

Fig. 3. Stereoview of the packing of the molecules. Only the H atoms of the hydrogen bonds in the dimers are included. The unit cell is oriented with the *c* axis horizontal, the *a* axis vertical and the *b* axis pointing towards the reader.

present structure and the corresponding distance in dibenzofuran of 1.480 (6) Å (Banerjee, 1973) and 1.481 (3) Å (Dideberg, Dupont & André, 1972).

The C(1)–C(13) bond distance may also be compared to the theoretically calculated distance of Banerjee (1973) of 1.468 Å. The shortening of the C(1)–C(13) bond in the present structure indicates an increased  $\pi$  bond order, compared to the dibenzofuran structure. CNDO calculations show a slight degree of asymmetry in the furan ring, the total net charge on C(1) being +0.034 and on C(13) –0.035 e.

The C(4)–C(5)–O(14) angle is enlarged to 128.1°, which is also the case for the corresponding angle in leucothelephoric acid hexamethyl ether (Silverton, 1973), deoxyanisoin and *p,p*-dimethoxybenzophenone (Norment & Karle, 1962). This is probably due to steric interactions between H(4) and the H atoms of the methyl groups of the side chain [e.g. the H(4)···H(15A1) distance is 2.56 Å], as proposed by Norment & Karle (1962).

Two centrosymmetrically related molecules form a dimer held together by hydrogen bonds at the carboxylic ends of the molecules at a distance of 2.632 (3) Å. Fig. 3 shows the dimers and the packing of the molecules. The dibenzofuran groups are not parallel

(Banerjee, 1973; Dideberg, Dupont & André, 1972; Silverton, 1973) but oriented perpendicularly towards each other.

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#### References

- BANERJEE, A. (1973). *Acta Cryst.* B29, 2070–2074.  
 BERG, J. E., KARLSSON, B., PILOTTI, A. M. & SÖDERHOLM, A. C. (1978). *Acta Cryst.* B34, 2071–2072.  
 BONDESSON, G., HEDBOM, C., HÖGBERG, T., MAGNUSSON, O., STJERNSTRÖM, N. E. & CARLSSON, L. A. (1974). *J. Med. Chem.* 17, 108–112.  
 BONDESSON, G., HÖGBERG, T., STJERNSTRÖM, N. E. & WÄGNER, A. (1979). To be published.  
 DIDEBERG, O., DUPONT, L. & ANDRÉ, J. M. (1972). *Acta Cryst.* B28, 1002–1007.  
 EL-SOHLI, M. A., SLATKIN, D. J., KNAPP, J. E., DOORENBOS, N. J., QUIMBY, M. W., SCHIFF, P. L. JR, GOPALAKRISHNA, E. M. & WATSON, W. H. (1977). *Tetrahedron*, 33, 1711–1715.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B26, 274–285.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 NORMENT, H. G. & KARLE, I. L. (1962). *Acta Cryst.* 15, 873–878.  
 SILVERTON, J. V. (1973). *Acta Cryst.* B29, 293–298.  
 WÄGNER, A. (1979). To be published.  
 WÄGNER, A. & MALMROS, G. (1979). *Acta Cryst.* B35, 2222–2225.

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## 2-[2-(Phenoxy)phenoxy]-2-methylpropionic Acid

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**Abstract.** C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.005 (3), *b* = 20.023 (3), *c* = 8.119 (3) Å,  $\beta$  = 105.91 (3)°, *d*<sub>c</sub> = 1.28 Mg m<sup>-3</sup>, *Z* = 4. The structure was solved by direct methods and refined by least-squares methods to an *R* value of 0.041. The two benzene rings are twisted

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out of the C–O–C plane linking the two phenyl groups together, with torsion angles of 177 and –75°.

**Introduction.** 2-[2-(Phenoxy)phenoxy]-2-methylpropionic acid was synthesized as part of a programme of © 1979 International Union of Crystallography

studies on hypolipidemic agents (Bondesson, Hedbom, Högberg, Magnusson, Stjernström & Carlsson, 1974). The present structure determination was carried out in order to investigate the structure-activity relationship of these agents when considering the hypolipidemic effect (Bondesson, Högberg, Stjernström & Wägner, 1979; Wägner & Malmros, 1979). The cell dimensions were obtained from a powder photograph taken in a Guinier-Hägg focusing camera with strictly monochromatized Cu  $K\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) using KCl ( $a = 6.2930 \text{ \AA}$ ) as internal standard. The photograph was measured by an automatic film-scanner system described by Malmros & Werner (1973). Intensity data were collected with a computer-controlled single-crystal diffractometer (Philips PW 1100) using graphite-monochromatized Cu  $K\alpha$  radiation. 2316 reflections up to  $2\theta = 120^\circ$  were collected using  $\theta$ - $2\theta$  scans at a scan width of  $1.5^\circ$  and a speed of  $0.02^\circ \text{ s}^{-1}$ . Of these, 1510 with  $\sigma(I)/I < 0.303$  were used in the subsequent calculations. Lorentz and polarization factors were applied. No corrections for absorption or extinction were made.

The structure was solved by the multiresolution program system *MULTAN* (Germain, Main & Woolfson, 1970) and refined by the full-matrix least-squares procedure. Weights were assigned as  $1/\sigma^2(F_o)$  where  $\sigma(F_o)$  was determined from the value  $\sigma_{cs}$  yielded by counting statistics with a 2% addition for instrumental instability according to the formula:  $\sigma(F_o)/F_o = \{[\sigma_{cs}(F_o)/F_o]^2 + (0.02)^2\}^{1/2}$ . Full-matrix least-squares refinement of all non-hydrogen atomic positions with anisotropic thermal parameters gave an  $R$  value of 0.085. The positions of all H atoms could be deduced

Table 1. Fractional coordinates ( $\times 10^4$ ) for the non-hydrogen atoms

Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$
C(1)	535 (4)	3937 (1)	9307 (4)
C(2)	1642 (4)	4301 (2)	10487 (4)
C(3)	3078 (3)	4377 (1)	10260 (3)
C(4)	3453 (3)	4082 (1)	8873 (3)
C(5)	2362 (2)	3708 (1)	7706 (3)
C(6)	891 (3)	3640 (1)	7942 (3)
C(8)	-916 (2)	3475 (1)	5210 (3)
C(9)	-665 (3)	4099 (1)	4641 (3)
C(10)	-1450 (3)	4289 (1)	2995 (3)
C(11)	-2480 (3)	3865 (1)	1950 (4)
C(12)	-2722 (3)	3240 (2)	2529 (4)
C(13)	-1941 (3)	3040 (1)	4162 (4)
C(15A)	4002 (2)	3410 (1)	5846 (3)
C(15B)	3607 (4)	3077 (2)	4094 (4)
C(16)	5292 (3)	3033 (1)	7114 (4)
O(7)	4437 (2)	4128 (1)	5589 (3)
O(14)	-206 (2)	3240 (1)	6837 (2)
O(15A)	2564 (1)	3386 (1)	6300 (2)
O(16A)	3314 (2)	4527 (1)	4927 (2)
O(16B)	5814 (2)	4291 (1)	5926 (2)

from several difference Fourier syntheses. Further least-squares refinement for all atoms with the H atoms given isotropic thermal parameters resulted in an  $R$  value of 0.041 for  $R = \sum |F_o| - |F_c| / \sum |F_o|$  and 0.048 for  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . Owing to extinction, the four strongest low-angle reflections were excluded in the last refinement cycle. The  $R$  value computed for all reflections was 0.045.\* The atomic scattering factors used for C and O were taken from *International Tables for X-ray Crystallography* (1974) and for the H atoms from Stewart, Davidson & Simpson (1965). Final positional parameters are listed in Tables 1 and 2.

**Discussion.** Bond lengths and bond angles for the non-hydrogen atoms are shown in Fig. 1. Fig. 2 shows the

\* Lists of structure factors, anisotropic thermal parameters for the non-hydrogen atoms and isotropic for the hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34442 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ( $\times 10^3$ ) for the H atoms

Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$
H(1)	454 (3)	111 (1)	441 (3)
H(2)	141 (3)	450 (1)	146 (4)
H(3)	390 (3)	464 (1)	108 (3)
H(4)	448 (3)	416 (1)	870 (3)
H(9)	8 (3)	440 (1)	535 (3)
H(10)	374 (3)	27 (1)	758 (3)
H(11)	196 (3)	99 (1)	575 (4)
H(12)	154 (3)	206 (2)	684 (4)
H(13)	293 (3)	239 (1)	961 (3)
H(15A1)	332 (3)	262 (1)	422 (3)
H(15A2)	448 (3)	309 (1)	363 (3)
H(15A3)	274 (3)	332 (1)	328 (4)
H(15B1)	124 (3)	195 (1)	175 (3)
H(15B2)	499 (3)	257 (2)	708 (4)
H(15B3)	50 (3)	176 (2)	325 (4)
H(16A)	136 (4)	-2 (2)	29 (4)

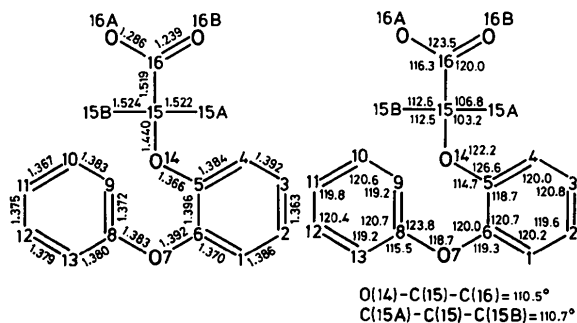


Fig. 1. Bond distances (Å) and bond angles ( $^\circ$ ) including atomic numbering. The e.s.d.'s range between 0.003-0.004 Å and 0.2-0.3 $^\circ$ .

conformation and the ring system of the title compound. The two benzene rings are twisted out of the C(6)–O(7)–C(8) plane and the torsion angles are  $177^\circ$  for C(8)–O(7) and  $-75^\circ$  for O(7)–C(6). Relevant torsion angles are listed in Table 3. The benzene rings are planar, deviating less than 0.007 and 0.005 Å from their respective mean-squares planes. The dihedral angle between the two rings is  $104.5(4)^\circ$ .

The H–C bond distances vary between 0.923 and 1.005 Å having e.s.d.'s of 0.02–0.04 Å, the average H–C distance being 0.973 Å. The H–C–H angles range from  $107.5$  to  $121.7^\circ$  having e.s.d.'s of  $1.2$ – $1.8^\circ$ . The H–O distance is 0.99(4) Å and the C–O–H angle  $121.8(11)^\circ$ .

Potential-energy calculations were made to account for the rotational freedom of the two benzene rings. The potential interaction energies were calculated from the sum of the Lennard–Jones potential  $\sum_{i>j} (B_{ij}r_{ij}^{-6} + A_{ij}r_{ij}^{-12})$  and the electrostatic 'monopole' approximation  $\sum_{i>j} q_i q_j \epsilon^{-1} r_{ij}^{-6}$  ( $\epsilon = 1$ ) where  $q_i$  is the electric charge of the  $i$ th atom and  $\epsilon$  the dielectric constant. The  $A_{ij}$  values were derived from the Slater & Kirkwood (1931) equation:  $A_{ij} = 3/2 ehm^{-1/2} \alpha_i \alpha_j \times [(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}]^{-1}$ . The  $B_{ij}$  values were derived from the requirement that the Lennard–Jones potentials have minima at the sum of the van der Waals distances ( $R_i + R_j$ ). The values of  $\alpha_i$  (the atomic polarizabilities),  $N_i$  (the effective valence electron numbers) and  $R_i$  (the van der Waals distances) were taken from Scheraga (1968). The charges  $q_i$  were calculated by CNDO and are shown in Fig. 3.

A potential-energy map was calculated by rotating the C(6)–O(7) and O(7)–C(8) bonds independently. The result of this calculation shows that the observed solid-state structure does not correspond to a

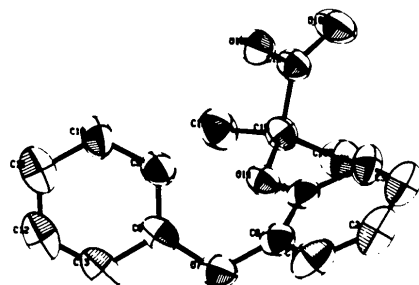


Fig. 2. Conformation and ring system of the title compound.

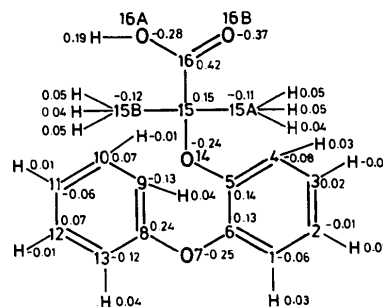


Fig. 3. The result of the CNDO calculation.

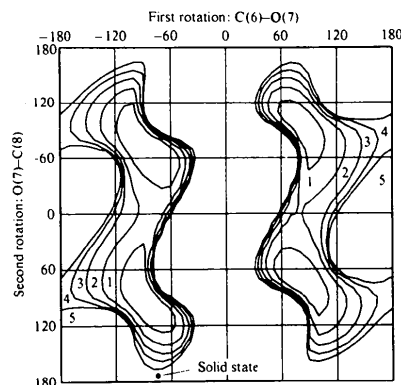


Fig. 4. The result of the potential-energy calculation in kcal mol<sup>-1</sup> (1 kcal mol<sup>-1</sup> = 4.2 kJ mol<sup>-1</sup>). The solid state is marked ●.

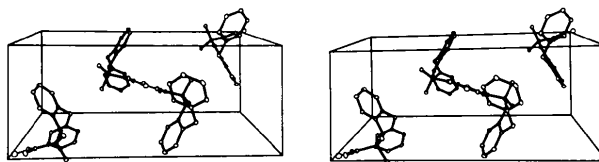


Fig. 5. Stereoview of molecular packing. Only H atoms involved in the hydrogen bonds are included. The unit cell is oriented with the  $b$  axis horizontal, the  $c$  axis vertical and the  $a$  axis pointing towards the reader.

Table 3. Torsion angles ( $^\circ$ )

Estimated standard deviations are given in parentheses.

C(13)–C(8)–O(7)–C(6)	177.3 (3)
C(8)–C(7)–C(6)–C(5)	-75.0 (3)
C(5)–O(14)–C(15)–C(16)	-58.0 (2)
O(14)–C(15)–C(16)–O(16A)	-35.2 (3)
C(6)–C(5)–O(14)–C(15)	179.1 (3)

minimum-energy conformation (*cf.* Fig. 4). As can be seen in Fig. 4 the torsion angle C(6)–O(7) lies within the minima, but is displaced owing to the second torsion angle O(7)–C(8). This indicates that the two benzene rings are allowed a certain rotational freedom, mainly around the O(7)–C(8) bond, with only minor energy differences between the various conformations.

The dimerization involves two centrosymmetrically related molecules which form a dimer at the carboxylic ends of the molecules. The dimer is held together by hydrogen bonds at a distance of 2.643(2) Å. The packing arrangement is shown in Fig. 5. A discussion concerning the structure–activity relationship for the hypolipidemic effect for this and related compounds will be presented elsewhere (Bondesson, Högberg, Stjernström & Wägner, 1979).

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#### References

- BONDESSON, G., HEDBOM, C., HÖGBERG, T., MAGNUSSON, O., STJERNSTRÖM, N. E. & CARLSSON, L. A. (1974). *J. Med. Chem.* **17**, 108–112.
- BONDESSON, G., HÖGBERG, T., STJERNSTRÖM, N. E. & WÄGNER, A. (1979). To be published.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MALMROS, G. & WERNER, P. E. (1973). *Acta Chem. Scand.* **27**, 493–502.
- SCHERAGA, A. A. (1968). *Adv. Phys. Org. Chem.* **6**, 103–184.
- SLATER, I. C. & KIRKWOOD, I. G. (1931). *Phys. Rev.* **37**, 682–697.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WÄGNER, A. & MALMROS, G. (1979). *Acta Cryst.* **B35**, 2220–2222.

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## The Structure of Racemic 7-Benzyl-9-methoxy-8-phenyl-7-phospha-*cis*-bicyclo[4.3.0]non-8-ene *anti*-7-Oxide\*†

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**Abstract.**  $C_{22}H_{25}O_2P$ ,  $M_r = 352.42$ , orthorhombic, *Pbca*,  $a = 16.728$  (4),  $b = 22.557$  (5),  $c = 10.001$  (3) Å,  $Z = 8$ ,  $D_m$  (floatation) = 1.294,  $D_c = 1.240$  Mg m<sup>-3</sup>. The structure was solved by the *MULTAN* program and refined by full-matrix least-squares calculations to a final  $R$  of 0.098 for 1757 reflections. The phospholene ring has a conformation intermediate between sofa and half-chair whereas the cyclohexane ring is in a slightly distorted chair conformation. The two rings have a *cis* junction.

**Introduction.** The present study is the first in a series of X-ray investigations of the structures of phosphaindole derivatives, especially of the conformations of the fused phospholane (or phospholene) and cyclohexane rings. So far, only four similar structures, 1-benzyl-3-hydroxy-4,5-dimethyl-2-phenylphosphol-2-ene (Washecheck, Helm, Purdum & Berlin, 1974), 1-hydroxy-1-oxophospholane (Alver & Kjøge,

1969), 1-benzylphosphole (Coggon, Engel, McPhail & Quin, 1970) and 1-hydroxydibenzo-1*H*-phosphole 1-oxide (Boer & Bright, 1974), have been examined by the X-ray method. Better known are structures containing a 1,3-dioxaphospholane ring.

Intensities from a crystal of irregular shape were collected on a Syntex *P2*<sub>1</sub> four-circle diffractometer with graphite-monochromated Cu *K* $\alpha$  radiation, up to  $2\theta = 96^\circ$ . From the 1757 recorded reflections 1275 were contributed to the last cycles of refinement [ $F \geq 3\sigma(F)$ ]. The structure was solved by a multisolution technique (*MULTAN*; Germain, Main & Woolfson, 1971). The  $E$  map based on  $340 E \geq 1.3$  revealed all the heavy atoms. The structure was refined by least-squares calculations,  $\sum w(\Delta F)^2$  being minimized. After four cycles with isotropic ( $R = 0.135$ ,  $R_w = 0.090$ ) and a further four cycles of full-matrix refinement with anisotropic temperature factors, the agreement factor was equal to 0.122 ( $R_w = 0.073$ ). During the anisotropic refinement the molecule was divided into two parts. One part was refined while the other was kept fixed because there were too many variables for the program. A difference synthesis revealed the positions of all H atoms, which were not refined (the C–H bond lengths differ considerably from the 'standard' value especially after test refinement). Finally three cycles of

\* Conformational Studies of 7-Phosphabicyclo[4.3.0]non-8-ene 7-Oxides. I.

† Note: The atom numbering used in the text, Fig. 1 and tables of this paper is arbitrary and does not correspond to that used in naming the compound.