Structure of 1,4-Dioxaspiro[4.5]dec-8-yl *p*-Toluenesulphonate*

By Gabriele Bocelli

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Istituti di Chimica Generale e di Strutturistica Chimica, Università degli Studi di Parma, Via M. D'Azeglio 85, 43100 Parma, Italy

and Marie-Florence Grenier-Loustalot and Pierre Iratçabal

Institut Universitaire de Recherche Scientifique, Avenue Philippon, 64000 Pau, France

Abstract. $C_{15}H_{20}O_5S$, $M_r = 312.4$, triclinic, $P\bar{1}$, $a = 11.593$ (3), $b = 11.258$ (2), $c = 6.808$ (1) Å, $\alpha = 104.6$ (3), $\beta = 94.7$ (1), $\gamma = 112.8$ (3)°, $V = 776.9$ (2) Å^3, $D_x = 1.34$ Mg m^{-3}, $Z = 2$, $\mu = 1.974$ mm^{-1} (Cu $K\alpha$ radiation). $R = 0.0637$ for 2585 observed reflections. The structure was solved by direct methods and refined by least-squares calculations. The structure as a whole is not planar, and the cyclohexane and dioxolane rings, which adopt the chair and the envelope conformation respectively, are practically perpendicular to each other.

Introduction. In an attempt to establish the possible correlations between NMR spectroscopy data and X-ray single-crystal diffractometry information one needs a great number of analyses in both these fields of research.

The present paper describes one of the steps carried out in our laboratories to correlate such data for cyclic compounds.

Crystals of the title compound were recrystallized from petroleum ether/chloroform mixture as colourless prisms.

Lattice constants were determined on the diffractometer using the program *CTDIF* (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) which repeatedly improves the angular values of θ, χ, φ of 29 reflections to reach the maximum of the peak until the angles do not change by more than 0.01°.

Intensity data were collected on a Siemens AED single-crystal diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The intensity of each reflection was obtained from a profile analysis following the Lehmann & Larsen (1974) notation. With this procedure 2856 reflections were collected and 263 of them, having $I < 2\sigma(I)$, were considered unobserved. A check reflection, measured periodically, revealed no

decomposition of the specimen. No absorption correction was made.

The structure was solved by direct methods using the *SHELX* system (Sheldrick, 1976). The initial R value, based on the coordinates of the heavy atoms obtained by direct methods and with isotropic thermal parameters, was 0.321. Full-matrix least-squares refinement with isotropic thermal parameters lowered R to 0.159, with anisotropic ones to 0.112. Hydrogen atoms, except for those of the methyl group, were clearly defined in a difference-Fourier map. The function minimized was $\sum w|F_o - F_c|^2$ and the weight was unity at first, while at the end of the refinement process the weighting scheme employed was $w = [\sigma^2 F_o + 0.003 F_o^2]^{-1}$. The final refinement of all atoms [the methyl hydrogens were put in their theoretical positions calculated with *CALCO* (Nardelli, 1982) and refined isotropically] gave an R of 0.064, $R_w = 0.077$ (observed reflections only). Eight strong reflections, having large values of $|F_o - F_c|$, were omitted in the last cycles of refinement. The atomic scattering factors used (corrected for the anomalous dispersion of the S atom) were taken from *International Tables for X-ray Crystallography* (1974).

All the calculations were performed on the General Automation SPC/16 computer using a local set of programs and on the CDC Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna, with financial support from the University of Parma.

Discussion. The final atomic coordinates are given in Table 1, bond distances and angles in Table 2.† A

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* Stereochemistry of Rings. VII. Cyclohexane Derivatives. 2. Part VI: Bocelli & Grenier-Loustalot (1982). Cyclohexane Derivatives Part 1: Bocelli & Grenier-Loustalot (1981).

† Lists of structure factors, anisotropic thermal parameters of heavy atoms, atomic coordinates of hydrogens with isotropic thermal parameters and equations of least-squares planes of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36747 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (×10⁴)

	x	y	z	B_{eq} (Å²)*
S	4490 (1)	2008 (1)	9073 (1)	3·83 (6)
O(1)	4388 (2)	2880 (2)	7929 (3)	5·33 (19)
O(2)	4889 (2)	981 (2)	8175 (3)	5·07 (18)
O(3)	3120 (2)	1374 (2)	9529 (3)	4·52 (16)
O(4)	855 (2)	−2706 (3)	13074 (5)	6·68 (19)
O(5)	−109 (2)	−1559 (3)	11857 (5)	6·82 (20)
C(1)	2813 (2)	278 (3)	10484 (4)	3·99 (15)
C(2)	1718 (3)	−965 (3)	9038 (5)	4·62 (16)
C(3)	1378 (3)	−2089 (3)	10037 (5)	5·11 (17)
C(4)	1068 (3)	−1667 (3)	12137 (5)	4·82 (17)
C(5)	2140 (4)	−360 (4)	13540 (5)	5·38 (19)
C(6)	2473 (3)	764 (3)	12549 (5)	5·00 (16)
C(7)	−856 (4)	−2181 (5)	13109 (8)	6·85 (22)
C(8)	−413 (4)	−3237 (6)	13300 (9)	6·95 (24)
C(9)	5461 (2)	2986 (2)	11502 (4)	3·63 (15)
C(10)	5973 (3)	2392 (3)	12661 (5)	4·61 (17)
C(11)	6677 (3)	3154 (3)	14624 (6)	5·27 (19)
C(12)	6888 (3)	4497 (3)	15452 (5)	4·67 (16)
C(13)	6385 (3)	5067 (3)	14259 (5)	4·99 (17)
C(14)	5668 (3)	4320 (3)	12292 (5)	4·38 (16)
C(15)	7623 (5)	5301 (6)	17619 (8)	7·41 (21)

* Defined according to Hamilton (1959).

Fig. 1. Projection of the molecule.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

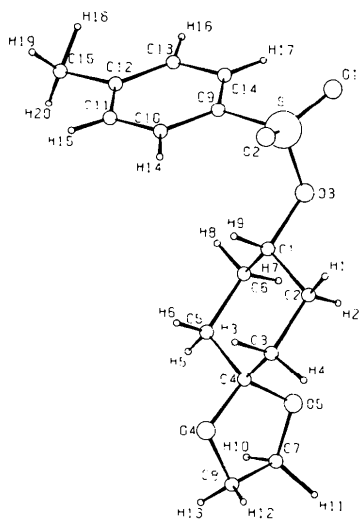|			
S—O(1)	1·429 (4)	C(2)—H(1)	1·01 (3)
S—O(2)	1·426 (4)	C(2)—H(2)	0·81 (4)
S—O(3)	1·563 (4)	C(3)—H(3)	1·13 (5)
S—C(9)	1·743 (7)	C(3)—H(4)	1·03 (3)
O(3)—C(1)	1·474 (5)	C(5)—H(5)	0·99 (6)
O(4)—C(4)	1·419 (6)	C(5)—H(6)	0·82 (7)
O(4)—C(8)	1·394 (6)	C(6)—H(7)	0·95 (4)
O(5)—C(4)	1·418 (5)	C(6)—H(8)	0·93 (4)
O(5)—C(7)	1·385 (7)	C(1)—H(9)	0·97 (4)
C(1)—C(2)	1·506 (8)	C(7)—H(10)	1·20 (6)
C(1)—C(6)	1·517 (5)	C(7)—H(11)	1·10 (4)
C(2)—C(3)	1·520 (6)	C(8)—H(12)	1·09 (6)
C(3)—C(4)	1·508 (5)	C(8)—H(13)	0·92 (6)
C(4)—C(5)	1·519 (9)	C(10)—H(14)	0·99 (5)
C(5)—C(6)	1·516 (7)	C(11)—H(15)	0·90 (7)
C(7)—C(8)	1·495 (10)	C(13)—H(16)	0·96 (3)
C(9)—C(10)	1·385 (6)	C(14)—H(17)	0·96 (7)
C(9)—C(14)	1·377 (5)	C(15)—H(18)	1·02 (9)
C(10)—C(11)	1·376 (7)	C(15)—H(19)	0·91 (9)
C(11)—C(12)	1·388 (6)	C(15)—H(20)	0·80 (7)
C(12)—C(13)	1·373 (6)		
C(12)—C(15)	1·500 (8)		
C(13)—C(14)	1·380 (6)		
O(1)—S—O(2)	119·2 (3)	C(3)—C(4)—C(5)	111·4 (6)
O(1)—S—O(3)	102·9 (7)	O(5)—C(4)—C(5)	112·2 (9)
O(2)—S—O(3)	110·8 (7)	O(4)—C(4)—C(5)	109·4 (5)
O(1)—S—C(9)	109·4 (6)	C(4)—C(5)—C(6)	111·7 (4)
O(2)—S—C(9)	109·1 (7)	C(1)—C(6)—C(5)	108·2 (6)
O(3)—S—C(9)	104·4 (4)	O(5)—C(7)—C(8)	103·7 (9)
S—O(3)—C(1)	118·5 (10)	O(4)—C(8)—C(7)	104·1 (10)
C(4)—O(4)—C(8)	109·4 (9)	S—C(9)—C(14)	120·0 (5)
C(4)—O(5)—C(7)	108·6 (8)	S—C(9)—C(10)	119·4 (6)
O(3)—C(1)—C(6)	107·6 (7)	C(10)—C(9)—C(14)	120·5 (4)
O(3)—C(1)—C(2)	108·4 (4)	C(9)—C(10)—C(11)	118·8 (9)
C(2)—C(1)—C(6)	111·9 (7)	C(10)—C(11)—C(12)	121·5 (7)
C(1)—C(2)—C(3)	108·6 (4)	C(11)—C(12)—C(15)	120·8 (9)
C(2)—C(3)—C(4)	111·7 (8)	C(11)—C(12)—C(13)	118·5 (5)
O(4)—C(4)—C(3)	109·6 (4)	C(13)—C(12)—C(15)	120·6 (9)
O(5)—C(4)—C(3)	108·4 (6)	C(12)—C(13)—C(14)	121·0 (9)
O(4)—C(4)—O(5)	105·6 (8)	C(9)—C(14)—C(13)	119·7 (9)
S—O(3)—C(1)—C(2)	−120·0 (10)	C(2)—C(1)—C(6)—C(5)	60·4 (11)
S—O(3)—C(1)—C(6)	118·9 (10)	C(3)—C(4)—O(4)—C(8)	115·0 (10)
O(3)—C(1)—C(2)—C(3)	−178·7 (9)	C(5)—C(4)—O(4)—C(8)	−122·6 (10)
O(3)—C(1)—C(6)—C(5)	179·4 (9)	C(3)—C(4)—O(5)—C(7)	−134·9 (10)
C(1)—C(2)—C(3)—C(4)	56·4 (11)	C(5)—C(4)—O(5)—C(7)	101·7 (11)
C(2)—C(3)—C(4)—C(5)	−54·3 (12)	C(4)—O(5)—C(7)—C(8)	−28·1 (11)
C(2)—C(3)—C(4)—O(4)	−175·5 (9)	O(5)—C(7)—C(8)—O(4)	28·2 (12)
C(2)—C(3)—C(4)—O(5)	69·7 (11)	C(4)—O(4)—C(8)—C(7)	−18·3 (12)
C(3)—C(4)—C(5)—C(6)	54·6 (12)	C(8)—O(4)—C(4)—O(5)	1·7 (12)
C(4)—C(5)—C(6)—C(1)	−56·5 (11)	O(4)—C(4)—O(5)—C(7)	−17·4 (12)

perspective drawing of the molecule is illustrated in Fig. 1.

Bond-length values of the two six-membered rings are in the range often observed for these molecular fragments. The average distances in the phenyl and the cyclohexane rings are 1·380 (2) and 1·514 (2) Å, respectively.

While the phenyl ring is planar with C(15) out of the mean plane by 0·053 (7) Å, the cyclohexane adopts the chair conformation. In terms of the ring-puckering coordinates proposed by Cremer & Pople (1975), the puckering values for this ring are: $Q = 0·58$ Å, $\varphi =$

335·4° and $\theta = 4·33°$. Two of the internal angles of this ring [C(1)—C(2)—C(3) = 108·6 (4), C(1)—C(6)—C(5) = 108·2 (6)°] are far from the standard value indicated by Dunitz (1968) (111·5°) probably because of a 'thrust' effect by the sulphonyloxy group on the C(6), C(1), C(2) moiety, which also influences the two external angles O(3)—C(1)—C(6) [107·6 (7)°] and O(3)—C(1)—C(2) [108·4 (4)°].

The dioxolane ring shows an envelope conformation. For this ring the puckering parameter ($\varphi = 285·5°$) is very close to the ideal value of 288°. The apex at C(7) is out by 0·42 (5) Å from the mean plane of the other four atoms. The envelope conformation is not often observed in similar spiro compounds, which seem to prefer the half-chair (Braun, Hornstra, Knobler, Rutten & Romers, 1973; Karle, 1975) or twist conformation (Chadwick, Dunitz & Schweizer, 1977; Chadwick & Dunitz, 1978). In the present case the angle between the mean cyclohexane (C1—C6) and the mean acetal (C4, O4, C8, C7, O5) rings is 86·0 (4)°
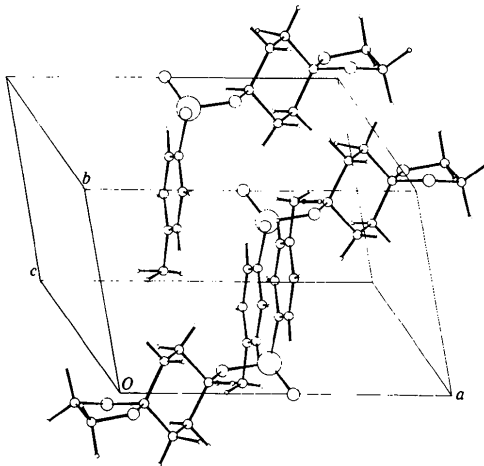
Fig. 2. View of the molecules in the crystallographic unit cell.

and, consequently, the two oxygens, each occupying an axial position, can influence the ring conformation.

The O(1)—S—O(2) plane is almost perpendicular to the C(9)—S—O(3) plane [87·0 (3)°] and some angles around the sulphur show a significant deviation from the tetrahedral value [O(1)—S—O(2) = 119·2 (3); O(1)—S—O(3) = 102·9 (7); O(3)—S—C(9) = 104·4 (4)°]. The same effect has been observed in other sulphones (Andreetti, Bocelli & Sgarabotto, 1973; Yasuoka, Kasai, Tanaka, Nagai & Tokura, 1972; Bordner, Levine, Mazur & Morrow, 1973). The sulphur—carbon and sulphur—oxygen bond lengths are as expected.

The packing scheme is illustrated in Fig. 2. There are no unusually short intermolecular contacts.

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Structure of 3-Phenyl-1-oxacyclohexane-2,6-dione*

By Gabriele Bocelli

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Istituti di Chimica Generale e di Strutturistica Chimica, Università degli Studi di Parma, Via M. D'Azeglio 85, 43100 Parma, Italy

and Marie-Florence Grenier-Loustalot

Institut Universitaire de Recherche Scientifique, Avenue Philippon, 64000 Pau, France

Abstract. $C_{11}H_{10}O_3$, $M_r = 190·2$, monoclinic, $P2_1/n$, $a = 10·990$ (3), $b = 10·115$ (3), $c = 8·662$ (2) Å, $\beta = 107·1$ (3)°, $V = 920·3$ (2) Å³, $Z = 4$, $D_x = 1·37$ Mg m⁻³, μ(Cu Kα) = 0·79 mm⁻¹. Final $R = 0·085$ for 760 observed reflections. The structure was solved by direct methods. The non-aromatic ring shows a half-boat conformation and the two carbonyl oxygens are both equatorial.

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* Stereochemistry of Rings VIII. Cyclohexane Derivatives. 3. Part VII and Part 2: Bocelli, Grenier-Loustalot & Iratçabal (1982).