organic papers

Methyl (*RS*)-[1-hydroxy-1-(3-nitrophenyl)-3-oxo-1,3-dihydroisoindol-2-yl]acetate

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Key indicators

Single-crystal X-ray study
$T = 123$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.109
Data-to-parameter ratio = 16.5

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

The benzophenone derivative, methyl [2-(3-nitrobenzoyl)-benzoylamino]acetate, (3), exists in equilibrium with the title compound, $C_{17}H_{14}N_2O_6$, (4), a tricyclic tertiary alcohol, with the position of the equilibrium lying strongly in favour of (4). The crystal structure consists of discrete molecules of (4) stabilized by O—H···O and C—H···O hydrogen bonds.

Comment

The benzophenone derivative (3) was of interest as a simplified representative of a proposed peptide mimic. In an attempt to prepare (3), the benzoic acid (1) (DeTar & Relyea, 1954) was coupled with glycine methyl ester, which was in turn liberated from the corresponding hydrochloride (2). The major product of this reaction was found to be the tricyclic tertiary alcohol (4), which had presumably formed by ring closure of the secondary amide in (3) with the adjacent ketone. This type of ring-chain tautomerism is not unprecedented in *o*-benzoylbenzamides (Bhatt & Ravindranathan, 1973) and electron-withdrawing substituents, such as the nitro substituent in (3), are thought to shift the position of the equilibrium in favour of the cyclized form.
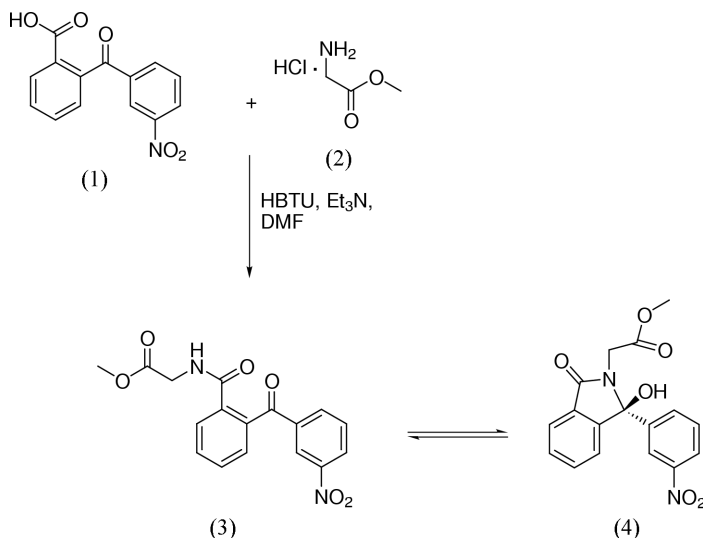
The crystal structure consists of discrete molecules of (4) stabilized by intermolecular O—H···O and C—H···O hydrogen bonds (Table 1). The dihydroisoindole ring system is planar, the maximum deviation being 0.045 (2) Å for atom C1. The side chain attached to the pyrrolidine ring adopts a *trans*-planar configuration and this plane forms a dihedral angle of 81.82 (7)° with the dihydroisoindole plane, while the planar

nitrophenyl group forms a dihedral angle of 78.44 (7)° with the dihydroisoindole plane.

Experimental

Glycine methyl ester hydrochloride (2) (44 mg, 0.35 mmol) was added to 2-(3-nitrobenzoyl)benzoic acid (1) (44 mg, 0.16 mmol) in DMF (10 ml). Et_3N (0.08 ml, 0.8 mmol) was then added, followed by HBTU [N,N,N',N'-tetramethyl-O-(1H-benzotriazol-1-yl)uronium hexafluorophosphate; 107 mg, 0.28 mmol]. The resulting reaction mixture was stirred for 5 h then poured into EtOAc (30 ml), washed with 2 M HCl (3 × 20 ml), saturated $NaHCO_3$ (3 × 20 ml) and saturated brine (2 × 20 ml). After drying ($MgSO_4$) and filtering, the organic solution was evaporated to dryness to give the title compound (4) (56.8 mg, 68%) as a white amorphous solid, which was then dissolved in ether (1.5 ml); MeOH (1.5 ml) was slowly added along the walls of the vessel. Upon standing for 30 min, colourless crystals formed. These were triturated with cold ether (2 × 5 ml) and analysed by X-ray crystallography (m.p. 430–432 K). Spectroscopic analysis, IR (ATR, ν cm^{-1}): 3256, 3088, 2955, 2941, 1752, 1677, 1527; ^{1}H NMR (methanol$_{d4}$, p.p.m.): 8.24–8.43 (m, 2H), 7.35–7.92 (m, 6H), 4.20 (d, J = 17.5 Hz, 1H), 3.98 (d, J = 17.5 Hz, 1H), 4.65 (brs, 1H), 3.62 (s, 3H); ^{13}C NMR (methanol$_{d4}$, p.p.m.): 170.8, 167.8, 148.3, 140.9, 133.4, 132.3, 130.1, 129.8, 129.4, 123.9, 123.8, 122.8, 121.6, 90.1, 52.8, 40.5; HRMS calculated for $C_{17}H_{14}N_2O_6$ 365.07495 (M + Na$^+$), found 365.0745.

Crystal data

$C_{17}H_{14}N_2O_6$	D_x = 1.466 Mg m^{-3}
M_r = 342.30	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 18 179
a = 15.0330 (3) Å	reflections
b = 6.8414 (1) Å	θ = 2.9–28.3°
c = 16.1593 (4) Å	μ = 0.11 mm^{-1}
β = 111.0117 (8)°	T = 123 (2) K
V = 1551.42 (5) Å^3	Prism, colourless
Z = 4	0.15 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.078
Thick-slice ω and φ scans	θ_{max} = 28.3°
18 179 measured reflections	h = −19 → 19
3764 independent reflections	k = −9 → 9
2085 reflections with $I > 2\sigma(I)$	l = −21 → 21

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.047	$+ 0.1011P]$
$wR(F^2)$ = 0.109	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max} < 0.001$
3764 reflections	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
228 parameters	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O2^i	0.84	1.99	2.819 (2)	171
C5—H5$\cdots$O3^{ii}	0.95	2.45	3.371 (2)	163
C12—H12$\cdots$O4^{iii}	0.95	2.38	3.301 (2)	165

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.
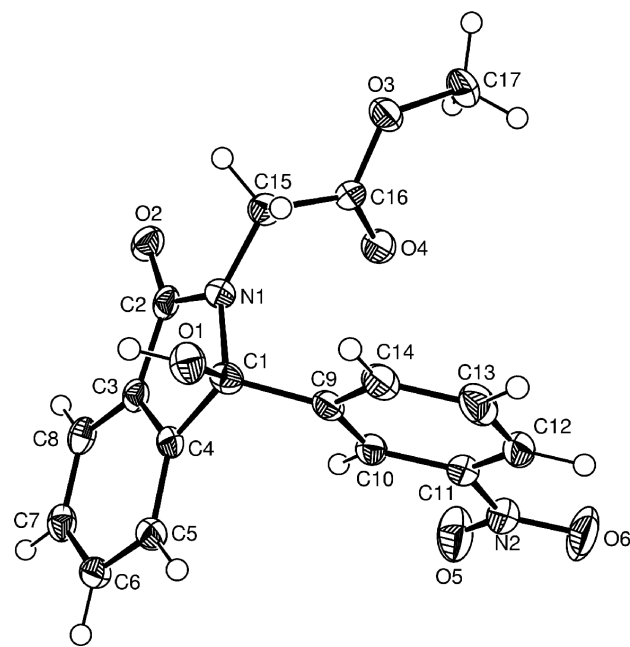

Figure 1
ORTEP-3 (Farrugia, 1997) view of (4). Displacement ellipsoids are drawn at the 50% probability level.

All H atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 0.99 Å, and O—H distances of 0.84 Å. They were included in the refinement in a riding-model approximation, with U_{iso}(H) = 1.2U_{eq} of the carrier atom (1.5 U_{eq} for methyl and hydroxyl H atoms).

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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