Acta Cryst. (1993). C**49**, 1098–1103

Structures of Some Methylenecyclobutanols and Transposed Derivatives

By S. Ianelli and M. Nardelli*

Istituto di Chimica Generale, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffrattometrica, Viale delle Scienze, I-43100 Parma, Italy

D. Belletti

Istituto di Strutturistica Chimica, Università degli Studi di Parma, Centro di Studio CNR per la Strutturistica Diffrattometrica, Viale delle Scienze, I-43100 Parma, Italy

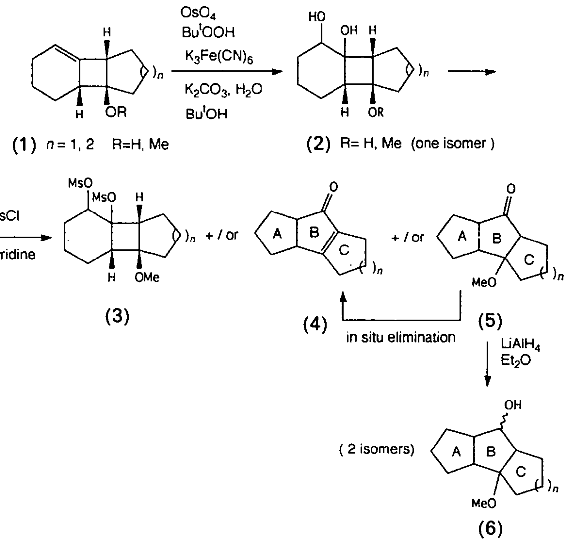
and B. Jamart-Grégoire, N. Brosse and P. Caubère

Laboratoire de Chimie Organique I, UA CNRS No. 457, Université de Nancy I, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France

(*Received* 25 *February* 1992; *accepted* 7 *December* 1992)

Abstract. *cis,syn,cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-2,3,8-triol (2), $C_{12}H_{20}O_3$, $M_r = 212.3$, triclinic, $P\bar{1}$, $a = 8.440\,(1)$, $b = 11.723\,(2)$, $c = 13.016\,(2)$ Å, $\alpha = 67.17\,(1)$, $\beta = 76.08\,(1)$, $\gamma = 71.40\,(1)^\circ$, $V = 1114.8\,(4)$ Å^3, $Z = 4$, $D_x = 1.265$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1.540562$ Å, $\mu = 0.682$ mm^{-1}, $F(000) = 464$, $T = 293\,(2)$ K, $R = 0.0462$ for 3438 observed reflections. *cis,syn,cis*-8-Methoxytricyclo[6.3.0.0^{2,7}]undecane-2,3-diyl bis(methanesulfonate) (3), $C_{14}H_{24}S_2O_7$, $M_r = 368.5$, monoclinic, $C2/c$, $a = 11.688\,(3)$, $b = 12.208\,(3)$, $c = 24.328\,(6)$ Å, $\beta = 90.98\,(1)^\circ$, $V = 3471\,(1)$ Å^3, $Z = 8$, $D_x = 1.410$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1.540562$ Å, $\mu = 3.019$ mm^{-1}, $F(000) = 1568$, $T = 293\,(2)$ K, $R = 0.0610$ for 2897 observed reflections. *cis,syn,cis*-1-Methoxytricyclo[6.3.0.0^{2,6}]undecan-7-ol (6), $C_{12}H_{20}O_2$, $M_r = 196.3$, orthorhombic, $P2_12_12_1$, $a = 14.317\,(2)$, $b = 12.020\,(2)$, $c = 6.490\,(1)$ Å, $V = 1116.9\,(3)$ Å^3, $Z = 4$, $D_x = 1.167$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1.540562$ Å, $\mu = 0.576$ mm^{-1}, $F(000) = 432$, $T = 293\,(2)$ K, $R = 0.0412$ for 798 observed reflections. These compounds contain a core formed by three fused rings with the terminal rings *syn* with respect to the central ring. The substituents at the junctions are *cis* in all cases. This knowledge is of fundamental importance in order to understand the mechanisms of the reactions in which these compounds are involved. There are two independent molecules in the asymmetric unit of the triclinic crystals of compound (2), which, in the crystal structure, differ from each other by the orientation of the hydroxyl groups which are involved, as both donors and acceptors, in a system of O—H···O hydrogen bonds. In compound (3), the orientations of the bulky methanesulfonate groups and of the methoxy group are mainly imposed by intramolecular steric hindrance. This is also observed for the methoxy group of compound (6), while the orientation of the hydroxyl group is determined by an intermolecular O—H···O hydrogen bond which the molecule forms with an adjacent molecule.

Introduction. The synthesis of new polycyclic compounds having potential biological activity has been carried out starting from previously described methylene cyclobutenols (1) (Caubère & Brunet, 1972) according to the scheme below (Jamart-Grégoire, Brosse, Ianelli, Nardelli & Caubère, 1991).



One of the problems to be solved in the course of this work was the determination of the structures of the synthesized products, since usual spectroscopic

---

* Author to whom correspondence should be addressed.

0108-2701/93/061098-06$06.00

methods did not provide unambiguous proof of the molecular structures.

The crystals of compound (2) ($n = 2$, $R = \mathrm{H}$) were studied in order to obtain structural evidence of the factors responsible for the stereoselectivity of the oxidation reaction of (1) ($n = 2$). Well formed crystals of (3) ($n = 1$) were obtained and its structure studied, firstly because the formation of the tertiary methanesulfonate is quite unusual and, secondly, because knowledge of its structure allowed us to define that of the corresponding diol (2) ($n = 1$). To obtain the structural information necessary to understand the mechanism of the transposition of compound (2), we studied the structure of one of the two isomers of (6) ($n = 1$) formed by reduction of the corresponding liquid ketone (5) ($n = 1$).

In the present paper the crystal structures of compounds (2) ($n = 2$, $R = \mathrm{H}$), (3) ($n = 1$) and (6) ($n = 1$) [hereafter called simply (2), (3) and (6), respectively] are reported.

Table 1. *Experimental data for the crystal structure analyses*

	(2)	(3)	(6)
No. of reflections for lattice parameters	29	30	30
θ range (°)	31–41	28–40	20–39
Crystal size (mm)	0.35 × 0.37 × 0.51	0.63 × 0.65 × 0.75	0.26 × 0.39 × 0.62
Extinction parameter, g	$0.19\,(2) \times 10^{-6}$	$0.17\,(3) \times 10^{-9}$	$0.62\,(4) \times 10^{-8}$
Scan speed (° min^{-1})	3–12	3–12	3–12
Scan width (°)	$1.1 + 0.14\tan\theta$	$1.1 + 0.14\tan\theta$	$1.1 + 0.14\tan\theta$
θ range (°)	3–70	3–70	3–70
h range	− 10 to 10	− 14 to 14	0 to 17
k range	− 14 to 14	0 to 14	0 to 14
l range	0 to 20	0 to 29	0 to 7
Standard reflection	$1\bar{5}7$	752	811
Intensity variation (%)	None	34	None
Reflections measured	3442	2991	1269
Reflections observed	3438	2897	798
Condition for observation	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	-	0.0177	-
Anisotropic LS on F	Full matrix	Full matrix	Full matrix
Max. LS shift to e.s.d. ratio	0.004	0.007	0.003
Min./max. height in final $\Delta\rho$ map (e Å^{-3})	−0.18/0.14	−0.21/0.21	−0.13/0.09
Refined parameters	431	302	207
R	0.0462	0.0610	0.0412
wR	0.0550	0.0837	0.0534
S	1.5653	2.6338	0.6603
k, g $\{w = k/[\sigma^2(F_o) + gF_o^2]\}$	1, 0.0005	1, 0.0005	1, 0.005

Experimental. Details of the experimental parameters are given in Table 1. For all three compounds Cu $K\alpha$ Ni-filtered radiation was used with the sample mounted on a Siemens-AED diffractometer. The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Corrections for Lorentz and polarization effects were applied but none for absorption, and a correction for extinction was considered for all three structures according to Zachariasen (1963). For compond (3), crystal decay (max. 34%) was observed during data collection, the data being scaled up to correct for this deterioration.

The structures were determined by direct methods with *SHELXS*86 (Sheldrick, 1986) and refined by anisotropic full-matrix least squares on F, using *SHELX*76 (Sheldrick, 1976). The H atoms were located from final difference Fourier syntheses, excepting those of the methyls which were placed at calculated positions; all were refined isotropically. The localization of the hydroxyl H atoms in the case of compound (2) deserves special comment. At the end of refinement, only three (those bound to O1*A*, O1*B* and O2*B*) were found from a $\Delta\rho$ map; for the others, the tetrahedral positions about the O atoms were calculated by the *PARST* program (Nardelli, 1983*a*), then all contacts with surrounding atoms were calculated by the same program, and the positions giving steric hindrance were rejected, while those found to give contacts with adjacent O atoms suitable for hydrogen bonding were assumed. The H atoms bound to O2*A*, O3*A* and O3*B* were localized by this procedure and their contributions added to the structure-factor calculations. Further isotropic refinement not only gave quite significant improvement of the residual error indices and goodness-of-fit ($R = 0.054$, $wR = 0.070$, $S = 1.98$ to $R = 0.046$, $wR = 0.055$, $S = 1.56$), but also gave quite acceptable values of the displacement coefficients (thermal parameters) and bond distances and angles for these atoms.

There are no significant differences between the two crystallographically independent molecules in compound (2). The correctness of the space group choice was checked using *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988) and *MISSYM* (Le Page, 1987). From the *PLUTO* (Motherwell & Clegg, 1976) drawing of the cell contents (Fig. 3) and from the non-bonded contacts calculated by *PARST*, it appears that the two independent molecules differ in terms of the role of the hydroxyl groups in the hydrogen bonds in which they are involved.

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic coordinates are given in Table 2.* Throughout the paper the averaged values are means weighted according to the reciprocals of the variances, and the corresponding e.s.d.'s are the largest of the values of the 'external' and 'internal' standard deviations (Topping, 1960). The calculations were carried out on Encore-Gould-Powernode 6040 and Encore91 computers at the Centro di Studio per la

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55867 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1008]

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^4$) *with e.s.d.'s in parentheses*

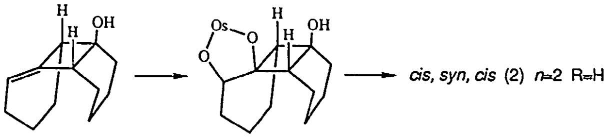
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Compound (2)				
O1*A*	9489 (2)	819 (1)	6439 (1)	400 (6)
O2*A*	7401 (2)	947 (1)	3686 (1)	378 (5)
O3*A*	5940 (2)	3323 (1)	2749 (1)	456 (6)
C1*A*	8155 (2)	1660 (2)	5787 (1)	296 (6)
C2*A*	7398 (2)	2835 (2)	6146 (2)	392 (8)
C3*A*	8472 (3)	3799 (2)	5597 (2)	533 (11)
C4*A*	8532 (3)	4279 (2)	4322 (2)	545 (10)
C5*A*	9341 (3)	3196 (2)	3842 (2)	444 (9)
C6*A*	8783 (2)	1961 (2)	4516 (1)	297 (6)
C7*A*	7174 (2)	1693 (1)	4381 (1)	271 (6)
C8*A*	5710 (2)	2843 (2)	3959 (1)	323 (7)
C9*A*	4037 (2)	2486 (2)	4448 (2)	406 (8)
C10*A*	3754 (2)	2186 (2)	5716 (2)	466 (9)
C11*A*	5124 (2)	1040 (2)	6300 (2)	417 (8)
C12*A*	6912 (2)	994 (2)	5669 (1)	303 (6)
H1O*A*	9015 (34)	658 (25)	7135 (23)	782 (88)
H2O*A*	8450 (38)	335 (28)	3752 (24)	979 (100)
H3O*A*	6416 (40)	2553 (31)	2605 (27)	1090 (117)
O1*B*	8270 (2)	115 (1)	8729 (1)	379 (5)
O2*B*	4768 (2)	−1987 (1)	10998 (1)	484 (6)
O3*B*	6474 (2)	−4243 (1)	11985 (1)	567 (7)
C1*B*	8229 (2)	−1196 (1)	9330 (1)	298 (6)
C2*B*	9988 (2)	−1983 (2)	9054 (2)	377 (8)
C3*B*	11196 (3)	−2052 (2)	9787 (2)	514 (10)
C4*B*	10644 (3)	−2766 (2)	11015 (2)	547 (10)
C5*B*	8898 (3)	−2086 (2)	11441 (2)	483 (9)
C6*B*	7606 (2)	−1526 (2)	10608 (1)	327 (7)
C7*B*	6481 (2)	−2278 (2)	10483 (1)	317 (6)
C8*B*	7113 (2)	−3735 (2)	10822 (2)	356 (7)
C9*B*	6554 (3)	−4223 (2)	10079 (2)	450 (9)
C10*B*	7328 (3)	−3693 (2)	8862 (2)	490 (10)
C11*B*	6733 (3)	−2233 (2)	8396 (2)	468 (9)
C12*B*	6698 (2)	−1566 (2)	9201 (1)	325 (7)
H1O*B*	7278 (33)	600 (25)	8913 (21)	739 (81)
H2O*B*	4723 (45)	−2756 (33)	11677 (30)	1260 (126)
H3O*B*	6470 (38)	−5047 (29)	12058 (25)	947 (99)
Compound (3)				
S1	527.9 (7)	2299.4 (6)	1091.3 (4)	568 (3)
S2	2634.3 (7)	4442.7 (7)	2248.7 (3)	575 (3)
O1	−355 (2)	2758 (2)	775 (1)	795 (10)
O2	1387.3 (19)	3220.4 (17)	1260.4 (9)	563 (7)
O3	1158 (3)	1413 (2)	870 (2)	1055 (14)
O4	2725.7 (17)	4911.4 (19)	1648.6 (9)	559 (7)
O5	1510 (2)	4121 (2)	2386 (1)	701 (9)
O6	3179 (3)	5205 (3)	2584 (1)	1221 (16)
O7	1162 (3)	7726 (2)	1470 (1)	770 (10)
C1	1590 (3)	4183 (2)	914 (1)	460 (9)
C2	1763 (2)	5154 (2)	1285 (1)	407 (8)
C3	2063 (3)	6197 (2)	947 (1)	449 (9)
C4	2349 (4)	5996 (3)	346 (2)	655 (13)
C5	3139 (4)	5018 (3)	294 (2)	751 (15)
C6	2600 (4)	3979 (3)	534 (2)	666 (13)
C7	961 (3)	6742 (2)	1163 (1)	538 (10)
C8	727 (3)	5762 (2)	1550 (1)	504 (10)
C9	−487 (3)	5371 (4)	1434 (2)	757 (16)
C10	−767 (5)	5842 (5)	876 (3)	1131 (25)
C11	−66 (4)	6817 (5)	791 (2)	877 (18)
C12	14 (4)	1937 (4)	1744 (2)	779 (16)
C13	3458 (5)	3228 (6)	2172 (2)	974 (21)
C14	1561 (7)	8621 (3)	1138 (3)	1024 (24)
Compound (6)				
O1	9388 (2)	3793 (2)	649 (4)	663 (9)
O2	10029 (2)	7416 (3)	1051 (5)	812 (11)
C1	8636 (3)	5555 (3)	−325 (6)	640 (12)
C2	8547 (4)	6153 (5)	−2383 (8)	950 (20)
C3	7864 (5)	7067 (5)	−1956 (10)	1071 (23)
C4	8060 (5)	7471 (5)	197 (10)	958 (21)
C5	8516 (3)	6483 (3)	1308 (6)	666 (13)
C6	9491 (3)	6664 (3)	2248 (6)	644 (12)
C7	9907 (3)	5490 (3)	2232 (6)	653 (13)
C8	9554 (3)	4959 (3)	213 (5)	568 (10)
C9	10398 (4)	5088 (5)	−1197 (8)	848 (18)
C10	11221 (3)	4846 (6)	226 (12)	1079 (26)
C11	10976 (3)	5396 (5)	2212 (11)	932 (20)
C12	9068 (5)	3153 (4)	−1030 (9)	845 (18)
H2O	10223 (45)	7839 (57)	1750 (103)	1250 (260)

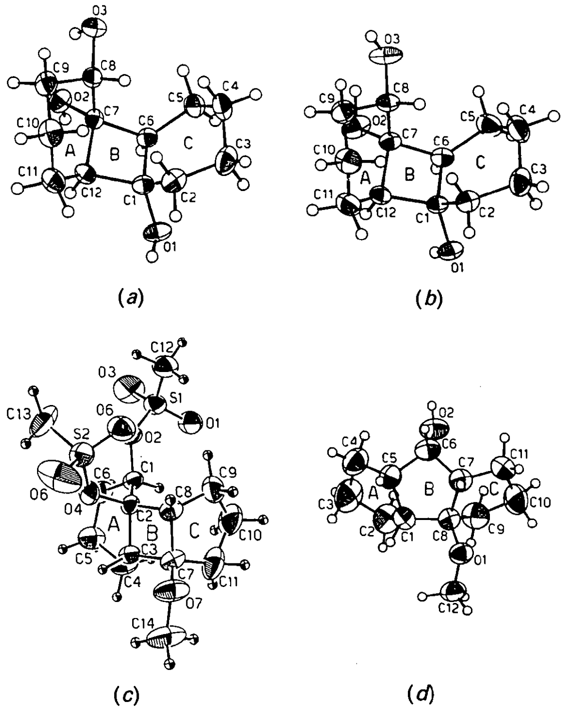
Strutturistica Diffrattometrica del CNR (Parma). In addition to the quoted programs, *LQPARM* (Nardelli & Mangia, 1984) and *ORTEP* (Johnson, 1965) have been used.

Discussion. As shown by the *ORTEP* drawings in Fig. 1, the molecules of the three compounds are built up of a central core formed by a system of three fused rings with the terminal rings *syn* with respect to the central one. The substituents are *cis* in all cases; this finding is important for understanding the mechanism of the reactions in which these compounds are involved.

In particular, the *cis,syn,cis* structure of (2) indicated that the bishydroxylation process is directed by steric interactions and takes place on the less hindered face of (1) leading to the less strained compound (2) according to:



The 'all *cis*' configuration of (5) allows us to assign a *cis* junction to compound (4) ($n = 1$ and $n = 2$), by comparison of the coupling constants of the ring-



(*a*) (*b*)

(*c*) (*d*)

Fig. 1. *ORTEP* drawings of the molecules projected onto planes approximately parallel to the *B* rings, with ellipsoids at 50% probability. (*a*) Compound (2) molecule *A*, (*b*) compound (2) molecule *B*, (*c*) compound (3), (*d*) compound (6).

junction protons from the ^{1}H NMR spectra. The values of the coupling constant of the *B* and *C* ring-junction protons are $n = 1$ and $J = 10$ Hz, for (5), and $n = 2$ and $J = 6$ Hz, for (4). These values are in agreement with a *cis* junction as described in the literature (Grebe, Lange, Rieckers, Kieslich, Viergutz, Waskausen & Winterfeldt, 1991; Mehta, Narayana Murthy, Sivakumar Reddy & Veera Reddy, 1986; Eaton, Srikrishna & Uggeri, 1984). The chemical relevance of these results is that, firstly they show that during transposition the *cis* junction between the *B* and *C* rings is preserved from the corresponding *cis* junction of (2), and thus no isomerization takes place once the keto group is formed, and secondly, the results raise the question of whether the reaction is stereoselective or specific on the one hand, or if, on the other hand, there is epimerization during the reaction leading to the more stable *cis A*/*B* junction. At this point we have no answer to this question.

There are several chiral centres in the molecules of the three compounds, whose relative configurations, according to the labelling of Fig. 1, are: compound (2) *S*(C1), *S*(C6), *R*(C7), *S*(C8), *R*(C12); compound (3) *S*(C2), *R*(C3), *R*(C7), *S*(C8); and compound (6) *R*(C1), *S*(C5), *S*(C6), *S*(C7), *S*(C8).

The values of bond distances and angles presented in Table 3 for the central tricyclic systems are as expected, and thus warrant no further comment. However, some attention needs to be devoted to the conformation of the substituents.

The conformations of the rings (Table 4) are influenced not only by their size, but also by their substituents. This is particularly true of compound (3) where the bulky methanesulfonate groups, attached to adjacent C atoms of the hexatomic *A* ring, produce an increased total puckering amplitude (Cremer & Pople, 1975) of this ring. These substituents also influence the dihedral angle between the mean planes through the rings, which in compound (3) becomes narrower for the *A* and *B* and wider for the *B* and *C* rings [compared with compounds (2) and (6)]. It is worth noting the local pseudo-mirror symmetry [indicated by the asymmetry displacement parameters (Nardelli, 1983*b*)] through atoms C6 and O2 and the midpoint of the C1—C8 bond in compound (6), which is maintained in spite of the presence of the O1—C12 methoxy substituent.

Fig. 1 parts (*a*) and (*b*), and the Newman projections of Fig. 2 clearly show that the two independent molecules of the asymmetric unit in compound (2) differ by the orientations of the hydroxyl groups as a result of their differing roles in the hydrogen-bonding scheme. To check the results of the analysis carried out on F's for compound (2), particularly with regard to the positions of the hydroxyl atoms, a refinement was carried out on F^2 using the

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Compound (2)

	A	*B*	*Δ*/*σ*		*A*	*B*	*Δ*/*σ*
O1—C1	1.436 (2)	1.436 (2)		C5—C6	1.528 (3)	1.535 (3)	
O2—C7	1.429 (3)	1.432 (2)		C6—C7	1.551 (3)	1.557 (3)	
O3—C8	1.438 (2)	1.432 (2)		C7—C8	1.528 (2)	1.531 (2)	
C1—C2	1.523 (3)	1.521 (2)		C7—C12	1.550 (2)	1.544 (2)	
C1—C6	1.545 (3)	1.550 (3)		C8—C9	1.520 (3)	1.518 (4)	
C1—C12	1.559 (3)	1.550 (3)		C9—C10	1.523 (3)	1.524 (3)	
C2—C3	1.524 (4)	1.521 (4)		C10—C11	1.536 (3)	1.530 (3)	
C3—C4	1.526 (4)	1.524 (3)		C11—C12	1.530 (3)	1.523 (4)	
C4—C5	1.525 (4)	1.522 (3)					
O1—C1—C12	115.0 (2)	115.1 (3)		C6—C7—C12	88.9 (3)	88.8 (2)	
O1—C1—C6	110.8 (3)	115.4 (2)	12.8	C6—C7—C8	117.6 (3)	118.3 (4)	
O1—C1—C2	109.1 (2)	105.5 (2)	12.7	O2—C7—C12	116.4 (2)	112.8 (3)	10.0
C6—C1—C12	88.8 (2)	88.8 (2)		O2—C7—C8	104.2 (2)	107.7 (3)	9.7
C2—C1—C12	117.6 (3)	118.1 (2)		C8—C7—C12	113.4 (2)	114.2 (2)	
C2—C1—C6	114.4 (2)	113.8 (2)		O3—C8—C7	109.8 (2)	106.4 (2)	12.0
C1—C2—C3	111.4 (3)	111.0 (2)		C7—C8—C9	110.4 (2)	110.8 (2)	
C2—C3—C4	110.0 (3)	109.7 (4)		O3—C8—C9	112.3 (3)	112.8 (3)	
C3—C4—C5	111.7 (2)	111.9 (3)		C8—C9—C10	109.5 (4)	110.3 (3)	
C4—C5—C6	114.8 (2)	115.0 (2)		C9—C10—C11	112.0 (2)	111.4 (2)	
C1—C6—C5	119.5 (2)	119.5 (3)		C10—C11—C12	114.8 (2)	114.5 (2)	
C5—C6—C7	124.4 (2)	124.7 (2)		C7—C12—C11	119.8 (3)	119.9 (2)	
C1—C6—C7	88.8 (3)	88.4 (2)		C1—C12—C11	125.0 (2)	124.8 (3)	
O2—C7—C6	116.6 (3)	114.4 (2)	6.1	C1—C12—C7	88.4 (2)	88.8 (3)	

Compound (3)

S1—O1	1.395 (3)	C1—C6	1.533 (5)
S1—O2	1.558 (2)	C2—C3	1.559 (4)
S1—O3	1.420 (3)	C2—C8	1.568 (4)
S1—C12	1.764 (5)	C3—C4	1.525 (5)
S2—O4	1.573 (2)	C3—C7	1.550 (4)
S2—O5	1.417 (3)	C4—C5	1.516 (6)
S2—O6	1.385 (4)	C5—C6	1.535 (6)
S2—C13	1.780 (7)	C7—C8	1.549 (4)
O2—C1	1.468 (4)	C7—C11	1.495 (6)
O4—C2	1.450 (3)	C8—C9	1.519 (5)
O7—C7	1.431 (4)	C9—C10	1.507 (9)
O7—C14	1.441 (6)	C10—C11	1.461 (8)
C1—C2	1.503 (4)		
O3—S1—C12	109.7 (2)	O4—C2—C8	116.3 (2)
O2—S1—C12	99.9 (2)	O4—C2—C3	108.0 (2)
O2—S1—O3	108.3 (2)	C3—C2—C8	90.7 (2)
O1—S1—C12	109.7 (2)	C2—C3—C7	88.6 (2)
O1—S1—O3	118.8 (2)	C2—C3—C4	115.5 (2)
O1—S1—O2	108.9 (1)	C4—C3—C7	126.3 (3)
O6—S2—C13	112.2 (3)	C3—C4—C5	110.5 (3)
O5—S2—C13	107.4 (3)	C4—C5—C6	111.4 (4)
O5—S2—O6	117.8 (2)	C1—C6—C5	114.8 (3)
O4—S2—C13	99.2 (2)	O7—C7—C3	114.1 (3)
O4—S2—O6	105.3 (2)	C3—C7—C11	118.9 (3)
O4—S2—O5	113.4 (1)	C3—C7—C8	91.8 (2)
S1—O2—C1	122.4 (2)	O7—C7—C11	112.8 (3)
S2—O4—C2	125.2 (2)	O7—C7—C8	111.2 (3)
C7—O7—C14	113.3 (3)	C8—C7—C11	105.5 (3)
O2—C1—C6	110.5 (2)	C2—C8—C7	88.3 (2)
O2—C1—C2	107.9 (2)	C7—C8—C9	107.8 (3)
C2—C1—C6	113.2 (3)	C2—C8—C9	120.1 (3)
O4—C2—C1	107.5 (2)	C8—C9—C10	103.5 (4)
C1—C2—C8	121.6 (2)	C9—C10—C11	109.0 (5)
C1—C2—C3	110.8 (2)	C7—C11—C10	108.1 (4)

Compound (6)

O1—C8	1.449 (4)	C4—C5	1.535 (8)
O1—C12	1.411 (6)	C5—C6	1.539 (6)
O2—C6	1.420 (5)	C6—C7	1.532 (6)
C1—C2	1.522 (7)	C7—C8	1.543 (5)
C1—C5	1.548 (6)	C7—C11	1.535 (6)
C1—C8	1.537 (5)	C8—C9	1.523 (7)
C2—C3	1.496 (9)	C9—C10	1.526 (8)
C3—C4	1.506 (9)	C10—C11	1.490 (10)
C8—O1—C12	115.5 (3)	C6—C7—C11	117.1 (4)
C5—C1—C8	106.0 (3)	C6—C7—C8	105.1 (3)
C2—C1—C8	119.4 (4)	C8—C7—C11	106.8 (4)
C2—C1—C5	104.6 (4)	C1—C8—C7	106.3 (3)
C1—C2—C3	103.8 (4)	O1—C8—C7	106.7 (3)
C2—C3—C4	106.7 (5)	O1—C8—C1	110.8 (3)
C3—C4—C5	105.4 (5)	C7—C8—C9	102.0 (3)
C1—C5—C4	106.4 (4)	C1—C8—C9	119.6 (3)
C4—C5—C6	117.5 (4)	O1—C8—C9	110.2 (3)
C1—C5—C6	105.8 (3)	C8—C9—C10	103.3 (4)
O2—C6—C5	111.5 (3)	C9—C10—C11	104.9 (4)
C5—C6—C7	102.7 (3)	C7—C11—C10	105.9 (4)
O2—C6—C7	111.8 (3)		

Table 4. *Total puckering amplitudes* (Q_T; *Cremer & Pople*, 1975), *asymmetry displacement parameters* (*ADP*; *Nardelli*, 1983*b*) *and dihedral angles* (*DA*) *formed by the least-squares planes through the rings*

	Compound (2)			
	Molecule *A*	Molecule *B*	Compound (3)	Compound (6)
Q_T (Å)				
Ring *A*	0.525 (3)	0.514 (6)	0.702 (5)	0.340 (9)
Ring *B*	0.0601 (8)	0.0603 (8)	0.020 (1)	0.377 (7)
Ring *C*	0.511 (6)	0.517 (4)	0.221 (6)	0.403 (8)
ADP				
Ring *A*	Δ_S(C9) = 0.034 (2)	Δ_S(C9) = 0.006 (3)	Δ_2(C3) = 0.078 (2)	Δ_S(C2) = 0.030 (4)
Ring *B*	–	–	–	Δ_2(C1) = 0.038 (3)
Ring *C*	Δ_S(C3) = 0.006 (3)	Δ_S(C3) = 0.022 (2)	Δ_2(C7) = 0.006 (2)	Δ_S(C9) = 0.006 (4)
DA (°)				
A/*B*	51.4 (1)	52.1 (2)	33.5 (2)	41.0 (2)
B/*C*	52.8 (2)	51.6 (1)	63.1 (2)	45.0 (2)

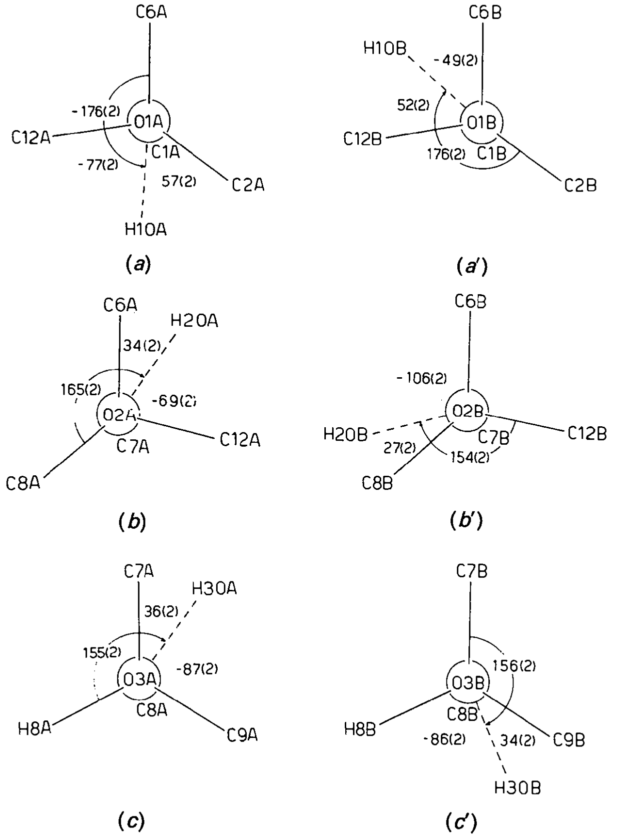


Fig. 2. Newman projections showing the orientations of the OH groups in the two independent molecules of compound (2): (*a*) and (*a'*) along O1—C1, (*b*) and (*b'*) along O2—C7, and (*c*) and (*c'*) along O3—C8.

*SHELXL*92 program (Sheldrick, 1992) assuming all the H atoms in the positions calculated by the program according to the riding model. For hydroxyl groups we chose the HFIX147 option, which calculates a difference electron-density synthesis around the circle representing the locus of possible H-atom position (for a fixed O—H distance and C—O—H angle). The position of maximum electron density is then taken as the starting position for the atom in subsequent least-squares refinement.

The following general indicators of the accuracy of the analysis were obtained: $wR2 = 0.1010$ for 4217 independent data and 281 parameters (31 reflections having $\Delta/\sigma > 3.5$ were omitted from the refinement), $S = 0.992$, $wR2 = 0.1139$ for all 4248 data, $R1 = 0.0362$ for 3411 $F_o > 4\sigma(F_o)$, $R1 = 0.0475$ for all 4248 data, $S = 1.119$. No significant differences (*i.e.* less than 3σ) were observed for the results (bond distances, angles, *etc.*) obtained from the two refinements. In Table 4 the relevant data concerning the geometry of the hydrogen bonds in compound (2) are compared for the two refinements.

The topological scheme is shown in Fig. 4 and Table 5 gives the relevant geometric parameters of the hydrogen-bonding system present in the crystals of this compound. From that scheme and projection

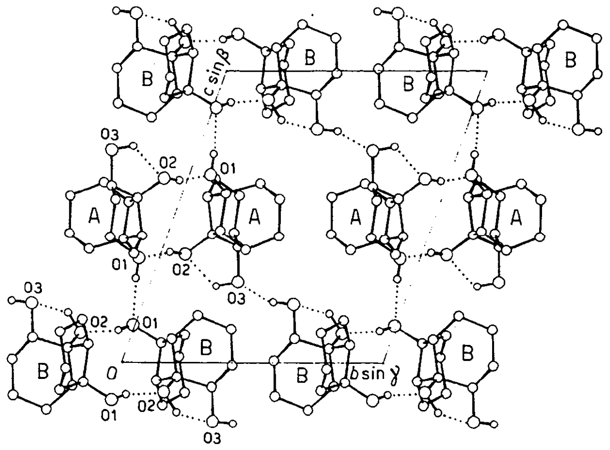


Fig. 3. Packing of the structure of (2) along the crystallographic *a* axis. *A* and *B* designate the two independent molecules in the asymmetric unit. Hydrogen bonds may be identified by the O atoms which act as acceptors (Table 4).

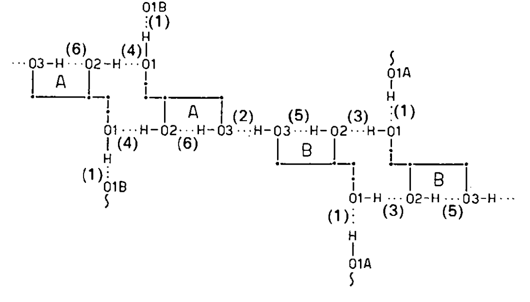


Fig. 4. Topological scheme of the hydrogen-bonding system of compound (2).

Table 5. *Geometric parameters* (Å, °) *of the hydrogen-bonding system of compound* (2) *determined from refinements on* F *(first row) and* F^2 *(second row)*

AA is the antecedent atom, ω is the torsion angle H···A—AA—AB, χ is the angle formed by the D—H bond direction with the lone pair (sp^3) plane, χ' is the angle formed by the D—H bond direction with the AA—A—H plane, and θ_1 and θ_2 are the angles between the H···A vector and the assumed directions of the two lone-pair orbitals on the O atom (sp^3).

	D—H	D···A	H···A	D—H···A	H···A—AA	ω	χ	χ'	θ_1	θ_2
(1) O1A—H1OA···O1B	0.87 (3)	2.789 (3)	1.92 (3)	172 (3)	120 (1)	−180 (1)	3 (4)	37 (2)	166 (4)	83 (3)
	0.85	2.787 (1)	1.94	176	120	177	0	42	165	85
(2) O3B—H3OB···O3A^{iii}	0.91 (4)	2.782 (2)	1.92 (3)	157 (3)	116 (1)	−110 (1)	31 (4)	22 (3)	154 (3)	95 (4)
	0.85	2.786 (2)	1.95	169	113	−113	18	30	155	95
(3) O1B—H1OB···O2B^{i}	0.89 (2)	2.845 (2)	1.97 (2)	167 (2)	145 (1)	−54 (2)	31 (5)	11 (2)	134 (5)	112 (4)
	0.85	2.843 (1)	2.00	170	146	−53	32	10	132	113
(4) O2A—H2OA···O1A^{ii}	0.94 (3)	2.791 (2)	1.86 (3)	168 (3)	138 (1)	19 (2)	24 (4)	12 (2)	140 (4)	108 (3)
	0.85	2.793 (1)	1.96	167	138	21	27	11	139	109
(5) O2B—H2OB···O3B	0.99 (3)	2.558 (2)	1.87 (3)	124 (3)	85 (1)	28 (1)	73 (4)	14 (3)	152 (3)	67 (4)
	0.85	2.558 (1)	2.02	120	83	29	79	9	153	62
(6) O3A—H3OA···O2A	0.94 (4)	2.581 (2)	1.93 (3)	125 (3)	116 (1)	−106 (1)	74 (4)	14 (2)	149 (4)	78 (3)
	0.85	2.580 (1)	2.09	116	113	−104	78	4	150	76

Symmetry code: (i) $1-x, -y, 2-z$; (ii) $2-x, -y, 1-z$; (iii) $x, y-1, 1+z$.

of Fig. 3, the following graph-set is deduced according to the rules proposed by Etter, MacDonald & Bernstein (1990); for molecule A: H1 D, H2 $R_2^2(12)$, H3 $S(5)$; for molecule B: H1 $R_2^2(12)$, H2 $S(5)$, H3 D. The graph set is similar for each of the two molecules, but chemically different H atoms are involved for the different motifs.

From the geometric parameters it seems that there is some tendency for lone-pair directionality to an sp^3 acceptor O atom in the case of the intermolecular hydrogen bond of (1), while for the other hydrogen bonds the geometries far from indicate defined directionalities; this is particularly true of the intramolecular hydrogen bonds of (5) and (6) where hindrance effects, imposed by the rigid core of the molecule, are of the greatest importance.

The observed differences in hydrogen bonding for compound (2) justify the significant differences ($\Delta/\sigma \gg 3$) found for bond angles involving the O atoms of the two molecules (Table 2), which do not show any significant difference in bond distances.

The relevant geometrical parameters of the hydrogen bond in compound (6) are as follows: O2—H(O2) 0.74 (7), O2···O1 2.832 (4), H(O2)···O1 2.11 (7) Å, O2—H(O2)···O1 165 (7)° (where O1 has the symmetry operation $2-x, y+\frac{1}{2}, \frac{1}{2}-z$).

Non-bonded energy calculations show that the orientation of the methoxy groups in the molecules of compounds (3) and (6) and that of the two bulky methanesulfonate groups in compound (3) are determined mainly by intramolecular hindrance, *i.e.* packing effects should not significantly influence their conformations.

The authors are indepted to Professor G. M. Sheldrick who kindly made his *SHELXL*92 program available to them at the beta-test stage. Financial support from the European Community Commission under grant No. SC1000657 is gratefully acknowledged.

References

BELLETTI, D., UGOZZOLI, F., CANTONI, A. & PASQUINELLI, G. (1979). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens-AED con Sistema General Automation Jumbo* 220. Internal Reports 1-3/79. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

CAUBÈRE, P. & BRUNET, J. J. (1972). *Tetrahedron*, **28**, 4835–4845.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

EATON, P. E., SRIKRISHNA, A. & UGGERI, F. (1984). *J. Org. Chem.* **49**, 1728–1732.

ETTER, M. C., MACDONALD, J. C. & BERNSTEIN, J. (1990). *Acta Cryst.* **B46**, 256–262.

GREBE, H., LANGE, A., RIECKERS, H., KIESLICH, K., VIERGUTZ, W., WASKAUSEN, P. & WINTERFELDT, E. (1991). *J. Chem. Soc. Perkin Trans.* 1, pp. 2651–2655.

JAMART-GRÉGOIRE, B., BROSSE, N., IANELLI, S., NARDELLI, M. & CAUBÈRE, P. (1991). *Tetrahedron Lett.* **32**, 3069–3070.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

LAWTON, S. L. & JACOBSON, R. A. (1965). *The Reduced Cell and Its Crystallographic Applications*, Ames Laboratory. Available from the Clearing-house for Federal Scientific and Technical Information, National Bureau of Standards, US Department of Commerce, Springfield, Virginia, USA.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–589.

LE PAGE, Y. (1987). *J. Appl. Cryst.* **A20**, 264–269.

MEHTA, G., NARAYANA MURTHY, A., SIVAKUMAR REDDY, D. & VEERA REDDY, A. (1986). *J. Am. Chem. Soc.* **108**, 3443–3452.

MOTHERWELL, W. D. S. & CLEGG, W. (1976). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

MUGNOLI, A. (1985). *J. Appl. Cryst.* **18**, 183–184.

NARDELLI, M. (1983*a*). *Comput. Chem.* **7**, 95–98.

NARDELLI, M. (1983*b*). *Acta Cryst.* **C39**, 1141–1142.

NARDELLI, M. & MANGIA, A. (1984). *Ann. Chim.* (*Rome*), **74**, 163–174.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

SHELDRICK, G. M. (1992). *SHELXL*92. Program for crystal structure refinement. Univ. of Göttingen, Germany.

SPEK, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.

TOPPING, H. (1960). *Errors of Observation and their Treatment*, p. 91. London: Chapman and Hall.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.