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Structure of *cis*-2-Methyl-4-tosyloxymethyl-1,3-dioxolane

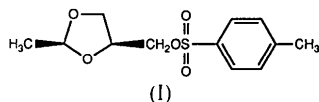
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Abstract. $C_{12}H_{16}O_5S$, $M_r = 272.3$, orthorhombic, *Pbca*, $a = 20.301$ (5), $b = 8.952$ (2), $c = 14.707$ (6) Å, $V = 2673$ (2) Å³, $Z = 8$, $D_x(105\text{ K}) = 1.353\text{ Mg m}^{-3}$, m.p. (hot-stage microscope) 339.5–340.5 K (uncorrected), $\lambda(\text{Mo } K\alpha) = 0.71073\text{ Å}$, $\mu = 0.240\text{ mm}^{-1}$, $F(000) = 1152$, $T = 105\text{ K}$, $R = 0.047$ for 764 observed reflections [$I \geq 3\sigma(I)$]. The conformation of the 1,3-dioxolane ring is a distorted envelope, E_2 , with the pseudo-rotational parameters $P = 131.3$ (7)° and $\theta_m = 38.7$ (4)°. The five-membered ring is more puckered than expected from *ab initio* calculations [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358], but the overall conformation is a favoured low-energy form. The tosyloxymethyl group adopts a conformation with $\tau(\text{O8—S9—C21—C26}) = \pm 89.3$ (6)°. This is the usual orientation of the tosyloxymethyl group, illustrated by a search in the *Cambridge Structural Database* (1991, version 4.4). Crystal packing is governed by electrostatic interactions and van der Waals contacts.

Experimental. The title compound (I) was prepared by the method described by Triggle & Belleau (1962). Single crystals were obtained by slow cooling of a saturated hot solution in toluene. Intensity data was



sampled from a crystal of size $0.05 \times 0.20 \times 0.30\text{ mm}$ on an Enraf–Nonius CAD-4 diffractometer with low-temperature device. Graphite-monochromated Mo $K\alpha$ radiation was used. Temperature was recorded with a thermocouple, variation within 1 K. Cell parameters and orientation matrix were

determined from 17 reflections ($11.47 \leq \theta \leq 18.48^\circ$). No corrections for absorption were performed. Three intensity control reflections measured every 10^4 s showed no systematic variation. ω scan, $\theta_{\text{max}} = 23^\circ$, range of *hkl* $-22 \leq h \leq 22$, $0 \leq k \leq 9$, $-16 \leq l \leq 16$. 4993 reflections were measured of which 1851 were unique and 1087 unobserved [$I < 3\sigma(I)$], $R_{\text{int}} = 0.031$ (on *I*).

All non-H atoms were localized by direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, German, Declercq & Woolfson, 1980). The positions of all H atoms were observed in the $\Delta\rho$ map in expected positions. Structure refinement on *F* (positional parameters for all non-H atoms, anisotropic displacement parameters for eight non-H atoms, isotropic displacement parameters for the remaining ten non-H atoms, H atoms fixed) by least squares, $w^{-1} = \sigma^2(F_o) + \frac{1}{4}(0.08F_o)^2$, $R = 0.047$, $wR = 0.063$ for 764 observed reflections [$I \geq 3\sigma(I)$] and 113 variables. $S = 1.19$, $(\Delta/\sigma)_{\text{max}} = 0.02$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.53/-0.24\text{ e Å}^{-3}$. Atomic scattering factors for uncharged atoms were used as implemented in the *SDP Structure Determination Package* (B. A. Frenz & Associates, Inc., 1982), which was used for all calculations (including *MULTAN80*). Final atomic coordinates and displacement parameters are listed in Table 1.* The bond lengths, bond angles, selected torsion angles and pseudo-rotational parameters involving the non-H atoms are listed in Table 2. Fig.

* Lists of structure factors, anisotropic displacement parameters for eight non-H atoms, atomic coordinates for H atoms and information on selected intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54952 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0261]

Table 1. Fractional atomic coordinates and isotropic and equivalent isotropic displacement parameters (Å²)

Equivalent isotropic displacement parameters for C6, C27, S9 and all O atoms, $B_{eq} = (4/3)\sum_i \beta_j \mathbf{a}_i \cdot \mathbf{a}_j$; all other C atoms refined with isotropic displacement parameters.

	x	y	z	B_{iso}/B_{eq}
O1	0.3747 (2)	0.2539 (5)	0.3952 (4)	3.3 (1)
C2	0.3497 (3)	0.1140 (8)	0.4174 (5)	3.4 (2)
O3	0.2939 (2)	0.0923 (5)	0.3615 (4)	3.1 (1)
C4	0.2638 (3)	0.2374 (7)	0.3536 (5)	2.6 (1)
C5	0.3183 (4)	0.3459 (8)	0.3802 (5)	3.2 (2)
C6	0.3994 (4)	-0.0070 (7)	0.3993 (6)	3.3 (2)
C7	0.2431 (3)	0.2596 (8)	0.2562 (5)	2.8 (1)
O8	0.1920 (2)	0.1486 (5)	0.2384 (3)	2.9 (1)
S9	0.1642 (1)	0.1352 (2)	0.1389 (1)	2.77 (3)
O10	0.2172 (2)	0.1434 (5)	0.0760 (3)	3.1 (1)
O11	0.1228 (3)	0.0058 (5)	0.1420 (4)	4.1 (1)
C21	0.1155 (3)	0.2952 (7)	0.1275 (4)	2.1 (1)
C22	0.0492 (4)	0.2900 (9)	0.1525 (6)	3.5 (2)
C23	0.0137 (4)	0.4218 (8)	0.1450 (5)	3.9 (2)
C24	0.0401 (4)	0.5542 (9)	0.1169 (5)	3.6 (2)
C25	0.1061 (4)	0.5545 (8)	0.0935 (5)	3.2 (2)
C26	0.1433 (3)	0.4269 (7)	0.0977 (5)	2.3 (1)
C27	-0.0015 (4)	0.694 (1)	0.1083 (6)	5.9 (2)

Table 2. Bond lengths (Å), bond angles (°), selected torsion angles (°) and pseudo-rotational parameters (°)

O1—C2	1.390 (9)	S9—O11	1.431 (5)
O1—C5	1.426 (8)	S9—C21	1.748 (6)
C2—O3	1.414 (9)	C21—C22	1.40 (1)
C2—C6	1.50 (1)	C22—C23	1.39 (1)
O3—C4	1.440 (8)	C23—C24	1.37 (1)
C4—C5	1.52 (1)	C24—C25	1.38 (1)
C4—C7	1.51 (1)	C25—C26	1.37 (1)
C7—O8	1.460 (8)	C26—C21	1.380 (9)
O8—S9	1.573 (5)	C24—C27	1.52 (1)
S9—O10	1.422 (5)		
C2—O1—C5	105.4 (5)	O10—S9—O11	120.5 (3)
O1—C5—C4	104.8 (5)	O10—S9—C21	108.9 (3)
O1—C2—O3	106.2 (6)	O11—S9—C21	109.5 (3)
O1—C2—C6	111.2 (6)	S9—C21—C22	119.5 (5)
O3—C2—C6	109.6 (6)	S9—C21—C26	119.9 (5)
C2—O3—C4	105.2 (5)	C22—C21—C26	120.5 (6)
O3—C4—C5	104.3 (5)	C21—C22—C23	116.9 (7)
O3—C4—C7	108.3 (6)	C22—C23—C24	124.0 (7)
C5—C4—C7	111.3 (6)	C23—C24—C25	117.2 (7)
C4—C7—O8	106.2 (5)	C23—C24—C27	121.6 (7)
C7—O8—S9	118.2 (4)	C25—C24—C27	121.2 (7)
O8—S9—O10	109.2 (3)	C24—C25—C26	121.4 (7)
O8—S9—O11	104.0 (3)	C21—C26—C25	120.0 (6)
O8—S9—C21	103.3 (3)		
Dioxolane ring		Tosyloxymethyl group	
C2—O1—C5—C4	-25.0 (7)	O3—C4—C7—O8	65.0 (6)
O3—C4—C5—O1	3.4 (7)	C4—C7—O8—S9	-175.2 (4)
C2—O3—C4—C5	19.0 (7)	C7—O8—S9—C21	-73.3 (5)
O1—C2—O3—C4	-36.0 (7)	O8—S9—C21—C22	-89.3 (6)
C5—O1—C2—O3	38.4 (7)	O8—S9—C21—C26	87.8 (6)

Pseudorotational parameters (reference bond O1—C5) (Rao, Westhof & Sundaralingam, 1981)

Phase $P = 131.3 (7)$
Amplitude $\theta_m = 38.7 (4)$

1 shows the molecule with displacement ellipsoids and atomic numbering. Fig. 2 presents the crystal packing.

Related literature. The present structure determination is one in a series for compounds which have a five-membered ring in the molecule (Frydenvang & Jensen, 1990, 1992). The title compound is an intermediate in the synthesis of the iodide salt of the muscarinic agonist, 2-methyl-4-*N,N,N*-trimethylammoniummethyl-1,3-dioxolane, described by

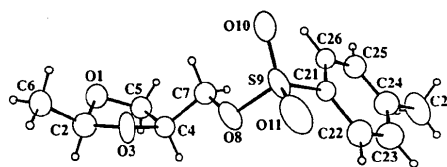


Fig. 1. ORTEP drawing (Johnson, 1976) of the title compound with the atom-labelling scheme. The molecule is shown with displacement ellipsoids at the 50% probability level.

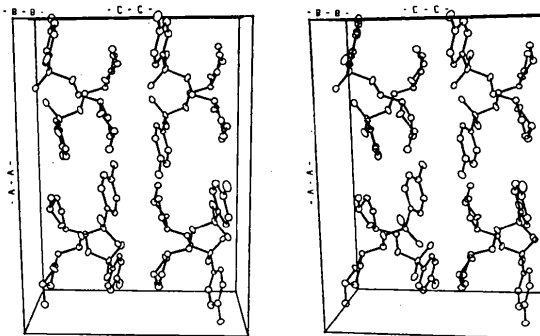


Fig. 2. Stereo drawing of the crystal packing. The axis directions are *c* horizontal, *a* vertical and *b* into the plane of the paper.

Triggle & Belleau (1962). A crystal structure of this muscarinic agonist has been published (Pauling & Petcher, 1971). This crystal-structure determination is based on very few observed reflections. The same is the case for the present structure, although the data were sampled at low-temperature. The two structures are therefore not very well determined, and probably different ring conformations are present in the crystals. This indicates that the dioxolane ring is very flexible. The *Cambridge Structural Database* (1991, version 4.4) has been examined for other compounds containing a dioxolane ring, and disorder in the dioxolane ring fragment was observed for several of these compounds (Lagersted, Frydenvang & Jensen, 1992).

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Structure of Choline Picrate

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Abstract. $C_5H_{14}NO^+ \cdot C_6H_2N_3O_7^-$, $M_r = 332.2$, monoclinic, $P2_1/n$, $a = 6.7895$ (9), $b = 22.054$ (2), $c = 9.713$ (1) Å, $\beta = 103.50$ (1)°, $V = 1414.2$ (5) Å³, $Z = 4$, D_x (105 K) = 1.561 Mg m⁻³, m.p. (hot-stage microscope) 516–518 K (corrected), $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.116$ mm⁻¹, $F(000) = 696$, $T = 105$ K, $R = 0.039$ for 2581 observed reflections [$I \geq 3\sigma(I)$]. The choline ion adopts a folded conformation, $\tau(\text{O—C—C—N}) = \pm 90.1$ (1)°. Strands of choline ions are formed *via* C··O contacts of length 3.305 (2) Å [C9··O4 ($x - 1, y, z$)] oriented along the a axis. Only weaker contacts are observed between parallel strands, which together form layers perpendicular to the b axis. The picrate ions are stacked in columns along the a axis with an average distance of 3.263 Å between the benzene rings. The parallel columns of picrate ions form layers perpendicular to the b axis. The picrate ions are not stacked exactly on top of each other; the shift releases strain. One nitro group overlaps the neighbouring benzene ring. The other nitro group close to the phenolate O atom makes an angle of 40.35 (4)° to the plane of the benzene ring, and is found on the outside of the column. The choline hydroxy group donates a hydrogen bond [O4··O21 2.781 (1) Å] to the phenolate O atom of the picrate ion. Many weak contacts, shorter than the sum of the van der Waals radii, are found involving the quaternary ammonium group and O atoms of the picrate ion.

Experimental. Choline picrate was prepared following *Pharmacopoea Nordica, Editio Danica* (1963). Single crystals were obtained by slow cooling of a saturated hot ethanol–water solution. Crystal size 0.1 × 0.2 × 0.4 mm. Intensity data were sampled on an Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature device, using graphite-

Table 1. Atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	x	y	z	B_{eq}
O4	0.4383 (2)	0.23339 (4)	-0.0540 (1)	2.05 (2)
C5	0.2444 (2)	0.25310 (6)	-0.1306 (1)	1.68 (2)
C6	0.2051 (2)	0.31654 (6)	-0.0839 (1)	1.47 (2)
N7	0.1020 (2)	0.32010 (5)	0.0388 (1)	1.24 (2)
C8	0.2104 (2)	0.28263 (6)	0.1613 (1)	1.76 (2)
C9	-0.1142 (2)	0.29968 (6)	-0.0063 (1)	1.68 (2)
C10	0.1048 (2)	0.38522 (6)	0.0848 (1)	1.62 (2)
C21	0.2846 (2)	0.06509 (6)	-0.1272 (1)	1.35 (2)
C22	0.2023 (2)	0.02199 (6)	-0.2398 (1)	1.25 (2)
C23	0.1551 (2)	-0.03724 (6)	-0.2209 (1)	1.40 (2)
C24	0.1748 (2)	-0.05805 (6)	-0.0827 (1)	1.43 (2)
C25	0.2370 (2)	-0.01983 (6)	0.0325 (1)	1.52 (2)
C26	0.2868 (2)	0.03943 (6)	0.0115 (1)	1.45 (2)
O21	0.3510 (2)	0.11557 (4)	-0.15114 (9)	1.91 (2)
N22	0.1750 (2)	0.04245 (5)	-0.3861 (1)	1.42 (2)
O221	0.1035 (2)	0.09327 (4)	-0.4167 (1)	1.88 (2)
O222	0.2219 (2)	0.00755 (4)	-0.47176 (9)	1.94 (2)
N24	0.1234 (2)	-0.12023 (5)	-0.0601 (1)	1.82 (2)
O241	0.0789 (2)	-0.15417 (4)	-0.1638 (1)	2.62 (2)
O242	0.1254 (2)	-0.13671 (5)	0.0619 (1)	2.50 (2)
N26	0.3477 (2)	0.07652 (6)	0.1379 (1)	1.82 (2)
O261	0.3618 (2)	0.05255 (6)	0.2539 (1)	3.43 (3)
O262	0.3811 (2)	0.13041 (5)	0.1258 (1)	3.58 (3)

monochromated Cu $K\alpha$ radiation. Temperature, recorded with a thermocouple, showed variation within 1 K. Cell parameters and orientation matrix were determined from 18 reflections ($38.96 \leq \theta \leq 45.10^\circ$). No corrections for absorption were made. Three intensity control reflections were measured every 10⁴ s and decay (-4.3% in 130 h) corrections were applied. $\omega/2\theta$ scan, $\theta_{\max} = 75^\circ$, range of hkl : $-8 \leq h \leq 8$, $-27 \leq k \leq 27$, $-12 \leq l \leq 11$. 7720 reflections were measured, of which 2950 were unique and 369 unobserved [$I < 3\sigma(I)$]; $R_{\text{int}} = 0.018$ (on F_{obs}).

All non-H atoms except O4 were localized by direct methods (*MULTAN80*; Main *et al.*, 1980). The atom O4 of the choline ion was only found in a $\Delta\rho$ map. This indicated that large displacements could