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## Bis(triphenylmethyl) Peroxide

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**Abstract.**  $C_{38}H_{30}O_2$ , triclinic,  $P\bar{1}$ ,  $a = 10.809$  (3),  $b = 9.062$  (2),  $c = 8.852$  (2) Å,  $\alpha = 115.47$  (1),  $\beta = 91.50$  (1),  $\gamma = 112.98$  (1)°,  $M_r = 518.62$ ,  $V = 700.75$  Å<sup>3</sup>,  $D_c = 1.229$  Mg m<sup>-3</sup>,  $Z = 1$ ,  $\mu(Mo K\alpha) = 0.04$  mm<sup>-1</sup>. The final  $R$  for 2220 reflections is 0.0638. The central COOC fragment is *trans*-planar with C–O = 1.461 (2), O–O = 1.480 (2) Å, and a COO angle of 107.5 (2)°.

**Introduction.** The compound was prepared by the reaction of  $Ph_3CCl$  with Zn amalgam in the presence of air; crystals were grown from benzene, and a crystal  $0.20 \times 0.15 \times 0.10$  mm was used for data collection on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. The intensities of 2374 unique reflections in the hemisphere  $\pm h$ ,  $\pm k$ ,  $\pm l$  having  $3 \leq \theta \leq 30^\circ$  were measured with the  $\omega$ - $2\theta$  scan technique. Lorentz and polarization corrections were applied, but no correction was made for absorption.

The  $E$  statistics suggested space group  $P\bar{1}$ , but attempts to solve the structure by direct methods with *SHELX* failed in both  $P1$  and  $P\bar{1}$ : the structure was eventually solved in  $P\bar{1}$  with negative quartets (Sheldrick, 1978). The structure was refined by full-matrix least squares with complex neutral-atom scattering factors (Cromer & Mann, 1968) and weights  $w = 1/\sigma^2(F)$  for 2220 unique reflections having  $F_o \geq 6\sigma(F_o)$ . Anisotropic temperature factors were employed for the O and C atoms; H atom coordinates

Table 1. *Atom coordinates* ( $\times 10^4$ , for H  $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>
O	4737 (1)	4170 (2)	4150 (2)
C(1)	3309 (2)	3722 (3)	3509 (2)
C(11)	3251 (2)	5244 (3)	3200 (3)
C(12)	3472 (2)	6906 (3)	4592 (3)
C(13)	3400 (2)	8272 (3)	4332 (3)
C(14)	3109 (3)	8027 (3)	2694 (4)
C(15)	2875 (3)	6395 (4)	1318 (4)
C(16)	2951 (3)	5013 (3)	1561 (3)
C(21)	2940 (2)	1959 (2)	1819 (2)
C(22)	1636 (2)	491 (3)	1239 (3)
C(23)	1304 (3)	-1089 (3)	-300 (3)
C(24)	2269 (3)	-1221 (3)	-1261 (3)
C(25)	3561 (3)	219 (4)	-711 (3)
C(26)	3899 (2)	1810 (3)	823 (3)
C(31)	2437 (2)	3353 (3)	4745 (2)
C(32)	2768 (3)	2624 (3)	5708 (3)
C(33)	1925 (3)	2170 (3)	6742 (3)
C(34)	746 (3)	2437 (4)	6845 (4)
C(35)	409 (3)	3144 (3)	5897 (4)
C(36)	1234 (2)	3592 (3)	4846 (3)
H(12)	362 (2)	707 (3)	579 (3)
H(13)	357 (2)	940 (3)	531 (3)
H(14)	310 (2)	903 (3)	255 (3)
H(15)	273 (3)	621 (3)	17 (3)
H(16)	284 (2)	388 (3)	56 (3)
H(22)	95 (2)	57 (3)	190 (3)
H(23)	36 (3)	-214 (3)	-67 (3)
H(24)	204 (2)	-234 (3)	-234 (3)
H(25)	423 (2)	17 (3)	-139 (3)
H(26)	484 (3)	289 (3)	125 (3)
H(32)	364 (3)	250 (3)	566 (3)
H(33)	219 (2)	166 (3)	739 (3)
H(34)	16 (2)	216 (3)	761 (3)
H(35)	-43 (2)	330 (3)	595 (3)
H(36)	100 (3)	411 (3)	416 (3)

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were refined, with a common isotropic temperature factor. The refinement converged to  $R = \sum A / \sum F_o = 0.0638$ , and  $R_G = (\sum wA^2 / \sum wF_o^2)^{1/2} = 0.0568$ . At each stage of the refinement the reduction in  $R_G$  was significant at the 99.9% level (Hamilton, 1965). When the space group was relaxed to  $P1$ , the reduction in  $R_G$  was not significant at the 50% level, so  $P1$  can be rejected.

The final atom coordinates are in Table 1, the geometrical parameters of the central  $C_3COOCC_3$  fragment in Table 2, and the parameters for the phenyl rings in Table 3. Fig. 1 shows the molecule and the numbering of the atoms.\*

**Discussion.** The C—O distance, 1.461 (2) Å, is identical to the mean in  $(Ph_3C)_2O$  (Glidewell & Liles, 1978), but significantly longer than that in  $(CH_3)_2O$ , 1.416 (3) Å (Kimura & Kubo, 1959). The O—O distance, 1.480 (2) Å, is typical of those found in

\* Lists of structure factors, anisotropic thermal parameters and geometrical parameters involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34024 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Geometry of the central  $C_3COOCC_3$  fragment

(a) Distances (Å)			
O—O'	1.480 (2)	C(1)—C(11)	1.540 (3)
O—C(1)	1.461 (2)	C(1)—C(21)	1.538 (3)
O...C(1)'	2.371 (3)	C(1)—C(31)	1.523 (3)
(b) Angles (°)			
O—C(1)—C(11)	110.6 (1)	C(11)—C(1)—C(21)	112.3 (2)
O—C(1)—C(21)	99.5 (1)	C(21)—C(1)—C(31)	111.4 (2)
O—C(1)—C(31)	109.9 (2)	C(31)—C(1)—C(11)	112.4 (1)
C(1)—O—O'	107.5 (2)	C(1)—O—O'—C(1)'	180.0

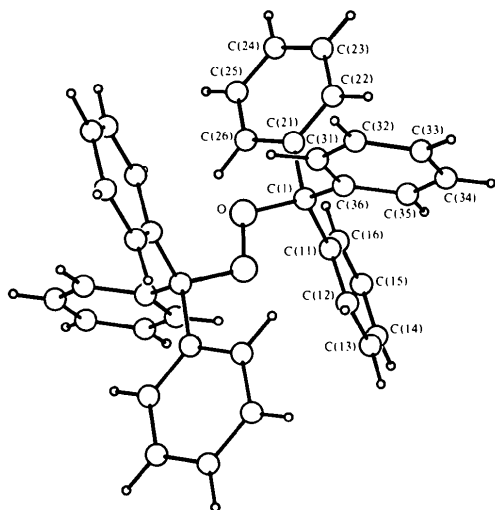


Fig. 1. The molecule of bis(triphenylmethyl) peroxide, showing the numbering of the atoms. H atoms have the same numbers as the C atoms to which they are bonded.

Table 3. Geometry within the phenyl rings

	Ring (i)			
	i = 1	i = 2	i = 3	Mean
(a) Distances (Å): C(ij)—C(ik)				
j—k				
1—2	1.397 (3)	1.389 (3)	1.394 (3)	1.393 (3)
2—3	1.382 (3)	1.389 (3)	1.383 (3)	1.385 (4)
3—4	1.377 (4)	1.372 (3)	1.385 (4)	1.378 (5)
4—5	1.370 (4)	1.373 (4)	1.370 (4)	1.371 (2)
5—6	1.390 (3)	1.391 (3)	1.382 (3)	1.388 (4)
6—1	1.384 (3)	1.387 (3)	1.399 (3)	1.390 (6)
(b) Angles (°): C(ij)—C(ik)—C(il) or C(ij)—C(ik)—C(1)				
j—k—l(1)				
6—1—2	117.7 (2)	118.4 (2)	118.3 (2)	118.1 (3)
1—2—3	120.9 (2)	120.7 (2)	120.3 (2)	120.6 (3)
2—3—4	120.8 (2)	120.2 (2)	120.7 (3)	120.6 (3)
3—4—5	118.9 (2)	119.9 (2)	119.4 (3)	119.4 (4)
4—5—6	120.9 (3)	120.3 (2)	120.6 (3)	120.6 (3)
5—6—1	120.9 (2)	120.5 (2)	120.7 (2)	120.7 (2)
2—1—C(1)	120.2 (2)	121.0 (2)	120.1 (2)	120.4 (4)
6—1—C(1)	122.0 (2)	120.6 (2)	121.5 (2)	121.4 (6)

Table 4. Geometrical parameters in some molecular peroxides (XOOY)

X	Y	r(O—O) (Å)	Dihedral angle (°)	Reference
H	H	1.453 (7)	90.2 (6)	(a)
F	F	1.217 (3)	87.5 (5)	(b)
CF <sub>3</sub>	H	1.447 (3)	95.0*	(c)
CF <sub>3</sub>	F	1.366 (11)	97.1 (20)	(c)
CF <sub>3</sub>	Cl	1.447 (5)	93.2 (23)	(c)
CF <sub>3</sub>	CF <sub>3</sub>	1.419 (7)	123.3 (13)	(d)
Me <sub>3</sub> C	Me <sub>3</sub> C	1.480*	165.8 (24)	(e)
Me <sub>3</sub> Si	Me <sub>3</sub> Si	1.481 (8)	143.5 (60)	(e)
Ph <sub>3</sub> C	Ph <sub>3</sub> C	1.480 (2)	180†	(f)
PhCO	PhCO	1.46 (2)	91	(g)
SF <sub>5</sub>	SF <sub>5</sub>	1.47 (3)	107 (5)	(h)
C <sub>8</sub> H <sub>17</sub> CO	H	1.44	133	(i)
O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CO	H	1.478	146	(j)
O <sub>3</sub> S <sup>-</sup>	O <sub>3</sub> S <sup>-</sup>	1.46	180†	(k)
(NH <sub>3</sub> ) <sub>5</sub> Co <sup>3+</sup>	(NH <sub>3</sub> ) <sub>5</sub> Co <sup>3+</sup>	1.47	146	(l)

References: (a) Busing & Levy (1965); (b) Jackson (1962); (c) Marsden, Desmarreau & Bartell (1977); (d) Marsden, Bartell & Diodati (1977); (e) Käss, Oberhammer, Brandes & Blaschette (1977); (f) this work; (g) Sax & McMullen (1967); (h) Harvey & Bauer (1954); (i) Belitskus & Jeffrey (1965); (j) Sax, Beurskens & Chu (1965); (k) Zachariasen & Mooney (1934); (l) Shaeffer (1968).

\* Parameter not refined.  
† By symmetry.

molecular peroxides not containing an O—F bond (Table 4). The mean C(aryl)—C(quaternary) distance, 1.533 (8) Å, is not significantly different from those in  $(Ph_3C)_2O$ , 1.543 (6) Å (Glidewell & Liles, 1978), and  $Ph_3CH$ , 1.524 (23) Å (Riche & Pascard-Billy, 1974), although it is somewhat shorter than that in the sterically crowded  $Ph_4C$ , 1.550 (3) Å (Robbins, Jeffrey, Chesick, Donohue, Cotton, Frenz & Murillo, 1975).

The angle at O,  $107.5(2)^\circ$ , is markedly smaller than that in  $(\text{Ph}_3\text{C})_2\text{O}$ ,  $127.9(1)^\circ$ , which was ascribed to repulsive interactions between the two  $\text{Ph}_3\text{C}$  groups (Glidewell & Liles, 1978). A similar substantial reduction in interbond angle at O has been observed on going from  $(\text{Me}_3\text{Si})_2\text{O}$  (Csákvári, Wagner, Gömöry, Mijlhoff, Rozsondai & Hargittai, 1976) to  $(\text{Me}_3\text{Si})_2\text{O}_2$  (Käss, Oberhammer, Brandes & Blaschette, 1977): in this case also the wider angle in the oxo compound can be ascribed to steric factors.

The angle between the two COO planes is  $180^\circ$ ; such a large dihedral angle occurs only rarely in peroxo compounds. In the simplest peroxide,  $\text{H}_2\text{O}_2$ , the dihedral angle in the solid state is  $90.2(6)^\circ$  (Busing & Levy, 1965), but the barrier to rotation about the O—O bond is very small, being  $4.62\text{ kJ mol}^{-1}$  towards the *trans* conformation and  $29.4\text{ kJ mol}^{-1}$  towards the *cis* (Hunt, Leacock, Peters & Hecht, 1965). However, marked deviations from a dihedral angle of *ca*  $90^\circ$  usually occur only as a consequence of either hydrogen bonding or steric repulsion (Table 4), although the value of  $180^\circ$  in  $M_2\text{S}_2\text{O}_8$  ( $M = \text{NH}_4$  or Cs) (Zachariassen & Mooney, 1934) has no obvious interpretation.

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## The *meso* Condensation Dimer from 2-(3-Bromopropyl)-6-hydroxy-2-methyl-1-indanone

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**Abstract.**  $\text{C}_{26}\text{H}_{28}\text{O}_4$ ,  $M_r = 404.5$ , triclinic,  $P\bar{1}$ ,  $a = 6.04(1)$ ,  $b = 8.73(2)$ ,  $c = 10.65(4)$  Å,  $\alpha = 99.90(3)$ ,  $\beta = 95.28(3)$ ,  $\gamma = 69.33(3)^\circ$  from diffractometer measurements (Mo  $K\alpha$  radiation).  $V = 516$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.296$  Mg m<sup>-3</sup>,  $F(000) = 216$ ,  $\mu = 0.049$  mm<sup>-1</sup>. The molecule was shown to be the *meso* isomer.

**Introduction.** The title compound was recrystallized from chloroform.

Weissenberg and precession photographs indicated a triclinic space group. Data were collected for 0–6kl

with  $\theta_{\text{max}} = 27.5^\circ$  on a Stoe STADI-2 diffractometer (graphite-monochromated Mo  $K\alpha$  radiation). This gave 2175 data of which 1843 unique reflexions with  $I > 3\sigma(I)$  were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data were scaled by a Wilson plot. The structure was solved by direct methods with *SHELX 76* (Sheldrick, 1976), which was used for all calculations. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Weighted full-matrix least-