

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

2-Benzoylspiro[1*H*-isoindole-1,3'-isochromene]-1',3,4'(2*H*,3'*H*)-trione

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2-Benzoylspiro[1*H*-isoindole-1,3'-isochromene]-1',3,4'(2*H*,3'*H*)-trione**Nigel McSweeney,^a Albert C. Pratt,^a Bernadette S. Creaven,^{a,‡} Conor Long^a and R. Alan Howie^{b,*}**^aSchool of Chemical Sciences, Dublin City University, Dublin 9, Ireland, and ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

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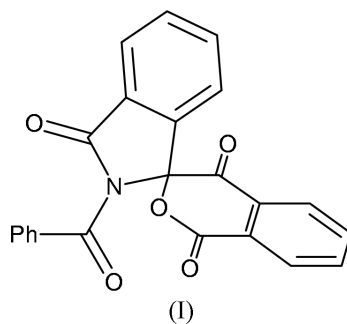
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Key indicatorsSingle-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
Disorder in main residue
R factor = 0.087
wR factor = 0.168
Data-to-parameter ratio = 8.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{23}\text{H}_{13}\text{NO}_5$, was isolated following irradiation of *N*-benzoylphthalimide in toluene. The bond lengths and angles are typical of a molecule of this kind, but the molecule itself is of some interest. The most challenging aspect of the refinement was to devise a model to cater for disorder in one part of the molecule.

Comment

The photochemistry of phthalimides has been extensively investigated over the past three decades. Many of the observed processes have proven to be of fundamental mechanistic interest and have yielded a diversity of molecular transformations. The topic has been reviewed by Oelgemöller & Griesbeck (2002), Coyle (1984) and Kanaoka (1978).



The structure determination of the title compound, (I), was undertaken in the context of a study of the photochemistry of *N*-benzoylphthalimide. Compound formation most likely results from initial photopinacolization, followed by thermal ring-opening and subsequent lactonization involving displacement of benzamide.

Fig. 1 shows the molecule of (I) and selected bond lengths and angles are given in Table 1. These are not, in themselves, remarkable, although the molecule itself, a spiro-keto-lactone, is unusual. Although the spiro atom, C8, is an asymmetric centre, the crystal structure, being centrosymmetric, is of necessity racemic. The presence of the asymmetric centre, however, is the source of a particular problem in the refinement of the structure because the enantiomers, instead of occupying the available sites in an orderly manner, are disordered in such a way that each site is occupied by a 69.2 (3)% majority of one enantiomer along with 30.8 (3)% of the other. In the structural model, this disorder only affects the keto-lactone component of the molecule, *i.e.* atoms C9–C16 (and the associated H atoms) and O2–O4. The disorder takes the form of interchange of the positions of the keto (C9 and O2) and carboxyl (C16, O3 and O4) fragments between the

Received 4 October 2004

Accepted 7 October 2004

Online 16 October 2004

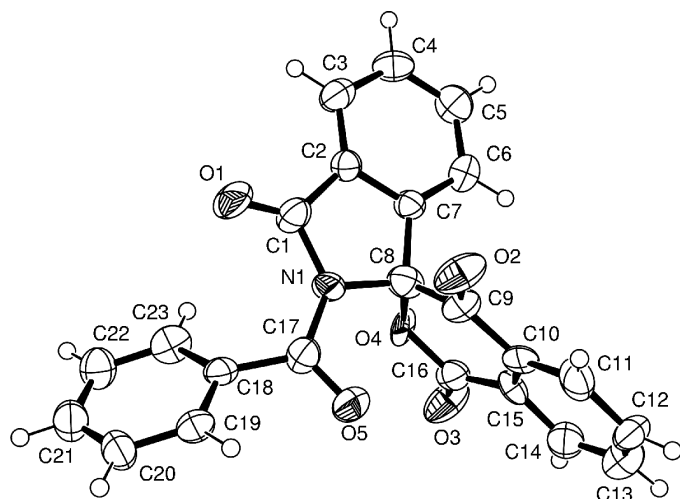


Figure 1
The molecule of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The atoms of the minor component of the disorder in the molecule (see text) have been omitted.

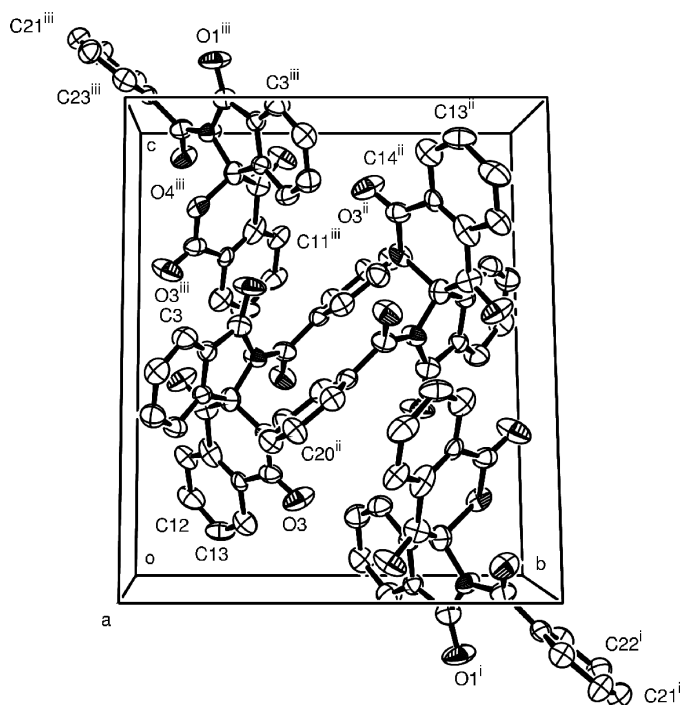


Figure 2
The unit cell contents of (I). Displacement ellipsoids are drawn at the 50% probability level. The atoms of the minor component of the disorder in the molecule and all H atoms have been omitted. The direction of view is approximately along a^* . [Symmetry codes: (i) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

superposed enantiomers which generate the disordered molecule. In effect, to a first approximation, the relationship between the orientations of the keto-lactone fragment in the two enantiomers is by rotation by 180° about a line joining the spiro atom, C8, and the centroid of the C10–C15 benzene ring. There is no strong evidence for any disorder affecting any of the other atoms, not even the spiro atom, C8. In the asymmetric unit, the atoms of the major component of the disorder

are labelled without suffix, while those of the minor component have suffix *A* and have been omitted from the Figures. The overall shape of the molecule can be discussed in terms of three more or less planar components as (a) the benzoyl substituent (least-squares plane defined by atoms C18–C23); (b) the isoindole fragment (plane defined by atoms N1 and C1–C8) and (c) the keto-lactone or isochromene entity (plane defined by atoms C8–C16 and O4). On this basis, the shape of the molecule can be described as that of a flattened letter Y (shown somewhat tilted in Fig. 1), with fragment *c* as the stem and fragments *a* and *b* as the arms of the Y. The dihedral angles between the planes defined above for pairs as *a/b*, *b/c* and *a/c* are 48.44 (18), 84.50 (15) and 77.0 (2) $^\circ$, respectively. This arrangement is largely determined by the spiro linkage at C8, the point of fusion of fragments *b* and *c*. The dihedral angle *a/b* is due, as indicated by the torsion angles in Table 1, to rotation of fragments *a* and *b* relative to one another about the C17–C18 and N1–C17 bonds.

Fig. 2 shows the unit cell contents for (I) and, while it gives a general indication of the packing of the molecules, it makes no attempt to display any of the intermolecular contacts which are, in fact, present in the structure. These include the weak C–H \cdots O hydrogen bonds listed in Table 2, the C–H \cdots π contacts given in Table 3 and, in addition, the face-to-face arrangement, in centrosymmetrically related pairs (symmetry code: $1 - x, -y, 1 - z$), of the C2–C7 benzene rings. For this π – π interaction, where the least-squares planes of the rings of the pair are parallel by symmetry, the distance between the ring centroids, the perpendicular distance between the rings and the slippage or lateral displacement of one ring relative to the other are 3.705, 3.436 and 1.386 Å, respectively.

Experimental

Compound (I) was among the products produced by irradiation of *N*-benzoylphthalimide (1.51 g, 6.0 mmol) in toluene (300 ml) for 40 h by a 400 W medium-pressure mercury vapour lamp fitted with a Pyrex filter. The product mixture, as a brown oil resulting from removal under vacuum of the toluene, was filtered through a silica column (10 \times 4 cm), using dichloromethane as eluant, in order to remove baseline impurities. The dichloromethane was removed under vacuum and the resulting mixture separated using a Chromatotron with a 4 mm plate with a mixture of ethyl acetate and light petroleum (b.p. 313–333 K) (2:98, increased stepwise to 30:70) as eluant. This gave, in order of recovery from the plate, a mixture of two minor products as an oil (7 mg), unchanged *N*-benzoylphthalimide (1.26 g), identified by comparison of its IR spectrum with that of an authentic sample, and lastly (I) as a colourless crystalline solid (95 mg, 50%; m.p. 493–495 K) after recrystallization from chloroform/light petroleum (b.p. 363–373 K).

λ_{\max} (MeCN): 305 (3065), 295 (sh) (3,602), 253 (27,586), 218 nm (ϵ 52,874 dm 3 mol $^{-1}$ cm $^{-1}$); ν_{\max} : 1745, 1703, 1668 (C=O), 1286 and 1261 cm $^{-1}$; ^1H NMR (270 MHz, CDCl $_3$): δ 7.95–7.43 (*m*, ArH); ^{13}C NMR (CDCl $_3$): δ 184.7, 169.0, 164.3, 160.2 (carbonyl C), 141.2, 136.0, 135.3, 135.2, 133.0, 132.5, 132.0, 131.2, 131.0, 129.8, 129.6, 128.1, 128.0, 126.4, 126.0, 121.9 (aromatic C), 94.8 (spiro C). Analysis found: C 71.7, H 3.4, N 3.6%; C $_{23}$ H $_{13}$ NO $_5$ requires: C 72.1, H 3.4, N 3.7%. *m/e*: 383 (1), 326 (18), 236 (18), 235 (100), 133 (13), 132 (92), 105 (56), 104 (90), 77 (11), 76 (10%).

Crystal data

C₂₃H₁₃NO₅
M_r = 383.34
 Monoclinic, *P*₂₁/*c*
a = 11.040 (7) Å
b = 11.782 (7) Å
c = 14.363 (9) Å
 β = 105.76 (4)°
V = 1798.0 (19) Å³
Z = 4

D_x = 1.416 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 15 reflections
 θ = 9.5–11.0°
 μ = 0.10 mm⁻¹
T = 298 (2) K
 Block, colourless
 0.30 × 0.25 × 0.20 mm

Data collection

Nicolet *P3* four-circle diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 2450 measured reflections
 2450 independent reflections
 1181 reflections with *I* > 2σ(*I*)

θ_{\max} = 25.1°
h = 0 → 13
k = -14 → 0
l = -17 → 16
 2 standard reflections every 50 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.087
wR (*F*²) = 0.168
S = 1.02
 2450 reflections
 306 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1–C17	1.381 (7)	C16–O3	1.183 (10)
N1–C1	1.422 (7)	C16–O4	1.349 (11)
N1–C8	1.464 (7)	C8–C9A	1.400 (14)
C1–O1	1.207 (6)	C8–O4A	1.607 (17)
C1–C2	1.474 (8)	C9A–O2A	1.198 (19)
C7–C8	1.492 (8)	C9A–C10A	1.51 (2)
C8–C9	1.449 (10)	C15A–C16A	1.46 (2)
C8–O4	1.566 (11)	C16A–O3A	1.198 (18)
C9–O2	1.209 (13)	C16A–O4A	1.33 (2)
C9–C10	1.503 (17)	C17–O5	1.226 (6)
C15–C16	1.454 (17)	C17–C18	1.485 (8)
C17–N1–C1	129.9 (5)	O3–C16–O4	116.4 (10)
C17–N1–C8	117.8 (5)	O3–C16–C15	125.6 (10)
C1–N1–C8	111.8 (5)	O4–C16–C15	117.9 (11)
O1–C1–N1	125.6 (6)	C16–O4–C8	122.0 (9)
O1–C1–C2	128.4 (6)	C9A–C8–N1	116.5 (8)
N1–C1–C2	105.9 (5)	C9A–C8–C7	121.0 (8)
C3–C2–C7	121.9 (6)	C9A–C8–O4A	115.7 (12)
C3–C2–C1	130.0 (6)	N1–C8–O4A	99.9 (11)
C7–C2–C1	108.1 (5)	C7–C8–O4A	98.2 (10)
C2–C7–C8	111.4 (5)	O2A–C9A–C8	109.5 (17)
C6–C7–C8	128.2 (6)	O2A–C9A–C10A	129 (2)
C9–C8–N1	113.6 (6)	C8–C9A–C10A	121.0 (16)
C9–C8–C7	116.8 (7)	C15A–C10A–C9A	118 (2)
N1–C8–C7	102.0 (5)	C11A–C10A–C9A	117 (2)
C9–C8–O4	115.1 (7)	C10A–C15A–C16A	126 (2)
N1–C8–O4	103.0 (5)	C16A–C15A–C14A	113 (2)
C7–C8–O4	104.6 (5)	O3A–C16A–O4A	120 (2)
O2–C9–C8	115.1 (9)	O3A–C16A–C15A	122.4 (19)
O2–C9–C10	125.1 (10)	O4A–C16A–C15A	118 (2)
C8–C9–C10	119.5 (10)	C16A–O4A–C8	120.7 (18)
C15–C10–C9	118.5 (13)	O5–C17–N1	117.2 (6)
C11–C10–C9	115.0 (13)	O5–C17–C18	121.7 (6)
C10–C15–C16	125.6 (16)	N1–C17–C18	121.0 (5)
C16–C15–C14	115.8 (11)		
C1–N1–C17–O5	–158.8 (6)	N1–C17–C18–C19	–151.4 (6)
C1–N1–C17–C18	25.4 (10)	N1–C17–C18–C23	37.1 (9)
C8–N1–C17–O5	12.1 (8)	O5–C17–C18–C19	33.0 (9)
C8–N1–C17–C18	–163.7 (6)	O5–C17–C18–C23	–138.5 (6)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C4–H4···O2 ⁱ	0.93	2.58	3.400 (10)	148
C5–H5···O3 ⁱⁱ	0.93	2.54	3.205 (10)	129

Symmetry codes: (i) 1 – *x*, –*y*, 1 – *z*; (ii) 1 – *x*, *y* – $\frac{1}{2}$, $\frac{1}{2}$ – *z*.

Table 3

Geometric parameters (Å, °) for C–H···π contacts in (I).

C–H··· <i>Cg</i>	H··· <i>Cg</i> ^{<i>a</i>}	H _{perp} ^{<i>b</i>}	γ ^{<i>c</i>}	C–H··· <i>Cg</i>	C··· <i>Cg</i>
C6–H6···Cg5 ^{iv}	2.76	2.74	8	142	3.54
C13–H13···Cg5 ^v	2.99	2.97	5	140	3.74
C19–H19···Cg4 ⁱⁱⁱ	2.87	2.86	6	130	3.55
C22–H22···Cg3 ⁱⁱ	2.96	2.78	20	119	3.51

Notes: (a) Cg3–Cg5 are, respectively, the centroids of the benzene rings defined by atoms C2–C7, C10–C15 and C18–C23; (b) H_{perp} is the perpendicular distance of H from the π-acceptor ring; (c) γ is the angle at H between H···Cg and H_{perp}. Symmetry codes: (ii) 1 – *x*, 1 – *y*, 1 – *z*; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

The initial solution and refinement of the structure, prior to the introduction of disorder into the structural model, even with H atoms included in geometrical positions, with C–H = 0.93 Å, and refined with a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(C), attained *R* [*I* > 2σ(*I*)] no better than 0.127, with particularly extreme anisotropy in the displacements of atoms C16 and O2, and with highly improbable bond lengths and angles in this part of the molecule. It was concluded, therefore, that some degree of disorder was present, but there was no clear indication as to its nature. Consideration of the nature of the compound and the manner of its synthesis led, however, to implementation of the disordered model described here. The disordered component, C9A–C16A and O2A–O4A, was created in stages as follows. First, all H atoms were removed from the structural model. Secondly, atom C8 was artificially split into two components, C8 and C8A, with identical coordinates. At this point, the six-membered ring which includes the spiro atom was created, using the known fragment C8–C10, C15, C16 and O2–O4 as a template to generate the corresponding part of the minor component (C8A–C10A, C15A, C16A and O2A–O4A) by adjusting, relative to C8A, the coordinates of (a) C9A placed midway between the original C16 and O4; (b) copies of C15 and C10 as C10A and C15A, respectively, and in that order (so that the cyclic order of the atoms is identical as to function and type in both the existing major and the generated minor components) and (c) dummy atoms for C16A and O2A–O4A. Finally, the disordered fragment was completed by a second application of the template, now extended by the addition of C11–C14 and with copies of these atoms, but in reverse order, for C11A–C14A of the minor component. Once the minor component had been completed, least-squares refinement was recommenced. In the initial stages, similarity restraints were applied to the disorder components, and equal isotropic displacement parameters were assigned to corresponding atoms in the two components, the complementary occupancies of which were refined. Subsequently, H atoms were introduced and refined as before. In the final stages, the occupancies of the atoms in the two components were fixed at the most recently obtained values and anisotropic displacement parameters were refined for all non-H atoms except those of the minor component.

The incompleteness of the early to mid-1980s data set upon which this refinement is based is due to the suppression, at the time when

data reduction was carried out and contrary to current practice, of reflections with intensities measured as negative. As a consequence, as perusal of the structure-factor file will show, the omissions are scattered throughout the data set, although they are more prevalent at high θ .

Data collection: *Nicolet P3 Software* (Nicolet, 1980); cell refinement: *Nicolet P3 Software*; data reduction: *RDNIC* (Howie, 1980); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

NM and BC thank Dublin City University for studentships.

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