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1-(12-Benzoyl-10-oxa-12-azatetracyclo-[6.3.1.0^{2,7}.0^{9,11}]dodeca-2,4,6-trien-1-yl)-ethan-1-one

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The title compound, $C_{19}H_{15}NO_3$, is non-planar with a dihedral angle between the benzonorbornadiene benzene ring and the benzoyl aromatic ring of 28.7 (1)°. In the crystal structure, there are three intermolecular C—H···O bonds.

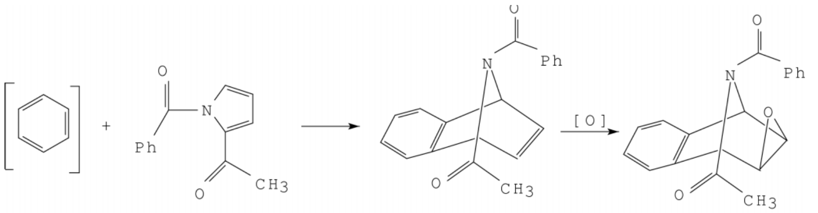
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.097
Data-to-parameter ratio = 8.3

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

Comment

The most general preparative method for 7-azobenzonorbornadiene (1,4-dihydronaphthalene-1,4-imine) involves benzyne cycloadditions to suitable conjugated dienes (Wolthuis & De Boer, 1965; Wolthuis *et al.*, 1966). 7–Azobenzonorbornadiene itself is of great synthetic interest because of its ready conversion to other types of compounds (Carpino & Barr, 1966; Kaupp *et al.*, 1970; Swenton *et al.*, 1974; Motyka, 1985). In this class of compounds, the configurations of the *R* groups bound to the nitrogen are variable; however, the exact configuration can be indentified by spectroscopic studies, as shown in the literature (Quin *et al.*, 1986; Davies *et al.*, 1992).



(1) (2) (3) (4)

In our synthetic strategy, based on the Diels–Alder cycloaddition of benzyne (1) to *N*-benzoyl-2-acetylpyrrole, (2), we obtained the novel 1,4-iminonaphthalene derivative (3). NMR data of (3) indicated that the molecule exists as a single isomer. However, the configuration of the benzoyl group bound to the N atom could not be determined by NMR spectroscopy. Epoxidation of *N*-benzoyl-1,4-iminonaphthalene, (3), with *m*-chloroperbenzoic acid resulted in the formation of only one isomer, namely the *exo*-epoxide (4), whose structure analysis is reported here.

The N1—C12 bond length of 1.386 (3) Å is shorter than is typical for a single bond, due to the influence of the neighbouring C12=O2 bond [1.220 (3) Å]. The average value of the O1—C8 and O1—C9 distances is 1.360 (4) Å; the corresponding value in a related structure is 1.455 (2) Å (Usman *et al.*, 2002). The C8—C9 distance of 1.452 (3) Å and the average value of 114.21 (19)° for the O1—C8—C7 and O1—C9—C10 angles are almost in agreement with the values of 1.426 (16) Å and 112.6 (10)°, respectively, in the same structure. The remaining bond lengths and angles in the title compound are normal, and are in agreement with those observed in similar compounds (Mague *et al.*, 1993; Jones *et al.*, 1992).

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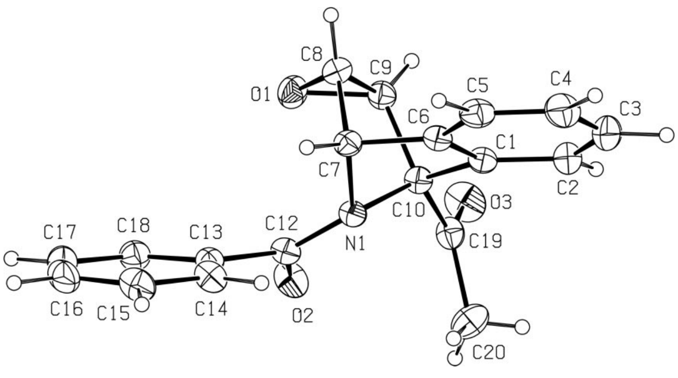

Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the title compound, showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

The five-membered rings N1/C7/C6/C1/C10 and N1/C7/C8/C9/C10 exhibit envelope conformations, with atom N1 as the flap. The puckering parameters (Cremer & Pople, 1975) for these rings are Q_2 = 0.553 (2) Å and φ_2 = 0.7 (3)°, and Q_2 = 0.536 (2) Å and φ_2 = 178.6 (3)°, respectively.

Plane *A* (C1–C7/C10) is almost perfect [maximum deviations at C3, C6 and C7 are −0.024 (3), 0.031 (2) and −0.024 (2) Å, respectively]. The dihedral angle between plane *A* and plane *B* (C13–C18) is 28.2 (1)°, and that between plane *A* and plane *C* (C7—C10) is 73 (1)°. The epoxy ring, formed by atoms O1, C8 and C9, is aligned parallel to plane *A*, but pointing in the opposite direction.

Hydrogen-bonding contacts are summarized in Table 2. The crystal structure is stabilized by three C—H···O intermolecular hydrogen bonds in addition to van der Waals forces (Fig. 2).

Experimental

A solution of 1.74 mmol (500 mg) *N*-benzoyl-1,4-iminonaphthalene, (3), and 2.09 mmol (362 mg) of *m*-chloroperbenzoic acid in 30 ml of CH_2Cl_2 was stirred for 20 h at room temperature in the presence of solid $NaHCO_3$ (1 g). The reaction mixture was extracted with 10% $NaHSO_3$ (2 × 50 ml), then with 10% $NaHCO_3$ (2 × 20 ml). The organic layer was dried over $MgSO_4$. The solvent was then evaporated and the residue recrystallized from 1:2 $CHCl_3$–hexane, m.p. 481–484 K, giving colourless crystals in 78% (416 mg) yield. ^1H NMR (200 MHz, $CDCl_3$): δ 7.68–7.12 (*m*, aromatic, 9H), 5.09 (*s*, bridgehead, 1H), 3.97 (*d*, *J* = 3.5 Hz, 1H), 3.39 (*d*, *J* = 3.5 Hz, 1H), 2.42 (*s*, methyl, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.20, 175.78, 145.79, 145.33, 136.07, 132.97, 130.47, 130.16, 129.64, 129.57, 123.49, 123.02, 82.51, 67.91, 58.54, 54.52, 29.77. IR (KBr) cm^{-1}: 3027, 2931, 2858, 1708, 1631, 1581, 1457, 1427, 1373, 1276, 1130, 1064, 1025, 944, 887, 848, 755, 698.

Crystal data

$C_{19}H_{15}NO_3$
M_r = 305.32
Orthorhombic, $P2_12_12_1$
a = 7.829 (1) Å
b = 13.874 (1) Å
c = 14.079 (1) Å
V = 1529.3 (2) $Å^3$
Z = 4
D_x = 1.326 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 74 reflections
θ = 2.9–15.0°
μ = 0.09 mm^{-1}
T = 298 (2) K
Block, colourless
0.55 × 0.50 × 0.40 mm

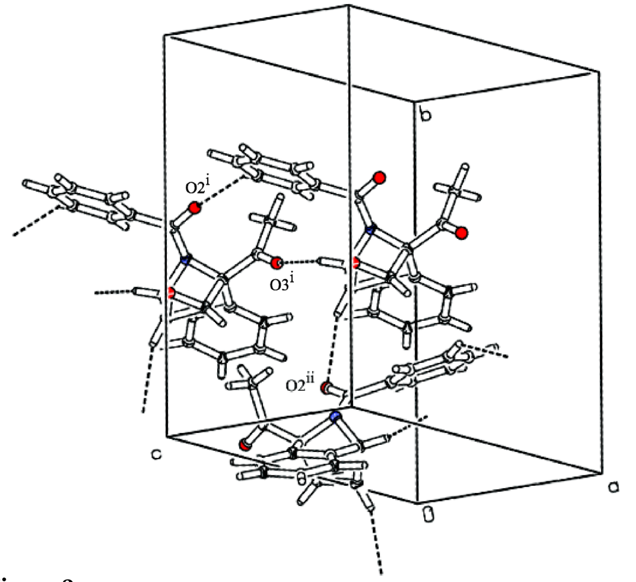

Figure 2
A view of the crystal packing. Short hydrogen-bond contacts are indicated by dashed lines.

Data collection

Siemens *P*4 diffractometer
Profile data from ω scans
Absorption correction: none
4236 measured reflections
2118 independent reflections
1622 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

θ_{max} = 28.0°
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -18 \rightarrow 18$
3 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.097
S = 0.98
2118 reflections
254 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.0258P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.15 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.024 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.450 (3)	N1—C7	1.486 (3)
O1—C9	1.454 (3)	N1—C10	1.488 (3)
O2—C12	1.220 (3)	N1—C12	1.386 (3)
O3—C19	1.208 (3)		
C8—O1—C9	60.00 (15)	O1—C9—C10	114.76 (19)
C7—N1—C10	97.20 (16)	N1—C10—C1	98.78 (17)
C7—N1—C12	125.01 (18)	N1—C10—C9	100.72 (17)
C10—N1—C12	118.12 (17)	N1—C10—C19	118.15 (19)
N1—C7—C6	99.08 (18)	O2—C12—N1	120.8 (2)
N1—C7—C8	101.45 (18)	O2—C12—C13	121.8 (2)
O1—C8—C7	113.66 (19)	N1—C12—C13	117.25 (19)
O1—C8—C9	60.16 (15)	O3—C19—C10	119.0 (2)
O1—C9—C8	59.84 (15)	O3—C19—C20	122.4 (2)
C10—C1—C6—C7	−0.9 (2)	O1—C9—C10—C1	−131.24 (19)
C6—C1—C10—C19	−159.13 (19)	C1—C10—C19—O3	−104.3 (3)
C2—C1—C10—C19	23.4 (4)	C1—C10—C19—C20	69.7 (3)
C6—C7—C8—O1	134.12 (19)	O2—C12—C13—C18	−37.8 (3)
N1—C7—C8—O1	31.8 (2)	N1—C12—C13—C14	−35.4 (3)
O1—C8—C9—C10	−110.43 (19)	N1—C12—C13—C18	146.7 (2)
O1—C9—C10—N1	−29.4 (2)	O2—C12—C13—C14	140.2 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H7$\cdots$O3^{i}	0.99 (4)	2.57 (4)	3.427 (3)	145 (2)
C8—H8$\cdots$O2^{ii}	0.98 (4)	2.56 (4)	3.501 (3)	161 (3)
C15—H15$\cdots$O2^{i}	1.03 (4)	2.48 (4)	3.317 (4)	138 (2)

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

All H atoms were placed in geometrically idealized positions and their coordinates were freely refined; however, their U values were not refined.

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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