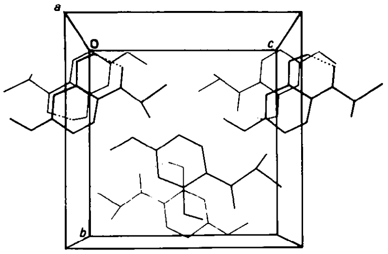


Fig. 2. Perspective view of the molecular packing of 2,2-dichloro-2′-hydroxy-4′-methoxyacetophenone.

A positive charge on H(O2) and a negative charge on O(1) and the geometry O(2)···O(1) = 2·589 (6), O(2)—H(O2) = 1·05 (7), O(1)···H(O2) = 1·72 (7) Å, O(2)—H(O2)···O(1) = 136 (6)° indicate that the conformation of the molecule is stabilized by an intramolecular 'O—H···O(keto)' hydrogen bond.

The *endo* conformation of the carbonyl group, as shown by the C(2)—C(1)—C(7)—O(1) torsion angle, favours this intramolecular hydrogen bonding which results in the formation of a six-membered ring. The O(1)···H(O2) and O(2)···O(1) distances are shorter than the mean values [1·818 (9) and 2·76 (7) Å] observed by Ceccarelli, Jeffrey & Taylor (1981). A corresponding increase in the O(2)—H(O2) distance compared to the mean O(donor)—H distance [0·969 (1) Å] indicates that the hydrogen bond is a strong one (Ceccarelli *et al.*, 1981). The molecules are packed in three dimensions through van der Waals forces. A perspective view of the molecular packing is shown in Fig. 2.

We thank our colleagues S. Chaudhuri and A. K. Basak for their active cooperation.

References

Banerjee, T. (1983). *Crystal and Molecular Structure of Biologically Active Molecules*. PhD Thesis, Univ. of Calcutta.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Ceccarelli, C., Jeffrey, G. A. & Taylor, R. (1981). *J. Mol. Struct.* **70**, 255–271.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

De, A. (1984). *Acta Cryst.* C**40**, 1972–1974.

Dennis, E. W. & Berberian, D. A. (1954). *Antibiot. Chemother.* (*Washington, D.C.*), **4**, 554–560.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 1630–1641.

Eliopoulos, E., Sheldrick, B. & Hamodrakas, S. (1983). *Acta Cryst.* C**39**, 1693–1695.

Haisa, M., Kashino, S. & Maeda, H. (1974). *Acta Cryst.* B**30**, 2510–2512.

Haisa, M., Kashino, S., Yuasa, T. & Akigawa, K. (1976). *Acta Cryst.* B**32**, 1326–1328.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Khaskin, I. G., Shomova, E. A. & Stolper, A. L. (1967). *Mikrobiologiya*, **36**(6), 1019–1023.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Podder, G. (1976). *Chemistry of Natural Products and Studies on Dichloroacetyl Compounds*. PhD Thesis, Univ. of Calcutta.

Pople, J. A. & Beveridge, D. L. (1970). In *Approximate Molecular Orbital Theory*. New York: McGraw-Hill.

Ravindra Acharya, K., Sake Gowda, D. S. & Post, M. (1979). *Acta Cryst.* B**35**, 1360–1363.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Tanimoto, Y., Kobayashi, H., Nagakura, S. & Saito, Y. (1973). *Acta Cryst.* B**29**, 1822–1826.

Vainshtein, B. K., Lobanova, G. M. & Gurskaya, G. V. (1974). *Kristallografiya*, **19**, 531–538.

Acta Cryst. (1985). C**41**, 289–292

rel-Methyl (3*R*,3a*R*,4a*S*,5*S*,7*R*,8*R*,8a*S*,9a*S*)-5-Bromododecahydro-3-isopropyl-8,9a-dimethyl-10-oxo-4a,8-(epoxymethano)-4a*H*-benz[*f*]indene-7-carboxylate (1) and *rel*-Methyl (3*R*,3a*S*,4a*S*,5*S*,7*R*,8*R*,8a*S*,9a*S*)-5-Bromododecahydro-3-isopropyl-8,9a-dimethyl-10-oxo-4a,8-(epoxymethano)-4a*H*-benz[*f*]indene-7-carboxylate (2), $C_{21}H_{31}BrO_4$

By E. J. Corey, T. A. Engler and Jeremy M. Berg

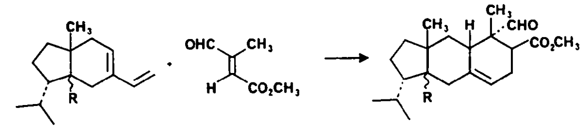
Department of Chemistry, Harvard University, 12 *Oxford Street, Cambridge, Massachusetts* 02138, *USA*

(*Received* 20 *July* 1984; *accepted* 22 *October* 1984)

Abstract. (1) $M_r = 427{\cdot}43$, triclinic, $P\bar{1}$, $a = 7{\cdot}042$ (2), $b = 11{\cdot}760$ (2), $c = 13{\cdot}160$ (2) Å, $\alpha = 102{\cdot}21$ (1), $\beta = 96{\cdot}25$ (2), $\gamma = 95{\cdot}20$ (2)°, $V = 1051{\cdot}1$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}35$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 19{\cdot}48$ cm^{-1}, $F(000) = 448$, $T = 296$ K, final $R = 3{\cdot}38$% for 2110 unique reflections. (2) $M_r = 427{\cdot}43$, monoclinic, $P2_1/c$, $a = 11{\cdot}855$ (4), $b = 7{\cdot}190$ (3), $c = 24{\cdot}571$ (6) Å, $\beta = 97{\cdot}59$ (3)°, $V = 2076$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}37$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 19{\cdot}80$ cm^{-1}, $F(000) = 896$, $T = 296$ K, final $R = 3{\cdot}62$% for 1922 unique reflections. Ring *B* in (1) has a chair conformation and in (2) has a twist-boat conformation. Largest bond-angle differences involve the ring-junction C atoms.

0108-2701/85/020289-04$01.50

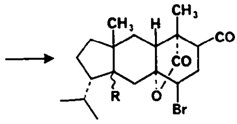
Introduction. In studies directed toward the synthesis of retigeranic acid (3) (Kaneda, Takahashi, Iitaka & Shibata, 1972), the 4 + 2 cycloaddition between dienes (4) and (5) and methyl (*E*)-3-formylbut-2-enoate (6) (Sisido, Kondo, Nozaki, Tuda & Udo, 1960) to afford (7) and (8), respectively, was examined. In order to ascertain the stereochemical course of the cycloaddition, the heavy-atom-labeled derivatives (1) and (2) of (7) and (8), respectively, were prepared and their X-ray crystal structures are reported herein.



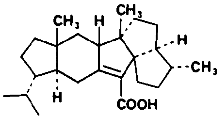
(4) R = α-H (5) R = β-H

(6)

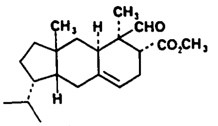
(7) R = α-H (8) R = β-H



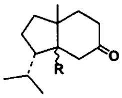
(1) R = α-H
(2) R = β-H



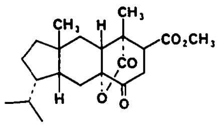
(3)



(9)



(11) R = α-H
(12) R = β-H



(10)

Experimental. For both (1) and (2): Nicolet *R*3 diffractometer; solution by direct methods using *SHELXTL* package and refinement by cascaded blocked-diagonal least squares (*SHELXTL User Manual*, 1981) based on *F* using 250 least-squares parameters; non-hydrogen atoms refined anisotropically and H atoms placed by calculation with temperature factors equal to 1·2 times the equivalent isotropic temperature factor of the C atom to which they are bonded; methyl groups assumed rigid; no secondary extinction used; atomic scattering factors and f', f'' values obtained from *International Tables for X-ray Crystallography* (1974).

(1). Aldehyde (7) was the major thermal cycloaddition adduct of (4) and (6) (neat, 373–376 K, 110 h, 54%). Two minor isomers (15% and 11%) were also found. Oxidation of (7) with chromic acid ($Na_2Cr_2O_7$/aq. H_2SO_4/acetone, 273–278 K) and bromolactonization of the tetra-*n*-butylammonium salt [1 equivalent (n-Bu)$_4$N$^+$.OH$^-$ in CH_3OH, 298 K] of the resulting acid with bromine (1·3 equivalents, $CHCl_3$, 273–278 K) gave (1) [81% from (7)].

Crystal of (1) (0·5 × 0·4 × 0·12 mm) was obtained from pentane/ether, m.p. 382–383·5 K. Lattice parameters determined using 25 reflections in the range $20 < 2\theta < 23°$. No systematic absences observed. Empirical absorption correction based on ψ scans applied (max. 0·941, min. 0·542). Max. $(\sin\theta)/\lambda = 0{\cdot}538$ Å^{-1}. Intensity measurements in the range $3 < 2\theta < 45°$ ($0 \le h \le 7$, $-12 \le k \le 12$, $-14 \le l \le 14$). Three standard reflections (06$\bar{1}$, 0$\bar{3}$7, 313) monitored every sixty scans indicated a 12% decrease in intensity and the data were corrected based on these reflections. Total of 2621 reflections measured of which 511 rejected [$F^2 < 3\sigma(F^2)$]; $R_{\text{merge}} = 1{\cdot}51\%$. Weights calculated from $1/(\sigma^2F + 0{\cdot}001\,F^2)$. $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·007. Final $R = 3{\cdot}38\%$, $wR = 3{\cdot}60\%$, $S = 1{\cdot}093$. Max. and min. heights in final difference Fourier synthesis 0·430 and −0·245 e Å^{-3}.

(2). Reaction of (5) with (6) (neat, 383 K, 22 h) produced a 1:1 mixture of Diels–Alder adducts (8) and (9) (75%) which were separated by column chromatography on silica gel (5% ethyl acetate:hexanes). Chromic acid oxidation ($Na_2Cr_2O_7$/aq. H_2SO_4/acetone, 273–278 K) of (8) afforded ketone (10) (29%) and an acid (27%) of which the tetra-*n*-butylammonium salt [1 equivalent (n-Bu)$_4$N$^+$OH$^-$, $CHCl_3$] reacted with bromine (2 equivalents, $CHCl_3$, 273–278 K) to yield bromolactone (2) (95%).

Crystal of (2) (0·4 × 0·4 × 0·3 mm) obtained from ether, m.p. 425–427 K. Lattice parameters acquired using 25 reflections in the range $16 < 2\theta < 23°$ and systematic absences *h*0*l* with $h \ne 2n$ and 0*k*0 with $k \ne 2n$ found. Empirical absorption correction based on ψ scans applied (max. 0·160, min. 0·110). Max. $(\sin\theta)/\lambda = 0{\cdot}538$ Å^{-1}. Reflections in the range $3 \le 2\theta \le 45°$ ($0 \le h \le 10$, $0 \le k \le 7$, $-26 \le l \le 26$) measured. Three standard reflections (500, 031, 0,0,10) monitored every sixty scans. A 12% decrease in intensity of the 0,0,10 reflection was found and the data were corrected based on the standards. 615 reflections rejected [$F^2 < 2{\cdot}5\sigma(F^2)$] of a total of 2537; $R_{\text{merge}} = 2{\cdot}31\%$. Weights calculated from $1/(\sigma^2F + 0{\cdot}0005\,F^2)$. $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·004. Final $R = 3{\cdot}62\%$, $wR = 3{\cdot}71\%$, $S = 1{\cdot}350$. Final difference Fourier synthesis had max. and min. heights of 0·23 and −0·28 e Å^{-3}.

Discussion. The atomic coordinates, bond distances and bond angles for (1) and (2) are given in Tables 1–3, respectively.* *ORTEP* drawings (Johnson, 1965) of (1) and (2) are shown in Figs. 1 and 2. The data demonstrate a close similarity in molecular structure for (1) and (2) which differ only in the configuration at C(3a) (see Figs. 1 and 2). The existence of a *trans A–B*

---

* Lists of anisotropic temperature factors, H-atom coordinates and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39811 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (1) *and* (2)

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Compound (1)				
Br	7402 (1)	7234 (1)	8637 (1)	60 (1)
O(1)	4661 (3)	9219 (2)	6782 (2)	51 (1)
O(2)	3660 (4)	8699 (3)	5066 (2)	78 (1)
O(3)	7029 (4)	5018 (2)	6132 (2)	68 (1)
O(4)	9363 (5)	6408 (3)	6065 (3)	75 (1)
C(1)	10322 (5)	11996 (3)	7664 (3)	54 (1)
C(2)	9935 (5)	12799 (3)	8682 (3)	52 (1)
C(3)	8326 (5)	12108 (3)	9112 (3)	46 (1)
C(3a)	7680 (5)	11041 (3)	8213 (3)	41 (1)
C(4)	6625 (5)	9962 (5)	8455 (3)	42 (1)
C(4a)	6241 (4)	8952 (3)	7497 (3)	41 (1)
C(5)	5433 (5)	7797 (3)	7750 (3)	48 (1)
C(6)	4694 (5)	6845 (3)	6777 (3)	53 (1)
C(7)	6004 (5)	6803 (3)	5908 (3)	50 (1)
C(8)	6663 (5)	8052 (3)	5771 (3)	47 (1)
C(8a)	7847 (5)	8763 (3)	6794 (2)	39 (1)
C(9)	8932 (5)	9909 (3)	6676 (3)	43 (1)
C(9a)	9515 (4)	10762 (3)	7722 (3)	39 (1)
C(10)	4845 (6)	8677 (3)	5789 (3)	55 (1)
C(11)	6757 (6)	12827 (4)	9519 (4)	68 (2)
C(11a)	7545 (7)	13740 (4)	10521 (4)	90 (2)
C(11b)	5696 (7)	13372 (4)	8712 (5)	107 (3)
C(12)	7688 (7)	6100 (3)	6049 (3)	54 (2)
C(13)	8482 (8)	4260 (4)	6272 (4)	88 (2)
C(14)	7517 (7)	8035 (4)	4758 (3)	70 (2)
C(15)	10946 (5)	10264 (4)	8425 (3)	54 (1)
Compound (2)				
Br	2422 (1)	6666 (1)	386 (1)	55 (1)
O(1)	2298 (2)	8859 (4)	1940 (1)	49 (1)
O(2)	3558 (3)	8682 (5)	2700 (1)	78 (1)
O(3)	5296 (2)	4707 (4)	1091 (1)	64 (1)
O(4)	3960 (3)	2979 (4)	1406 (2)	74 (1)
C(1)	−1034 (4)	5278 (8)	1886 (2)	67 (2)
C(2)	−1741 (4)	6728 (6)	1540 (2)	56 (2)
C(3)	−1316 (3)	6654 (5)	983 (2)	43 (1)
C(3a)	−36 (3)	6275 (4)	1123 (1)	34 (1)
C(4)	671 (3)	8042 (5)	1278 (2)	38 (1)
C(4a)	1917 (3)	7634 (5)	1465 (1)	37 (1)
C(5)	2757 (3)	8144 (5)	1065 (2)	41 (1)
C(6)	3999 (4)	7920 (5)	1310 (2)	49 (2)
C(7)	4229 (3)	6212 (5)	1690 (2)	45 (1)
C(8)	3283 (3)	5995 (6)	2069 (2)	49 (2)
C(8a)	2146 (3)	5693 (5)	1708 (2)	40 (1)
C(9)	1150 (3)	5132 (6)	2008 (2)	46 (1)
C(9a)	43 (3)	4882 (5)	1609 (2)	42 (1)
C(10)	3102 (4)	7958 (7)	2289 (2)	55 (2)
C(11)	−1670 (4)	8296 (5)	599 (2)	53 (2)
C(11a)	−1180 (4)	8135 (7)	56 (2)	68 (2)
C(11b)	−2957 (4)	8494 (7)	494 (3)	88 (2)
C(12)	4441 (3)	4440 (6)	1386 (2)	52 (2)
C(13)	5658 (5)	3062 (8)	819 (3)	96 (3)
C(14)	3617 (4)	4636 (8)	2538 (2)	75 (2)
C(15)	5 (5)	2896 (6)	1387 (2)	73 (2)

Table 2. *Bond distances* (Å) *for* (1) *and* (2)

	(1)	(2)		(1)	(2)
Br—C(5)	1·966 (4)	1·973 (4)	O(1)—C(4a)	1·478 (4)	1·484 (4)
O(1)—C(10)	1·354 (4)	1·359 (5)	O(2)—C(10)	1·203 (5)	1·200 (5)
O(3)—C(12)	1·346 (5)	1·336 (5)	O(3)—C(13)	1·440 (6)	1·451 (7)
O(4)—C(12)	1·199 (6)	1·199 (5)	C(1)—C(2)	1·535 (5)	1·524 (6)
C(1)—C(9a)	1·532 (5)	1·550 (6)	C(2)—C(3)	1·561 (5)	1·522 (6)
C(3)—C(3a)	1·528 (4)	1·535 (5)	C(3)—C(11)	1·527 (6)	1·535 (6)
C(3a)—C(4)	1·524 (5)	1·542 (5)	C(3a)—C(9a)	1·539 (5)	1·551 (5)
C(4)—C(4a)	1·520 (4)	1·516 (5)	C(4a)—C(5)	1·543 (5)	1·533 (6)
C(4a)—C(8a)	1·541 (5)	1·528 (5)	C(5)—C(6)	1·519 (4)	1·524 (5)
C(6)—C(7)	1·544 (6)	1·545 (6)	C(7)—C(8)	1·555 (5)	1·557 (6)
C(7)—C(12)	1·523 (6)	1·514 (6)	C(8)—C(8a)	1·537 (4)	1·527 (5)
C(8)—C(10)	1·533 (6)	1·536 (6)	C(8)—C(14)	1·521 (6)	1·523 (7)
C(8a)—C(9)	1·535 (5)	1·527 (6)	C(9)—C(9a)	1·513 (4)	1·541 (5)
C(9a)—C(15)	1·535 (5)	1·527 (6)	C(11)—C(11a)	1·529 (6)	1·529 (7)
C(11)—C(11b)	1·519 (8)	1·519 (6)			

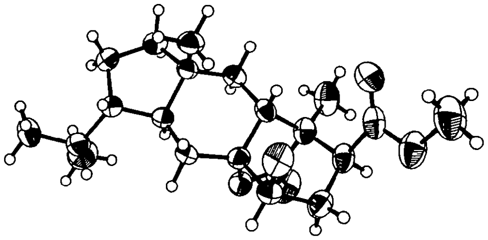


Fig. 1. *ORTEP* drawing of (1).

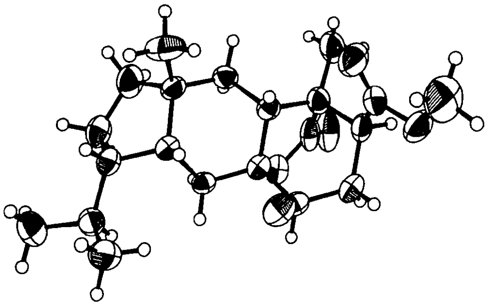


Fig. 2. *ORTEP* drawing of (2).

Table 3. *Bond angles* (°) *for* (1) *and* (2)

	(1)	(2)		(1)	(2)		(1)	(2)
C(4a)—O(1)—C(10)	108·5 (3)	109·2 (3)	C(5)—C(4a)—C(8a)	111·6 (3)	111·9 (3)	C(8a)—C(9)—C(9a)	111·8 (3)	111·8 (3)
C(12)—O(3)—C(13)	115·4 (4)	115·1 (4)	Br—C(5)—C(4a)	110·2 (2)	109·7 (2)	C(1)—C(9a)—C(3a)	99·7 (3)	104·5 (3)
C(2)—C(1)—C(9a)	105·3 (3)	107·8 (4)	Br—C(5)—C(6)	109·8 (3)	110·6 (3)	C(1)—C(9a)—C(9)	115·2 (3)	112·4 (3)
C(1)—C(2)—C(3)	106·5 (3)	104·7 (4)	C(4a)—C(5)—C(6)	113·1 (3)	113·4 (3)	C(1)—C(9a)—C(15)	109·8 (3)	110·0 (4)
C(2)—C(3)—C(3a)	102·9 (3)	103·8 (3)	C(5)—C(6)—C(7)	112·9 (3)	114·0 (3)	C(3a)—C(9a)—C(9)	108·2 (2)	111·9 (3)
C(2)—C(3)—C(11)	114·8 (3)	115·4 (3)	C(6)—C(7)—C(8)	111·4 (3)	110·9 (3)	C(3a)—C(9a)—C(15)	112·8 (3)	109·4 (3)
C(3a)—C(3)—C(11)	116·6 (3)	117·2 (3)	C(6)—C(7)—C(12)	113·2 (3)	113·5 (3)	C(9)—C(9a)—C(15)	110·6 (3)	108·6 (3)
C(3)—C(3a)—C(4)	118·3 (3)	113·4 (3)	C(8)—C(7)—C(12)	112·3 (3)	112·9 (3)	O(1)—C(10)—O(2)	121·3 (4)	121·7 (4)
C(3)—C(3a)—C(9a)	104·9 (2)	104·2 (3)	C(7)—C(8)—C(8a)	109·2 (3)	108·5 (3)	O(1)—C(10)—C(8)	110·4 (3)	109·5 (3)
C(4)—C(3a)—C(9a)	111·9 (3)	111·6 (3)	C(7)—C(8)—C(14)	112·6 (3)	112·4 (3)	O(2)—C(10)—C(8)	128·3 (3)	128·8 (4)
C(3a)—C(4)—C(4a)	111·3 (3)	113·0 (3)	C(8a)—C(8)—C(10)	100·0 (3)	100·5 (3)	C(3)—C(11)—C(11a)	111·0 (3)	111·9 (3)
O(1)—C(4a)—C(4)	107·4 (3)	107·9 (3)	C(8a)—C(8)—C(14)	117·6 (3)	118·0 (4)	C(3)—C(11)—C(11b)	114·2 (4)	111·3 (4)
O(1)—C(4a)—C(5)	103·8 (2)	101·9 (3)	C(10)—C(8)—C(14)	111·0 (3)	111·0 (4)	C(11a)—C(11)—C(11b)	111·7 (4)	110·4 (4)
O(1)—C(4a)—C(8a)	102·4 (3)	102·4 (3)	C(4a)—C(8a)—C(8)	100·1 (3)	101·2 (3)	O(3)—C(12)—O(4)	122·7 (4)	123·2 (4)
C(4)—C(4a)—C(5)	112·7 (3)	116·6 (3)	C(4a)—C(8a)—C(9)	113·4 (3)	108·7 (3)	O(3)—C(12)—C(7)	109·7 (4)	109·5 (3)
C(4)—C(4a)—C(8a)	117·5 (3)	114·3 (3)	C(8)—C(8a)—C(9)	113·4 (3)	115·9 (3)	O(4)—C(12)—C(7)	127·6 (4)	127·3 (4)

ring (Fig. 3) fusion in (1) and a *cis* ring fusion in (2) necessitates the following differences. Ring *B* in (1) is in a chair conformation as is easily seen in the figure and by the torsional angles around this ring (3a—4—4a—8a—9—9a, beginning with ∠9a—3a—4—4a: −53·1, 40·2, −37·8, 47·6, −60·1, 64·0°). In contrast, in (2) ring *B* has a twist-boat conformation (torsional angles 57·6, −25·9, −33·6, 66·2, −34·6, −25·4°). In addition, there are certain bond-angle differences as shown in Table 3. The largest differences are seen at the ring-junction C atoms 3a, 4a, 8a and 9a.

Dienes (4) and (5) were synthesized from hydrindanones (11) and (12), respectively.* Stereospecific syntheses of (11) and (12) have been previously reported (Corey & Engler, 1984) and the crystal structures presently reported establish the relative configuration of the ring fusion of (11) and (12) as well as the stereochemical course of the 4 + 2 cycloadditions between dienes (4) and (5) and dienophile (6).

This research was supported by the National Institutes of Health and the National Science Foundation. X-ray equipment used in this research was obtained by NSF Grant CHE 8000670. The authors thank Jay Ponder and James Fox for help with the structure determinations.

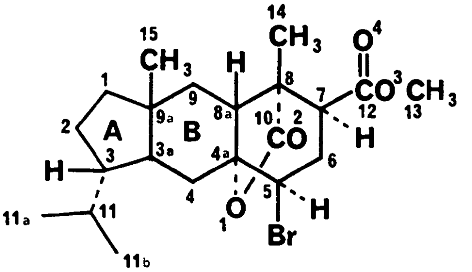


Fig. 3. IUPAC numbering scheme for (1) and (2).

---

* The details of the syntheses of (4) and (5) will be reported at a later date.

References

Corey, E. J. & Engler, T. A. (1984). *Tetrahedron Lett.* **25**, 149–152.

International Tables for X-ray Crystallography (1974). Tables 2.2B and 2.3.1. Birmingham: Kynoch Press.

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

Kaneda, M., Takahashi, R., Iitaka, Y. & Shibata, S. (1972). *Tetrahedron Lett.* **13**, 4609–4611.

SHELXTL User Manual (1981). Nicolet XRD Corporation.

Sisido, K., Kondo, K., Nozaki, H., Tuda, M. & Udo, Y. (1960). *J. Am. Chem. Soc.* **82**, 2286–2288.

Acta Cryst. (1985). C**41**, 292–294

Hexaphenylcyclotrisiloxane, $C_{36}H_{30}O_3Si_3$, a Redetermination

By P. E. Tomlins,* J. E. Lydon,† D. Akrigg and B. Sheldrick

Astbury Department of Biophysics, University of Leeds, Leeds LS2 9JT, England

(*Received* 19 *March* 1984; *accepted* 26 *September* 1984)

Abstract. $M_r = 594·89$, orthorhombic, $P2_12_12_1$, $a = 20·247 (6)$, $b = 15·807 (3)$, $c = 10·109 (2)$ Å, $V = 3235·3$ Å^3, $Z = 4$, $D_m = 1·234$, $D_x = 1·221$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1·514$ mm^{-1}, $F(000) = 1248$, $T = 293$ K. Final $R = 0·0718$ for 2211 unique observed reflections. A redetermination of the structure described by Bokii, Zakharova & Struchkov [*Zh. Strukt. Khim.* (1972), **13**, 291–297] who had insufficient data to carry out an independent refinement of every atom and assumed that the phenyl groups were perfect hexagons (their *R* 17%) is presented. This structure determination gives the same major features and shows that there are small but significant distortions of the phenyl rings, presumably resulting from the ±*M* effect of the silicon atoms.

Introduction. This structure determination is part of a programme of investigation of cyclic oligomers of silane derivatives, prompted by our interest in the unique liquid-crystalline phase of diisobutylsilanediol which we have suggested is of the columnar discotic type.

In general, discogenic molecules have well defined and clearly characteristic types of structures with a central rigid aromatic core, surrounded by an annulus of radiating alkyl chains (usually of the range C_5—C_9). When viewed in this light, diisobutylsilanediol appears to be totally unsuitable for mesophase formation and we have therefore postulated that the basic structural unit of the mesophase was actually a cyclic dimer rather than an individual molecule. Following a preliminary investigation of the crystalline solid, we modified our model to a cyclic trimer.

The structure of the title compound (I) has previously been determined by Bokii *et al.* (1972). The model, which they used for refinement, assumed that the phenyl rings had idealized bond lengths (of 1·4 Å)

---

* Present address: Department of Chemical Engineering, Imperial College, Prince Consort Road, London SW7 2BZ, England.

† To whom correspondence should be addressed.

0108-2701/85/020292-03$01.50