

- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MISUMI, S., OHFUNE, Y., FURUSAKI, A., SHIRAHAMA, H. & MATSUMOTO, T. (1976). *Tetrahedron Lett.* pp. 2865–2868.
- MISUMI, S., OHTSUDA, T., HASHIMOTO, H., OHFUNE, Y., SHIRAHAMA, H. & MATSUMOTO, T. (1979). *Tetrahedron Lett.* pp. 35–38.
- MISUMI, S., OHTSUDA, T., OHFUNE, Y., SUGITA, K., SHIRAHAMA, H. & MATSUMOTO, T. (1979). *Tetrahedron Lett.* pp. 31–34.
- SUTHERLAND, J. K. (1974). *Tetrahedron*, **30**, 1651–1660.
- TRAUER, H. (1985). Doctoral Dissertation, Karl-Marx-Universität Leipzig, German Democratic Republic.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1987). **C43**, 1964–1966

Structure of Racemic Isoptychanolide

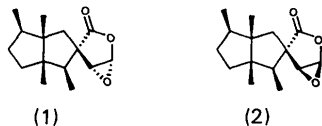
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(Received 4 February 1987; accepted 18 May 1987)

Abstract. C₁₅H₂₂O₃, $M_r = 250.34$, triclinic, $P\bar{1}$, $a = 6.890(1)$, $b = 6.971(1)$, $c = 15.829(2)$ Å, $\alpha = 87.15(2)$, $\beta = 80.33(2)$, $\gamma = 61.97(1)^\circ$, $V = 661.2(2)$ Å³, $Z = 2$, $D_x = 1.26$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.80$ cm⁻¹, $F(000) = 272$, $T \approx 130$ K, $R = 0.057$ for 6933 reflections. The configurations of all asymmetric carbon atoms except those in the oxirane ring are equal to those in ptychanolide.

Introduction. Ptychanolide (1) is a natural product whose crystal structure has been published previously (Takeda, Naoki, Iwashita, Mizukawa, Hirose, Isida & Inoue, 1983). The diastereoisomer isoptychanolide (2) has been synthesized in racemic form (Huguet, Karpf & Dreiding, 1983; Šolaja, Huguet, Karpf & Dreiding, 1987). To establish the configuration at the spiro centre and at the oxirane moiety, we have determined its crystal structure.



Experimental. A colourless parallelepiped, $ca\ 0.6 \times 0.35 \times 0.3$ mm, crystallized from pentane at room temperature, was mounted on a Nicolet R3 four-circle diffractometer with LT-1 low-temperature device and graphite monochromator. Unit-cell parameters were obtained from least-squares refinement (Stewart,

Kruger, Ammon, Dickinson & Hall, 1972) of both 'positive' and 'negative' 2θ values of 72 automatically centered reflection positions, $45 < |2\theta| < 54^\circ$. 6934 unique reflections, $0 \leq h \leq 11$, $-10 \leq k \leq 11$, $-26 \leq l \leq 27$, were measured in the ω -scan technique within $(\sin\theta)/\lambda = 0.857$ Å⁻¹. Owing to beam-stop impairment 001 was omitted. Three standard reflections, repeated after each 100 reflections, varied at most by 3.5% from their initial intensities. The intensities were corrected for standard intensity variation and Lp effects but not for absorption. Reflections with $I < 0.5\sigma(I)$ were set to $I = 0.25\sigma(I)$. The structure was solved by direct methods and the 251 parameters (isotropic temperature factors for the H atoms after their location in a difference density map, anisotropic temperature factors for the other atoms, positional parameters for all atoms) were refined by a blocked-cascade least-squares refinement algorithm with $ca\ 100$ variables per block using all 6933 unique structure factors, $R = 0.057$, $wR = 0.054$, $w = [\sigma^2(F) + 0.0004F^2]^{-1}$, $S = 2.1$, $(\Delta/\sigma)_{\max} = 0.04$, $(\Delta\rho)_{\max} = 0.47$ (on a bond), $(\Delta\rho)_{\min} = -0.25$ e Å⁻³, 0.35 Å apart from C(10). Scattering and dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Unless otherwise stated the program system *SHELXTL* (Sheldrick, 1981) was used for all computerized calculations.

Discussion. Fractional atomic coordinates are given in Table 1, § bond lengths and bond angles in

§ 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 44061 (43 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 ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for the non-H atoms of isoptychanolide (2)

	x	y	z	U_{eq}^*
C(1)	8072 (1)	3714 (1)	1473 (1)	20 (1)
C(2)	10597 (1)	2210 (1)	1318 (1)	25 (1)
C(3)	11025 (1)	255 (1)	1896 (1)	24 (1)
C(4)	8713 (1)	518 (1)	2316 (1)	18 (1)
C(5)	7931 (1)	1768 (1)	3198 (1)	16 (1)
C(6)	5338 (1)	3063 (1)	3298 (1)	16 (1)
C(7)	4805 (1)	3350 (1)	2370 (1)	22 (1)
C(8)	7040 (1)	2175 (1)	1756 (1)	18 (1)
C(9)	4093 (1)	2058 (1)	3873 (1)	24 (1)
O(9)	1660 (1)	3410 (1)	3950 (1)	33 (1)
C(10)	2769 (1)	3572 (1)	4592 (1)	28 (1)
O(10)	3099 (1)	5419 (1)	4523 (1)	27 (1)
C(11)	4500 (1)	5236 (1)	3771 (1)	19 (1)
O(11)	4940 (1)	6683 (1)	3561 (1)	29 (1)
C(12)	7229 (1)	5128 (1)	716 (1)	29 (1)
C(13)	8700 (1)	-1670 (1)	2390 (1)	27 (1)
C(14)	8835 (1)	414 (1)	3962 (1)	26 (1)
C(15)	6775 (1)	1135 (1)	985 (1)	27 (1)

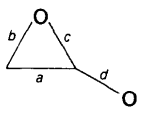
* Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensor.

 Table 2. Bond lengths (\AA) and angles ($^\circ$) for isoptychanolide (2)

C(1)—C(2)	1.534 (1)	C(1)—C(8)	1.555 (1)
C(1)—C(12)	1.524 (1)	C(2)—C(3)	1.540 (1)
C(3)—C(4)	1.547 (1)	C(4)—C(5)	1.558 (1)
C(4)—C(8)	1.562 (1)	C(4)—C(13)	1.528 (1)
C(5)—C(6)	1.561 (1)	C(5)—C(14)	1.525 (1)
C(6)—C(7)	1.554 (1)	C(6)—C(9)	1.515 (1)
C(6)—C(11)	1.528 (1)	C(7)—C(8)	1.542 (1)
C(8)—C(15)	1.530 (1)	C(9)—O(9)	1.474 (1)
C(9)—C(10)	1.451 (1)	O(9)—C(10)	1.409 (1)
C(10)—O(10)	1.405 (1)	O(10)—C(11)	1.370 (1)
C(11)—O(11)	1.200 (1)		
C(2)—C(1)—C(8)	104.5 (1)	C(2)—C(1)—C(12)	113.5 (1)
C(8)—C(1)—C(12)	115.8 (1)	C(1)—C(2)—C(3)	106.8 (1)
C(2)—C(3)—C(4)	106.7 (1)	C(3)—C(4)—C(5)	110.8 (1)
C(3)—C(4)—C(8)	105.2 (1)	C(5)—C(4)—C(8)	102.4 (1)
C(3)—C(4)—C(13)	111.6 (1)	C(5)—C(4)—C(13)	112.0 (1)
C(8)—C(4)—C(13)	114.3 (1)	C(4)—C(5)—C(6)	105.4 (1)
C(4)—C(5)—C(14)	116.1 (1)	C(6)—C(5)—C(14)	115.3 (1)
C(5)—C(6)—C(7)	105.5 (1)	C(5)—C(6)—C(9)	115.2 (1)
C(7)—C(6)—C(9)	112.6 (1)	C(5)—C(6)—C(11)	109.8 (1)
C(7)—C(6)—C(11)	112.5 (1)	C(9)—C(6)—C(11)	101.4 (1)
C(6)—C(7)—C(8)	107.3 (1)	C(1)—C(8)—C(4)	102.6 (1)
C(1)—C(8)—C(7)	111.8 (1)	C(4)—C(8)—C(7)	105.4 (1)
C(1)—C(8)—C(15)	111.6 (1)	C(4)—C(8)—C(15)	114.1 (1)
C(7)—C(8)—C(15)	111.0 (1)	C(6)—C(9)—O(9)	111.7 (1)
C(6)—C(9)—C(10)	107.4 (1)	O(9)—C(9)—C(10)	57.6 (1)
C(9)—O(9)—C(10)	60.4 (1)	C(9)—C(10)—O(9)	62.0 (1)
C(9)—C(10)—O(10)	110.5 (1)	O(9)—C(10)—O(10)	113.0 (1)
C(10)—O(10)—C(11)	108.7 (1)	C(6)—C(11)—O(10)	111.8 (1)
C(6)—C(11)—O(11)	128.0 (1)	O(10)—C(11)—O(11)	120.2 (1)

Table 2. As can be seen from Figs. 1 and 2, (2) differs from (1) only in the position of the epoxide oxygen, which is on the other side of the lactone ring plane. The differences in the bond lengths generally do not exceed 0.028 (9) \AA shorter, and all three oxirane bonds, which are significantly shorter in (1). The reason for this is not clear. Stereoelectronic effects (Kirby, 1983) between

 Table 3. Bond lengths (\AA) in oxyoxiranes



CSD Refcode/ Compound No.	a	b	c	d	e.s.d.'s (class)
BURRAH/(1)	1.422	1.442	1.368	1.412	0.007–0.011
(2)	1.451	1.474	1.409	1.405	0.001
BINJOX	1.473	1.467	1.444	1.369	0.011–0.03
BUHSEC	1.489	1.466	1.423	1.392	not given
ECOTDA	1.451	1.461	1.411	1.432	0.001–0.005
FLOCOS	1.463	1.444	1.443	1.363	0.001–0.005

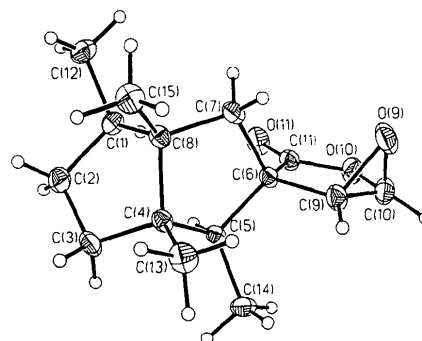


Fig. 1. Molecular drawing of (2). The H atoms are depicted with an arbitrary radius, the other atoms with their 50% thermal ellipsoids.

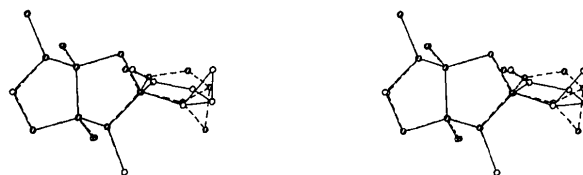


Fig. 2. Stereoscopic overlay plot of (1) and (2) by minimizing the distances between equivalent atoms of the bicyclic skeletons. (1) is shown with dashed bonds. H atoms were omitted.

O(9) and O(10) should be almost the same in the two structures, the torsion angle O(9)C(10)O(10)C(11) being -64.6 (1) $^\circ$ in (2) and 62.6 (7) $^\circ$ in (1). In a comparison with four other structures taken from the Cambridge Structural Database (Allen *et al.*, 1979), which have an oxirane function and an additional O atom attached to it by a single bond (see Table 3), the three above-mentioned distances are again shortest in (1). In all structures bond c is shorter than bond b but with differing significance.

The two *cis*-fused pentacycles may be approximately described as envelopes in (1) and (2). In ring C(1),C(2),C(3),C(4),C(8) atom C(8) is out of plane, in ring C(4),C(5),C(6),C(7),C(8) it is C(4). The largest intra-annular torsion angles in these rings are below

39° (absolute values). The lactone rings are much less puckered. That of (1) is close to the twist form. Its largest intra-annular torsion angle is C(9)C(6)C(11)-O(10) with $-12.2(7)^\circ$. The lactone ring of (2) is almost flat. Its largest torsional angle, C(10)O(10)-C(11)C(6), is $-3.7(1)^\circ$.

References

- ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* B35, 2331–2339.
 HUGUET, J., KARPF, M. & DREIDING, A. S. (1983). *Tetrahedron Lett.* p. 4177.

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KIRBY, A. J. (1983). *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, pp. 52–61. Berlin: Springer.
 SHELDRIK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Revision 3.0. Univ. of Göttingen, Federal Republic of Germany.
 ŠOLAJA, B., HUGUET, J., KARPF, M. & DREIDING, A. S. (1987). *Tetrahedron*. Submitted.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The XRAY72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
 TAKEDA, R., NAOKI, H., IWASHITA, T., MIZUKAWA, K., HIROSE, Y., ISIDA, T. & INOUE, M. (1983). *Bull. Chem. Soc. Jpn.* 56, 1125–1132.

Acta Cryst. (1987). C43, 1966–1968

Conformational Effects in Methoxybenzenes Caused by *Ortho* Disubstitution. I. Pentachloromethoxybenzene

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(Received 9 January 1987; accepted 18 May 1987)

Abstract. $C_7H_3Cl_5O$, $M_r = 280.37$, monoclinic, $P2_1$, $a = 8.636(3)$, $b = 3.935(5)$, $c = 16.925(7)$ Å, $\beta = 120.30(5)^\circ$, $V = 496.6$ Å³, $Z = 2$, $D_x = 1.87$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.42$ mm⁻¹, $F(000) = 276$, $T = 296$ K, final $R = 0.054$ for 775 unique observed reflections. *Ortho* disubstitution forces the methoxy group to move out of the benzene plane, so that the methoxy C atom [C(7)] is 1.182(13) Å above and the methoxy O atom [O(1)] 0.135(9) Å below the calculated least-squares plane [C(1)–C(6)]. The angle C(7)–O(1)–C(1) is $112.2(9)^\circ$. The rest of the molecule is nearly planar: maximum distance from the least-squares plane is 0.037(4) Å [Cl(2)].

Introduction. Chlorinated methoxybenzenes (anisoles) and 1,2-dimethoxybenzenes (veratroles) have been shown to be formed by bacterial biomethylation of chlorinated phenols, 1,2-benzenediols (pyrocatechols) and 2-methoxyphenols (guaiacols), which are produced in chlorobleaching processes in kraft pulp mills (Knuutinen, 1984). These same compounds are considered as potential off-flavour compounds and are frequently detected in environmental samples (Paasivirta *et al.*, 1983).

Quantum-chemical and spectroscopic studies (Anderson, Kollman, Domelsmith & Houk, 1979; Kolehmainen & Knuutinen, 1983) have revealed that

ortho disubstitution causes drastic changes in the spatial arrangement of the methoxy group. Methoxybenzenes lacking *ortho* disubstitution are planar, but when *ortho* disubstitution occurs the methoxy group moves out of the benzene plane.

The purpose of our study was to solve the molecular structure of pentachloromethoxybenzene and determine the degree of out-of-plane displacement of the methoxy group caused by *ortho* disubstitution.

Experimental. Colourless crystals (m.p. 377–379 K) synthesized by refluxing pentachlorophenol with potassium carbonate and methyl iodide in acetone (Knuutinen & Korhonen, 1987), $0.40 \times 0.50 \times 0.65$ mm, mounted on a glass fibre; Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized Mo $K\alpha$; ω - 2θ method; lattice parameters from 25 reflections with $9 < \theta < 17^\circ$; two standard reflections measured every hour, no loss of intensity; 1000 reflections (h : 0→10, k : 0→4, l : -20→20) with $\theta < 25^\circ$, 1000 independent, 775 with $I > 3\sigma(I)$; Lp correction; empirical absorption correction (Walker & Stuart, 1983), correction factors: max. = 1.195 and min. = 0.934; direct methods; refinement by full-matrix least-squares method using unit weights and F^2 s; all non-H atoms anisotropic; all H atoms calculated and used as riding atoms in final refinement (C–H distance