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Abstract

The title compound, C₂₆H₃₀O₄, is one of the first alkyl bis-peroxides to be structurally characterized. The molecule lies on a centre of inversion and therefore the terminal phenyl rings are parallel. Although there are three aromatic rings in the molecule, the C—O—O—C torsion angle of 163.10 (10)° is close to the value found in Me₃COOCMe₃.

Keywords

phenylethyl, 4, bis, benzene, methyl, 1, peroxymethyl

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1,4-Bis[(1-methyl-1-phenylethyl)-peroxymethyl]benzene

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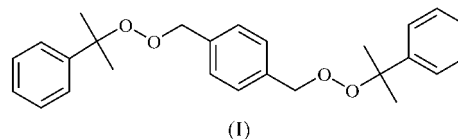
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The title compound, C₂₆H₃₀O₄, is one of the first alkyl bisperoxides to be structurally characterized. The molecule lies on a centre of inversion and therefore the terminal phenyl rings are parallel. Although there are three aromatic rings in the molecule, the C—O—O—C torsion angle of 163.10 (10)° is close to the value found in Me₃COOCMe₃.

Comment

Growing interest in fine chemicals has resulted in, *inter alia*, a rapid development in studies of organic peroxides. These compounds are able both to initiate polymerization processes and to crosslink unsaturated compounds (Sanchez & Myers, 1996). Recently, work has focused on molecules with several

initiating peroxide and/or azo groups (Hazer, 1997), which may act as precursors for block or graft copolymers. Our previous study has shown that bisperoxides can be obtained in good yield under phase-transfer-catalysis conditions (Zawadiak *et al.*, 2001). To our surprise, a search of the Cambridge Structural Database (April 2002, Version 1.4; Allen & Kennard, 1993) indicated only one crystal structure of an alkyl bisperoxide (bisperoxyacetate; Jefford *et al.*, 1984). We report here the results of the X-ray crystallographic study of 1,4-bis[(1-methyl-1-phenylethyl)peroxymethyl]benzene, (I).



The molecule of (I) (Fig. 1) is symmetrical, with the central phenyl ring lying on a centre of inversion at $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$. The C4—O1—O2—C5 torsion angle of 163.10 (10)° is very close to that found in the simple analogous compound Me₃COOCMe₃ [166 (2)°; Käss *et al.*, 1977]. The C—O—O—C torsion angles in peroxides span a broad range, from 90.2 (6)° for H₂O₂ (Busing & Levy, 1965) to 180° for peroxides with very bulky groups near the COOC fragment [*e.g.* Ph₃COOCPh₃ (Glide-well *et al.*, 1979) or isopropylphenyl-9-fluorenyl peroxide (Robinson *et al.*, 1999)]. The O—O bond distance in the peroxide group of (I) is 1.476 (2) Å (1.480 Å in Me₃COOCMe₃). Thus, it seems that the presence of aryl substituents on both sides of the C—O—O—C group and the absence of methyl substituents on one of its sides have no influence on the geometry of this group in comparison with Me₃COOCMe₃, or the effects cancel each other out.

Because the environment of each C atom in the C—O—O—C fragment is different, we also observe different C—O bond lengths and angles on each side of the bond. For the

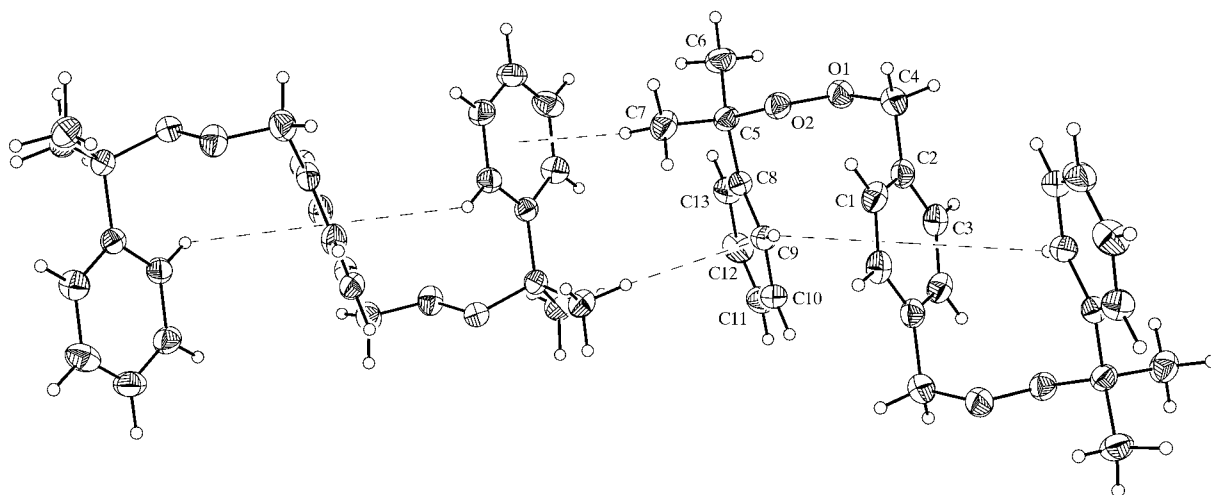


Figure 1

A perspective view of two molecules of (I), connected *via* weak C—H... π interactions, which are drawn as dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. For clarity, the labels on the symmetry-related part of the molecule have been omitted.

quaternary atom C5, C5—O2 is 1.438 (2) Å and C5—O2—O1 is 107.3 (1)°, while for the secondary atom C4, C4—O1 is 1.430 (2) Å and C4—O1—O2 is 104.3 (2)°. The small differences in the geometry of these C atoms, while statistically relevant, are easily explained by the presence of two more relatively bulky methyl groups attached to atom C5. For the same reason, we observe a slight lengthening of the C_{alkyl}—C_{aryl} bond in the case of the quaternary atom C5 [C5—C8 1.522 (2) Å] in comparison with the secondary atom C4 [C4—C2 1.495 (3) Å].

The terminal aromatic rings are parallel to each other (by symmetry), and the mean planes of the terminal and central aromatic rings form a dihedral angle of 42.9 (1)°. Weak intramolecular C—H... π interactions for C9—H9...Cg1 [C—H 0.95 (2), H...Cg1 2.84 (2) and C...Cg1 3.480 (2) Å, and C—H...Cg1 126 (1)°; Cg1 is the centroid of the central ring, C1/C2/C3/C1A/C2A/C3A] may, to some extent, control the twisted conformation of the whole molecule. Another weak C—H... π interaction is intermolecular, namely C7—H7...Cg2($\frac{3}{2} - x, y, -z$) [C—H 0.99 (2), H...Cg2 2.80 (2) and C...Cg2 3.785 (2) Å, and C—H...Cg2 175 (1)°; Cg2 is the centroid of either terminal aromatic ring, C8—C13 or C8A—C13A], and this seems to influence the crystal packing. In addition to these, van der Waals interactions also determine the crystal packing.

Experimental

The title compound was obtained from the sodium salt of cumene hydroperoxide and 1,4-bis(bromomethyl)benzene under phase-transfer-catalysis conditions, similar to the method previously described by Zawadiak *et al.* (2001). The detailed synthetic procedure, together with a description of the thermal behaviour of the compound, will be published elsewhere. Appropriate crystals of (I) were obtained by crystallization from a solution in ethanol. The crystals were stored in a fridge in order to limit the slow decomposition of (I) at room temperature.

Crystal data

C ₂₆ H ₃₀ O ₄	$D_x = 1.221 \text{ Mg m}^{-3}$
$M_r = 406.50$	Mo $K\alpha$ radiation
Monoclinic, $I2/a$	Cell parameters from 94 reflections
$a = 15.368 (3) \text{ \AA}$	$\theta = 3.2\text{--}16.7^\circ$
$b = 6.2200 (12) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 23.142 (5) \text{ \AA}$	$T = 295 \text{ K}$
$\beta = 90.44 (3)^\circ$	Block, colourless
$V = 2212.1 (8) \text{ \AA}^3$	$0.4 \times 0.3 \times 0.2 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 diffractometer	$h = -18 \rightarrow 18$
$\omega/2\theta$ scans	$k = 0 \rightarrow 7$
2007 measured reflections	$l = 0 \rightarrow 27$
1951 independent reflections	3 standard reflections
1198 reflections with $I > 2\sigma(I)$	every 100 reflections
$R_{\text{int}} = 0.012$	intensity decay: 0.6%
$\theta_{\text{max}} = 25.1^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
1951 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
197 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.0123 (10)

The choice of the non-standard space group $I2/a$ (instead of $C2/c$) was as a result of the large value of the β angle in the latter case [123.29 (1)°].

Data collection: *KM-4 Software* (Kuma, 1991); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1111). Services for accessing these data are described at the back of the journal.

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