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3-(Benzotriazol-1-yl)-*p*-nitropropiophenone: sheets built from weak three-centred C—H···O hydrogen bonds

John Nicolson Low,[a]* Justo Cobo,[b] Manuel Nogueras,[b] Adolfo Sánchez,[b] Paola Andrea Cuervo[c] and Rodrigo Abonia[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad del Valle, AA25360 Cali, Colombia

Correspondence e-mail: jnlow111@hotmail.com

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.058
wR factor = 0.155
Data-to-parameter ratio = 14.3

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

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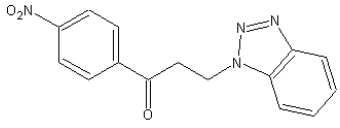
Molecules of the title compound, $C_{15}H_{12}N_4O_3$, are hydrogen bonded into undulating sheets lying perpendicular to the *b* axis by three-centred weak C—H···O hydrogen bonds involving the O atoms of the nitro group in molecules related by the *c*-axis glide plane.

Comment

The title compound, (I), was prepared for use as an intermediate (after α-bromination) in the synthesis of benzotriazolyl derivatives of dihydroquinoxalines, compounds with interesting optical (Schaller *et al.*, 1967) and biological properties (Takahashi *et al.*, 1977; Billhardt *et al.*, 1993).



(I)

There are no unusual bond distances or angles in the molecule, which is shown in Fig. 1.

The molecules of (I) are hydrogen bonded into undulating sheets parallel to (010) by three-centred weak C5—H5···O hydrogen bonds involving the O atoms, O141 and O142, of the nitro group (see Table 1 for hydrogen-bonding data and for the symmetry codes). Each molecule links head-to-tail to two other molecules related to it by a *c*-glide plane. C5—H5 links to O141^{i} and to O142^{ii}. The angle sum at H5 is 356°. These hydrogen bonds form interlocking *C*(15) chains (Bernstein *et al.*, 1995), as shown in Fig. 2, with the result that H5^{i} and H5^{ii} link to the molecule at (1+*x*, *y*, 1+*z*) to form an $R^4_3(34)$ ring (Bernstein *et al.*, 1995), thus generating a sheet of interlocked rings. Fig. 2 shows a view of the sheet.

In addition, there are several short C—H···π contacts in the range 2.68 to 2.84 Å with C—H···*Cg* angles in the range 121 to 130°, in which the centres of gravity are *Cg*1 (ring 1 C3*A*/C4/C5/C6/C7/C7*A*) and *Cg*2 (ring 2 C11/C12/C13/C14/C15/C16). These contacts are from H13 and H16 of ring 2 to *Cg*1^{iii} and *Cg*1^{iv}, respectively, whilst there are contacts from H4^{iii} and H7^{iv} to *Cg*2. Since the molecules are stacked head-to-tail, there are similar contacts from H4 and H7 to *Cg*2^{iii} and *Cg*2^{iv}, respectively, whilst there are contacts from H13^{iii} and H16^{iv} to *Cg*1. These contacts are short and, despite the low angular range at H, appear to act co-operatively in stabilizing the packing of the structure. Fig. 3 shows a view of these contacts, which link the molecules in the different sheets. Their parameters are listed in Table 1.

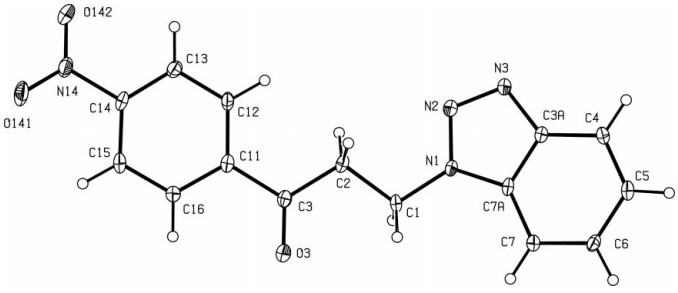


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Examination of the structure with *PLATON* (Spek, 2002) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

A solution of 3-(dimethylamino)-*p*-nitropropiophenone hydrochloride (0.5 g, 1.93 mmol), benzotriazole (0.23 g, 1.93 mmol) and 5 ml of water was heated at 323 K for 5 min. After cooling, the solution was left overnight at room temperature. The resulting precipitate was filtered, washed with water, and purified by column chromatography on silica gel, with chloroform as eluent, giving a white solid (93% yield; m.p. 405 K). Crystals suitable for X-ray diffraction were collected from the solution in chloroform. Found: C 60.81, H 4.08, N 18.91%; calculated for $C_{15}H_{12}N_4O_3$: C 60.78, H 4.12, N 18.89%.

Crystal data

$C_{15}H_{12}N_4O_3$
M_r = 296.29
Monoclinic, $P2_1/c$
a = 5.9554 (2) Å
b = 6.9671 (3) Å
c = 31.8248 (13) Å
β = 96.8560 (17)°
V = 1311.03 (9) Å^3
Z = 4
D_x = 1.501 Mg m^{-3}
Mo Kα radiation
Cell parameters from 2852 reflections
θ = 3.0–27.5°
μ = 0.11 mm^{-1}
T = 120 (2) K
Prism, orange
0.50 × 0.35 × 0.08 mm

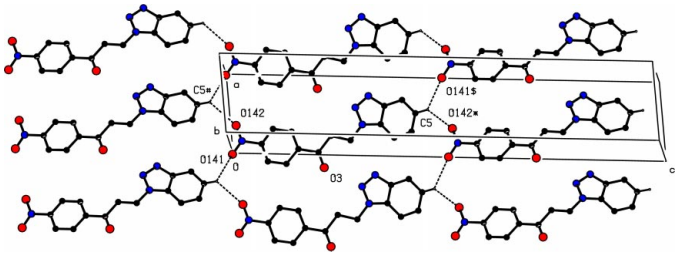


Figure 2
A view the (010) sheets composed of $R^4_3(34)$ rings formed by the interlocking $C(15)$ chains. The atoms labelled with an asterisk (*), dollar sign ($) or hash mark (#) are at the symmetry positions (x, $-y$+1/2, z+1/2), (1+x, $-y$+1/2, z+1/2) and (x, $-y$+1/2, z−1/2), respectively.

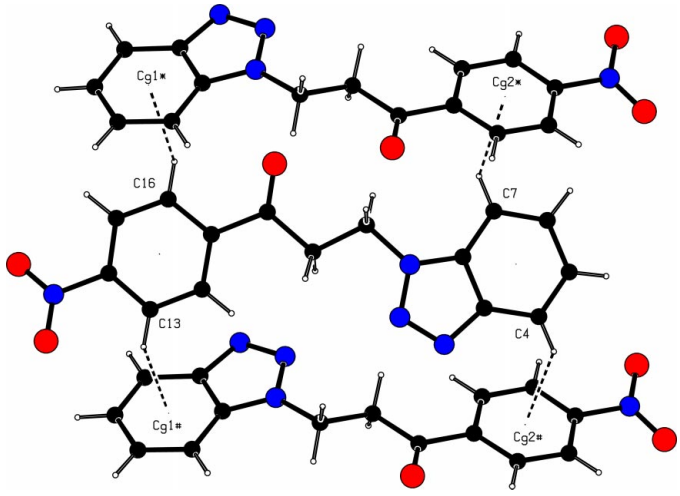


Figure 3
A view of the short C—H···π contacts between the molecules at (−x, y−1/2, −z+1/2), labelled with an asterisk (*), and at (1−x, y+3/2, −z+1/2), labelled with a hash mark (#). The unit cell is not shown, for clarity.

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.927, T_{max} = 0.991
6931 measured reflections
2852 independent reflections
1820 reflections with $I > 2\sigma(I)$
R_{int} = 0.093
θ_{max} = 27.5°
$h = -7 \rightarrow 5$
$k = -9 \rightarrow 8$
$l = -40 \rightarrow 41$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.155
S = 1.00
2852 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O141^{i}	0.95	2.59	3.286 (3)	131
C5—H5···O142^{ii}	0.95	2.58	3.264 (3)	129
C4—H4···*Cg*2^{iii}	0.95	2.84	3.425 (2)	121
C7—H7···*Cg*2^{iv}	0.95	2.83	3.464 (2)	125
C13—H13···*Cg*1^{iii}	0.95	2.68	3.321 (2)	125
C16—H16···*Cg*1^{iv}	0.95	2.83	3.516 (2)	130

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

H atoms were treated as riding atoms, with C—H distances in the range 0.95–0.99 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton. The authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

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