Acta Cryst. (1985). C**41**, 295–298

2,3,4aβ,6,7,8aβ-Hexamethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4α(and 4β)-yl Acetate,* $C_{18}H_{26}O_3$

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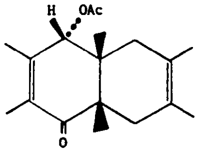
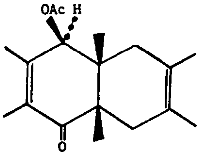
(*Received* 13 *June* 1984; *accepted* 3 *October* 1984)

Abstract. $M_r = 290{\cdot}40$, $T = 295$ K, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}75$ cm^{-1}. Crystals of the 4α-acetate are monoclinic, $P2_1/c$, $a = 14{\cdot}826$ (3), $b = 6{\cdot}900$ (1), $c = 17{\cdot}511$ (4) Å, $\beta = 109{\cdot}87$ (1)°, $V = 1684{\cdot}7$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}145$ g cm^{-3}, $F(000) = 632$, final $R = 0{\cdot}054$ for 2066 observed reflections. The 4β-acetate is triclinic, $P\bar{1}$, $a = 8{\cdot}993$ (3), $b = 9{\cdot}228$ (3), $c = 10{\cdot}770$ (3) Å, $\alpha = 100{\cdot}29$ (2), $\beta = 94{\cdot}26$ (2), $\gamma = 106{\cdot}71$ (2)°, $V = 834{\cdot}6$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}155$ g cm^{-3}, $F(000) = 316$, final $R = 0{\cdot}047$ for 2639 observed reflections. The molecules have different ring-flipped conformations, so that in each molecule the acetate group is pseudo-equatorial to the cyclohexenone ring. The two conformations produce different intramolecular nonbonded contacts, which account for the varying photochemical reactivities in the solid state.

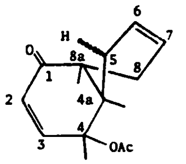
Introduction. Compounds (1) and (2) when irradiated in the solid state were expected to undergo two different photorearrangements (path *A* and path *B*, Fig. 1) as a result of their different molecular conformations, (3) and (4), with the acetate groups occupying more sterically favoured pseudo-equatorial positions (Trotter, 1983). Both reactions are initiated by intramolecular allylic hydrogen-atom transfer to the β-carbon atom of the enone moiety. However, while enone (2) behaved as expected (path *B*), irradiation of enone (1) in the crystalline phase led exclusively to the product resulting from initial hydrogen-atom abstraction by the α-carbon atom of the enone chromophore (path *C*) (Ariel, Askari, Scheffer, Trotter & Walsh, 1984). The present crystallographic study of (1) and (2) was undertaken to establish whether the crystal structures and molecular conformations can explain the unexpected reactivity in the solid state.



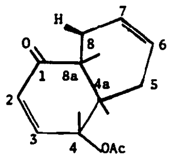
(1) (4α-acetate)



(2) (4β-acetate)



(3)



(4)

Experimental. The indices for boundary planes (6 faces) for (1) ±(110), ±(100) and ±(101), with distances from crystal centre of 0·24, 0·15 and 0·25 mm; for (2) (12 faces) ±($\bar{1}$01), ±($\bar{1}$10), ±($\bar{1}$1$\bar{1}$), ±(01$\bar{1}$), ±(011) and ±(001) with distances 0·12, 0·12, 0·14, 0·11, 0·19 and 0·14 mm; CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting of 21 reflections with $18 \leq \theta \leq 21°$ for (1), 25 reflections with $20 \leq \theta \leq 25°$ for (2). 2659 unique reflections with $\theta \leq 25°$, $h = -17$ to $+15$, $k = 0$–8, $l = 0$–20 for (1), 3297 with $\theta \leq 27°$, $h = -11$ to $+10$, $k = -11$ to $+11$, $l = 0$–13 for (2); ω–$\frac{1}{3}\theta$ scan for (1), ω–2θ for (2); ω-scan width $(1{\cdot}0 + 0{\cdot}3\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(1{\cdot}0 + \tan\theta)$ mm, vertical aperture 4 mm, Lp corrections. Three standard reflections measured every 60 min displayed <2% average fluctuation. Structures solved by direct methods using *SHELX* (Sheldrick, 1976) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$. All H atoms located in a difference synthesis and refined isotropically. 294 parameters, consisting of 141 positional

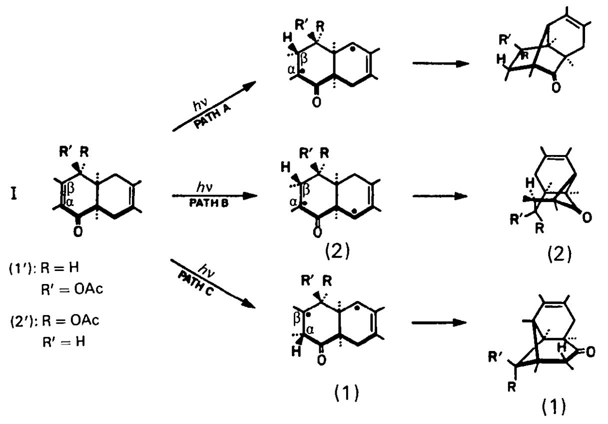


Fig. 1. Reactants and products in solid-state photorearrangements.

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* IUPAC names: 2,3,4aβ,6,7,8aβ-hexamethyl-4(1*H*)-oxo-4a,5,8,8a-tetrahydro-1α(and 1β)-naphthyl acetate (Note this numbering differs from that used throughout the paper.)

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Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic temperature factors* (Å² × 10³)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Compound (1) (4α-acetate)				Compound (2) (4β-acetate)			
	x	y	z	$U_{\rm eq}$	x	y	z	$U_{\rm eq}$
O(1)	7930 (1)	3355 (3)	1574 (1)	75	2765 (2)	1370 (2)	10369 (1)	70
O(2)	6820 (1)	357 (2)	3914 (1)	50	3098 (2)	2358 (2)	5715 (1)	45
O(3)	5596 (1)	1660 (3)	4209 (1)	82	1015 (2)	1671 (2)	4209 (2)	72
C(1)	7585 (1)	2980 (3)	2098 (1)	46	2425 (2)	1392 (3)	9256 (2)	43
C(2)	6786 (1)	1589 (3)	1924 (1)	46	2753 (2)	283 (2)	8224 (2)	41
C(21)	6427 (3)	789 (7)	1076 (2)	77	3186 (4)	−1054 (4)	8618 (3)	65
C(3)	6405 (1)	1131 (3)	2497 (1)	41	2630 (2)	475 (2)	7021 (2)	38
C(31)	5534 (2)	−122 (5)	2328 (2)	62	2871 (4)	−657 (3)	5921 (3)	57
C(4)	6818 (1)	1911 (3)	3345 (1)	40	2136 (2)	1788 (2)	6668 (2)	35
C(4a)	7844 (1)	2675 (3)	3583 (1)	40	2313 (2)	3163 (2)	7767 (2)	38
C(4a1)	8110 (2)	3684 (5)	4414 (2)	62	4050 (3)	4099 (3)	8164 (3)	55
C(5)	8548 (1)	1008 (3)	3642 (2)	42	1403 (3)	4196 (3)	7331 (2)	49
C(6)	9536 (1)	1608 (3)	3672 (1)	45	−359 (3)	3571 (3)	7240 (2)	48
C(61)	10278 (2)	47 (6)	3967 (2)	63	−1225 (4)	4436 (4)	6555 (3)	72
C(7)	9706 (1)	3355 (3)	3427 (1)	49	−1062 (2)	2390 (3)	7750 (2)	44
C(71)	10678 (2)	4063 (6)	3446 (2)	67	−2815 (3)	1718 (4)	7698 (3)	66
C(8)	8924 (2)	4826 (4)	3112 (2)	56	−154 (2)	1562 (3)	8447 (2)	42
C(8a)	7900 (1)	4066 (3)	2907 (1)	44	1585 (2)	2500 (2)	8889 (2)	38
C(8a1)	7211 (2)	5803 (4)	2761 (2)	62	1681 (3)	3774 (3)	10058 (2)	57
C(9)	6196 (2)	440 (4)	4320 (1)	57	2387 (3)	2217 (3)	4530 (2)	47
C(10)	6355 (3)	−1194 (7)	4902 (3)	86	3569 (4)	2851 (4)	3702 (3)	65

parameters, 126 anisotropic temperature factors, 26 isotropic temperature factors and a scale factor. Final $R = 0.054$, $R_w = 0.052$ for 2066 reflections for (1), $R = 0.047$, $R_w = 0.046$ for 2639 reflections for (2), for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, S = scan count, B = time-averaged background count. For all data $R = 0.074$, $R_w = 0.057$ for (1), $R = 0.064$, $R_w = 0.076$ for (2), $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{\rm max} = 0.6$ for (1), 0.2 for (2); ± 0.26 e Å^{-3} for (1), ± 0.21 e Å^{-3} for (2) in final difference synthesis; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion. Final atomic coordinates are in Table 1, bond distances and bond angles in Table 2.* The molecular structures of (1) and (2) (Fig. 2) show that the two molecules have fused six-membered rings with half-chair conformations which are folded and twisted about the C(4a)—C(8a) bond. They have different ring-flipped conformations, (3) for the 4α-acetate and (4) for the 4β-acetate. The acetate groups occupy the more sterically favoured pseudo-equatorial positions in both molecules. The degree of twist in the molecules is indicated by the bridgehead torsion angles: 4α-acetate, C(4a1)—C(4a)—C(8a)—C(8a1) = −61·3 (3), C(5)—C(4a)—C(8a)—C(1) = 62·4 (2)°; 4β-acetate, C(4a1)—C(4a)—C(8a)—C(8a1) = 59·6 (2), C(4)—C(4a)—C(8a)—C(8) = −58·9 (2)°. The twists are thus similar in the two molecules, and to those in the tetrahydronaphthoquinone analogue, 60·0 (6) and −61·4 (5)° (Phillips & Trotter, 1976).

The consequence of these conformations is that there is a close intramolecular nonbonded approach in the 4α-acetate of H(51) to the enone carbon atoms C(2) and C(3); in the 4β-acetate the close approach is from H(81) to C(2) and C(3). In the 4α-acetate the C(2)···H(51) and C(3)···H(51) distances are 2·74 (2) and 2·70 (2) Å, respectively, not significantly different from each other, but shorter than the normal van der Waals contact distance of 2·90 Å. In the 4β-acetate the C(2)···H(81) and C(3)···H(81) distances are 2·79 (2) and 2·84 (2) Å, respectively, comparable to the 4α-acetate. The solid-state photochemical reaction of the 4α-acetate proceeds *via* initial H(51) abstraction by the α-enone carbon, C(2) (path *C*, Fig. 1), the 4β-acetate reacts *via* initial H(81) abstraction by the β-enone carbon, C(3) (path *B*, Fig. 1). The C(2)—C(3)···H(*n*) angle (Δc) and τc [angle between the C(3)···H(*n*) vector and the enone plane defined by C(21)—C(2)—C(3)—C(31); H(*n*) is H(51) in the 4α-acetate, and H(81) in the 4β-acetate] are quite similar in the two molecules, 77 (1) and 55 (1)° in (1), and 74 (1) and 50 (1)° in (2). The C(3)—C(2)···H(51) angle ($\Delta'c$) and $\tau'c$ for the 4α-acetate are 74 (1) and 54 (1)°, similar and suitable for H abstraction by C(2) (path *C*, Fig. 1).

Recent work (Appel, Jiang, Scheffer & Walsh, 1983) has shown that enones of general structure I, when irradiated in the crystalline phase, undergo one of two possible photorearrangements (path *A* or path *B*, Fig. 1), both of which are initiated by intramolecular allylic hydrogen-atom transfer to the β-carbon atom of the enone moiety. We believe that the change in reactivity of enone (1) is caused by specific crystal-lattice packing effects near the reaction site, which are unique to (1). The hydrogen transfer to C_α or C_β is accompanied by change in hybridization of C_α or C_β from sp^2 to sp^3. Inspection of the crystal-packing diagram for enone (2) [Fig. 3(*b*)] shows that these changes in hybridization of C_α and C_β would force both

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39805 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

	Compound (1) (4α-acetate)	Compound (2) (4β-acetate)
C(1)–O(1)	1·220 (2)	1·221 (2)
C(1)–C(2)	1·474 (2)	1·478 (3)
C(2)–C(3)	1·346 (2)	1·339 (3)
C(2)–C(21)	1·502 (2)	1·515 (3)
C(3)–C(4)	1·500 (2)	1·503 (3)
C(3)–C(31)	1·498 (2)	1·507 (3)
C(4)–C(4a)	1·528 (2)	1·535 (3)
C(4)–O(2)	1·464 (2)	1·464 (2)
C(4a)–C(4a1)	1·538 (2)	1·537 (3)
C(4a)–C(5)	1·533 (2)	1·533 (3)
C(5)–C(6)	1·506 (2)	1·511 (3)
C(6)–C(7)	1·331 (2)	1·326 (3)
C(6)–C(61)	1·500 (2)	1·507 (3)
C(7)–C(8)	1·498 (2)	1·513 (3)
C(7)–C(71)	1·511 (2)	1·512 (3)
C(8)–C(8a)	1·530 (2)	1·544 (3)
C(1)–C(8a)	1·528 (2)	1·522 (3)
C(4a)–C(8a)	1·548 (2)	1·555 (3)
C(8a)–C(8a1)	1·539 (2)	1·540 (3)
C(9)–C(10)	1·484 (3)	1·496 (3)
C(9)–O(2)	1·345 (2)	1·351 (2)
C(9)–O(3)	1·192 (2)	1·188 (3)
C(2)–C(1)–O(1)	119·7 (1)	120·5 (2)
C(8a)–C(1)–O(1)	121·2 (1)	121·3 (2)
C(8a)–C(1)–C(2)	118·8 (1)	118·2 (2)
C(3)–C(2)–C(1)	120·7 (1)	120·2 (2)
C(21)–C(2)–C(1)	115·7 (1)	116·0 (2)
C(3)–C(2)–C(21)	123·6 (1)	123·8 (2)
C(31)–C(3)–C(2)	122·7 (1)	122·7 (2)
C(4)–C(3)–C(31)	115·9 (1)	115·3 (2)
C(4)–C(3)–C(2)	121·4 (1)	121·9 (2)
C(4a)–C(4)–O(2)	107·1 (1)	107·9 (2)
C(3)–C(4)–O(2)	108·5 (1)	107·4 (2)
C(4a)–C(4)–C(3)	115·3 (1)	115·6 (2)
C(5)–C(4a)–C(4)	110·6 (1)	108·9 (2)
C(8a)–C(4a)–C(4)	108·2 (1)	107·4 (2)
C(4a1)–C(4a)–C(4)	109·1 (1)	110·4 (2)
C(5)–C(4a)–C(4a1)	109·0 (1)	109·9 (2)
C(8a)–C(4a)–C(4a1)	112·3 (1)	111·0 (2)
C(8a)–C(4a)–C(5)	107·7 (1)	109·3 (2)
C(6)–C(5)–C(4a)	115·4 (1)	115·6 (2)
C(7)–C(6)–C(5)	121·7 (1)	122·4 (2)
C(61)–C(6)–C(5)	113·9 (1)	114·0 (2)
C(7)–C(6)–C(61)	124·4 (1)	123·6 (2)
C(8)–C(7)–C(6)	121·7 (1)	122·2 (2)
C(71)–C(7)–C(6)	124·6 (2)	124·9 (2)
C(8)–C(7)–C(71)	113·7 (2)	112·9 (2)
C(8a)–C(8)–C(7)	115·9 (1)	113·9 (2)
C(8)–C(8a)–C(1)	110·6 (1)	107·5 (2)
C(4a)–C(8a)–C(1)	109·0 (1)	108·9 (2)
C(8)–C(8a)–C(4a)	109·9 (1)	109·2 (2)
C(8a1)–C(8a)–C(4a)	113·8 (1)	112·6 (2)
C(8a1)–C(8a)–C(1)	104·6 (1)	109·9 (2)
C(8a1)–C(8a)–C(8)	108·8 (1)	108·6 (2)
O(3)–C(9)–O(2)	123·6 (1)	124·1 (2)
C(10)–C(9)–O(3)	125·7 (2)	125·6 (2)
C(10)–C(9)–O(2)	110·7 (2)	110·3 (2)
C(9)–O(2)–C(4)	119·1 (1)	118·6 (2)

methyl groups at these centres, C(21) and C(31), into close contacts with the C(71) methyl hydrogens on neighbouring molecules and thus sterically impede the reaction [C(21), C(31) and C(71) are filled circles in Fig. 3(*b*)]. However, while pyramidalization of the C_β methyl of enone (1) is sterically inhibited [pyramidalization of C(31) would force these methyl hydrogens into close proximity, 1·71 and 1·87 Å, with neighbouring stationary C(31) methyl hydrogens; the appropriate C(31) atoms are filled circles in Fig. 3(*a*)], pyramidalization of the C_α methyl is totally unimpeded (computer simulations of the pyramidalization at C_α and C_β were performed, and all new intermolecular H···H contacts were calculated). We believe that it is the void space surrounding the C_α methyl group of enone (1) which allows reaction and pyramidalization at this centre in contrast to steric compression which would attend reaction and pyramidalization at C_β.

Bond distances and angles (Table 2) are very similar to those in the parent compounds (Greenhough & Trotter, 1980), the only significant differences being associated with the replacement of the 4—OH by the acetoxy group. C(4)—O(2), 1·464 (2) Å in both 4α- and 4β-acetate, is increased in length by 0·037 Å (9σ) relative to 4α–OH (1·427 Å), and 0·043 Å (11σ) relative to 4β–OH (1·421 Å). This change is accompanied by a small reduction (4σ) in C(4)—C(3). The C(3)—C(4)—C(4a) angle increases [from 114·0 (1) to 115·3 (1)° in 4α, and from 114·2 (2) to 115·6 (2)° in 4β]. Similar variations were observed in the 4α-benzoate derivative (Secco & Trotter, 1983). Intermolecular distances correspond to normal van der Waals interactions.

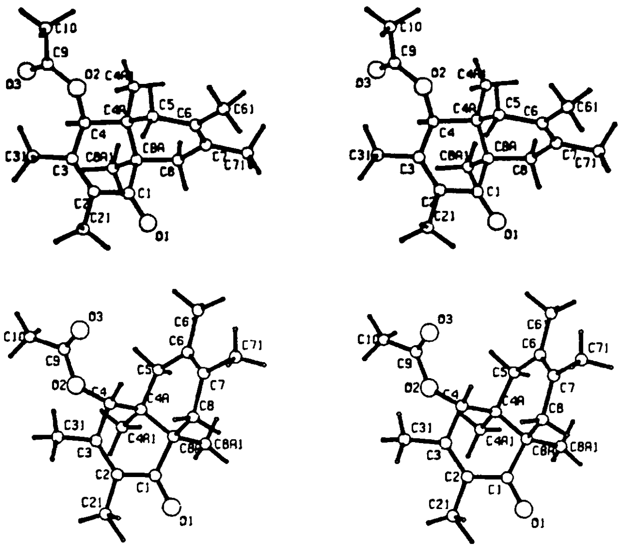
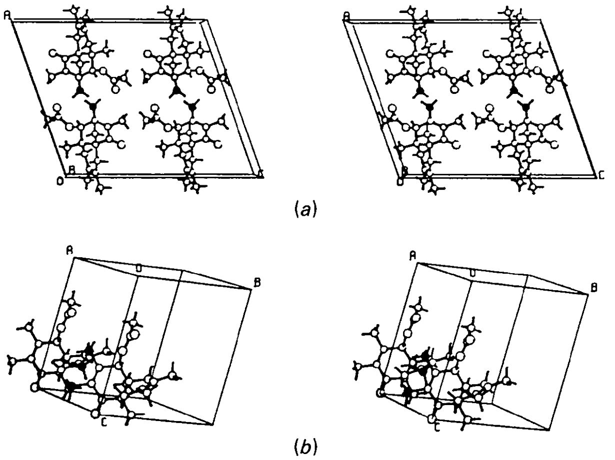


Fig. 2. Stereoscopic view of (1′) (top) and (2′) with atomic labelling [enantiomorphs of (1) and (2)].



(*a*)

(*b*)

Fig. 3. Packing diagrams of (*a*) (1) and (*b*) (2).

We thank Professor J. R. Scheffer and Ms L. Walsh for their collaborative studies on the solid-state photochemistry, the Natural Sciences and Engineering Research Council of Canada for financial support, and the University of British Columbia Computing Centre for assistance.

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Acta Cryst. (1985). C**41**, 298–300

Diphthalimide Phthalate,* $C_{24}H_{12}N_2O_8$

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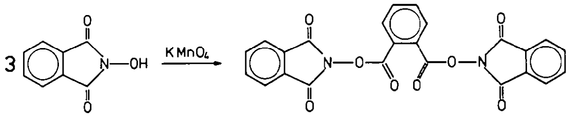
(*Received* 27 *June* 1984; *accepted* 1 *October* 1984)

Abstract. $M_r = 456{\cdot}37$, triclinic, $P\bar{1}$, $a = 8{\cdot}025$ (2), $b = 12{\cdot}910$ (1), $c = 20{\cdot}589$ (2) Å, $\alpha = 73{\cdot}90$ (1), $\beta = 88{\cdot}72$ (1), $\gamma = 77{\cdot}87$ (1)°, $V = 2002{\cdot}1$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}514$ (1) g cm^{-3}, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}1$ cm^{-1}, $F(000) = 936$, $T = 296$ K, $R = 0{\cdot}046$ for 3938 independent reflections. The two independent molecules differ only in the relative orientation of one of the side groups. One carboxyl group is coplanar with the central phenyl group, the other forms an angle of 101·2 (4)° (I) and 111·2 (4)° (II). The phthalimide groups are almost perpendicular to the carboxyl groups. The packing shows stacks of parallel phthalimide groups along **a**.

Introduction. The title compound (m.p. 497–498 K) was obtained by the oxidation of *N*-hydroxyphthalimide by $KMnO_4$ in acetone. The reaction occurs by dehydrogenation and oxidative elimination of nitrogen from each third molecule of the starting material. The product corresponds in some ways to the well known class of activated esters. The formation of such a compound in the present case is quite unusual.



As the nature of the reaction product was not clear from a chemical analysis, a crystal structure determination was undertaken.

Experimental. Colorless transparent lath-shaped crystals from acetone, sample dimensions 0·075 × 0·25 × 0·62 mm, cell constants from setting angles of 25 reflections with $7 < \theta < 13°$, CAD-4 diffractometer, hemisphere up to $2\theta = 42°$, $0 \leq h \leq 8$, $-12 \leq k \leq 13$, $-20 \leq l \leq 20$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}50$ Å^{-1}, ω scan, total number of reflections 4811, independent reflections 4382; three standards every 5000 s remained stable; empirical absorption correction based on ψ scans (North, Phillips & Mathews, 1968), correction range 1·00–1·035; internal agreement of equivalent reflections $R_{\text{int}} = 0{\cdot}02$, 3938 reflections with $I > 0{\cdot}5\sigma(I)$ used, $w(I) = 1/[\sigma^2(I) + (0{\cdot}03I)^2]$, structure determination by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), H atoms from difference synthesis and refined with fixed isotropic thermal parameters, refinement on F, extinction parameter $g = 37$ (4) $\times 10^{-8}$, the two independent molecules refined in alternating cycles, peaks in final difference synthesis less than 0·22 e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}06$, $R = 0{\cdot}046$, $wR = 0{\cdot}040$, $S = 1{\cdot}52$, scattering factors from *International Tables for X-ray Crystallography* (1974), calculations performed with the *SDP* program system (Enraf–Nonius, 1982).

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* Bis(1,3-dioxo-2*H*-isoindol-2-yl) phthalate.

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