

Fig. 2. Stereoview of the hydrogen-bonding geometry. Only the relevant portions of the side chains are shown; hydrogen bonds are indicated by dashed lines (drawn with *CRISTEP*, De Wet, 1980).

Fig. 2 shows the hydrogen-bonding arrangement in the crystal. The shortest Cl<sup>-</sup>...Cl<sup>-</sup> distance is that between ions related by the inversion centre at  $\frac{1}{2}, 0, 0$ . These ions link centrosymmetrically related cations *via* N—H...Cl<sup>-</sup> hydrogen bonds involving both amino H atoms (Table 2).

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#### References

- AMMON, H. L., BALSAMO, A., MACCHIA, B., MACCHIA, F., HOWE, D. B. & KEEFE, W. E. (1975). *Experientia*, **31**, 644–645.
- BEALE, J. P. & STEPHENSON, N. C. (1972). *J. Pharm. Pharmacol.* **24**, 277–280.
- DE WET, J. F. (1980). *J. Appl. Cryst.* **13**, 625–629.
- DUKES, M. & SMITH, L. H. (1971). *J. Med. Chem.* **14**, 326–328.
- HOWE, R. & RAO, B. S. (1968). *J. Med. Chem.* **11**, 1118–1121.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MURRAY-RUST, P., MURRAY-RUST, J., HARTLEY, D., HALLETT, P. & CLIFTON, J. (1984). *Acta Cryst.* **C40**, 825–828.
- PATTANAYEK, R. R., DATTAGUPTA, J. K., BHATTACHARYYA, S. C. & SAHA, N. N. (1984). *Acta Cryst.* **C40**, 294–297.
- PAXTON, K. & HAMOR, T. A. (1977). *Acta Cryst.* **B33**, 2143–2146.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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## 2,2'-[*o*-Phenylenebis(methyleneoxy)]diacetophenone, C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>

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**Abstract.**  $M_r = 374.4$ , monoclinic,  $P2_1$ ,  $a = 10.842$  (2),  $b = 5.131$  (1),  $c = 17.390$  (3) Å,  $\beta = 92.12$  (1)°,  $V = 966.7$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.29$ ,  $D_m = 1.25$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.76$  cm<sup>-1</sup>,  $F(000) = 396.0$ ,  $T = 297$  K,  $R = 0.044$  for 1383 observations. Although the molecule could possess symmetry 2 or  $m$ , it is crystallographically asymmetric, with the two acetophenone rings forming dihedral angles of 98.5 (2) and 159.5 (3)° with the *o*-phenylene ring. This is in contrast with the structure in solution, where the two chemically equivalent halves are, on a time-averaged basis, conformationally equivalent.

**Introduction.** In the course of our studies utilizing 2,3-bis(2-substituted-phenyl)-2-butenes as models for intramolecular reactions (Tirado-Rives, Oliver, Fronczek & Gandour, 1984), the title compound's crystal

structure has been determined. This structure serves as a reference for predicting the stereochemistry of the low-valent titanium-induced reductive coupling of the carbonyl groups.

**Experimental.** Title compound prepared previously (Tirado-Rives *et al.*, 1984). Suitable crystals, needles, from hexane/ether. Crystal size 0.32 × 0.20 × 0.44 mm.  $D_m$  by flotation in aq. KBr. Space-group determination by systematic absences  $0k0$  with  $k$  odd and successful refinement in non-centrosymmetric space group. Cell dimensions determined from setting angles of 25 reflections having  $12 < \theta < 13$ °. Enraf-Nonius CAD-4 diffractometer, Mo  $K\alpha$  radiation, graphite monochromator.  $\omega$ - $2\theta$  scans designed to yield  $I = 25\sigma(I)$ . Scan rates ( $\omega$ ) varied, 0.31–5.0° min<sup>-1</sup>. Measured reflections (1597) having  $0.025 \leq \sin\theta/\lambda \leq 0.550$  Å<sup>-1</sup>,  $1 < \theta < 23$ °,  $0 \leq h \leq 11$ ,  $0 \leq k \leq 5$ ,  $-19 \leq l \leq 19$ , corrected for background, Lorentz, and polarization effects, equivalent data ( $0kl$  and  $0k\bar{l}$ )

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averaged to yield 1522 unique reflections ( $R_{\text{int}} = 0.022$ ). Crystal decay (3% variation in three standards) and absorption negligible. Structure solved using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares based upon  $F$ , using data with  $F_o > 0$  (139 unobserved reflections) and weights  $w = \sigma^{-2}(F_o)$ , with *SHELX76* (Sheldrick, 1976) and *Enraf-Nonius SDP* (Frenz & Okaya, 1980). Atomic scattering factors from Cromer & Mann (1968). Non-H atoms anisotropic, H positions located by  $\Delta F$  map and included as fixed contributions, isotropic thermal parameters assigned, based on those of C atoms. Final  $R = 0.063$  (for all data),  $wR = 0.039$ ,  $S = 1.318$ . Max. shift  $0.10\sigma$  in final cycle; residual density within  $\pm 0.16 \text{ e } \text{\AA}^{-3}$ , extinction  $1.4(2) \times 10^{-6}$ .

**Discussion.** The atomic parameters are given in Table 1.\* Bond distances and angles are presented in Table 2. Fig. 1 illustrates that the title compound adopts an asymmetric conformation in the crystal. Three different least-squares planes ( $P1$ ,  $P2$  and  $P3$ ) are formed by the six atoms of each aromatic ring. The angles that are formed by the intersection of the *o*-phenylene plane ( $P2$ ) with each of the acetophenone planes are  $P1-P2$  [ $98.5(2)^\circ$ ] and  $P2-P3$  [ $159.5(3)^\circ$ ]. The asymmetric disposition of the two chemically equivalent rings with respect to the central *o*-phenylene ring is in contrast with the structure in solution. The  $^{13}\text{C}$  NMR spectrum recorded in  $\text{CDCl}_3$  shows only twelve signals (Tirado-Rives *et al.*, 1984). In solution the two chemically equivalent halves are, on a time-averaged basis, conformationally equivalent.

\* Lists of H-atom coordinates, anisotropic thermal parameters, ring torsion angles and deviations from least-squares planes, and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39896 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

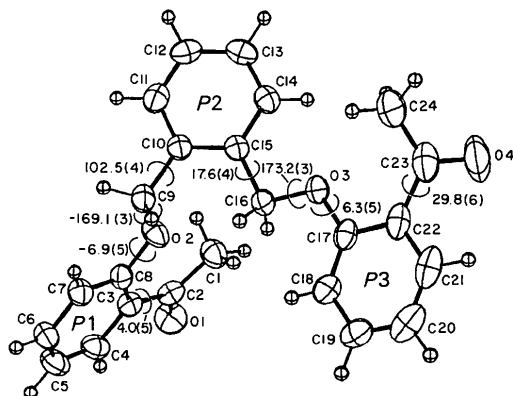


Fig. 1. Drawing of 2,2'-[*o*-phenylenebis(methyleneoxy)]-diacetophenone (40% contours) with selected torsion angles ( $^\circ$ ).  $P1$ ,  $P2$  and  $P3$  refer to ring planes (see text).

Table 1. Fractional coordinates and equivalent isotropic thermal parameters

Origin of polar axis defined by  $y = 0$  for O(1).

	$x$	$y$	$z$	$B_{\text{eq}}^*(\text{\AA}^2)$
O(1)	0.8578 (2)	0	0.51422 (11)	6.12 (5)
O(2)	0.8407 (1)	0.3541 (5)	0.30004 (8)	4.87 (4)
O(3)	1.2100 (1)	0.5795 (5)	0.18988 (9)	4.25 (4)
O(4)	1.5568 (2)	0.6932 (9)	0.12290 (1)	9.69 (9)
C(1)	0.9625 (3)	0.0128 (7)	0.3990 (2)	5.29 (7)
C(2)	0.8638 (2)	0.0994 (7)	0.4507 (1)	4.18 (6)
C(3)	0.7756 (2)	0.3122 (6)	0.4286 (1)	3.66 (5)
C(4)	0.6964 (2)	0.3952 (7)	0.4849 (1)	4.58 (7)
C(5)	0.6125 (2)	0.5889 (7)	0.4729 (1)	5.05 (7)
C(6)	0.6040 (2)	0.7128 (7)	0.4024 (1)	4.66 (6)
C(7)	0.6795 (2)	0.6351 (6)	0.3441 (1)	4.25 (6)
C(8)	0.7645 (2)	0.4369 (6)	0.3571 (1)	3.70 (6)
C(9)	0.8208 (2)	0.4571 (7)	0.2242 (1)	4.00 (6)
C(10)	0.8977 (2)	0.2981 (6)	0.1719 (1)	3.52 (5)
C(11)	0.8394 (2)	0.1086 (7)	0.1258 (1)	4.52 (6)
C(12)	0.9040 (2)	-0.0453 (7)	0.0773 (1)	4.69 (7)
C(13)	1.0294 (3)	-0.0149 (7)	0.0739 (1)	4.59 (6)
C(14)	1.0899 (2)	0.1718 (7)	0.1191 (1)	4.12 (6)
C(15)	1.0256 (2)	0.3298 (6)	0.1681 (1)	3.25 (5)
C(16)	1.0896 (2)	0.5287 (6)	0.2180 (1)	3.92 (6)
C(17)	1.2766 (2)	0.7783 (6)	0.2242 (1)	4.09 (6)
C(18)	1.2378 (2)	0.9117 (7)	0.2883 (1)	4.83 (7)
C(19)	1.3060 (3)	1.1152 (8)	0.3193 (2)	5.56 (7)
C(20)	1.4154 (3)	1.1840 (8)	0.2890 (2)	6.63 (8)
C(21)	1.4577 (3)	1.0459 (8)	0.2281 (2)	6.22 (8)
C(22)	1.3904 (2)	0.8400 (8)	0.1931 (1)	4.92 (7)
C(23)	1.4459 (2)	0.7054 (8)	0.1264 (2)	5.91 (8)
C(24)	1.3705 (3)	0.6094 (14)	0.0613 (2)	9.7 (1)

$$* B_{\text{eq}} = \frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha).$$

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

O(1)-C(2)	1.221 (3)	C(10)-C(11)	1.396 (4)
O(2)-C(8)	1.382 (3)	C(10)-C(15)	1.400 (3)
O(2)-C(9)	1.429 (3)	C(11)-C(12)	1.368 (4)
O(3)-C(16)	1.434 (3)	C(12)-C(13)	1.372 (4)
O(3)-C(17)	1.373 (3)	C(13)-C(14)	1.388 (4)
O(4)-C(23)	1.208 (3)	C(14)-C(15)	1.383 (3)
C(1)-C(2)	1.490 (4)	C(15)-C(16)	1.494 (4)
C(2)-C(3)	1.492 (4)	C(17)-C(18)	1.387 (4)
C(3)-C(4)	1.393 (3)	C(17)-C(22)	1.401 (3)
C(3)-C(8)	1.399 (3)	C(18)-C(19)	1.378 (5)
C(4)-C(5)	1.359 (4)	C(19)-C(20)	1.362 (5)
C(5)-C(6)	1.380 (4)	C(20)-C(21)	1.368 (5)
C(6)-C(7)	1.386 (3)	C(21)-C(22)	1.409 (5)
C(7)-C(8)	1.385 (4)	C(22)-C(23)	1.495 (4)
C(9)-C(10)	1.498 (3)	C(23)-C(24)	1.456 (5)
C(8)-O(2)-C(9)	118.4 (2)	C(11)-C(12)-C(13)	119.4 (3)
C(16)-O(3)-C(17)	117.2 (2)	C(12)-C(13)-C(14)	120.2 (3)
O(1)-C(2)-C(1)	119.0 (3)	C(13)-C(14)-C(15)	121.0 (2)
O(1)-C(2)-C(3)	118.9 (2)	C(10)-C(15)-C(14)	118.9 (3)
C(1)-C(2)-C(3)	122.1 (2)	C(10)-C(15)-C(16)	119.4 (2)
C(2)-C(3)-C(4)	116.7 (2)	C(14)-C(15)-C(16)	121.6 (2)
C(2)-C(3)-C(8)	126.6 (2)	O(3)-C(16)-C(15)	109.6 (2)
C(4)-C(3)-C(8)	116.7 (3)	O(3)-C(17)-C(18)	123.0 (2)
C(3)-C(4)-C(5)	122.8 (3)	O(3)-C(17)-C(22)	117.2 (3)
C(4)-C(5)-C(6)	119.7 (2)	C(18)-C(17)-C(22)	119.8 (3)
C(5)-C(6)-C(7)	119.7 (3)	C(17)-C(18)-C(19)	120.9 (3)
C(6)-C(7)-C(8)	119.9 (2)	C(18)-C(19)-C(20)	120.5 (3)
O(2)-C(8)-C(3)	117.6 (2)	C(19)-C(20)-C(21)	119.1 (3)
O(2)-C(8)-C(7)	121.3 (2)	C(20)-C(21)-C(22)	122.7 (3)
C(3)-C(8)-C(7)	121.1 (2)	C(17)-C(22)-C(21)	116.8 (3)
O(2)-C(9)-C(10)	106.9 (2)	C(17)-C(22)-C(23)	125.5 (3)
C(9)-C(10)-C(11)	118.5 (2)	C(21)-C(22)-C(23)	117.7 (3)
C(9)-C(10)-C(15)	122.7 (2)	O(4)-C(23)-C(22)	119.5 (3)
C(11)-C(10)-C(15)	118.8 (2)	O(4)-C(23)-C(24)	118.3 (3)
C(10)-C(11)-C(12)	121.7 (2)	C(22)-C(23)-C(24)	121.9 (3)

$\chi^2$  tests indicate planarity of two of the rings, but slight non-planarity of the third [C(17) through C(22)], with maximum deviation 0.019 (3) Å. Atoms of this ring also exhibit the largest thermal parameters of the structure, causing observed bond distances to be systematically shorter than those of the chemically equivalent ring, P1. The possibility that the apparent thermal motion is actually a static effect involving a slight crystal disorder cannot be discounted.

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#### References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst. A* **24**, 321–324.  
 FRENZ, B. A. & OKAYA, Y. (1980). *Enraf-Nonius Structure Determination Package*. Delft, Holland.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.  
 TIRADO-RIVES, J., OLIVER, M. A., FRONCZEK, F. R. & GANDOUR, R. D. (1984). *J. Org. Chem.* **49**, 1627–1634.

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## Structural Studies of Colchicine Derivatives. IV. The Structure of Colchicine Benzoate Monohydrate, C<sub>28</sub>H<sub>27</sub>NO<sub>7</sub>·H<sub>2</sub>O

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**Abstract.**  $M_r = 507.5$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.324$  (4),  $b = 11.348$  (6),  $c = 22.944$  (9) Å,  $V = 2688$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.24$  (2),  $D_x = 1.254$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.86$  cm<sup>-1</sup>,  $F(000) = 1072$ ,  $T = 293$  K,  $R = 0.052$  for 1399 unique reflections. The troponoid ring *C* exhibits a definite bond-length alternation with an arrangement corresponding to an isocolchicine-like structure. The three shorter C–C bonds are of lengths 1.329 (8)–1.386 (8) Å, and the longer bonds are in the range 1.407 (8)–1.448 (10) Å. The other seven-membered ring has a similar conformation to those of similar compounds. The normals to the three rings *A*, *B*, *C* of colchicine are  $A-B = 43.7$  (4),  $B-C = 36.3$  (4) and  $A-C = 52.1$  (4)°. The molecules are held together by hydrogen bonds between molecules of colchicine benzoate and the water.

**Introduction.** As part of a study on the molecular geometry of some colchicine derivatives (Part I: Miravittles, Solans, Bladé-Font, Germain & Declercq, 1982; Part II: Miravittles, Rius, Bladé-Font & Germain, 1983; Part III: Rius, Molins, Miravittles & Bladé-Font, 1984), the structure of colchicine benzoate has been determined.

This derivative was synthesized in order to determine whether it belongs to the colchicine (II) or the isocolchicine series (I), and to study the equilibrium in solution of the two forms in relation to that of colchicine acetate (Elguero, Muller, Bladé-Font, Faure & Vincent, 1980). The biological activity of colchicine derivatives depends, principally, on the position of the oxygen functions of the troponoid ring *C*. Thus, the derivatives belonging to the colchicine series (II) are considerably more active biologically than those of the isocolchicine series (I) (Santavý, 1979).

The present structure determination has shown that the title compound belongs to the isocolchicine series [(I);  $R = C_6H_5CO$ ].

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