

Structure of Trimethyl[(*cis*-2-methyl-1,3-oxathiolan-5-yl)methyl]ammonium Iodide, $C_8H_{18}NOS^+I^-$

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Abstract. $M_r = 303.2$, monoclinic, $P2_1/c$, $a = 8.389$ (4), $b = 12.820$ (5), $c = 12.098$ (5) Å, $\beta = 102.7$ (1)°, $Z = 4$, $U = 1269.3$ Å³, $D_m = 1.58$ (floatation), $D_x = 1.586$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 2.68$ mm⁻¹. The structure has been solved from 1430 diffractometer-measured intensities and refined by full-matrix least squares to $R = 0.061$ ($R_w = 0.065$). The conformation of the molecule, described by the torsion angle N–C–C–O (+77°), is similar to that of L-(+)-muscarine.

Introduction. The simple cation acetylcholine (Me)₃N⁺–CH₂–CH₂–O–C(=O)–Me is an important neurotransmitter molecule (Barlow, 1968). The molecule is flexible: rotation about the single bonds C–C and C–O allows the molecule to assume different conformations of similar energy (Canepa, Pauling & Sörum, 1966; Liquori, Damiani & De Coen, 1968; Chothia & Pauling, 1968; Herdtklotz & Sass, 1970). One of the difficulties in determining the conformation of acetylcholine on its interaction with muscarinic nerve receptors has been the apparent absence of analogues with rigid conformations and high activity (Baker, Chothia, Pauling & Petcher, 1971). The crystal structure of the title compound (TMSO) has been determined as part of an investigation of the conformational properties of some muscarinic agents, which we are examining in an attempt to correlate molecular conformation and biological activity.

Experimental. Single crystals obtained by slow evaporation of a solution in absolute ethanol, under reduced constant pressure in a dry atmosphere; approximate unit-cell parameters estimated from preliminary Weissenberg and precession photographs, crystal $\sim 0.35 \times 0.35 \times 0.07$ mm, Philips PW 1100 four-circle diffractometer, graphite monochromator, $2\theta = 12.16^\circ$, accurate unit-cell parameters and crystal-orientation matrices (together with their estimated standard errors) obtained from least-squares refinement

of $2\theta, \omega, \chi$ and φ values of 20 carefully centred high-angle reflections; θ – 2θ scan, scan speed 0.03°s^{-1} , 2θ range 4 – 50° , two standard reflections (310, $3\bar{1}0$) every 180 min, 2224 data measured, 1430 with $I \geq 3\sigma(I)$, Lorentz and polarization corrections, intensities placed on an absolute scale by Wilson's method, experimental absorption correction applied (North, Phillips & Mathews, 1968); trial structure obtained by heavy-atom method and refined by full-matrix least-squares procedure, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 3.412[\sigma^2(F_o) + 0.0016 F_o^2]^{-1}$, adequacy of the weighting scheme confirmed by analysis of the variation of the mean $w(|F_o| - |F_c|)^2$ with $|F_o|$ and $\lambda^{-1} \sin \theta$, scattering factors from *International Tables for X-ray Crystallography* (1974), both real and imaginary components of anomalous dispersion included for iodine only (*International Tables for X-ray Crystallography*, 1974). The refinement was carried out allowing all non-H atoms to vibrate anisotropically. Although most of the H atoms could be located from a difference Fourier map, all H atoms were included in their calculated idealized positions (C–H = 1.0 Å), as a fixed contribution. Final conventional $R = 0.061$ ($R_w = 0.065$) for the 1430 observed reflections, $\dagger F(000) = 600$; calculations carried out on the CYBER 76 computer of 'CINECA' with the *SHELX 76* program for crystal-structure determination (Sheldrick, 1976).

Discussion. The final positional parameters are given in Table 1, \ddagger and interatomic distances and interbond angles with e.s.d.'s calculated from the full variance-covariance matrix are in Table 2.

A perspective view of the cation, with the atom-numbering scheme and selected intramolecular non-bonding distances, is presented in Fig. 1.

\dagger Lists of structure factors, anisotropic thermal parameters, least squares planes data, torsion angles and Fig. 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38098 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Interatomic distances and angles of the cation, as determined in this analysis, correspond within experimental error to those normally found for similar atomic contacts. The most relevant aspect of the structure of the molecule is the orientation of the oxathiolane ring with respect to the ammonium tetrahedral N. Therefore the molecular structure of TMSO is essentially a one-parameter problem as in the

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

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

	x	y	z	U_{eq}
I(1)	2994 (1)	3901 (1)	1640 (1)	74 (7)
S(1)	7018 (4)	4250 (3)	5817 (3)	59 (2)
O(1)	7861 (10)	4109 (6)	3881 (7)	51 (5)
N(1)	7949 (12)	5859 (8)	2060 (9)	49 (6)
C(1)	8171 (22)	4810 (12)	1595 (11)	78 (10)
C(2)	6246 (17)	6225 (13)	1588 (11)	62 (9)
C(3)	9114 (22)	6611 (15)	1698 (14)	79 (12)
C(4)	8296 (16)	5870 (9)	3340 (10)	47 (7)
C(5)	7285 (15)	5152 (10)	3890 (10)	47 (7)
C(6)	6953 (17)	3500 (11)	4506 (10)	57 (8)
C(7)	7676 (21)	2427 (11)	4729 (14)	74 (10)
C(8)	7441 (16)	5447 (11)	5138 (10)	53 (8)

Table 2. Final interatomic distances (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

N(1)—C(1)	1.485 (19)	C(5)—C(8)	1.535 (17)
N(1)—C(2)	1.493 (17)	C(8)—S(1)	1.812 (14)
N(1)—C(3)	1.505 (22)	S(1)—C(6)	1.844 (13)
N(1)—C(4)	1.512 (16)	C(6)—O(1)	1.419 (17)
C(4)—C(5)	1.502 (19)	C(6)—C(7)	1.504 (20)
C(5)—O(1)	1.422 (15)		
C(1)—N(1)—C(2)	109.2 (1.1)	C(4)—C(5)—C(8)	110.5 (1.0)
C(1)—N(1)—C(3)	109.1 (1.1)	C(5)—C(8)—S(1)	104.7 (9)
C(1)—N(1)—C(4)	112.6 (9)	C(6)—S(1)—C(8)	91.4 (6)
C(2)—N(1)—C(3)	108.4 (1.1)	S(1)—C(6)—O(1)	104.7 (8)
C(2)—N(1)—C(4)	109.9 (1.0)	C(6)—O(1)—C(5)	106.9 (9)
C(3)—N(1)—C(4)	107.5 (1.0)	O(1)—C(5)—C(8)	106.5 (1.0)
N(1)—C(4)—C(5)	116.6 (1.0)	S(1)—C(6)—C(7)	112.8 (9)
C(4)—C(5)—O(1)	110.3 (1.0)	C(7)—C(6)—O(1)	110.9 (1.2)

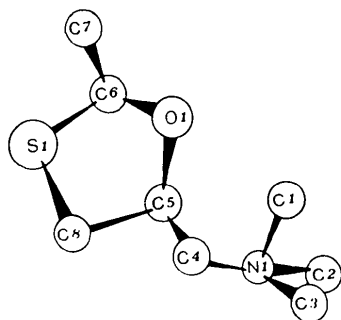


Fig. 1. Perspective view of the cation with the atom-numbering scheme. Selected intramolecular non-bonding distances are C(1)...O(1) 2.97 (2), N(1)...O(1) 3.16 (1) and N(1)...C(7) 3.49 (2) \AA .

structure of L-(+)-muscarine (Jellinek, 1957). That one parameter is the N(1)—C(4)—C(5)—O(1) torsion angle. In principle there are several other torsion angles, as parameters, but all of these have threefold symmetry and all are expected to have $\tau = \pm 60$ or 180° . $\tau[\text{N}(1)\text{—C}(4)\text{—C}(5)\text{—O}(1)]$ is $+77^\circ$ in TMSO, very similar to the $+73^\circ$ in L-(+)-muscarine. The synclinal value for this torsion angle is generally found in $\text{N}^+\text{—C—O}$ systems (Sundaralingam, 1968; Baker *et al.*, 1971). A careful X-ray structure analysis of xylocholine bromide [(2,6-dimethylphenyl)choline bromide] (Coggon, Mcphail & Roe, 1969) has shown that none of the H atoms on C(1) are in positions to form hydrogen bonds with O(1) and therefore the stability of synclinal $\text{N}^+\text{—C—O}$ conformations is a result of electrostatic attraction between the positively charged quaternary group and the electronegative O atom. A similar conclusion was reached in the neutron diffraction study of erythro-acetyl- α,β -dimethylcholine (Brennan, Ross, Hamilton & Shefter, 1970). In TMSO the C(1)...O(1) and N(1)...O(1) distances, 2.97 (2) and 3.16 (1) \AA , do not differ from those in L-(+)-muscarine (2.87 and 3.07 \AA) (Jellinek, 1957) and in acetylcholine (3.02 and 3.29 \AA) (Canepa *et al.*, 1966). The other torsion-angle parameter $\tau[\text{C}(5)\text{—C}(4)\text{—N}(1)\text{—C}(3)]$ is -179° in TMSO and -175° in L-(+)-muscarine. In both cases this compares well with the 180° expected in an antiplanar bond.

It is evident that the five-membered ring C(5)—O(1)—C(6)—S(1)—C(8) cannot be planar. In particular, the puckering amplitude Q , which defines quantitatively the degree of puckering, is 0.457 (12) \AA (Cremer & Pople, 1975). In addition, there is a pseudo mirror plane through O(1) and C(8)—S(1) and a pseudo twofold axis through S(1) and C(5)—O(1). Fig. 2* and the asymmetry parameters of Duax, Weeks & Rohrer

*See previous footnote.

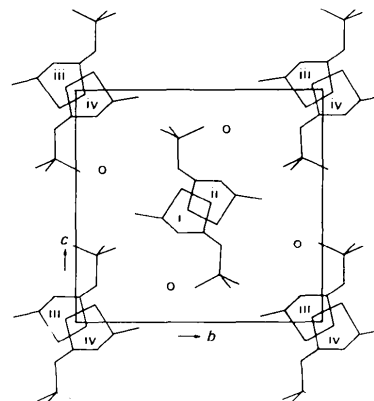


Fig. 3. The crystal structure projected down *a*. The symbols inside the ring represent the equivalent positions in space group $P2_1/c$ (No. 14) |(i) x, y, z ; (ii) $\bar{x}, \bar{y}, \bar{z}$; (iii) $\bar{x}_{1/2} + y_{1/2} - z$; (iv) $x_{1/2} - y_{1/2} + z$].

(1976), $\Delta C_s^2 = 14.5 (1.0)^\circ$ and $\Delta C_s^0 = 10.0 (1.0)^\circ$, indicate that the conformation of the ring is twisted and between 'half-chair' (C₂) and 'envelope' (C_s). Finally, C(8) is $-0.14 (1) \text{ \AA}$ out of the plane of C(5)–C(6)–S(1) on the same side as the methyl and the quaternary group.

The crystal packing, as viewed down **a**, is depicted in Fig. 3 and it is mainly determined by Coulombic and van der Waals forces. The intermolecular non-bonding distances are as expected for standard van der Waals values. The environment of the I⁻ anions is approximately tetrahedral with I⁻...N⁺ distances ranging from 4.3 to 5.0 Å.

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Tetramethylammonium Benzotriazolide, C₄H₁₂N⁺.C₆H₄N₃⁻

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Abstract. $M_r = 192.27$, orthorhombic, $P2_12_12_1$, $a = 8.342 (2)$, $b = 10.797 (2)$, $c = 12.265 (7) \text{ \AA}$, $Z = 4$, $V = 1104.7 (7) \text{ \AA}^3$, $D_x = 1.156 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$, $\mu(\text{Cu } K\alpha) = 0.590 \text{ mm}^{-1}$, final $R = 0.050$ for 941 reflections. The benzotriazolide ion is planar and has approximate *mm* symmetry.

Introduction. Benzotriazole is receiving increasing interest because of the biological activity of some of its derivatives on the one hand (Sparatore, La Rotonda, Paglietti, Ramundo, Silipo & Vittoria, 1978), and because of its use as a corrosion inhibitor for Cu and Cu alloys on the other (Søtofte & Nielsen, 1981a,b,c; Himes, Mighell & Siedle, 1981).

In order to gain a better knowledge of this heterocycle we have carried out X-ray investigations of crystal structures containing the benzotriazol-1-yl and -2-yl residues and the benzotriazolium cation (Giordano & Zagari, 1977, 1978; Giordano 1980). Here the structure of the benzotriazolide anion is presented.

Experimental. Deliquescent elongated prisms obtained by evaporation over P₂O₅ of an equimolar solution of

benzotriazole and tetramethylammonium hydroxide, $0.2 \times 0.3 \times 0.2 \text{ mm}$, Lindemann capillary tube, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$, three monitoring reflections, 1349 independent with $\theta < 75^\circ$, 941 with $I > 3\sigma(I)$, Lp correction, absorption ignored; direct methods (*MULTAN 78*; Main, Lessinger, Woolfson, Germain & Declercq, 1978), anisotropic full matrix, H (from ΔF synthesis) isotropic, final $R = 0.050$, $R_w = 0.064$, $w = 1/\sigma^2(F_o)$,* secondary-extinction value $G = 4.6(0.7) \times 10^{-6}$, $F(000) = 416$, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), PDP 11/34 computer, Enraf–Nonius SDP software.

Discussion. The final atomic parameters are listed in Table 1. The dimensions of the benzotriazolide and tetramethylammonium ions are shown in Fig. 1, together with the atomic numbering scheme. The benzotriazolide anion has approximate *mm* symmetry.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38145 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.