observed in similar conjugated alkyl systems (Denne & Mackay, 1974; Wong, 1978).

The molecule, (II), is essentially planar with an average deviation of 0.03 Å and with C(13) deviating 0.172 Å away from the least-squares plane (Hamilton, 1964) through all non-H atoms. Molecules are packed with the molecular plane parallel to the (202) plane (Fig. 2). The benzisothiazole ring (x, y, z) overlaps an adjacent ring ($x - \frac{1}{2}$, $\frac{1}{2} - y$, z) resulting in a π-stacked column of rings in the [100] direction.

The financial assistance of the National Sciences and Engineering Research Council of Canada is gratefully acknowledged. We also thank Drs James Trotter and Steven Rettig of the University of British Columbia for allowing one of us (ASS) to make use of their equipment for data collection and analysis.

References

BRUMMER, S. & WEISS, A. (1987). *Ber. Bunsenges. Phys. Chem.* **91**, 873–879.
BURKE-LAING, M. & LAING, M. (1976). *Acta Cryst.* B**32**, 3216–3224.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
DAVIS, M. (1985). *Adv. Heterocycl. Chem.* **38**, 105–133.
DAVIS, M., MACKAY, M. F. & DENNE, W. A. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 565–568.
DENNE, W. A. & MACKAY, M. F. (1974). *J. Cryst. Mol. Struct.* **4**, 141–148.
DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B**31**, 221–234.
GIEREN, A. & DEDERER, B. (1978). *Acta Cryst.* B**34**, 2046–2049.
GILMORE, G. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
HAMILTON, W. C. (1964). *Acta Cryst.* **14**, 185–189.
JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
KIGASAWA, K., OHKUBO, K., KOHAGISAWA, T., SHIMIZU, H., SAITOH, S. & KAMETANI, T. (1976). *Heterocycles*, **4**, 1257–1262.
LEBAN, I. (1976). *Acta Cryst.* B**32**, 1601–1604.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY* Structure Analysis Package. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SATO, S., KINOSHITA, T., HATA, T. & TAMURA, C. (1977). *Acta Cryst.* B**33**, 550–552.
SATO, S., KINOSHITA, T., HATA, T. & TAMURA, C. (1980). *Acta Cryst.* B**36**, 2703–2706.
SCRIVEN, E. F. V. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 2, edited by A. R. KATRITZKY & C. W. REES, pp. 165–314. Oxford: Pergamon.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WONG, R. Y. (1978). *Acta Cryst.* B**34**, 3482–3484.

Acta Cryst. (1992). C**48**, 686–690

Structure of 3-(2,4-Dimethyl-6-methylsulfonyloxyphenyl)-3-methylbutyric Acid

BY ANDRZEJ KATRUSIAK

Department of Crystal Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6,
60-780 *Poznań, Poland*

(*Received* 5 *April* 1991; *accepted* 12 *September* 1991)

Abstract. $C_{14}H_{20}O_5S$, $M_r = 300.38$, monoclinic, $P2_1/c$, $a = 10.5276\,(7)$, $b = 10.417\,(2)$, $c = 28.385\,(3)$ Å, $\beta = 104.583\,(9)°$, $V = 3012.0\,(3)$ Å^3, $Z = 8$, $D_x = 1.33$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 1.54178$ Å, $\mu = 18.6$ cm^{-1}, $F(000) = 1280$, $T = 292$ K, final $R = 0.046$ for 2977 observed reflections. Two symmetry-independent molecules, which have similar conformations, are interconnected by a pair of hydrogen bonds between their hydroxyl groups to form a dimer. In both molecules short intramolecular contacts between atoms of the side chains are observed. The deformations of the phenyl ring are similar to those previously observed in analogous structures and can be attributed to steric effects of the methyl substituents.

Introduction. This X-ray determination of the structure of 3-(2,4-dimethyl-6-methylsulfonyloxyphenyl)-3-methylbutyric acid (I) continues our studies on the influence of substituents and their intermolecular interactions on conformational restrictions in molecules. Milstein & Cohen (1972) and Borchardt & Cohen (1972*a*,*b*) described the influence of substituents, the methyl groups located mainly at C(3) and C(2′)* (see Fig. 1), on the rate of lactonization of *o*-hydroxyhydrocinnamic acid and its derivatives. They found that the rate of this reaction could be

---

* The atom labelling of the title compound (see Fig. 1) has been adopted, for the sake of clarity, for all other structures discussed in this paper.

enhanced by over 10^{11} when two methyl groups were substituted at C(3) and one at C(2′), compared with the rate of lactonization of the compounds with C(3) and C(2′) unsubstituted. They suggested that these methyl groups, which are all located close to each other in the molecule (see Fig. 1), form a trialkyl lock and restrict the conformation of the flexible side chain by interlocking it into a position which is favourable for the reaction. The very reactive *o*-hydroxyhydrocinnamic acid or its derivatives with methyl groups at C(3) or C(2′) are too unstable to obtain crystals suitable for X-ray analysis, therefore their analogues were prepared for crystallographic studies. Two X-ray crystal structure determinations, of a lactone, 4,4,5,7,8-pentamethyldihydrocoumarin, and of an alcohol analogue of the *o*-hydroxyhydrocinnamic acid, pentamethyl-*o*-hydroxydihydrocinnamyl alcohol, carried out by Karle & Karle (1972) in order to explain the large enhancement of the rate constants observed in the lactonization reactions, indicated that the conformational restrictions imposed by the 'trialkyl lock' are not as severe as was expected. This paper now reports on the structure of (I), another analogue of *o*-hydroxyhydrocinnamic acid, which follows previous structural determinations of two other over-methylated lactones: 6-amino-4,4,5,7,8-pentamethyldihydrocoumarin and 6-chloro-4,4,5,7-tetramethyldihydrocoumarin (Katrusiak, 1989*a*,*b*). The main aim of this study is to compare the conformation of the side chain in this structure with that observed by Karle & Karle (1972) in pentamethyl-*o*-hydroxydihydrocinnamyl alcohol (II).

Experimental. Crystals of (I), suitable for X-ray diffraction study, were obtained by slow evaporation of its ethanol solution. They were rectangular colourless plates with well developed faces. The size of the sample chosen for intensity measurements was 0.32 × 0.30 × 0.25 mm. A CAD-4 diffractometer and graphite-monochromated Mo $K\alpha$ radiation were used. Unit-cell dimensions were determined from the least-squares fit 25 automatically centred reflections ($9.0 < 2\theta < 23.0°$). Stationary background measurements and the $2\theta-\theta$ scan method were applied, the variable scan speed ranging from 2.0 to 20.0° min^{-1} depending on reflection intensity. Quadrant of reflections collected out to $2\theta = 60°$ ($\sin\theta/\lambda = 0.713$ Å^{-1}): h −14/14, k 0/14, l 0/40. Two control reflections monitored every 2 h showed no systematic variation in their intensity throughout the data collection. Of 4983 reflections, 2977 were independent with $I > 2.5\sigma(I)$ and were considered observed. Only Lp corrections were applied. The structure was solved by direct methods using the program *SHELXS*86 (Sheldrick, 1986) and refined with anisotropic thermal parameters for non-H atoms. All the H atoms were located in a difference Fourier map and were included in the refinement with isotropic thermal factors. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$. At final convergence: $R = 0.046$, $wR = 0.033$ for 2977 reflections, 261 parameters, $S = 1.06$, $(\text{shift}/\sigma)_{\max} = 0.1$ for non-H atoms; highest and lowest peaks on the final ΔF map 0.23 and −0.29 e Å^{-3}, respectively. Most of the calculations were performed with *SHELX76* (Sheldrick, 1976) on an ICL 2900 computer; the atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic parameters are listed in Table 1.*

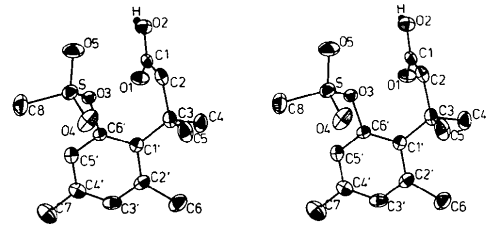

Fig. 1. Stereoscopic *ORTEP* (Johnson, 1970) drawing of (I) viewed along the direction perpendicular to its phenyl ring. Thermal ellipsoids enclose 50% probabilities; H atoms, except that in the carboxyl group taking part in the hydrogen bond, have been omitted for clarity.

Discussion. A stereoscopic view of (I) and the atom labelling are presented in Fig. 1. The asymmetric part of the unit cell of (I) contains two molecules, hereafter referred to as molecules *A* and *B*. These molecules are interconnected by a pair of hydrogen bonds linking their carboxyl groups; the geometry of the hydrogen bonds is described in Table 2. The dimer formed in this way is nearly symmetrical with respect to a non-crystallographic twofold axis perpendicular to the plane defined by the four O atoms forming the hydrogen bonds: O(1*A*)···HO(2*B*) and O(2*A*)H···O(1*B*). However, a statistically significant difference in the O···O distances of these hydrogen bonds of 0.059 (5) Å is observed; the other hydrogen-bond parameters agree well within error. The arrangement of the molecules in the unit cell is presented in Fig. 2. Except for the hydrogen bonds between the hydroxyl groups, there are no short intermolecular contacts other than van der Waals interactions in this structure.

The bond lengths and valency angles for both independent molecules are listed in Table 3. There

---

* Lists of structure factors, anisotropic thermal parameters, H-atom positions and least-squares planes fitted to the phenyl rings have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54652 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for* (I)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
Molecule *A*				
C(1*A*)	0.1656 (4)	0.5025 (4)	0.1799 (1)	0.041
O(1*A*)	0.2564 (3)	0.5602 (3)	0.17085 (9)	0.060
O(2*A*)	0.0987 (3)	0.4149 (3)	0.15091 (9)	0.060
C(2*A*)	0.1147 (3)	0.5237 (3)	0.2244 (1)	0.047
C(3*A*)	0.1783 (3)	0.6317 (3)	0.2595 (1)	0.047
C(4*A*)	0.1114 (4)	0.6280 (4)	0.3021 (1)	0.065
C(5*A*)	0.1404 (4)	0.7577 (4)	0.2305 (1)	0.063
C(1′*A*)	0.3294 (3)	0.6216 (3)	0.2809 (1)	0.040
C(2′*A*)	0.4062 (4)	0.7284 (3)	0.3035 (1)	0.046
C(6*A*)	0.3535 (4)	0.8584 (4)	0.3127 (2)	0.069
C(3′*A*)	0.5415 (4)	0.7153 (4)	0.3212 (3)	0.055
C(4′*A*)	0.6099 (4)	0.6054 (4)	0.3185 (1)	0.051
C(7*A*)	0.7561 (4)	0.5950 (5)	0.3388 (2)	0.078
C(5′*A*)	0.5368 (3)	0.5011 (3)	0.2977 (1)	0.045
C(6′*A*)	0.4017 (3)	0.5098 (3)	0.2812 (1)	0.036
O(3*A*)	0.3405 (2)	0.3914 (2)	0.26248 (8)	0.040
S(1*A*)	0.31191 (9)	0.28807 (9)	0.30006 (4)	0.047
O(4*A*)	0.2830 (3)	0.3531 (2)	0.33974 (9)	0.068
O(5*A*)	0.2181 (3)	0.2047 (3)	0.2710 (1)	0.072
C(8*A*)	0.4598 (4)	0.2042 (4)	0.3203 (2)	0.066
Molecule *B*				
C(1*B*)	0.2719 (4)	0.4507 (4)	0.0596 (1)	0.042
O(1*B*)	0.1820 (2)	0.3915 (2)	0.06794 (8)	0.050
O(2*B*)	0.3448 (3)	0.5308 (3)	0.0914 (1)	0.072
C(2*B*)	0.3177 (4)	0.4462 (4)	0.0136 (1)	0.041
C(3*B*)	0.2367 (3)	0.3696 (3)	−0.0302 (1)	0.039
C(4*B*)	0.3110 (5)	0.3856 (5)	−0.0701 (2)	0.053
C(5*B*)	0.1038 (5)	0.4410 (6)	−0.0445 (2)	0.060
C(1′*B*)	0.2160 (3)	0.2257 (3)	−0.0221 (1)	0.037
C(2′*B*)	0.1222 (3)	0.1525 (4)	−0.0568 (1)	0.047
C(6*B*)	0.0404 (5)	0.2010 (6)	−0.1047 (2)	0.065
C(3′*B*)	0.1026 (4)	0.0231 (4)	−0.0482 (2)	0.040
C(4′*B*)	0.1660 (4)	−0.0410 (4)	−0.0074 (2)	0.060
C(7*B*)	0.1430 (7)	−0.1821 (5)	−0.0005 (3)	0.099
C(5′*B*)	0.2595 (4)	0.0266 (4)	0.0262 (2)	0.038
C(6′*B*)	0.2852 (3)	0.1524 (3)	0.0176 (1)	0.037
O(3*B*)	0.3891 (2)	0.2105 (2)	0.05346 (8)	0.041
S(1*B*)	0.5366 (9)	0.19015 (9)	0.04936 (3)	0.044
O(4*B*)	0.5352 (2)	0.1782 (2)	−0.00055 (9)	0.055
O(5*B*)	0.6069 (2)	0.2930 (2)	0.0766 (1)	0.061
C(8*B*)	0.5855 (5)	0.0466 (5)	0.0801 (2)	0.053

Table 2. *Geometry of the hydrogen bonds* (Å, °) *between the carboxyl groups of the two symmetry-independent molecules of* (I)

O(2*B*)—H	0.84 (4)	O(2*A*)—H	0.91 (5)
O(1*A*)···H	1.82 (4)	O(1*B*)···H	1.82 (5)
O(2*B*)···O(1*A*)	2.664 (4)	O(2*A*)···O(1*B*)	2.723 (4)
O(2*B*)—H···O(1*A*)	176.3 (9)	O(2*A*)—H···O(1*B*)	175.4 (10)

are no statistically significant differences in lengths between the corresponding bonds in molecules *A* and *B*; the largest difference was found for C(3)—C(1′) for which $(d_A - d_B)/\sigma_d = 2.3$ [d_A and d_B are the corresponding bond lengths in molecules *A* and *B* and σ_d is the combined standard deviation of their difference]. The maximum difference/σ calculated for the corresponding valency angles reaches 5.1 and 5.4 for angles O(4)—S(1)—C(8) and C(1′)—C(6′)—O(3), respectively; although of some statistical significance, these values only reflect the influence of different environments of the molecules in the crystal lattice. Surprisingly small differences – as for molecules with flexible side chains – have been found in their conformation. The largest difference in torsion angles (listed in Table 4) reaches 5° and the difference/σ extends only to 10.7. Significant distortions from the ideal values of 120° are observed in the valency angles within and without the phenyl ring – the corresponding endocyclic valency angles are almost exactly the same (within 2σ's) in both independent molecules of (I) and very similar to those observed in the phenyl ring of (II). The transannular valency angles C(1′)—C(6′)—C(5′) and C(2′)—C(3′)—C(4′) are significantly wider than the ideal 120°, while angles C(3′)—C(4′)—C(5′) and C(2′)—C(1′)—C(6′) are significantly smaller (Table 3). The largest difference in the endocyclic valency angles between (I) and (II) is in angle C(4′)—C(5′)—C(6′), where C(5′) is methyl substituted in (II) and unsubstituted in (I). As suggested by Karle & Karle (1972) the distortions of the valency angles within and without the phenyl ring accommodate its overmethylation. Despite the strong angular distortions in the phenyl rings, their planarity has not been significantly affected in the molecules of (I). The χ^2 values of the least-squares planes fitted to the atoms of the phenyl rings in molecules *A* and *B* are 0.016 and 0.021, respectively. Small but statistically significant deviations from planarity are observed for the adjacent methyl substituents and atom O(3). In both molecules *A* and *B* short intermolecular contacts are observed between atom O(3) and carboxy groups: the distance between O(3) and C(1) is 2.814 (4) Å in molecule *A* and 2.837 (4) Å in molecule *B*. Short

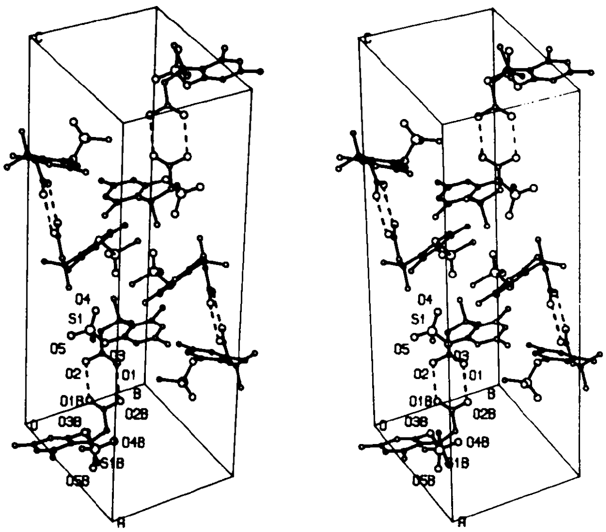

Fig. 2. Stereoscopic view (*PLUTO*; Motherwell, 1976) of the molecular packing in the structure of (I). To avoid overlapping of the molecules, the orientation of the structure in this drawing was obtained by rotating the cell, originally viewed along **a**, by 35° about **c** and then by 25° about the horizontal direction. H atoms have been omitted for clarity. Hydrogen bonds are represented as broken lines. Atom labels for molecule *A* omit the designation '*A*'.

Table 3. *Bond lengths* (Å) *and valency angles* (°) *in the two symmetry-independent molecules of* (I)

	Molecule *A*	Molecule *B*
C(1)—O(1)	1.210 (5)	1.203 (5)
C(1)—O(2)	1.311 (4)	1.325 (5)
C(1)—C(2)	1.507 (6)	1.501 (6)
C(2)—C(3)	1.541 (5)	1.541 (5)
C(3)—C(4)	1.545 (6)	1.540 (7)
C(3)—C(5)	1.548 (5)	1.547 (7)
C(3)—C(1′)	1.556 (5)	1.541 (5)
C(1′)—C(2′)	1.430 (5)	1.429 (5)
C(1′)—C(6′)	1.390 (5)	1.404 (5)
C(2′)—C(6)	1.512 (6)	1.502 (6)
C(2′)—C(3′)	1.393 (7)	1.395 (6)
C(3′)—C(4′)	1.364 (9)	1.358 (6)
C(4′)—C(7)	1.506 (5)	1.511 (7)
C(4′)—C(5′)	1.377 (5)	1.380 (6)
C(5′)—C(6′)	1.384 (5)	1.373 (5)
C(6′)—O(3)	1.431 (4)	1.428 (4)
O(3)—S(1)	1.597 (3)	1.601 (3)
S(1)—O(4)	1.412 (3)	1.419 (4)
S(1)—O(5)	1.415 (3)	1.416 (3)
S(1)—C(8)	1.751 (4)	1.743 (5)
O(2)—C(1)—C(2)	112.4 (3)	110.9 (3)
O(1)—C(1)—C(2)	125.0 (4)	126.7 (4)
O(1)—C(1)—O(2)	122.8 (3)	122.6 (4)
C(1)—C(2)—C(3)	117.5 (3)	119.0 (3)
C(2)—C(3)—C(1′)	116.0 (3)	117.1 (3)
C(2)—C(3)—C(5)	105.2 (3)	104.2 (3)
C(2)—C(3)—C(4)	106.2 (3)	105.0 (3)
C(5)—C(3)—C(1′)	111.5 (3)	110.8 (3)
C(4)—C(3)—C(1′)	108.6 (3)	109.5 (3)
C(4)—C(3)—C(5)	109.4 (3)	110.4 (4)
C(3)—C(1′)—C(6′)	124.4 (3)	125.8 (3)
C(3)—C(1′)—C(2′)	122.0 (3)	121.1 (3)
C(2′)—C(1′)—C(6′)	113.7 (3)	113.2 (3)
C(1′)—C(2′)—C(3′)	119.9 (3)	120.2 (4)
C(1′)—C(2′)—C(6)	125.8 (4)	125.9 (4)
C(6)—C(2′)—C(3′)	114.4 (4)	114.1 (4)
C(2′)—C(3′)—C(4′)	124.7 (6)	124.3 (4)
C(3′)—C(4′)—C(5′)	116.2 (4)	116.9 (4)
C(3′)—C(4′)—C(7)	122.9 (5)	122.0 (5)
C(7)—C(4′)—C(5′)	121.0 (4)	121.2 (5)
C(4′)—C(5′)—C(6′)	120.7 (3)	120.2 (4)
C(1′)—C(6′)—C(5′)	125.0 (3)	125.3 (4)
C(5′)—C(6′)—O(3)	113.5 (3)	115.4 (3)
C(1′)—C(6′)—O(3)	121.7 (3)	119.5 (3)
C(6′)—O(3)—S(1)	118.5 (2)	118.5 (2)
O(3)—S(1)—C(8)	104.8 (2)	104.3 (2)
O(3)—S(1)—O(5)	104.2 (2)	104.1 (2)
O(3)—S(1)—O(4)	109.0 (1)	108.6 (2)
O(5)—S(1)—C(8)	108.6 (2)	109.2 (2)
O(4)—S(1)—C(8)	109.4 (2)	110.7 (4)
O(4)—S(1)—O(5)	120.1 (2)	119.1 (2)

Table 4. *Selected torsion angles* (°) *in the two symmetry-independent molecules of* (I)

	Molecule *A*	Molecule *B*
O(2)—C(1)—C(2)—C(3)	−175.0 (8)	−173.1 (8)
O(1)—C(1)—C(2)—C(3)	3.9 (10)	6.9 (11)
C(1)—C(2)—C(3)—C(4)	−177.4 (8)	−179.5 (8)
C(1)—C(2)—C(3)—C(5)	66.7 (8)	64.6 (9)
C(1)—C(2)—C(3)—C(1′)	−56.9 (9)	−58.0 (9)
C(2)—C(3)—C(1′)—C(2′)	164.2 (8)	168.1 (8)
C(2)—C(3)—C(1′)—C(6′)	−17.6 (9)	−13.5 (10)
C(5)—C(3)—C(1′)—C(2′)	44.0 (9)	49.0 (9)
C(4)—C(3)—C(1′)—C(2′)	−76.5 (9)	−72.8 (9)
C(3)—C(1′)—C(6′)—O(3)	−1.2 (10)	−2.8 (10)
C(3)—C(1′)—C(2′)—C(6)	4.8 (10)	3.8 (10)
C(2′)—C(1′)—C(6′)—O(3)	177.1 (7)	175.8 (8)
C(6′)—C(1′)—C(2′)—C(6)	−173.6 (8)	−174.8 (9)
C(4′)—C(5′)—C(6′)—O(3)	−177.0 (8)	−175.9 (8)
C(1′)—C(6′)—O(3)—S(1)	−99.0 (8)	−96.7 (8)
C(6′)—O(3)—S(1)—O(4)	33.6 (7)	31.7 (10)
C(6′)—O(3)—S(1)—O(5)	162.9 (7)	159.4 (7)
C(6′)—O(3)—S(1)—C(8)	−83.2 (7)	−86.3 (7)

distances are also found between O(3) and C(2): 2.728 (5) and 2.725 (4) Å in molecules *A* and *B*; distance O(3)···H(21) is 2.40 (3) Å in *A* and 2.35 (5) Å in *B* and angle O(3)···H(21)—C(2) is 102 (1)° in both the molecules.

The conformation of the side chain and its position with respect to the phenyl ring and methylsulfonyloxy group was the main interest in this study. In theory, this side chain can rotate about the single bond C(1′)—C(3) and this motion could be hindered only by steric interactions between atoms C(2), C(4) and C(5) and the adjacent methyl group, C(6), as suggested by Milstien & Cohen (1972) and Borchardt & Cohen (1972*a*,*b*). Throughout the remaining discussion, we have assumed that the conformation of the molecules in the crystals reflects, to some extent at least, their favourable conformation in solution. The conformation of the side chain can be conveniently described by torsion angles (Table 4) or by the distances of the atoms in the chain to the least-squares plane fitted to the phenyl ring. If the positions of the methyl C(4) and C(5) atoms were determined by their intramolecular interactions with methyl group C(6), these methyl groups should lie on the opposite sides and at approximately equal distances from the plane. The distances of atoms C(4) and C(5) from the best plane are 1.355 (4) and −1.060 (4) Å in molecule *A* and 1.285 (5) and −1.188 (6) Å in molecule *B*, respectively (the negative values indicate the opposite sides of the phenyl-ring planes). Interestingly, the distances of atom C(6) from the phenyl plane can be correlated with the distances of the methyl groups at C(3): atom C(6) is 0.091 (4) Å from this plane in molecule *A* and 0.052 (6) Å in molecule *B*. The distances of atoms C(4) and C(5)* in the four symmetry-independent molecules of (II) were: 0.21 and 1.54 Å in molecule (II*A*), 0.26 and 1.42 Å in molecule (II*B*), −0.12 and 1.49 Å in molecule (II*C*) and −0.365 and 1.28 Å in molecule (II*D*). They showed that the intramolecular interactions between the methyl groups at C(3) and C(2′) have no strict influence on the position of the side chain with respect to the phenyl ring and that the side chain has considerable freedom of rotation about the C(1′)—C(3) bond (Karle & Karle, 1972). The present results for (I) are different from those observed in (II), as C(4) and C(5) in (I) lie at approximately equal distances on the opposite sides of the phenyl-ring plane. A similar situation was observed in the structures of the over-methylated lactones: 4,4,5,7,8-pentamethyldihydrocoumarin, −0.85 and 1.35 Å (Karle & Karle, 1972); 6-amino-4,4,5,7,8-pentamethyldihydrocoumarin, −1.160 (4) and 1.141 (3) Å in molecule *A* and −1.033 (4) and 1.164 (4) Å in molecule *B* (Katrusiak, 1989*a*); 6-chloro-4,4,5,7-tetramethyldihydrocoumarin, −1.017 (4) and 1.277 (4) Å in molecule *A*,

---

* See footnote to *Introduction*.

−1.008 (4) and 1.287 (4) Å in molecule *B*, −1.072 (5) and 1.230 (5) Å in molecule *C* and −1.088 (6) and 1.223 (5) Å in molecule *D* (Katrusiak, 1989*b*). Thus, the position of the side chain in (I) appears ideal for lactonization. In the light of the previous studies of Karle & Karle (1972) the 'trimethyl lock' is unlikely to be responsible for this side-chain conformation and further structural studies are needed to explain the influence of over-methylation on the rate of lactonization of these compounds.

The author is grateful to Professor Wiesław Antkowiak of the Faculty of Chemistry, Adam Mickiewicz University, Poznań, for stimulating discussions and for preparing and providing the substance, and to Dr Louis A. Cohen of the National Institute of Arthritis and Metabolic Diseases, Bethesda, Maryland, USA (where the substance was synthesized), for his encouragement to undertake the project and his informative correspondence. The author is also indebted to Drs R. O. Gould and A. J. Blake of the Department of Chemistry, University of Edinburgh, Scotland, for their help in solving this structure and to Dr R. J. Nelmes of the Department of Physics, University of Edinburgh, Scotland, where the data collection and most of the calculations were carried out.

References

Borchardt, R. T. & Cohen, L. A. (1972*a*). *J. Am. Chem. Soc.* **94**, 9166–9174.

Borchardt, R. T. & Cohen, L. A. (1972*b*). *J. Am. Chem. Soc.* **94**, 9175–9181.

Johnson, C. K. (1970). *ORTEP*. Report ORNL-3794, second version. Oak Ridge National Laboratory, Tennessee, USA.

Karle, J. M. & Karle, I. M. (1972). *J. Am. Chem. Soc.* **94**, 9182–9189.

Katrusiak, A. (1989*a*). *Acta Cryst.* C**45**, 275–278.

Katrusiak, A. (1989*b*). *Acta Cryst.* C**45**, 1201–1205.

Milstien, S. & Cohen, L. A. (1972). *J. Am. Chem. Soc.* **94**, 9158–9165.

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

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1992). C**48**, 690–693

Structures of Three 1-[(Diphenylphosphinoyl)methyl]cyclohexanols

By Peter J. Steel*

Chemistry Department, University of Canterbury, Christchurch, New Zealand

and Merle A. Battiste* and Curtis R. Campbell

Chemistry Department, University of Florida, Gainesville, Florida 32611, *USA*

(*Received* 18 *June* 1991; *accepted* 2 *September* 1991)

Abstract. (2*a*) 1-[(Diphenylphosphinoyl)methyl]cyclohex-2-en-1-ol, $C_{19}H_{21}O_2P$, $M_r = 312.4$, monoclinic, *Cc*, $a = 9.190$ (6), $b = 19.485$ (12), $c = 9.570$ (6) Å, $\beta = 103.66$ (5)°, $V = 1665$ Å^3, $Z = 4$, $D_x = 1.25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.16$ mm^{-1}, $F(000) = 664$, $T = 155$ K, $R = 0.045$ for 1553 independent observed reflections. (3*a*) (1*SR*,2*RS*,3*RS*)-1-[(Diphenylphosphinoyl)methyl]-2,3-epoxycyclohexan-1-ol, $C_{19}H_{21}O_3P$, $M_r = 328.4$, monoclinic, *Cc*, $a = 9.240$ (4), $b = 19.529$ (8), $c = 9.736$ (6) Å, $\beta = 103.88$ (4)°, $V = 1706$ Å^3, $Z = 4$, $D_x = 1.28$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.17$ mm^{-1}, $F(000) = 696$, $T = 175$ K, $R = 0.041$ for 2173 independent observed reflections. (5*b*) (1*SR*,2*RS*,3*SR*)-1-[(Diphenylphosphinoyl)methyl]-3-methylcyclohexane-1,2,3-triol, $C_{20}H_{25}O_4P$, $M_r = 360.4$, triclinic, $P\bar{1}$, $a = 5.836$ (3), $b = 11.837$ (8), $c = 13.242$ (7) Å, $\alpha = 75.09$ (5), $\beta = 81.25$ (4), $\gamma = 83.86$ (5)°, $V = 871.5$ Å^3, $Z = 2$, $D_x = 1.37$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.17$ mm^{-1}, $F(000) = 384$, $T = 155$ K, $R = 0.049$ for 2822 independent observed reflections. In (2*a*) and (3*a*) the six-membered ring exists in a half-chair conformation with the bulky diphenylphosphinoylmethyl substituent in a pseudo-axial position and involved in an intramolecular hydrogen bond to the hydroxyl group. In (5*b*) the six-membered ring exists in a chair conformation with the diphenylphosphinoylmethyl subsitituent in an equatorial orientation and involved in an intramolecular hydrogen bond. In addition a network of intermolecular hydrogen bonds exists that involves all three hydroxyl groups of (5*b*).

---

* Authors to whom correspondence should be addressed.

0108-2701/92/040690-04$03.00