

intermolecular contacts with nitro-group oxygen atoms: H(2A)···O(6) (at $-x, \frac{1}{2}+y, \frac{1}{2}-z$) = 2.33 (3) Å and H(4A)···O(4) (at $x, \frac{1}{2}-y, \frac{1}{2}+z$) = 2.27 (3) Å; N(4)···O(4) = 2.964 (3) and N(2)···O(6) = 3.018 (3) Å. The first of these contacts, together with the carboxylic acid dimer interaction, forms hydrogen-bond-linked ribbons approximately parallel to [101], while the second forms a lateral link to another ribbon.

The packing coefficients (PC = total molecular volume/unit-cell volume) for over 40 polynitro-organic compounds have been calculated (Holden & Dickinson, 1979), giving values ranging from 0.70 to 0.81. The PC 's calculated for (I)–(IV), 0.77, 0.79, 0.80 and 0.79, respectively, are near the top of the range of these values, suggesting that crystal-packing efficiency is an important contribution to the high crystal densities of these compounds.

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Structure of 3-Benzylidenephthalide, $C_{15}H_{10}O_2$

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Abstract. $M_r = 222$, $P2_1/n$, $a = 15.166$ (2), $b = 8.002$ (2), $c = 19.013$ (2) Å, $\beta = 103.64$ (1)°, $V = 2242.27$ Å³, $Z = 8$, $D_m = 1.32$ (8), $D_x = 1.32$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7093$ Å, $\mu = 0.81$ cm⁻¹, $F(000) = 928$, $T = 298$ K, final $R = 0.047$ for 1890 observed reflections. The title compound has the Z configuration with two molecules in the asymmetric unit related by a pseudo twofold axis. The molecule is almost planar with the phenyl ring *trans* to the benzene ring fused to phthalide. The benzene ring is slightly distorted by the five-membered ring fused to it.

Introduction. It is known (Knight & Pattenden, 1975) that alkylphthalides exist in two isomeric forms, E and Z , which give different melting points. The assignment of the form is purely based on proton NMR data. The title compound and 3-ethylidenephthalide were synthesized and their transformation to the other form could be observed by photochemical procedures (Lin, Wang, Koh & Ko, 1984). The chemical shifts on the

References

- AMMON, H. L. & BHATTACHARJEE, S. K. (1982). *Acta Cryst.* **B38**, 2083–2086.
- AMMON, H. L., BHATTACHARJEE, S. K. & HOLDEN, J. R. (1982). *Acta Cryst.* **B38**, 1851–1854.
- BHATTACHARJEE, S. K. & AMMON, H. L. (1981). *Acta Cryst.* **B37**, 2082–2085.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- HOLDEN, J. R. & DICKINSON, C. W. (1977). *J. Phys. Chem.* **81**, 1505–1514.
- HOLDEN, J. R. & DICKINSON, C. W. (1979). *Prediction of Crystal Density through Molecular Packing Analysis*. Report No. NSWC MP 79–185. Naval Surface Weapons Center, Silver Spring, Maryland.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- NYBURG, S. C. (1974). *Acta Cryst.* **B30**, 251–253.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. S. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

vinyl protons of the two forms are 6.33, 6.90 for the title compound and 5.6, 5.8 for 3-ethylidenephthalide. It is somewhat dangerous to assign the structure according to such small differences, so to confirm whether the synthetic product is the Z or E form, the single-crystal structure analysis was undertaken.

Experimental. Crystal $0.05 \times 0.3 \times 0.6$ mm. CAD-4 diffractometer. Unit-cell parameters refined by least-squares methods on the basis of 25 reflections, 2θ range 22 to 24°. D_m by flotation (n -hexane/ CCl_4). $2\theta_{max} = 50^\circ$. Ranges of h, k, l : 0 to 18, 0 to 9, -22 to 22. Three standard reflections monitored every 2 h: variation $< \pm 3\%$. 4268 unique reflections, 1890 observed with $I \geq 2\sigma(I)$. $R = 0.047$, $wR = 0.030$, $S = 1.71$ based on F . Weighting scheme from counting statistics. Structure solved by direct methods using *MULTAN* with 315 highest E 's, 100 smallest E 's and 2409 \sum_2 relationships. H atoms found in difference Fourier map after isotropic refinement and then refined. Other atoms refined anisotropically. $(\Delta/\sigma)_{max} = 0.26$. Peaks in final map -0.19 to 0.14 e Å⁻³. Atomic

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scattering factors from *International Tables for X-ray Crystallography* (1974). Computing programs: NRCC SDP PDP-11 Package (Gabe & Lee, 1981), *MULTAN* and *ORTEP* from Enraf-Nonius (1979) *Structure Determination Package*.

Table 1. Atomic parameters and B_{eq} values

$$B_{eq} = \frac{2}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1A)	0.1905 (2)	0.3809 (4)	0.2611 (2)	3.49 (2)
C(2A)	0.2653 (2)	0.4513 (4)	0.3098 (2)	3.88 (2)
C(3A)	0.2803 (2)	0.4225 (5)	0.3836 (2)	4.33 (2)
C(4A)	0.2202 (3)	0.3242 (5)	0.4103 (2)	4.55 (2)
C(5A)	0.1447 (2)	0.2565 (5)	0.3631 (2)	4.51 (2)
C(6A)	0.1293 (2)	0.2846 (5)	0.2892 (2)	4.22 (2)
C(7A)	0.1832 (2)	0.4077 (4)	0.1840 (2)	3.72 (2)
C(8A)	0.1227 (2)	0.3492 (4)	0.1267 (2)	3.61 (2)
C(9A)	-0.0047 (2)	0.2145 (5)	0.0636 (2)	4.80 (2)
C(10A)	0.0414 (2)	0.2865 (5)	0.0114 (2)	3.92 (2)
C(11A)	0.0178 (3)	0.2827 (5)	-0.0636 (2)	4.98 (2)
C(12A)	0.0767 (3)	0.3586 (5)	-0.0996 (2)	5.50 (2)
C(13A)	0.1563 (3)	0.4349 (5)	-0.0611 (2)	5.22 (2)
C(14A)	0.1790 (2)	0.4396 (5)	0.0136 (2)	4.24 (2)
C(15A)	0.1193 (2)	0.3653 (4)	0.0497 (2)	3.56 (2)
O(1A)	0.0469 (1)	0.2533 (3)	0.1328 (1)	4.55 (1)
O(2A)	-0.0731 (2)	0.1329 (4)	0.0568 (1)	6.55 (2)
C(1B)	0.8456 (2)	0.4370 (5)	0.4063 (2)	3.98 (2)
C(2B)	0.7676 (2)	0.5329 (5)	0.3825 (2)	4.91 (2)
C(3B)	0.7491 (3)	0.6033 (5)	0.3138 (2)	5.76 (2)
C(4B)	0.8058 (3)	0.5785 (5)	0.2683 (2)	5.91 (2)
C(5B)	0.8819 (3)	0.4816 (5)	0.2915 (2)	5.46 (2)
C(6B)	0.9029 (2)	0.4100 (5)	0.3599 (2)	4.73 (2)
C(7B)	0.8641 (2)	0.3720 (5)	0.4808 (2)	4.16 (2)
C(8B)	0.9334 (2)	0.2862 (4)	0.5192 (2)	3.74 (2)
C(9B)	1.0696 (2)	0.1440 (4)	0.5444 (2)	3.99 (2)
C(10B)	1.0330 (2)	0.1394 (4)	0.6091 (2)	3.52 (2)
C(11B)	1.0694 (2)	0.0674 (5)	0.6758 (2)	4.57 (2)
C(12B)	1.0214 (3)	0.0878 (5)	0.7288 (2)	5.00 (2)
C(13B)	0.9409 (3)	0.1796 (5)	0.7152 (2)	5.11 (2)
C(14B)	0.9040 (2)	0.2487 (5)	0.6474 (2)	4.50 (2)
C(15B)	0.9519 (2)	0.2270 (4)	0.5938 (2)	3.55 (2)
O(1B)	1.0075 (2)	0.2332 (3)	0.4916 (1)	4.01 (1)
O(2B)	1.1374 (2)	0.0886 (3)	0.5315 (1)	5.32 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) of the two independent molecules A and B

Molecule A		Molecule B		Molecule A		Molecule B	
C(1)–C(2)	1.402 (5)	1.393 (5)	C(9)–C(10)	1.461 (5)	1.466 (5)		
C(1)–C(6)	1.404 (5)	1.395 (5)	C(9)–O(1)	1.398 (4)	1.399 (4)		
C(1)–C(7)	1.460 (4)	1.472 (5)	C(9)–O(2)	1.207 (4)	1.197 (4)		
C(2)–C(3)	1.388 (5)	1.390 (5)	C(10)–C(11)	1.385 (5)	1.385 (5)		
C(3)–C(4)	1.387 (5)	1.369 (6)	C(10)–C(15)	1.385 (5)	1.386 (5)		
C(4)–C(5)	1.389 (5)	1.375 (6)	C(11)–C(12)	1.387 (5)	1.384 (5)		
C(5)–C(6)	1.387 (5)	1.387 (5)	C(12)–C(13)	1.396 (5)	1.396 (6)		
C(7)–C(8)	1.333 (5)	1.322 (5)	C(13)–C(14)	1.381 (5)	1.392 (5)		
C(8)–C(15)	1.459 (4)	1.460 (5)	C(14)–C(15)	1.392 (5)	1.394 (4)		
C(8)–O(1)	1.409 (4)	1.413 (4)					
Molecule A		Molecule B		Molecule A		Molecule B	
C(2)–C(1)–C(6)	118.3 (3)	119.2 (3)	C(10)–C(9)–O(2)	132.7 (3)	132.6 (3)		
C(2)–C(1)–C(7)	117.5 (3)	117.5 (3)	O(1)–C(9)–O(2)	119.8 (3)	120.6 (3)		
C(6)–C(1)–C(7)	124.2 (3)	123.3 (3)	C(9)–C(10)–C(11)	129.9 (3)	129.2 (3)		
C(1)–C(2)–C(3)	121.0 (3)	119.8 (3)	C(9)–C(10)–C(15)	108.0 (3)	107.8 (3)		
C(2)–C(3)–C(4)	119.9 (3)	121.2 (4)	C(11)–C(10)–C(15)	122.1 (3)	123.0 (3)		
C(3)–C(4)–C(5)	119.9 (3)	119.0 (3)	C(10)–C(11)–C(12)	117.3 (3)	117.0 (3)		
C(4)–C(5)–C(6)	120.5 (3)	121.6 (3)	C(11)–C(12)–C(13)	120.8 (3)	120.9 (3)		
C(1)–C(6)–C(5)	120.4 (3)	119.3 (3)	C(12)–C(13)–C(14)	121.7 (3)	121.6 (3)		
C(1)–C(7)–C(8)	130.1 (3)	131.4 (3)	C(13)–C(14)–C(15)	117.5 (3)	117.5 (3)		
C(7)–C(8)–C(15)	130.1 (3)	130.6 (3)	C(8)–C(15)–C(10)	108.1 (3)	109.0 (3)		
C(7)–C(8)–O(1)	122.7 (3)	123.4 (3)	C(8)–C(15)–C(14)	131.3 (3)	131.0 (3)		
C(15)–C(8)–O(1)	107.2 (3)	106.0 (3)	C(10)–C(15)–C(14)	120.6 (3)	120.0 (3)		
C(10)–C(9)–O(1)	107.5 (3)	106.8 (3)	C(8)–O(1)–C(9)	109.3 (2)	110.3 (2)		

Discussion. There are two molecules in the asymmetric unit; both appear to be the *Z* form with the phenyl ring *trans* to the benzene ring of the phthalide. The atomic coordinates and the equivalent isotropic temperature factors of the two molecules are listed in Table 1.* The molecular structure and labeling scheme are shown in Fig. 1 as a projection along the pseudo twofold rotation axis with the relative orientation marked in the center of the map. The bond distances and bond angles are listed in Table 2. The molecule is nearly planar with average carbon–carbon distances over both molecules of 1.389 (6) \AA for the benzene rings; the C=C, C=O double bonds average 1.328, 1.202 \AA respectively. The bond angles are all quite normal. The C–C–C angles with the central carbon at the *ortho* position to the five-membered ring, *i.e.* C(11), C(14), are significantly smaller than 120° , which can be explained as a small distortion of the benzene ring by the fused five-membered ring. The dihedral angle between the benzyl group and the phthalide plane is $7.1 (1)^\circ$. The angle between the two molecular (*A* and *B*) planes is $60.9 (1)^\circ$.

The synthetic products of 3-benzylidene-phthalide and 3-ethylidene-phthalide were both studied by X-ray diffraction. They were both found to have the *Z* configuration. Unfortunately, the structure of 3-ethylidene-phthalide [$P2_1/c$, $a = 5.288 (5)$, $b = 15.037 (8)$, $c = 10.142 (6) \text{\AA}$, $\beta = 81.69 (5)^\circ$] was not satisfactorily refined owing to decomposition of the sample, although the molecule could be seen in the *Z* configuration in the Fourier map. Based on these two structures, we propose that the major synthetic product is the *Z* form rather than the *E* form as stated previously (Knight & Pattenden, 1975). In addition, 3-(nitromethylene)-

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42038 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

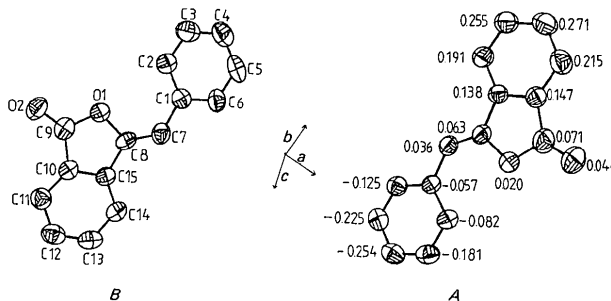


Fig. 1. An *ORTEP* drawing of the two molecules with 50% probability for the thermal ellipsoids. The pseudo twofold rotation axis is perpendicular to and passes through the center of the drawing, *i.e.* (0.53, y^+ , 0.32). Numbers on molecule *A* are Δy of *A* – *B* molecules.

phthalide was also confirmed to be in the *Z* form (Joshi, Hegde, Rogers & Williams, 1980).

The two molecules in the asymmetric unit do possess a pseudo twofold axis of rotation ($0.53, y^+, 0.32$) with the rotation axis about 18° away from the *b* axis. The relationship between molecules *A* and *B* is shown in Fig. 1 as the projection along this y^+ axis. The numbers listed on the atoms of *A* are the differences in the *y* coordinates of the two independent molecules. Therefore, the two independent molecules are very similar, but cannot pack to give higher symmetry.

Of course, this study cannot completely rule out the possibility of a different conformation in solution, but the rotation around the C=C double bond must go through a very high energy barrier. Therefore, the

conformation in the solution state (NMR data) and that of the solid state are assumed to be the same.

References

- ENRAF-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft.
- GABE, E. J. & LEE, F. L. (1981). *Acta Cryst.* **A37**, C339.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOSHI, B. S., HEGDE, V. R., ROGERS, D. & WILLIAMS, D. J. (1980). *Tetrahedron Lett.* **21**, 1163–1164.
- KNIGHT, D. W. & PATTENDEN, G. (1975). *J. Chem. Soc. Perkin Trans.* **1**, pp. 635–640.
- LIN, L. C., WANG, C. B., KOH, V. C. & KO, W. C. (1984). *Bull. Inst. Chem. Acad. Sin.* No. 31.

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4-Acetyl-3'-chlorobiphenyl, $C_{14}H_{11}ClO$

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Abstract. $M_r = 230.7$, monoclinic, $P2_1/c$, $a = 3.88$ (1), $b = 9.03$ (1), $c = 32.82$ (5) Å, $\beta = 98.5$ (2)°, $V = 1137.26$ Å³, $Z = 4$, $D_m = 1.29$, $D_x = 1.35$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 2.627$ mm⁻¹, $F(000) = 480$, $T = 293$ K, $R = 0.068$ for 1212 observed densitometer and visually measured equi-inclination Weissenberg data. The average C–C bond length in the phenyl rings is 1.391 Å. The molecule is non-planar; the angle between the phenyl rings is 37.7 (3)° and the acetyl group is rotated about its C–C bond by 4.1 (2)°. The C–Cl bond is 1.745 (6) Å and makes an angle of 1.3 (2)° with the phenyl plane.

Introduction. The structure determination of the title compound forms part of an investigation into liquid-crystal compounds and their chemical precursors.

Experimental. D_m measured by flotation in aqueous cadmium *n*-dodecatungstoborate. Thin transparent needle crystals, $0.3 \times 0.08 \times 0.05$ and $0.1 \times 0.1 \times 0.06$ mm, respectively, for *a*- and *b*-axis Weissenberg data. 1600 reflexions measured on a Joyce–Loebl flying-spot densitometer from multiple-film photographs using Cu $K\alpha$ radiation. Data merged to give 1212 unique observed reflexions; $h -3 \rightarrow 3$, $k 0 \rightarrow 11$, $l 0 \rightarrow 40$; $R_{int} = 0.05$. Structure solved by Patterson synthesis and refined (on *F*) by block-diagonal least squares with

anisotropic thermal parameters for the non-hydrogen atoms. H-atom positions, initially obtained from a difference synthesis and placed at geometrically reasonable positions, refined with isotropic thermal parameters. Final $R = 0.068$, unit weights used. $(\Delta/\sigma)_{max}$ in final refinement cycle 0.009 for positional and 0.004 for thermal parameters. Max. and min. heights in final $\Delta\rho$ map $+0.31$ and -0.27 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs used: *SHELX76* (Sheldrick, 1976) and locally written programs supplied by HHS and Drs C. Morgan and M. J. Mottram.

Discussion. Table 1* gives atomic parameters and Table 2 bond lengths and angles. The atomic numbering is shown in Fig. 1.

The phenyl rings are planar to within ± 0.01 Å with an average C–C bond length of 1.391 Å. In several 2' and 3' halogen-substituted biphenyls the halogen atom has been found to be displaced out of the plane of the

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, intermolecular distances and details of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42052 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.