# Structure of Trimethyl[(*cis*-5-methyl-1-oxolan-2-yl)methyl]ammonium Iodide, $C_9H_{20}NO^+.I^-$

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**Abstract.** $M_r = 285\cdot2$, orthorhombic, $Pna2_1$, $a = 14\cdot688$ (5), $b = 9\cdot954$ (6), $c = 8\cdot752$ (6) Å, $Z = 4$, $U = 1279\cdot6$ Å$^3$, $D_m = 1\cdot475$ (flotation), $D_x = 1\cdot480$ Mg m$^{-3}$, $T = 298$ K, $\lambda$(Mo $K\alpha$) $= 0\cdot7107$ Å, $\mu$(Mo $K\alpha$) $= 2\cdot44$ mm$^{-1}$, $F(000) = 568$. $R = 0\cdot064$ ($R_w = 0\cdot071$) for 922 observed reflections. The overall conformation of the molecule, described by the torsion angle N—C—C—O [68 (2)°], is similar to that of L-(+)-muscarine.

**Introduction.** One of the difficulties in determining the effect of 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 (TMO) has been determined as part of an investigation of the conformational properties of some muscarinic agents, 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 atomosphere; approximate unit-cell parameters from preliminary Weissenberg and precession photographs, crystal ~0·4 × 0·4 × 0·6 mm, Philips PW 1100 four-circle diffractometer, graphite monochromator; accurate unit-cell parameters and crystal-orientation matrices (with e.s.d.'s) from least-squares refinement of the $2\theta$, $\omega$, $\chi$ and $\varphi$ values of 20 carefully centred high-angle reflections; $\theta$–$2\theta$ scan, scan speed $0\cdot03°$s$^{-1}$, scan width $1\cdot20°$, $2\theta$ range 4–50°, two standard reflections (411, $\bar{4}$1$\bar{1}$) every 180 min, 1184 data measured, 922 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 and Mathews, 1968); trial structure obtained by the heavy-atom method and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$,

$w = 4\cdot314[\sigma^2(F_o) + 0\cdot00048\,F_o^2]^{-1}$; adequacy of the weighting scheme confirmed by analysis of the variation of the mean $w(|F_o| - |F_c|)^2$ with $|F_o|$ and sin $\theta/\lambda$, scattering factors from *International Tables for X-ray Crystallography* (1974); both real and imaginary components of anomalous dispersion were included for iodine only. The refinement was carried out allowing the I$^-$ anion to vibrate anisotropically; all the atoms of the cation were assigned isotropic thermal parameters. 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 $= 1\cdot0$ Å), as a fixed contribution. Final conventional $R = 0\cdot064$ ($R_w = 0\cdot071$) for the 922 observed reflections; maximum residual electron density in final difference map $\pm 0\cdot4$ e Å$^{-3}$; calculations carried out on the Cyber 76 computer of 'CINECA' with *SHELX*76 (Sheldrick, 1976).

**Discussion.** The final atomic parameters are given in Table 1,† 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.

Interatomic distances and angles in the cation correspond within experimental error to expected values, apart from C(6)–C(7) and C(8)–C(9) which seem unusually short. The most relevant aspect of the structure of the molecule is the orientation of the oxolane ring with respect to the tetrahedral N atom of the ammonium group. Therefore the molecular structure of TMO can be considered essentially a one-parameter problem as in L-(+)-muscarine (Jellinek, 1957). The one parameter is the N(1)–C(4)–C(5)–

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† Lists of structure factors, least-squares-planes' data, torsion angles, calculated H-atom coordinates and Fig. 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38377 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (× 10⁴) *and temperature factors* ($Å^2 × 10^3$) *with e.s.d.'s in parentheses*

|        | x         | y         | z         | U       |
|--------|-----------|-----------|-----------|---------|
| C(1)   | 2470 (13) | 4331 (18) | 4682 (22) | 102 (4) |
| C(2)   | 3438 (19) | 5709 (23) | 6277 (23) | 106 (5) |
| C(3)   | 3439 (19) | 6131 (21) | 3503 (26) | 106 (5) |
| C(4)   | 4217 (15) | 4167 (20) | 4414 (20) | 91 (4)  |
| C(5)   | 4287 (15) | 3042 (17) | 5505 (21) | 95 (4)  |
| C(6)   | 3992 (14) | 726 (21)  | 5382 (23) | 106 (5) |
| C(7)   | 3539 (18) | −152 (21) | 4397 (21) | 113 (4) |
| C(8)   | 5008 (14) | 995 (18)  | 5553 (22) | 108 (4) |
| C(9)   | 5216 (14) | 2354 (18) | 5367 (23) | 101 (4) |
| O(1)   | 3598 (8)  | 2043 (9)  | 5394 (14) | 84 (3)  |
| N(1)   | 3371 (9)  | 5077 (12) | 4741 (17) | 77 (3)  |
| I      | 8920 (1)  | 2005 (1)  | 0         | *       |

\* Anisotropic temperature factors

| $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|----------|----------|----------|----------|----------|----------|
| 78 (1)   | 83 (1)   | 106 (1)  | 1 (2)    | 1 (2)    | 18 (2)   |

Table 2. *Final interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

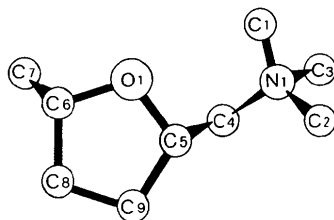| N(1)–C(1) | 1·52 (2) | C(1)–N(1)–C(2) | 107 (1) |
|-----------|----------|----------------|---------|
| N(1)–C(2) | 1·49 (2) | C(1)–N(1)–C(3) | 112 (1) |
| N(1)–C(3) | 1·51 (2) | C(1)–N(1)–C(4) | 114 (1) |
| N(1)–C(4) | 1·56 (2) | C(2)–N(1)–C(3) | 110 (1) |
| C(4)–C(5) | 1·47 (2) | C(2)–N(1)–C(4) | 111 (1) |
| C(5)–C(9) | 1·53 (3) | C(3)–N(1)–C(4) | 103 (1) |
| C(5)–O(1) | 1·42 (2) | N(1)–C(4)–C(5) | 112 (1) |
| O(1)–C(6) | 1·43 (2) | C(4)–C(5)–C(9) | 110 (1) |
| C(6)–C(7) | 1·40 (2) | C(4)–C(5)–O(1) | 116 (1) |
| C(6)–C(8) | 1·52 (3) | C(5)–O(1)–C(6) | 111 (1) |
| C(8)–C(9) | 1·40 (2) | O(1)–C(6)–C(7) | 113 (2) |
|           |          | O(1)–C(6)–C(8) | 104 (1) |
|           |          | C(7)–C(6)–C(8) | 130 (2) |
|           |          | C(6)–C(8)–C(9) | 112 (2) |
|           |          | C(8)–C(9)–C(5) | 103 (1) |
|           |          | C(9)–C(5)–O(1) | 108 (1) |



Fig. 1. Perspective view of the cation with the atom-numbering scheme. Selected intramolecular non-bonding distances are: C(1)···O(1) 2·88 (2), N(1)···O(1) 3·09 (1) and N(1)···C(7) 5·22 (2) Å.

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 $\tau = ± 60°$ or 180°. $\tau[N(1)–C(4)–C(5)–O(1)]$ is +68 (2)° in TMO and +73° in L-(+)-muscarine. The synclinal value for this torsion angle is generally found in N⁺–C–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 a position to

form H bonds with O(1) and therefore the stability of synclinal N⁺–C–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 TMO the C(1)···O(1) and N(1)···O(1) distances, 2·88 (2) and 3·09 (1) Å, are very close to those in L-(+)-muscarine (2·87 and 3·07 Å) (Jellinek, 1957) and in acetylcholine bromide (3·02 and 3·29 Å) (Canepa, Pauling & Sörum, 1966). The other torsion-angle parameter $\tau[C(5)–C(4)–N(1)–C(3)]$ is 180° in TMO [−175° in L-(+)-muscarine].

The five-membered ring C(5)–O(1)–C(6)–C(8)–C(9) is approximately planar, and the puckering amplitude $Q$ (Cremer & Pople, 1975), which defines quantitatively the degree of puckering, is low, 0·14 (2) Å. In addition also the asymmetry parameters $ΔC_s$ and $ΔC_2$ (Duax, Weeks & Rohrer, 1976), which measure the degree of departure from ideal symmetry at any of the possible symmetry locations, are always low (Fig. 2).*

The crystal packing, as viewed along c, is depicted in Fig. 3; it is mainly determined by Coulombic and van der Waals forces. The intermolecular non-bonding distances correspond to standard van der Waals values. The environment of the I⁻ anions is approximately tetrahedral with I⁻···N⁺ distances ranging from 4·4 to 5·1 Å.
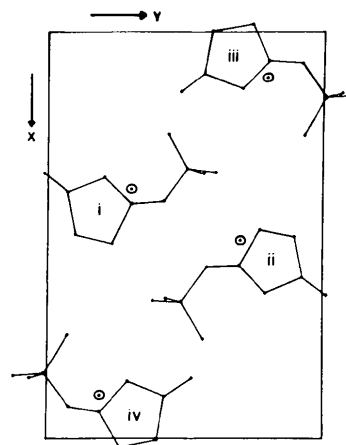
\* See deposition footnote.



Fig. 3. The crystal structure projected along c. The symbols inside the ring represent the equivalent positions (i) x, y, z; (ii) $\bar{x}, \bar{y}, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z$.

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# Structures of Substituted Perfluoropolyphenyls. III. Structure of 1-Bromo-4,5,6-trifluoro-2,3-bis(pentafluorophenyl)benzene, $C_{18}BrF_{13}$

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**Abstract.** $M_r = 543 \cdot 081$, triclinic, $P\bar{1}$, $a = 14 \cdot 671$ (5), $b = 10 \cdot 547$ (6), $c = 7 \cdot 29$ (4) Å, $\alpha = 78 \cdot 0$ (5), $\beta = 95 \cdot 2$ (5), $\gamma = 127 \cdot 4$ (5)°, $U = 875 \cdot 85$ Å³, $Z = 2$, $D_m$ (pycnometric) $= 2 \cdot 041$, $D_x = 2 \cdot 060$ g cm⁻³, $\lambda(\text{Cu}\,K\alpha) = 1 \cdot 5418$ Å, $\mu = 4 \cdot 930$ mm⁻¹, $F(000) = 520$, measurement temperature, $T = 293$ K. $R = 0 \cdot 083$ for 1576 observed reflexions with $I > 3\sigma$ ($I$). The dihedral angles between the central phenyl ring and those ortho and meta to bromine are $65 \cdot 6$ (15) and $63 \cdot 3$ (11)°, respectively. The corresponding inter-ring bond lengths are $1 \cdot 49$ (2) and $1 \cdot 50$ (2) Å (uncorrected for thermal libration).

**Introduction.** The title compound (I) and its isomer (II) have been synthesized by Cohen, Tomlinson, Wiles & Massey (1968) from 2-lithiononafluorobiphenyl and (pentafluorophenyl)lithium. They proposed an aryne mechanism for the reaction, elimination of LiF from 2-lithiononafluorobiphenyl giving 1-pentafluorophenyl-2,3,4-trifluorobenzyne. Addition of (pentafluorophenyl)-lithium to this aryne yields 1-lithio-4,5,6-trifluoro-2,3-bis(pentafluorophenyl)benzene (III) and 1-lithio-3,4,5-trifluoro-2,6-bis(pentafluorophenyl)benzene (IV). Li–Br exchange with (III) and (IV) in the presence of 2-bromononafluorobiphenyl produces isomers (I) and (II).
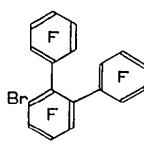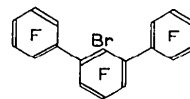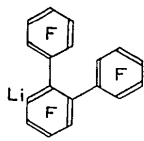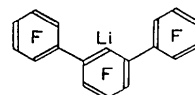


(I)  (II)  (III)  (IV)

The evidence for this mechanism has been strengthened by the confirmation of the structure of (II) (Bowen Jones & Brown, 1980). The structure of its isomer (I) is now reported.

This analysis is also part of a series of studies on the correlation between inter-ring bond lengths and dihedral angles in substituted perfluoropolyphenyls. No such correlation has been found in substituted perfluorobiphenyls (Goodhand, Hamor & Hamor, 1978; Bowen Jones & Brown, 1982).