

(*R,R,S,S*)-Bis[(*trans*-2-phenyl-1-cyclopropyl)carbonyl] Peroxide, C₂₀H₁₈O₄

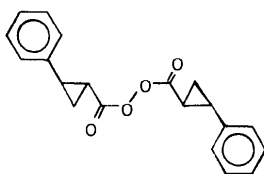
BY DONALD BETHELL, DEREK J. CHADWICK, MARJORIE M. HARDING AND GUY Q. MALING

Departments of Organic and Inorganic, Physical and Industrial Chemistry, University of Liverpool, Liverpool L69 3BX, England

(Received 23 May 1984; accepted 2 July 1984)

Abstract. $M_r = 322.34$, monoclinic, $P2_1/c$, $a = 8.11$ (1), $b = 18.50$ (3), $c = 11.45$ (2) Å, $\beta = 95.5$ (2)°, $U = 1710.0$ Å³, $Z = 4$, $D_x = 1.25$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.690$ mm⁻¹, $F(000) = 680$, $T = ca$ 293 K, final $R = 0.053$ for 1157 unique reflexions. The molecular structure of the title compound has been determined for comparison with those of the isomeric bis[(1-phenyl-1-cyclopropyl)carbonyl] peroxide and of *trans*-cinnamoyl peroxide. The torsion angle about the O–O bond is unusually large [-121.8 (7)°].

Introduction. In the course of a programme attempting to relate the structures of diacyl peroxides with their kinetic and spectroscopic behaviour on thermolysis, we have determined the molecular structures of bis[(1-phenyl-1-cyclopropyl)carbonyl] peroxide (Bethell, Chadwick, Harding & Maling, 1982) and *trans*-cinnamoyl peroxide (Bethell, Chadwick, Harding & Maling, 1984). The present peroxide (I) was investigated for determination particularly of the degree of conjugation of the phenyl, cyclopropyl and carbonyl groups in it in comparison with analogous moieties in the other two molecules.



(I)

Experimental. (I) [m.p. 384–385 K (dec.)] was prepared from the corresponding commercial (\pm) acid by the method of Greene & Kazan (1963). Crystals obtained from solutions in methylene chloride plus methanol exhibited a regular disorder and could not be used for structure determination. Slow recrystallization at 273 K from solution in hexachloroacetone yielded needle crystals from which a suitable section ($0.3 \times 0.2 \times 0.2$ mm) was cut. A further section from the same crystal was used for interlayer scaling. The peroxide crystals showed no deterioration on exposure

to the X-ray beam. D_m not determined. Reflexion intensities measured by the SERC Microdensitometer Service, Daresbury Laboratory, from Weissenberg photographs of layers $0kl$ to $6kl$ and $hk0$, giving 1157 data used for structure solution and refinement. Unit-cell dimensions from precession photographs. Structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1970) in space group $P2_1/c$, and refined using full-matrix least squares on F (*XRAY72*; Stewart, Kruger, Ammon, Dickinson & Hall, 1972); unit weight. In final refinement cycle $\Delta/\sigma = 0.0545$ (max.) and 0.0080 (av.). Majority of the H atoms located from a difference map and refined using isotropic thermal parameters; vibration parameters for O(2), O(14), C(5) and C(17) unexpectedly high and anisotropic; unexpectedly short contact of 3.2 Å between O(2) and C(17); attempts to assign two disordered positions to the carbonyl O's with longer C...O contact distances not successful; no extinction correction applied; peak heights in final difference map 0.17 (max.) and $-0.21 e \text{ \AA}^{-3}$ (min.).

Discussion. Positional and mean thermal parameters for C and O are in Table 1.* The molecular and crystal structures are depicted in Figs. 1 and 2 respectively, while Table 2 shows the bond lengths and bond angles. Torsion angles (excluding those in the two phenyl rings and those involving H) are in Table 3.

The molecular structure indicates that the crystals obtained from hexachloroacetone solution are of the *R,R,S,S* (*meso*) form. In the crystal all the O atoms show very anisotropic thermal parameters and close contacts with atoms on adjacent molecules, *viz* O(1)...O(13) 3.35, O(1)...C(16) 3.35, O(2)...C(9) 3.36, O(2)...C(17) 3.20, O(13)...O(13) 3.04, O(14)...C(23) 3.38 Å. Strong intermolecular interaction may thus be responsible for the difficulty in refinement of the carbonyl O and methylene C atoms.

* Lists of H-atom parameters, structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39621 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecules adopt an extended conformation in the crystal with an unusually large torsion angle about the O—O bond [$-121.8(7)^\circ$]; this value is more than 5° greater than the largest previously reported for a

diacyl peroxide (Gougoutas & Clardy, 1970) and some 30° more than the usual value seen, for example, in the structurally closely related *trans*-cinnamoyl peroxide. This observation may also be related to the inter-

Table 1. Atomic coordinates and mean temperature factors (\bar{U}) ($\times 10^4$) for C and O atoms, with e.s.d.'s in parentheses

	x	y	z	$\bar{U}(\text{\AA}^2)$
O(1)	8185 (5)	4847 (2)	8599 (4)	736 (33)
O(2)	5864 (5)	5451 (2)	8551 (6)	1135 (44)
O(13)	8904 (5)	5486 (2)	9185 (5)	694 (33)
O(14)	10453 (8)	5483 (3)	7645 (6)	1129 (50)
C(3)	6560 (7)	4938 (3)	8320 (6)	594 (46)
C(4)	5885 (7)	4281 (3)	7767 (6)	506 (44)
C(5)	4326 (10)	4344 (4)	6937 (8)	872 (64)
C(6)	4191 (7)	4047 (3)	8146 (7)	560 (47)
C(7)	3832 (7)	3291 (3)	8323 (6)	431 (41)
C(8)	4262 (7)	2766 (3)	7547 (6)	500 (43)
C(9)	3814 (9)	2073 (3)	7724 (7)	624 (51)
C(10)	2976 (9)	1880 (4)	8683 (7)	640 (53)
C(11)	2563 (8)	2393 (4)	9466 (6)	640 (52)
C(12)	3009 (7)	3081 (4)	9304 (6)	538 (46)
C(15)	10128 (9)	5736 (3)	8542 (8)	591 (51)
C(16)	10916 (7)	6333 (3)	9216 (6)	504 (44)
C(17)	12760 (8)	6413 (4)	9104 (8)	822 (60)
C(18)	11607 (7)	6923 (3)	8476 (6)	550 (44)
C(19)	11457 (7)	7670 (3)	8865 (6)	456 (41)
C(20)	12374 (9)	7938 (4)	9893 (7)	636 (51)
C(21)	12173 (12)	8640 (4)	10191 (7)	882 (66)
C(22)	11131 (12)	9069 (4)	9498 (10)	962 (75)
C(23)	10239 (9)	8813 (4)	8493 (9)	813 (66)
C(24)	10399 (7)	8119 (4)	8162 (6)	561 (46)

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

E.s.d.'s are 0.010 \AA and 0.6° respectively.

O(1)—C(3)	1.336	O(13)—C(15)	1.372
C(3)—O(2)	1.149	C(15)—O(14)	1.181
C(3)—C(4)	1.452	C(15)—C(16)	1.459
C(4)—C(5)	1.511	C(16)—C(17)	1.520
C(4)—C(6)	1.542	C(16)—C(18)	1.521
C(5)—C(6)	1.503	C(17)—C(18)	1.467
C(6)—C(7)	1.447	C(18)—C(19)	1.461
C(7)—C(8)	1.384	C(19)—C(20)	1.420
C(8)—C(9)	1.353	C(20)—C(21)	1.359
C(9)—C(10)	1.393	C(21)—C(22)	1.358
C(10)—C(11)	1.368	C(22)—C(23)	1.382
C(11)—C(12)	1.342	C(23)—C(24)	1.349
C(12)—C(7)	1.414	C(24)—C(19)	1.392
O(1)—O(13)	1.452		
O(13)—O(1)—C(3)	110.6	O(1)—O(13)—C(15)	107.8
O(1)—C(3)—O(2)	122.9	O(13)—C(15)—O(14)	124.5
O(1)—C(3)—C(4)	108.7	O(13)—C(15)—C(16)	105.9
O(2)—C(3)—C(4)	128.3	O(14)—C(15)—C(16)	129.6
C(3)—C(4)—C(5)	117.8	C(15)—C(16)—C(17)	114.3
C(3)—C(4)—C(6)	114.9	C(15)—C(16)—C(18)	114.5
C(5)—C(4)—C(6)	59.0	C(17)—C(16)—C(18)	57.7
C(4)—C(5)—C(6)	61.5	C(16)—C(17)—C(18)	61.2
C(4)—C(6)—C(5)	59.5	C(16)—C(18)—C(17)	61.1
C(4)—C(6)—C(7)	120.5	C(16)—C(18)—C(19)	117.6
C(5)—C(6)—C(7)	121.1	C(17)—C(18)—C(19)	121.9
C(6)—C(7)—C(8)	121.5	C(18)—C(19)—C(20)	122.0
C(6)—C(7)—C(12)	119.6	C(18)—C(19)—C(24)	117.0
C(8)—C(7)—C(12)	119.0	C(20)—C(19)—C(24)	121.0
C(7)—C(8)—C(9)	118.7	C(19)—C(20)—C(21)	118.4
C(8)—C(9)—C(10)	121.3	C(20)—C(21)—C(22)	119.7
C(9)—C(10)—C(11)	120.5	C(21)—C(22)—C(23)	122.2
C(10)—C(11)—C(12)	118.8	C(22)—C(23)—C(24)	120.2
C(11)—C(12)—C(7)	121.6	C(23)—C(24)—C(19)	118.4

Table 3. Torsion angles ($^\circ$) excluding those involving H and those within phenyl rings (e.s.d.'s $\sim 0.7^\circ$)

1-3-4-5	-154.5	4-6-7-8	-43.3	15-16-17-18	104.6
1-3-4-6	138.9	4-6-7-12	137.3	15-16-18-17	-104.3
1-13-15-14	3.2	5-4-6-7	110.4	15-16-18-19	142.6
1-13-15-16	174.8	5-6-7-8	27.3	16-17-18-19	-106.2
2-3-1-13	-1.7	5-6-7-12	-152.1	16-18-19-20	69.3
2-3-4-5	29.0	6-7-8-9	-176.5	16-18-19-24	-112.3
2-3-4-6	-37.6	6-7-12-11	176.0	17-16-18-19	-113.1
3-1-13-15	-121.8	13-15-16-17	146.8	17-18-19-20	-2.2
3-4-5-6	-103.6	13-15-16-18	-149.2	17-18-19-24	176.2
3-4-6-5	108.7	14-15-16-17	-31.1	18-19-20-21	179.6
3-4-6-7	-140.9	14-15-16-18	32.9	18-19-24-23	-179.7
4-5-6-7	-109.4				

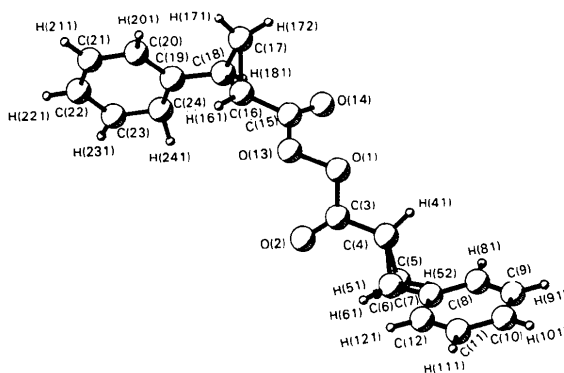


Fig. 1. A view of (I) drawn by *PLUTO* (Motherwell & Clegg, 1978).

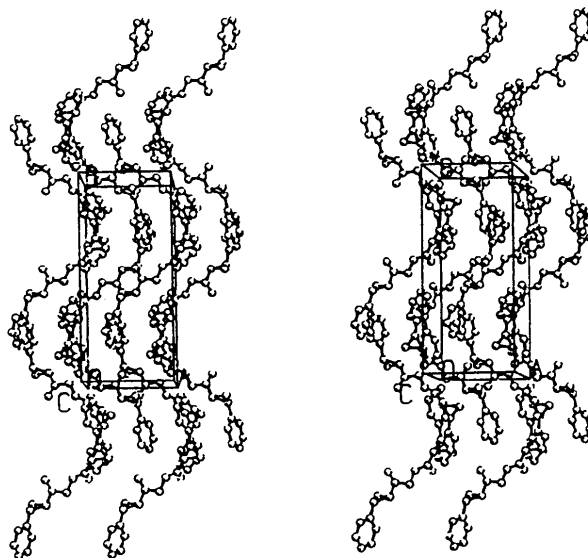


Fig. 2. Stereoscopic view of the crystal structure of (I) (drawn by *PLUTO*).

molecular interaction; the usual 90° torsion angle could bring adjacent molecules even closer together with a reduction in stability of the crystal lattice.

The phenyl and carbonyl groups are both able to adopt the preferred bisected conformation (Jason & Ibers, 1977) with respect to the cyclopropane ring C(4)–C(5)–C(6), unlike the situation in the isomeric bis[1-phenyl-1-cyclopropyl]carbonyl peroxide where there are steric constraints (Bethell, Chadwick, Harding & Maling, 1982). Further, the C–C bond lengths in the three-membered ring show a combination of vicinal bond lengthening and distal bond shortening as previously noted (Allen, 1980), the effect of the carbonyl group appearing to dominate as in the isomeric peroxide. This effect is exaggerated in the bond lengths of the cyclopropane ring C(16)–C(17)–C(18) since the attached carbonyl group adopts the bisected conformation but the phenyl group is twisted from it by some 30°. It should be noted, however, that the orbital interaction implied by these effects does not appear to lead to lengthening of the C=O bond which is substantially shorter than such bonds in unconjugated acyloxy groups (Allen, 1981), in common with other diacyl peroxides. We also note that, in the present compound as in its isomer, the carbonyl group adopts the bisected conformation in which its O atom lies

vertically above the three-membered ring. Bearing in mind the parallelism of behaviour often noted between cyclopropyl and vinyl groups (e.g. Noe & Young, 1982), this preference is analogous to that for the *s-cis* conformation found in *trans*-cinnamoyl peroxide.

References

- ALLEN, F. H. (1980). *Acta Cryst.* **B36**, 81–96.
 ALLEN, F. H. (1981). *Acta Cryst.* **B37**, 890–900.
 BETHELL, D., CHADWICK, D. J., HARDING, M. M. & MALING, G. Q. (1982). *Acta Cryst.* **B38**, 1677–1679.
 BETHELL, D., CHADWICK, D. J., HARDING, M. M. & MALING, G. Q. (1984). *Acta Cryst.* **C40**, 1628–1630.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
 GOUGOUTAS, J. Z. & CLARDY, J. C. (1970). *Acta Cryst.* **B26**, 1999–2008.
 GREENE, F. D. & KAZAN, J. (1963). *J. Org. Chem.* **28**, 2168–2171.
 JASON, M. E. & IBERS, J. A. (1977). *J. Am. Chem. Soc.* **99**, 6012–6021.
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 NOE, E. A. & YOUNG, R. M. (1982). *J. Am. Chem. Soc.* **104**, 6218–6220.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY72* system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1984). **C40**, 1911–1914

Stereochemistry and Absolute Structure of (+)-8β-Acetoxy-12-(4-bromobenzoyloxy)-13,14,15,16-tetranorlabdane,* C₂₅H₃₅BrO₄

BY G. BERNARDINELLI, A. DUNAND, H. D. FLACK AND K. YVON

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

AND W. GIERSCH AND G. OHLOFF

Firmenich SA, Research Laboratories, CH-1211 Genève 8, Switzerland

(Received 16 May 1984; accepted 2 July 1984)

Abstract. $M_r = 479.5$, orthorhombic, $P2_12_12_1$, $a = 7.3547(6)$, $b = 11.0209(10)$, $c = 30.025(3)$ Å, $V = 2433.7(3)$ Å³, $Z = 4$, $D_x = 1.308$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.693$ mm⁻¹, $F(000) = 1008$, room temperature, $R = 4.6\%$ for 2519 observed reflections (mostly Friedel pairs), $[\alpha]_D^{20} +31.6^\circ$ (1.2% in CHCl₃), m.p. 382–384 K. The absolute configuration for chiral centres was confirmed by least-squares

refinement to a high degree of precision using a new procedure for absolute structure assessment. The six-membered rings are *trans*-fused and both are in the chair conformation.

Introduction. Ambergris fragrances display a strong stereochemistry–odour relationship to norlabdane derivatives, Ambrox® (1) being the most typical example (Ohloff, 1982). The two diastereoisomeric ethers (2) and (3) differ in tonality and odour strength from (1). The steric effect at receptor level is held responsible for

* (+)-12-(4-Bromobenzoyloxy)-13,14,15,16-tetranorlabdan-8β-yl acetate.