$$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.2193P]$$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.028$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C2A—N2A	1.361 (2)	N9B—C10B	1.453 (4)
C6A—N6A	1.331 (2)	C2C—N2C	1.350 (11)
N9A—C10A	1.450 (2)	C6C—N6C	1.346 (11)
C2B—N2B	1.365 (12)	N9C—C10C	1.465 (4)
C6B—N6B	1.336 (11)		
N3A—C2A—N1A	127.55 (12)	N1B—C6B—C5B	119.8 (9)
N1A—C6A—C5A	118.13 (12)	N3C—C2C—N1C	128.0 (10)
N3B—C2B—N1B	128.2 (10)	N1C—C6C—C5C	118.1 (9)
C8A—N9A—C10A—C11A		93.0 (2)	
C8B—N9B—C10B—C11B		50.8 (6)	
C8C—N9C—C10C—C11C		−97.0 (6)	

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N2A—H2A···N1A^i	2.10 (2)	3.012 (2)	172 (2)
N6A—H4A···N7A^{ii}	2.10 (2)	2.973 (2)	162 (2)
N6A—H3A···O1W^i	2.08 (2)	2.932 (2)	162 (1)
N2A—H1A···O1W	2.47 (2)	3.180 (2)	137 (2)

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $1 - x, 2 - y, 2 - z$.

Direct methods revealed molecule *A*, but only ambiguous indications of the other molecule. Successive electron density maps gave a consensus position for most of the other heterocycle atoms, with clear indications of disorder in the side chain, N9 and C8. Molecules *B* and *C* were constructed and refined subject to 50% occupancy and the *SAME* restraint in *SHELXL93* (Sheldrick, 1993), which restrained bond and 1,3 distances to similar values to those in molecule *A*.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DATREDXL* (Brookhaven National Laboratory & University of Birmingham, 1986). Program(s) used to solve structure: *MULTAN11/84* (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1160). Services for accessing these data are described at the back of the journal.

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6-Nitrophthalide

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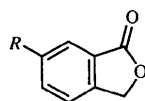
Abstract

In the title compound, $C_8H_5NO_4$, the heterocycle is planar within 0.02 Å, and the nitro group plane makes an angle of 10.0 (1)° to it. Dipolar interactions and possible weak C—H···O hydrogen bonding feature in the crystal packing. In a series of phthalides, bond lengths in the lactone ring can be related to substituent effects; in the title compound, the nitro group exerts less influence than it does in the homologous 3-nitromethylenephthalide.

Comment

With its hydrolysable (Kellog, Brown & McDonald, 1994) and electrophilic (Lesimple & Bigg, 1991; Tobia, Baranski & Rickborn, 1989) lactone ring, together with its ability to undergo ready electrophilic aromatic substitution at positions 6 and 4, phthalide, (2), is a versatile synthetic building block (Shibuya, Sakai & Naoe, 1995; Sugaya, Kato, Sakaguchi & Tomioka, 1995), particularly for the synthesis of carbocyclic (Epsztajn, Jozwiak & Szczesniak, 1993) and heterocyclic compounds (Nagao, Jeong, Lee & Sano, 1996; Hellwinkel & Goeke, 1995). 6-Nitrophthalide, (1), formed in near quantitative yield on mononitration of phthalide, (2), has recently found use in the synthesis of peralkylated isobenzofuranamines (Stanetty, Rodler & Krumpak, 1993) and the fused tricyclic compound triazolo[6,7-*d*]phthalide (Katritzky, Ji, Fan, Beretta & Bertoldi, 1992).

(1) $R = NO_2$
(2) $R = H$

In the title compound, (1) (Fig. 1), the heterocycle is planar to within ± 0.02 Å. Slight twisting about the C—N bond causes the nitro group plane (C6, N6, O8, O9) to intersect the ring plane at an angle of 10.0 (1)°. The high density (1.547 Mg m^{-3}) suggests close packing with favourable intermolecular interactions. Neighbouring molecules of (1) related by a screw axis exhibit an attraction between C=O dipoles; thus, the C1···O1^i contact is 3.221 (2) Å, while the repulsive O1···O1^i and C1···C1^i contacts are 3.837 (2) and 4.062 (2) Å, respectively, where equivalent position (i) is $(-x, -y, \frac{1}{2} + z)$. In addition, there appears to be weak intermolecular C—H···O hydrogen bonding to O8 in position (ii) $(\frac{1}{2} + x, \frac{1}{2} - y, 1 + z)$ as acceptor (Fig. 2), as shown by the following contact distances and angles: H3a···O8^{ii} 2.55 (2), H4···O8^{ii} 2.50 (3) Å, C3—H3a···O8^{ii} 111 (2) and C4—H4···O8^{ii} 134 (2)°. The *a* glide plane locates O9 adjacent to the lactone moiety of another molecule with closest contact 3.133 (2) Å to C1^{iii}, where position (iii) is $(-\frac{1}{2} + x, \frac{1}{2} - y, z)$. These interactions are generally consistent with charges from semi-empirical molecular-orbital calculations with *AM*1 parameters in *MOPAC* (Stewart, 1993). All four O atoms are negatively charged, especially the nitro O atoms: O1 −0.259, O2 −0.246, O8 −0.345 and O9 −0.353 e. Atom C1 has a strong positive charge (0.348 e). The positive charge on the H atoms involved in C—H···O contacts (H3a 0.130 and H4 0.161 e) are surpassed elsewhere (H5 0.179 and H7 0.194 e), but the latter atoms are more sterically hindered.

Resonance effects in phthalides are expected to move some electron density from the ring O atom to the car-
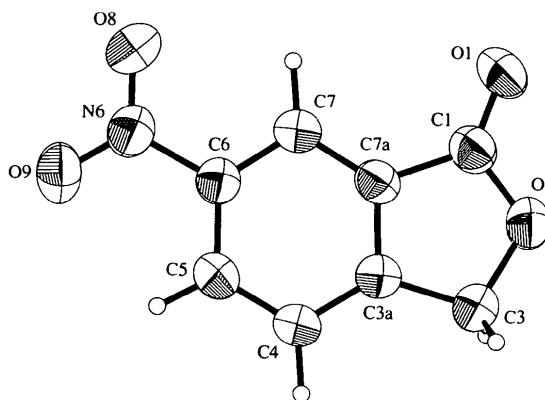

Fig. 1. *ORTEP*II view (Johnson, 1976) of the title molecule. Displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are drawn as small circles.
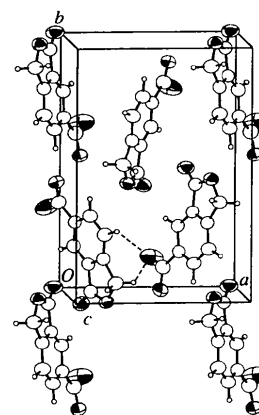

Fig. 2. *ORTEP*II view (Johnson, 1976) of the unit-cell contents. Displacement ellipsoids at the 50% probability level are shown in full for O atoms and in outline for other non-H atoms. H atoms are represented as small circles. Close C—H···O contacts are represented by dashed lines.

bonyl group, thus strengthening C1—O2 and weakening C1—O1; however, the electron-withdrawing nitro group provides an alternative sink for electron density. In (1), C1—O1 is 1.203 (2), C1—O2 is 1.346 (2) and C1—C7a is 1.473 (2) Å. In the homologue, where the nitro group is attached at C3 through a methylene bridge (Joshi, Hedge, Rogers & Williams, 1980), even less electron density reaches the carbonyl group; thus, these bond distances are 1.185, 1.415 and 1.477 Å. With a largely neutral substitution pattern, the phthalide form of 2-acetylbenzoic acid (Dobson & Gerkin, 1996) displays distances of 1.212 (2), 1.347 (2) and 1.466 (3) Å. When electron-donating substituents are introduced into the benzene ring, C1—C7a becomes shorter and C1—O1 longer. The relevant distances are 1.218 (8), 1.355 (6) and 1.447 (6) Å averaged over the four independent molecules of 7-hydroxy-5-methoxy-6-methyl-

phthalide (Gainsford, 1995), and 1.202 (4), 1.350 (5) and 1.460 (5) Å in 4,7-dimethoxy-5-methylphthalide (Whalley, Ferguson & Roberts, 1980). It should be noted that the two longest C=O bonds are affected by either intermolecular or intramolecular hydrogen-bond acceptance.

Experimental

The title compound was prepared by mononitration of phthalide according to the literature procedure (Katritzky *et al.*, 1992) and was recrystallized from ethyl acetate–hexane.

Crystal data

C$_8$H$_5$NO$_4$	Cu $K\alpha$ radiation
$M_r = 179.13$	$\lambda = 1.54178$ Å
Orthorhombic	Cell parameters from 25
$Pna2_1$	reflections
$a = 9.2511\,(10)$ Å	$\theta = 21.1-30.3°$
$b = 13.513\,(3)$ Å	$\mu = 1.098$ mm^{-1}
$c = 6.1542\,(3)$ Å	$T = 293\,(2)$ K
$V = 769.3\,(2)$ Å^3	Lath
$Z = 4$	$0.5 \times 0.2 \times 0.2$ mm
$D_x = 1.547$ Mg m^{-3}	Colourless
$D_m = 1.54$ Mg m^{-3}	
D_m measured by flotation in aqueous NaCl/KI	

Data collection

Enraf–Nonius CAD-4 diffractometer	1511 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$\theta_{max} = 73.93°$
Absorption correction:	$h = 0 \rightarrow 11$
ψ scan (North, Phillips & Mathews, 1968)	$k = 0 \rightarrow 16$
	$l = -7 \rightarrow 7$
$T_{min} = 0.71$, $T_{max} = 0.80$	3 standard reflections
1563 measured reflections	frequency: 120 min
1563 independent reflections	intensity decay: 3%

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.036$	SHELXL93 (Sheldrick,
$wR(F^2) = 0.099$	1993)
$S = 1.072$	Extinction coefficient:
1563 reflections	0.021 (2)
139 parameters	Scattering factors from
All H atoms refined	*International Tables for*
$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.0501P]$	*Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute structure: Flack
$(\Delta/\sigma)_{max} < 0.001$	(1983)
$\Delta\rho_{max} = 0.164$ e Å^{-3}	Flack parameter = 0.1 (2)
$\Delta\rho_{min} = -0.168$ e Å^{-3}	

Table 1. Selected geometric parameters (Å, °)

C1—O1	1.203 (2)	O2—C3	1.451 (2)
C1—O2	1.346 (2)	C3—C3a	1.491 (2)
C1—C7a	1.473 (2)		
O1—C1—O2	122.0 (2)	C1—O2—C3	110.82 (12)
O1—C1—C7a	129.9 (2)	O2—C3—C3a	104.53 (14)
O2—C1—C7a	108.13 (13)	C7—C6—C5	123.50 (15)
C7—C6—N6—O8	−9.0 (3)	C5—C6—N6—O9	−9.6 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CADABS* (Gould & Smith, 1993). Program(s) used to solve structure: *MUL-TAN84* (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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