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(1*RS*,2*SR*,7*RS*,8*RS*)-*N*-Benzoyltricyclo[6.2.2.0^{2,7}]dodeca-9,11-diene-1,10-dicarboximide

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The title 1,4-photoadduct, $C_{21}H_{19}NO_3$, was formed on irradiation of *N*-benzoylphthalimide in dichloromethane containing cyclohexene. The bond lengths and angles are generally within the normal ranges. A notable feature of the molecule is the presence within it of four contiguous chiral centres.

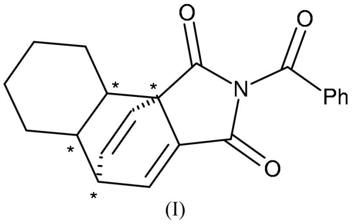
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.088
wR factor = 0.192
Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The photochemistry of phthalimides has been studied extensively and has been reviewed by Kanaoka (1978), Coyle (1984) and Oelgemöller & Griesbeck (2002). Schwack (1987) has reported the photo-induced *para*-cycloaddition of cyclohexene to *N*-trichloromethylthio-, *N*-methyl- and *N*-phenylphthalimides. Suau *et al.* (1989) have reported the *ortho*- and *para*-photocycloaddition of 3-methoxy-*N*-methylphthalimide to 1-hexene and Kubo *et al.* (1989) have reported analogous *ortho*- and *para*-cycloadditions of *N*-methylphthalimide to allyltrimethylsilane. In each case, the *para*-cycloaddition products are structurally analogous to the title compound, (I). However, the structures were only elucidated by spectroscopic means and lack stereochemical certainty. The determination of the structure of (I) presented here was undertaken in the context of a study of the photochemistry of *N*-benzoylphthalimide but is clearly of significance in relation to the analogous compounds.



(I)

The molecule of (I) is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The bond lengths, along with those of the phenyl group *R*1 defined by C16–C21 in the range 1.361 (6)–1.389 (5) Å, are not unusual excepting, perhaps, the C2—C3 and C6—C7 bond lengths of 1.493 (5) and 1.481 (5) Å, respectively. Likewise, with the sole exception of the angle C9—C10—C14 of 134.1 (3)°, the bond angles, including the internal angles of the phenyl group in the range 117.9 (3)–121.1 (4)°, are as expected. The cyclohexane ring, *R*3, defined by C2–C7, adopts the chair conformation, with puckering parameters (Cremer & Pople, 1975) Q = 0.564 (4) Å, θ = 168.5 (5) and φ = 151 (2)°. The dihedral angle between the least-squares planes of phenyl group *R*1 (r.m.s. displacement = 0.0006 Å) and five-membered ring *R*2, defined by C1/C10/C13–C14/N1 (r.m.s. displacement = 0.0143 Å) is 61.97 (15)°. Atom O3 is displaced from the least-squares planes of *R*1 and *R*2 by 0.145 (7) and 1.134 (6) Å, respectively. The packing of the molecules of (I) creates layers parallel to ($\bar{1}02$) (Fig. 2) in such a way as to generate the first two C—H$\cdots\pi$ interactions given in Table 2 (shown as dashed lines in Fig. 2). The only contact between the layers, other than van der Waals interactions, is the third, longer, C—H$\cdots\pi$ contact given in Table 2.

The racemic nature of (I), a prerequisite for the refinement of the structure in the centrosymmetric space group $P2_1/c$, is a natural consequence of the manner in which the compound has been formed from achiral reactants. In principle, given that the unsymmetrical 1,4-addition across the aromatic ring must of necessity be *cis*, there are four possible racemic products, two involving *trans* ring junctions at C2—C7 and two involving *cis* junctions at C2—C7. Formation of the single unsymmetrical product, (I), suggests a favoured approach by the cyclohexene to the excited phthalimide, possibly involving minimization of steric interactions between the *N*-benzoylimide and cyclohexene rings in the transition state. The stereochemistry at the C2—C7 ring junction is the outcome of overall *trans* addition across the cyclohexene double bond.

Experimental

Compound (I) was one of the products of irradiation for 40 h of *N*-benzoylphthalimide (2.90 g, 11.5 mmol) and cyclohexene (19.60 g, 239.0 mmol) in dichloromethane (300 ml) by a 400 W medium-pressure mercury vapour lamp fitted with a Pyrex filter. After removal of solvents under vacuum three products (previously detected by thin-layer chromatography) were isolated by means of a Chromatotron and a 4 mm silica plate with a mixture of dichloromethane and light petroleum (b.p. 313–333 K) (2:98 increased stepwise to 60:40) as eluant to yield: (i) recovered *N*-benzoylphthalimide (2.75 g); (ii) a mixture of minor products as a colourless oil (12 mg); (iii) compound (I), a white crystalline solid [160 mg, 80%; m.p. 411–413 K (from chloroform/light petroleum, b.p. 363–373 K)], λ_{max} (MeCN): 251 (ε 20,208 dm^3 mol^{-1} cm^{-1}); ν_{max} 2929 (aliphatic CH), 1717 and 1694 (C═O), 1297 and 1252 cm^{-1}; δ_H (270 MHz, CDCl$_3$): 7.89–7.47 (5H, *m*, ArH), 7.10 (1H, *d, J* 6.0 Hz, vinylic H), 6.82 (1*H*, *d* of *d*, *J* 6.0 Hz, *J* 7.0 Hz, vinylic H), 6.16 (1*H*, *d*, *J* 7.0 Hz, vinylic H), 3.76 (1H, *t, J* 6.0 Hz), 2.10–1.11 (10H, *m*, cyclohexane derived moiety); δ_C (67.8 MHz, CDCl$_3$): 173.0, 167.1, 162.3 (carbonyl C), 143.3, 141.7, 137.3, 134.8, 131.9, 130.4, 128.8, 123.5 (aromatic and vinylic C), 56.2, 52.5, 50.7, 45.7, 32.7, 30.2, 27.7 and 27.4 (aliphatic C); analysis found: C 75.3, H 5.8, N 3.9%; $C_{21}H_{19}NO_3$ requires: C 75.7, H 5.8, N 4.2%; m/e: 333 (1), 265 (47), 264 (31), 252 (56), 105 (100), 77 (63) and 67 (45%).

Crystal data

$C_{21}H_{19}NO_3$
$M_r = 333.37$
Monoclinic, $P2_1/c$
$a = 8.111$ (3) Å
$b = 12.999$ (7) Å
$c = 16.256$ (5) Å
$\beta = 100.76$ (3)°
$V = 1683.8$ (12) Å^3
$Z = 4$
$D_x = 1.315$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 11.0$–13.0°
$\mu = 0.09$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.60 × 0.40 × 0.26 mm

Data collection

Nicolet *P*3 four-circle diffractometer
θ–2θ scans
Absorption correction: none
3882 measured reflections
3882 independent reflections
1880 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30.1$°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = -22 \rightarrow 22$
2 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.088$
$wR(F^2) = 0.192$
$S = 1.03$
3882 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C13	1.408 (4)	C2—C3	1.493 (5)
N1—C14	1.425 (4)	C2—C7	1.514 (5)
N1—C15	1.444 (4)	C6—C7	1.481 (5)
O1—C13	1.203 (4)	C7—C8	1.584 (5)
O2—C14	1.200 (4)	C8—C9	1.506 (5)
O3—C15	1.194 (4)	C8—C12	1.519 (5)
C1—C11	1.500 (5)	C9—C10	1.330 (4)
C1—C13	1.504 (5)	C10—C14	1.462 (5)
C1—C10	1.504 (4)	C11—C12	1.323 (5)
C1—C2	1.571 (4)	C15—C16	1.473 (5)
C13—N1—C14	113.0 (3)	C12—C8—C7	100.8 (3)
C13—N1—C15	121.3 (3)	C10—C9—C8	112.1 (3)
C14—N1—C15	125.0 (3)	C9—C10—C14	134.1 (3)
C11—C1—C13	118.0 (3)	C9—C10—C1	115.4 (3)
C11—C1—C10	108.2 (3)	C14—C10—C1	110.3 (3)
C13—C1—C10	103.4 (3)	C12—C11—C1	113.2 (3)
C11—C1—C2	109.4 (3)	C11—C12—C8	114.5 (3)
C13—C1—C2	114.3 (3)	O1—C13—N1	124.0 (3)
C10—C1—C2	102.0 (3)	O1—C13—C1	127.9 (3)
C3—C2—C7	110.4 (3)	N1—C13—C1	108.1 (3)
C3—C2—C1	124.6 (3)	O2—C14—N1	123.9 (3)
C7—C2—C1	107.4 (3)	O2—C14—C10	130.9 (3)
C6—C7—C2	110.8 (3)	N1—C14—C10	105.1 (3)
C6—C7—C8	122.4 (3)	O3—C15—N1	118.4 (3)
C2—C7—C8	109.0 (3)	O3—C15—C16	123.8 (3)
C9—C8—C12	108.3 (3)	N1—C15—C16	117.7 (3)
C9—C8—C7	109.1 (3)		
C11—C1—C2—C3	−86.5 (4)	C6—C7—C8—C9	−87.4 (4)
C13—C1—C2—C3	48.3 (5)	C2—C7—C8—C9	44.1 (4)
C10—C1—C2—C3	159.1 (4)	C6—C7—C8—C12	158.8 (4)
C11—C1—C2—C7	44.9 (4)	C2—C7—C8—C12	−69.7 (4)
C13—C1—C2—C7	179.7 (3)	C8—C9—C10—C14	178.1 (3)
C10—C1—C2—C7	−69.5 (3)	C8—C9—C10—C1	3.3 (4)
C1—C2—C3—C4	−171.5 (3)	C13—C1—C10—C9	179.5 (3)
C5—C6—C7—C8	−170.5 (4)	C13—C1—C10—C14	3.4 (3)
C3—C2—C7—C6	−65.8 (4)	C1—C11—C12—C8	3.4 (4)
C1—C2—C7—C6	155.5 (3)	C9—C8—C12—C11	−54.9 (4)
C3—C2—C7—C8	156.7 (3)	C7—C8—C12—C11	59.5 (4)
C1—C2—C7—C8	18.0 (4)		

Table 2
Geometry (Å,°) of C—H$\cdots\pi$ contacts in (I).

C—H$\cdots$*Cg*^{a}	C—H	H$\cdots$Cg	H_{perp}^{b}	γ^c	C—H$\cdots$*Cg*	C$\cdots$*Cg*
C6—H6*A*$\cdots$*Cg*1^{i}	0.97	2.80	2.69	16	149	3.68
C6—H6*B*$\cdots$*Cg*1^{ii}	0.97	3.03	2.93	15	135	3.79
C4—H4*B*$\cdots$*Cg*2^{iii}	0.97	3.34	3.28	11	120	3.92

Notes: (*a*) *Cg*1 and *Cg*2 are the centroids of the rings defined by C16–C21 and C1/C10/C13–C14/N1, respectively; (*b*) H_{perp} is the perpendicular distance of the H atom from the mean plane of the ring; (*c*) γ is the angle at hydrogen between H_{perp} and H$\cdots$*Cg*. Symmetry codes (i) $1 - x, 1 - y, 1 - z$; (ii) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 + x, y, z$.

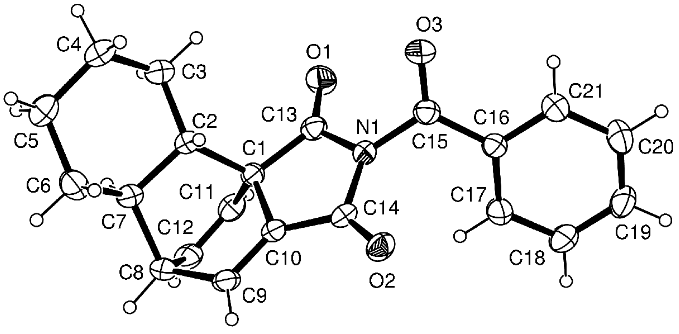


Figure 1
A view of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small circles of arbitrary radii.

The incompleteness (84.9% complete for $\theta_{\rm full} = 25°$) of the mid-1980s data set upon which this refinement is based is due to the suppression, during data reduction and contrary to current practice, of reflections with intensities measured as negative. As a consequence, the omissions are scattered throughout the data set although they are more prevalent at high θ. In the final stages of refinement, H atoms were introduced in calculated positions with C—H set at 0.93, 0.97 and 0.98 Å for aryl/alkene, methylene and tertiary H atoms, respectively, and refined with a riding model, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) in all cases.

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).

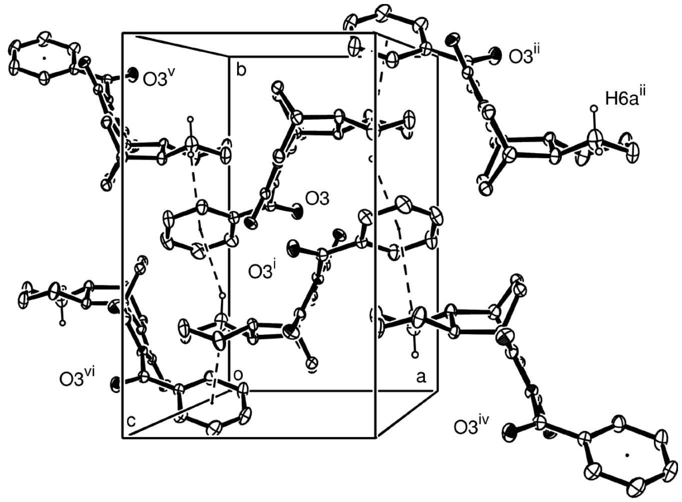


Figure 2
A layer of molecules of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms involved in C—H..π contacts (dashed lines) are shown as small circles of arbitrary radii. [Symmetry codes (i) $1 - x$, $1 - y$, $1 - z$; (ii) $1 + x$, $\frac{3}{2} - y$, $\frac{1}{2} + z$; (iv) $2 - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$; (v) $x - 1$, $\frac{3}{2} - y$, $z - \frac{1}{2}$; (vi) $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$.]

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References

Coyle, J. D. (1984). *Synthetic Organic Photochemistry*, edited by W. M. Horspool, pp. 259–284. New York: Plenum Press.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Howie, R. A. (1980). *RDNIC*. University of Aberdeen, Scotland.

Kanaoka, Y. (1978). *Acc. Chem. Res.* **11**, 407–413.

Kubo, Y., Taniguchi, E. & Araki, T. (1989). *Heterocycles*, **29**, 1857–1860.

Nicolet. (1980). *Nicolet P3/R3 Data Collection Operator's Manual*. Nicolet XRD Corporation, Cupertino, California, USA.

Oelgemöller, M. & Griesbeck, A. G. (2002). *J. Photochem. Photobiol. C*, **3**, 109–127.

Schwack, W. (1987). *Tetrahedron Lett.* **28**, 1869–1871.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Suau, R., Garcia-Segura, R. & Sosa-Olaya, F. (1989). *Tetrahedron Lett.* **30**, 3225–3228.