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Bis[(1-phenyl-1-cyclopropyl)carbonyl] Peroxide

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Abstract. $C_{20}H_{18}O_4$, $M_r = 322{\cdot}34$, monoclinic, $C2/c$ or Cc, $a = 14{\cdot}65\,(2)$, $b = 11{\cdot}21\,(2)$, $c = 11{\cdot}10\,(2)$ Å, $\beta = 106{\cdot}6\,(1)^\circ$, $U = 1747{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}25$, $D_x = 1{\cdot}26$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $R = 0{\cdot}060$ for 765 unique reflexions. The title compound decomposes in solution at a rate significantly greater than those of related peroxides: the molecular structure has been determined to explore possible steric reasons for this.

Introduction. The title compound (m.p. 365·5–366 K) was synthesized following the method of Greene & Kazan (1963) by the reaction between 1-phenyl-1-cyclopropanecarboxylic acid and hydrogen peroxide (6*M*) in the presence of *N*,*N'*-dicyclohexylcarbodiimide. Crystals were obtained by slow cooling to 268 K of a saturated solution in diethyl ether.

Intensities of 765 reflexions were measured by the SERC Microdensitometer Service, Daresbury Laboratory, from Weissenberg photographs of the layers *hk*0 to *hk*9 on a crystal of dimensions 0·3 × 0·3 × 0·2 mm. Interlayer scale factors and cell dimensions were determined from precession photographs. The structure was solved with the space group $C2/c$ by direct methods (*MULTAN*, Germain, Main & Woolfson, 1970) and refined satisfactorily by full-matrix least squares (XRAY system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The molecule has symmetry $\bar{1}$. There were no indications that the lower-symmetry space group Cc should be considered. At an intermediate stage, the positions of most of the H atoms were located from a difference map and subsequently refined with isotropic temperature factors; all other atoms were refined with anisotropic thermal parameters. Interlayer scale factors were refined individually in the final stages. An extinction correction was not required. Positional and mean thermal parameters are given in Table 1.* The molecular and

Table 1. *Atomic coordinates and mean temperature factors* ($\bar{U}$) ($\times10^4$; $\times10^3$ *for* H) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}$ (Å^2)
O(1)	377 (2)	4129 (3)	7188 (3)	452 (22)
C(1)	186 (4)	3287 (5)	6238 (5)	382 (30)
O(2)	−493 (3)	2651 (4)	6001 (4)	614 (27)
C(4)	946 (3)	3288 (5)	5584 (4)	365 (30)
C(5)	566 (4)	3192 (7)	4166 (5)	617 (39)
C(6)	996 (4)	2135 (5)	4887 (6)	555 (38)
C(7)	1841 (3)	3978 (4)	6173 (4)	365 (29)
C(8)	2054 (4)	4995 (5)	5598 (6)	524 (27)
C(9)	2907 (5)	5593 (6)	6121 (7)	756 (52)
C(10)	3520 (5)	5215 (7)	7227 (7)	723 (49)
C(11)	3315 (4)	4207 (7)	7811 (6)	678 (46)
C(12)	2471 (4)	3573 (5)	7294 (5)	497 (46)
H(51)	−10 (4)	326 (6)	375 (5)	70 (20)
H(52)	83 (5)	364 (6)	372 (6)	85 (23)
H(61)	156 (5)	192 (6)	502 (6)	98 (24)
H(62)	64 (4)	130 (5)	492 (5)	44 (17)
H(81)	161 (5)	525 (6)	472 (6)	102 (25)
H(91)	307 (6)	625 (9)	573 (9)	60*
H(101)	415 (4)	571 (6)	766 (5)	75 (21)
H(111)	363 (5)	389 (7)	854 (6)	60*
H(121)	237 (4)	278 (5)	766 (5)	43 (17)

* These parameters were unrefined.

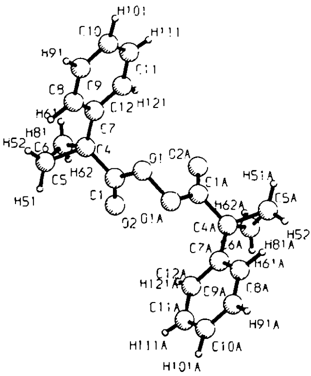

Fig. 1. A view of (1) drawn by the program *PLUTO* 78 (W. D. S. Motherwell, Cambridge Crystallographic Data Centre, UK).

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* Lists of structure factors and anisotropic thermal parameters (for C and O atoms) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36676 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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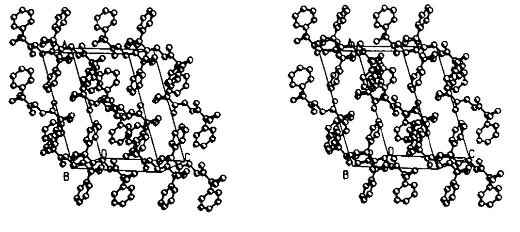


Fig. 2. Stereoscopic view of the crystal structure of (1) (drawn by *PLUTO* 78).

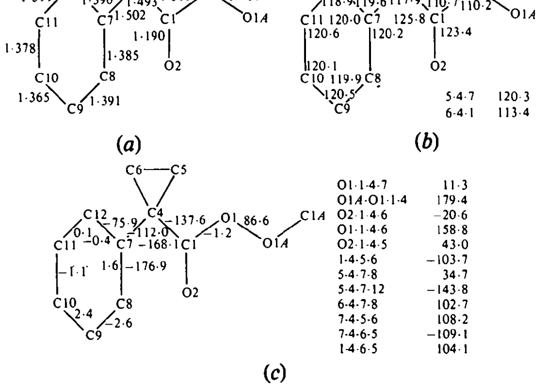
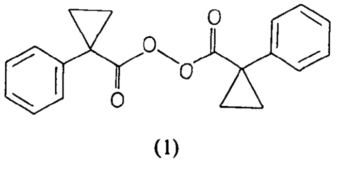


Fig. 3. (*a*) Bond lengths (Å), (*b*) bond angles (°) and (*c*) torsion angles (°). E.s.d.'s are *ca* 0·008 Å for bond lengths, 0·5° for bond angles and >0·5° for torsion angles, not involving H atoms. The ranges of bond lengths and angles involving H are C—H 0·838–1·074 Å, H—C—C 110·3–129·0 and H—C—H 101·6–103·7°.

crystal structures are depicted in Figs. 1 and 2 and the atomic numbering system, bond lengths, bond angles and torsion angles in Fig. 3.*

Discussion. The title compound (1) was synthesized as a precursor for the corresponding phenylcyclopropyl radical. Accurate geometric parameters were required for the calculation of its hyperfine coupling constants for use in interpretation of the CIDNP observed during thermolysis of (1) in hexachloroacetone. During the course of this work is emerged that (1) is unusually unstable compared with related peroxides and it was thought possible that this instability might be an indication of unusual geometric features associated with the peroxide bond. In the event, the O(1)—O(1*A*) bond length of 1·461 (5) Å found in the present study is not unusual compared with that found in other peroxides, *e.g.* 1·445 Å in acetyl benzoyl peroxide (Karch & McBride, 1972) and 1·481 Å in 4,4′-dichlorodibenzoyl peroxide (Caticha-Ellis & Abrahams, 1968).



(1)

The conformation of the phenyl ring and the carbonyl group with respect to the cyclopropyl moiety merits special comment. Both the phenyl ring and the carbonyl group can interact with the cyclopropyl ring by conjugation. We define τ as the angle between the line joining C(4) with the midpoint of the distal bond [C(5)···C(6)] and the line formed by the intersection of the nodal plane of the π system with the plane of the cyclopropane ring. The lowest-energy conformation for the interaction of a π system with the cyclopropyl $3e'$ orbitals is the bisected geometry, $\tau = 0$ (Jason & Ibers, 1977). Donation of electron density from the highest occupied molecular orbital (HOMO) of the cyclopropane ring into the lowest unoccupied molecular orbital (LUMO) of the attached π system causes distal [C(5)···C(6)] bond shortening and vicinal [C(4)···C(5) and C(4)···C(6)] bond lengthening (Allen, 1980); both are observed in (1).

An alternative, perpendicular conformation, $\tau = 90°$, allows electron donation from the HOMO of the attached π system into the cyclopropyl LUMO. This conformation is found (i) when powerful electron-donating groups are attached to the cyclopropyl ring, *e.g.* as in cyclopropylamine (Harmony, Bostrom & Hendricksen, 1975), and (ii) where steric repulsions render the bisected conformation unfavourable, *e.g.* in 1,1-dibromo-2,2-diphenylcyclopropane where $\tau \simeq 80°$ (Lauler & Ibers, 1975). Powerful electron donation leads to cyclopropane distal-bond lengthening and vicinal-bond shortening which is inconsistent with the effects observed in the structure of (1).

The bond distances and angles around the carbonyl group show no unusual features: however, the torsion angles show that the carbonyl group adopts a bisected ($\tau = 0$) conformation with its O atom [O(2)] lying over the cyclopropyl ring. It is not possible for both phenyl and carbonyl groups simultaneously to adopt the bisected conformation because of the potential interactions between the peroxide oxygen [O(1)] and an *ortho* hydrogen [H(81)] on the phenyl ring. In this event the carbonyl group adopts the bisected geometry while the phenyl ring is orientated with an angle $\tau = 69°$ between the phenyl and the cyclopropyl rings. The O(1)···H(81) interaction could be relieved by small rotations involving both the phenyl and carbonyl groups. Such rotations would, however, increase the interactions between the *ortho*-H atoms and the β-H atoms of the cyclopropane ring presumably rendering

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* Since the molecule lies on a crystallographic inversion centre, only the asymmetric unit is drawn in Fig. 3.

such a conformation unfavourable. The observed conformation is 21° from the perpendicular geometry. It appears, therefore, that the observed geometry is a consequence of a balance between two opposing constraints: (i) maximization of orbital overlap between the π system of the phenyl group and the cyclopropyl orbitals, and (ii) the unfavourable interaction between H(52) and H(81).

The steric compression which prevents the phenyl and carbonyl groups from adopting the bisected conformation could possibly account for the thermal instability of this compound provided that it is relieved in the transition state for decomposition. It is, therefore, difficult to reconcile this interpretation with simple homolytic cleavage of the peroxide bond in the rate-limiting step. Two-bond fission, *i.e.* synchronous cleavage of the C(4)···C(1) and O(1)···O(1*A*) bonds by either a homolytic mechanism as in certain peroxyesters (Bartlett & Hiatt, 1958) or more probably, in view of the relatively low intensity of CIDNP, a heterolytic mechanism (Taylor, Govindan & Kaelin, 1979), provides a more convincing explanation.

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Structure of 3,6-Dimethyl-1,4-dioxane-2,5-dione [D-,D-(L-,L-)Lactide]

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Abstract. $C_6H_8O_4$, $M_r = 144{\cdot}1$, $P2_1/c$, $a = 8{\cdot}050\ (2)$, $b = 9{\cdot}086\ (1)$, $c = 9{\cdot}713\ (2)$ Å, $\beta = 102{\cdot}86\ (3)^\circ$, $Z = 4$, $V = 693$ Å^3, $D_x = 1{\cdot}38$ g cm^{-3}, $\mu_{\mathrm{Mo}\,K} = 1{\cdot}1$ cm^{-1}. Data collection was carried out at 293 K. All hydrogen atoms were located. The molecule has approximate C_2 symmetry. $R = 4{\cdot}6$, $R_w = 3{\cdot}8\%$ for 872 reflexions. The compound D-,L-lactide is shown to be the racemate of D-,D- and L-,L-lactide.

Introduction. Over the past fifteen years there has been considerable interest in the application of poly(D-,L-lactic acid) in medicine and surgery (Kronenthal, 1975), for example as a grafting material for perforated eardrums (Feenstra, van der Ven, Kohn & Feijen, 1980). The preferred method of preparation is the ring-opening polymerization of racemic lactide [or dilactide, commonly known as D-,L-lactide (Kulkarni, Pani, Neuman & Leonard, 1966)], a six-membered cyclic diester synthesized from the commercially available racemate of L(+)- and D(−)-lactic acid.

Substantial synthetic evidence exists (Jungfleisch & Godschot, 1906; Deane & Hammond, 1960; Holten, Müller & Rehbinder, 1971) that the D-,L-lactide (m.p. 400 K) routinely used is in fact a racemate of L-,L- and D-,D-lactide (m.p. 368 K). This fact has not been appreciated generally. Some authors (Fouty, 1973; Gregory, Schwope & Wise, 1973; Sinclair, 1977) suggest that D-,L-lactide consists of *meso*-lactide molecules. In polymers derived from the *meso*-lactide the stereo sequence cannot contain more than two D- or L-lactate units in succession. A racemate of D-,D- and L-,L-lactide allows, in principle, the formation of stereo

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