effort to develop a bleomycin model based on our psoralen–18-crown-6 monoacid (1), we coupled this chiral crown ether (Basak & Dugas, 1986) to the EDTA derivative (2) (Taylor, Schultz & Dervan, 1984); the EDTA side chains of this adduct will serve to bind iron and oxygen (Nakamura, 1989). However, during this synthesis a side reaction always took place between the acid and the amide function of psoralen–18-crown-6 monoacid (1) resulting in the corresponding cyclic imide (3). In the present paper we present the crystal structure determination of this novel psoralen–imido-18-crown-6 molecule.



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Experimental. Compound (3) is a white crystalline solid, m.p. 466–467 K, IR (CHCl₃) cm⁻¹: 2290 (*s*), 1730 (*imide*), 1710 (*coumarine lactone*), 1598 (*arom. vs*), 1110 (*crown vs*). ¹H NMR (CDCl₃, 90 MHz): 7.82 (*s*, 1H), 6.24 (*s*, 1H), 4.69 (*s*, 2H), 4.43 (*s*, 2H), 4.08 (*m* 4H, *crown*), 3.62–3.75 (*m*, 16H, *crown*), 2.62 (*s*, 3H), 2.55 (*s*, 3H), 2.52 (*s*, 3H). MS: *m/e* 574 (*M*⁺, base peak), 573, 531, 440, 400, 258, 241, 223, 185, 180.

Crystals suitable for X-ray diffraction were obtained from a CH₂Cl₂/petroleum ether mixture (4:1). Crystal bounded by {100}, {010}, {001}; dimensions 0.023 × 0.49 × 0.21 mm. Unit cell from 25 well centered reflections in the range 20 ≤ θ ≤ 25°. Nonius CAD-4 diffractometer, graphite-monochromatized Cu Kα radiation, ω/2θ-scan technique, Δω = (1.00 + 0.14 tan θ)°, 2θ_{max} = 140.0° (0 ≤ h ≤ 23, 0 ≤ k ≤ 8, -29 ≤ l ≤ 25). Orientation monitored every 200 measurements, intensity checked every hour using seven standard reflections, largest intensity fluctuation ±2.4%. A set of 5289 independent reflections was collected at 170 K of which 3720, such that I ≥ 1.96σ(I), were retained for structure determination and refinement. Lp corrections, no absorption correction. The low temperature was maintained to ±2 K using a locally modified Nonius attachment.

The structure was solved by direct methods (*MULTAN80*)* and difference Fourier synthesis (*SHELX76*). There are two independent molecules (I and II) per asymmetric unit. As the refinement progressed, it was discovered that the atoms forming the 18-crown-6 moiety of molecule II are disordered. This disordered model was included in the refinement with an occupancy ratio, refined, then fixed in the last cycles at 0.67/0.33. Initially, full-matrix least-squares refinement based on *F*'s, block-diagonal approximation in the last cycles, all non-H atoms anisotropic (minor occupancy part of the molecule II isotropic). All H atoms were calculated at idealized positions (tetrahedral angles and D_{C-H} = 0.95 Å). B_{iso} = 2.5 Å² (psoralen), 4.5 Å² (methyl), 6.0 Å² (crown I) and 8.0 Å² (crown II) for all the H atoms fixed in the last cycles of refinement.

Function minimized: Σw(|F_o| - |F_c|)². Final R = 0.065, wR = 0.057 [weights derived from the counting statistics w = 1/σ²(*F*)] and S = 1.77 for 775 refined parameters and 14 reflections suffering extinction rejected. Maximum (Δ/σ) = 0.26, average (Δ/σ) = 0.05; in the final difference Fourier synthesis, general background in the range -0.45–0.30 e Å⁻³

and a few peaks in the range 0.32–0.50 e Å⁻³ found in the vicinity of O(127) and C(128). The relatively high residual electron density is to be associated with the disorder encountered in this structure.

The scattering curves for non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965). The final fractional atomic coordinates of both I and II are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles of the 18-crown-6 moiety, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53819 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates with their *e.s.d.*'s (× 10⁴) and U_{eq} values (× 10³) for the non-H atoms of the psoralen-imido-18-crown-6 compound

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq} (Å ²)
C11	4132 (4)	2789 (10)	2986 (3)	26
Me11	3225 (4)	2407 (11)	2653 (3)	32
C12	4555 (4)	3097 (10)	3606 (3)	26
C13	5421 (4)	3452 (10)	3939 (3)	25
O13	5854 (3)	3667 (7)	4506 (2)	33
O14	5803 (2)	3577 (7)	3592 (2)	26
C15	5392 (3)	3329 (9)	2949 (3)	19
C16	5854 (3)	3538 (9)	2651 (3)	19
Me16	6763 (4)	3937 (10)	3024 (3)	28
C17	5429 (3)	3252 (9)	2006 (3)	22
O18	5759 (2)	3375 (6)	1622 (2)	19
C19	5121 (3)	3010 (9)	1019 (2)	18
Me19	5339 (4)	3067 (11)	517 (3)	30
C110	4416 (3)	2654 (9)	1008 (2)	19
C111	4591 (3)	2810 (9)	1651 (2)	18
C112	4148 (3)	2659 (10)	1963 (3)	22
C113	4538 (3)	2947 (10)	2614 (3)	20
C114	3611 (4)	2140 (10)	451 (3)	23
N115	3084 (3)	3838 (8)	139 (2)	21
C116	2652 (3)	4782 (9)	378 (2)	18
O116	2535 (2)	4169 (7)	790 (2)	30
C117	2381 (3)	6070 (10)	30 (3)	25
O118	1639 (2)	7301 (7)	-21 (2)	29
C119	1436 (4)	9291 (11)	-228 (3)	34
C120	740 (4)	9951 (12)	-155 (3)	43
O121	26 (3)	8958 (8)	-595 (3)	61
C122	-692 (4)	9840 (13)	-648 (4)	66
C123	-1071 (4)	11263 (15)	-1172 (4)	64
O124	-510 (3)	12742 (9)	-1068 (2)	59
C125	-762 (5)	14025 (18)	-1575 (4)	89
C126	-18 (5)	15161 (14)	-1485 (4)	67
O127	575 (4)	14050 (13)	-1547 (3)	114
C128	462 (7)	13159 (17)	-2032 (6)	119
C129	1178 (5)	12463 (12)	-2009 (4)	67
O130	1451 (3)	10649 (8)	-1701 (2)	41
C131	2172 (4)	10022 (11)	-1707 (3)	33
C132	2331 (4)	7967 (11)	-1451 (3)	30
O133	2587 (2)	8028 (7)	-797 (2)	25
C134	2389 (3)	6347 (10)	-571 (3)	23
C135	3007 (3)	4673 (10)	-397 (3)	23
O135	3354 (2)	4179 (7)	-681 (2)	28
C21	5990 (3)	8519 (9)	2080 (3)	20
Me21	6888 (4)	8968 (11)	2392 (3)	29
C22	5570 (3)	8260 (9)	1453 (3)	22
C23	4699 (3)	7851 (10)	1123 (3)	22
O23	4279 (2)	7604 (7)	560 (2)	30
O24	4308 (2)	7777 (7)	1467 (2)	21
C25	4733 (3)	8003 (9)	2114 (2)	19
C26	4252 (3)	7810 (10)	2390 (3)	21
Me26	3346 (4)	7463 (11)	2018 (3)	30
C27	4675 (3)	8069 (9)	3041 (3)	18
O28	4337 (2)	7977 (7)	3423 (2)	23
C29	4966 (4)	8372 (10)	4040 (3)	29

* The programs used here are modified versions of *NRC-2*, data reduction, *NRC-10*, bond distances and angles and *NRC-22*, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *MULTAN80*, multi-solution program (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *SHELX76*, program for structure determination (Sheldrick, 1976) and *ORTEP*, stereodrawings (Johnson, 1965).

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Me29	4716 (4)	8309 (11)	4522 (3)	36
C210	5675 (3)	8697 (9)	4041 (3)	22
C211	5508 (3)	8486 (9)	3395 (3)	21
C212	5974 (3)	8648 (9)	3101 (3)	20
C213	5580 (3)	8419 (9)	2445 (3)	21
C214	6470 (4)	9260 (10)	4605 (3)	32
N215	7006 (3)	7608 (8)	4934 (2)	23
C216	7579 (4)	6901 (10)	4795 (3)	29
O216	7682 (3)	7553 (8)	4374 (2)	38
C217	8078 (4)	5327 (12)	5280 (3)	37
O218	8242 (3)	3832 (8)	4963 (2)	56
C219	8642 (5)	2230 (15)	5366 (5)	92
C220	9470 (6)	2426 (19)	5860 (5)	44
O221	9991 (3)	2980 (10)	5627 (3)	87
C222	10472 (5)	1657 (16)	5533 (4)	80
C223	11150 (5)	865 (14)	6099 (4)	54
O224	10975 (3)	-210 (9)	6517 (2)	51
C225	10756 (5)	-2211 (14)	6344 (4)	65
C226A	10426 (9)	-2718 (20)	6820 (6)	69
C226B	10521 (11)	-3406 (32)	6662 (9)	29
O227A	9621 (4)	-1792 (16)	6589 (3)	81
O227B	9783 (7)	-2809 (20)	6625 (5)	25
C228A	9382 (8)	-1943 (25)	7041 (5)	79
C228B	9925 (13)	-1324 (39)	7075 (10)	52
C229A	8572 (8)	-1137 (25)	6759 (7)	107
C229B	9179 (19)	-990 (56)	7148 (14)	102
O230A	8551 (4)	908 (11)	6819 (3)	39
O230B	8665 (9)	222 (27)	6634 (7)	58
C231A	7729 (6)	1542 (17)	6517 (4)	35
C231B	8147 (15)	1219 (46)	6799 (12)	67
C232A	7679 (6)	3706 (15)	6573 (4)	32
C232B	7519 (13)	2435 (38)	6222 (10)	45
O233A	8065 (4)	4749 (10)	6277 (3)	36
O233B	7994 (7)	3969 (20)	6121 (5)	27
C234	7556 (4)	4832 (12)	5575 (3)	44
C235	7004 (4)	6598 (11)	5430 (3)	32
O235	6639 (3)	7110 (8)	5694 (2)	46

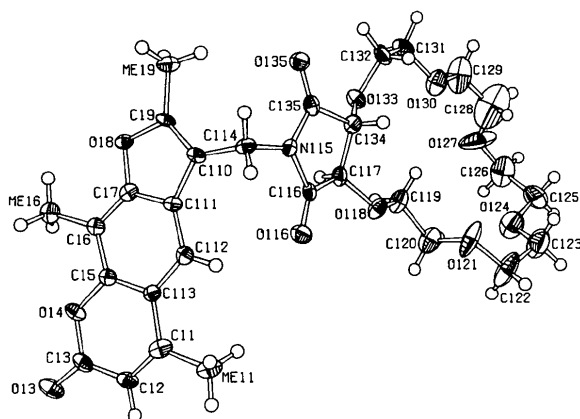


Fig. 1. View of molecule I in the crystal of the psoralen-imido-18-crown-6 compound showing the numbering scheme adopted. The H atoms are represented by spheres of arbitrary size. The ellipsoids are drawn at the 50% probability level.

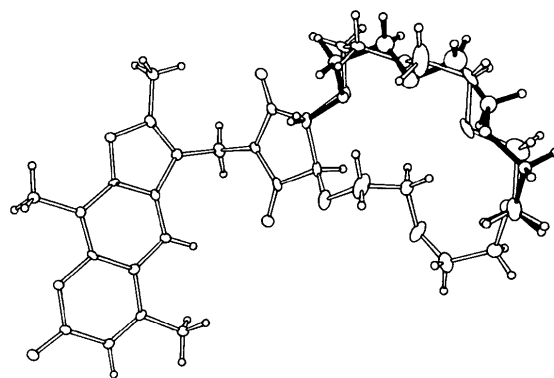


Fig. 2. Molecule II. The bonds of IIA have been darkened for easier identification.

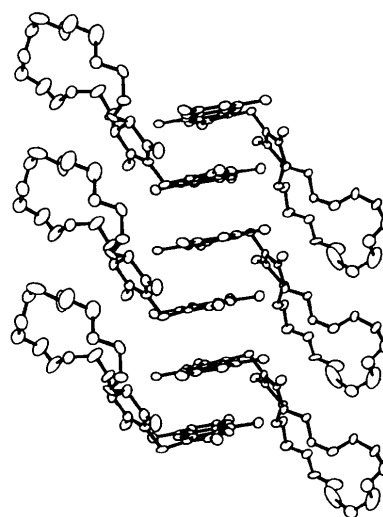


Fig. 3. View of the stacking arrangement of the psoralen parts found in the solid. H atoms and minor disorder omitted for clarity. Atoms drawn at the 30% probability level.

Discussion. There are two molecules in the asymmetric unit. Molecule I is well behaved while the 18-crown-6 part of molecule II is disordered over two sites with respective occupancies of 67% for IIA and 33% for IIB. The atomic numbering adopted is shown on molecule I in Fig. 1. Molecule II with the two orientations of the 18-crown-6 part is shown in Fig. 2. The mode of association of these molecules is shown in Fig. 3. The psoralen moieties in I and II are nearly centrosymmetrically related. This is not too surprising. The space group could have been $P2_1/c$ since of the 300 $h0l$ reflections, only 30 (10%) with l odd are significantly observed.

The bond distances and angles of the psoralen part are listed in Table 2. Those of the 18-crown-6 have been deposited. However, the torsion angles, reflecting the flexibility of the 18-crown-6, are compared in Table 3. A more revealing comparison is shown on the polar map of Fig. 4 (Ounsworth & Weiler, 1987).

This particular stacking arrangement of crown-ether and psoralen rings makes this molecule an interesting system to be studied in the presence of mono- and divalent cations. The presence of such ions should reduce the flexibility of the macrocyclic ring and increase the order in the packing. In this respect, suffice to mention the X-ray work on a chiral 18-crown-6 tetraamide whereby in the presence of K^+ ions, the molecular architecture resembles an ion channel with not only some K^+ ions in the

Table 2. Comparison of the interatomic distances (Å) and bond angles (°) for the psoralen part of molecules I and II with their e.s.d.'s

	Mol. I (x = 1)	Mol. II (x = 2)
C(x1)—Me(x1)	1.508 (10)	1.504 (10)
C(x1)—C(x2)	1.344 (8)	1.343 (8)
C(x1)—C(x13)	1.458 (10)	1.446 (10)
C(x2)—C(x3)	1.438 (10)	1.453 (10)
C(x3)—O(x3)	1.219 (7)	1.212 (7)
C(x3)—O(x4)	1.364 (8)	1.370 (8)
O(x4)—C(x5)	1.376 (7)	1.382 (6)
C(x5)—C(x6)	1.396 (10)	1.382 (9)
C(x5)—C(x13)	1.422 (9)	1.415 (9)
C(x6)—Me(x6)	1.514 (10)	1.503 (10)
C(x6)—C(x7)	1.383 (8)	1.394 (8)
C(x7)—O(x8)	1.365 (8)	1.372 (8)
C(x7)—C(x11)	1.407 (9)	1.396 (9)
O(x8)—C(x9)	1.386 (6)	1.406 (7)
C(x9)—Me(x9)	1.479 (9)	1.474 (10)
C(x9)—C(x10)	1.340 (10)	1.356 (11)
C(x10)—C(x11)	1.443 (8)	1.458 (8)
C(x10)—C(x14)	1.493 (9)	1.498 (9)
C(x11)—C(x12)	1.390 (10)	1.391 (10)
C(x12)—C(x13)	1.397 (8)	1.403 (8)
Me(x1)—C(x1)—C(x2)	121.2 (6)	118.8 (6)
Me(x1)—C(x1)—C(x13)	119.0 (6)	120.7 (6)
C(x2)—C(x1)—C(x13)	119.8 (6)	120.5 (6)
C(x1)—C(x2)—C(x3)	122.6 (6)	121.4 (6)
C(x2)—C(x3)—O(x3)	126.4 (6)	125.2 (6)
C(x2)—C(x3)—O(x4)	117.5 (6)	118.2 (6)
O(x3)—C(x3)—O(x4)	116.1 (6)	116.5 (6)
C(x3)—O(x4)—C(x5)	122.2 (5)	121.2 (5)
O(x4)—C(x5)—C(x6)	116.3 (5)	113.7 (5)
O(x4)—C(x5)—C(x13)	120.9 (5)	121.6 (5)
C(x6)—C(x5)—C(x13)	122.8 (6)	124.7 (6)
C(x5)—C(x6)—Me(x6)	121.3 (6)	123.0 (6)
C(x5)—C(x6)—C(x7)	115.1 (6)	113.9 (6)
Me(x6)—C(x6)—C(x7)	123.5 (6)	122.9 (6)
C(x6)—C(x7)—O(x8)	125.0 (6)	125.3 (6)
C(x6)—C(x7)—C(x11)	124.7 (6)	124.2 (6)
O(x8)—C(x7)—C(x11)	110.3 (5)	110.4 (5)
C(x7)—O(x8)—C(x9)	105.7 (5)	107.0 (5)
O(x8)—C(x9)—Me(x9)	115.3 (5)	114.8 (6)
O(x8)—C(x9)—C(x10)	112.4 (5)	109.8 (6)
Me(x9)—C(x9)—C(x10)	132.3 (6)	135.5 (6)
C(x9)—C(x10)—C(x11)	106.2 (6)	107.6 (6)
C(x9)—C(x10)—C(x14)	127.6 (6)	125.4 (6)
C(x11)—C(x10)—C(x14)	126.2 (6)	127.0 (6)
C(x7)—C(x11)—C(x10)	105.4 (5)	105.2 (5)
C(x7)—C(x11)—C(x12)	118.4 (6)	120.2 (6)
C(x10)—C(x11)—C(x12)	136.2 (6)	134.7 (6)
C(x11)—C(x12)—C(x13)	119.8 (6)	118.2 (6)
C(x1)—C(x13)—C(x5)	116.8 (6)	117.1 (6)
C(x1)—C(x13)—C(x12)	124.1 (6)	124.1 (6)
C(x5)—C(x13)—C(x12)	119.0 (6)	118.8 (6)

Table 3. Comparison of the torsion angles (°) of the crown portion of the psoralen-imido-18-crown-6 compound for molecules I and II

	Mol. I (x = 1)	Mol. II (x = 2)	
		A (67%)	B (33%)
C(x17)—O(x18)—C(x19)—C(x20)	-169.1 (6)	-70.5 (11)	
O(x18)—C(x19)—C(x20)—O(x21)	-69.0 (8)	-57.2 (13)	
C(x19)—C(x20)—O(x21)—C(x22)	-166.6 (6)	-99.5 (11)	
C(x20)—O(x21)—C(x22)—C(x23)	94.3 (8)	-70.3 (12)	
O(x21)—C(x22)—C(x23)—O(x24)	-60.4 (10)	61.0 (11)	
C(x22)—C(x23)—O(x24)—C(x25)	171.8 (8)	82.4 (10)	
C(x23)—O(x24)—C(x25)—C(x26)	-163.6 (8)	-168.2 (8)	-175.7 (13)
O(x24)—C(x25)—C(x26)—O(x27)	68.4 (10)	73.8 (10)	64.2 (19)
C(x25)—C(x26)—O(x27)—C(x28)	61.5 (14)	-170.5 (10)	-82.1 (20)
C(x26)—O(x27)—C(x28)—C(x29)	169.1 (9)	-175.9 (12)	-166.9 (21)
O(x27)—C(x28)—C(x29)—O(x30)	83.8 (12)	-85.5 (15)	-81.2 (27)
C(x28)—C(x29)—O(x30)—C(x31)	178.9 (8)	179.0 (12)	-156.5 (23)
C(x29)—O(x30)—C(x31)—C(x32)	-172.2 (6)	179.7 (10)	-175.1 (23)
O(x30)—C(x31)—C(x32)—O(x33)	-69.7 (7)	61.3 (11)	-66.9 (25)
C(x31)—C(x32)—O(x33)—C(x34)	151.5 (5)	77.5 (10)	167.3 (16)
C(x32)—O(x33)—C(x34)—C(x17)	-159.2 (5)	-161.4 (7)	-143.1 (13)
O(x33)—C(x34)—C(x17)—O(x18)	89.8 (7)	107.3 (7)	80.5 (10)
C(x34)—C(x17)—O(x18)—C(x19)	-73.4 (7)	-58.3 (9)	

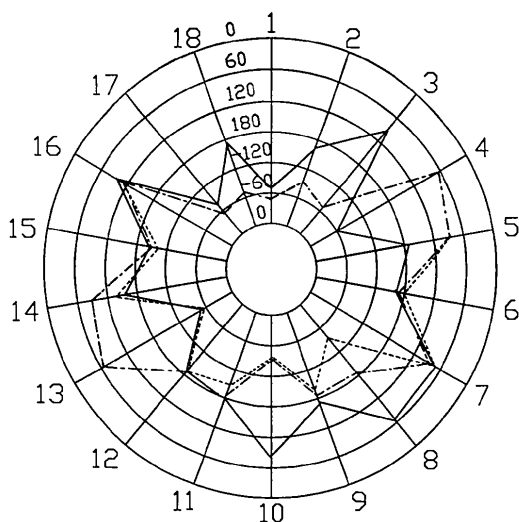


Fig. 4. Polar map showing the conformations of the 18-crown-6 moiety in I (—), IIA (---) and IIB (-.-).

We thank S. Cyr for preparing and recrystallizing a larger quantity of the imido-crown ether (3).

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crown cavity but some being sandwiched between two crown-ether rings (Behr, Lehn, Dock & Moras, 1985).

In our case, such sandwich-like disposition of the aromatic stacking domains and ion trapping domains could confer to this new crystalline material novel properties reminiscent of electrides and/or organic conductors (Dye, 1987). Furthermore, molecular channels are thought to be important in ion-exchange processes across membranes.

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Acta Cryst. (1991). **C47**, 1687–1689

Structures of Trimethyloxosulfonium Salts. I. The Iodide and the Bromide

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(Received 24 May 1990; accepted 18 December 1990)

Abstract. $[(\text{CH}_3)_3\text{SO}]\text{I}$, $M_r = 220.07$, orthorhombic, $Pnma$, $a = 11.289(3)$, $b = 7.701(2)$, $c = 8.298(2)$ Å, $V = 721.5(5)$ Å³, $Z = 4$, $D_x = 2.026$, $D_m = 2.0(1)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 4.56$ mm⁻¹, $F(000) = 416$, $T = 293$ K, final $R = 0.018$, $wR = 0.023$ for 528 independent observed reflections. $[(\text{CH}_3)_3\text{SO}]\text{Br}$, $M_r = 173.08$, orthorhombic, $Pnma$, $a = 10.978(2)$, $b = 7.462(2)$, $c = 8.062(2)$ Å, $V = 660.5(5)$ Å³, $Z = 4$, $D_x = 1.740$, $D_m = 1.71(5)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$, $\mu(\text{Mo } K\alpha) = 6.35$ mm⁻¹, $F(000) = 344$, $T = 293$ K, final $R = 0.018$, $wR = 0.019$ for 758 independent observed reflections. These two compounds have the same structure; a stacking of anions (I^- or Br^-) and pyramidal thiocations $(\text{CH}_3)_3\text{SO}^+$, which approximate closely to symmetry $3m$; the thiocation has only one symmetry plane (for $y = 0.25$ or 0.75) where the halogen atoms are also located.

Introduction. Very little is known about the structures of the trimethyloxosulfonium salts: only the structures of the perchlorate (Coulter, Gantzel & McCullough, 1963) and the fluoborate (Zimmerman, Barlow & McCullough, 1963) have been described at 293 K. Many other salts exist and may be easily prepared. In this first paper, we describe the structures of the iodide and the bromide.

Experimental. *The iodide.* Crystal obtained by recrystallization of the commercial product (Aldrich) in water, prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 2.0(1)$ Mg m⁻³. Crystal size $0.18 \times 0.20 \times 0.21$ mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Unit-cell constants from least-squares refinement of

25 reflections with $5 < \theta < 13^\circ$. Systematic absences $0kl$ ($k + l = 2n$) and $hk0$ ($h = 2n$). Space group $Pnma$ (No. 62) or $Pn2_1a$ (No. 33). $\omega/2\theta$ scan, scan width 1.2° . $1 < \theta < 30^\circ$. $-4 < h < 15$, $-6 < k < 11$, $-6 < l < 12$. Four orientation reference reflections (331, 400, 411, 442) every 200 scans, no significant variations. Four intensity reference reflections (331, 400, 601, 250) recorded every 2 h varied by -2.2% during 50.0 h; decay correction. 2045 measured reflections, 1648 with $I > 3\sigma(I)$. Lorentz and polarization corrections. Absorption corrections from ψ scans: relative transmission factor between 0.820 and 0.998. 528 reflections after averaging: $R_{\text{int}} = 0.017$. Crystal structure solved by direct methods with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), in $Pnma$. H atoms located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Extinction coefficient refined: $g = 1.5085 \times 10^{-6}$ (Stout & Jensen, 1968). Unit weights. 54 variables. Final refinement with 528 reflections gave $R = 0.018$, $wR = 0.023$ and $S = 1.109$. Maximum and minimum peak heights in final difference Fourier synthesis: 0.323 and -0.577 e Å⁻³; $\Delta/\sigma_{\text{max}} = 0$.

The bromide. The crystals were obtained by using the preparative method described elsewhere (de Brauer & Perret, to be published), prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 1.71(5)$ Mg m⁻³. Crystal size $0.20 \times 0.20 \times 0.21$ mm. Enraf–Nonius CAD-4 diffractometer used. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 14^\circ$. Systematic absences $0kl$ ($k + l = 2n$) and $hk0$ ($h = 2n$). Space group $Pnma$ (No. 62) or $Pn2_1a$ (No. 33). $\omega/2\theta$ scan, scan width