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2-(Benzotriazol-1-ylmethyl)-1-phenyl-3-pyrazolidinone: two weak hydrogen bonds combine to form molecular ladders

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.110
Data-to-parameter ratio = 15.3

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

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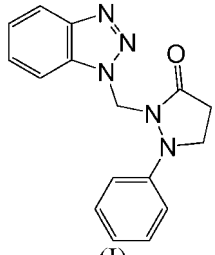
In the supramolecular structure of $C_{16}H_{15}N_5O$, weak C—H···O and C—H···N bonds combine to form molecular ladders, the former bonds acting as the rungs and the latter as the uprights.

Comment

The title compound, (I), was prepared for use as a precursor in the synthesis of new pyrazolo-1,2-benzodiazepines (Knight & Little, 2000, and references therein) using the benzotriazole methodology (Katritzky *et al.*, 1998).



(I)

The triazole ring and the benzene ring of the benzotriazole moiety are both planar and are inclined to one another at an angle of 0.55 (7)°. It is a feature of N1-substituted 1,2,3-benzotriazole molecular geometry that, although bond lengths do have values in the range expected for delocalized double bonds, there is a degree of bond fixation. The bond lengths of the benzene ring show an alternation of bonds, indicating a degree of double- and single-bond character around the ring. The triazole ring shows a marked bond fixation, the differences in length of the two N—N bonds being of the order of

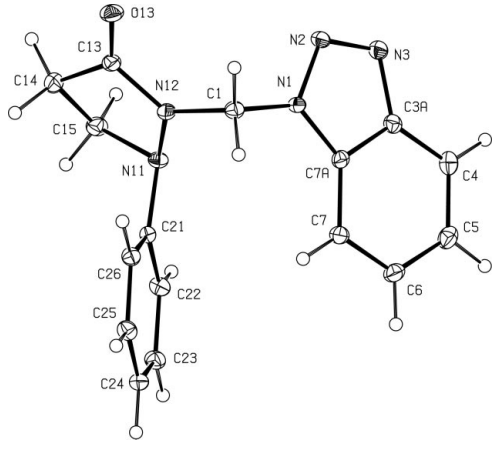


Figure 1
View of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

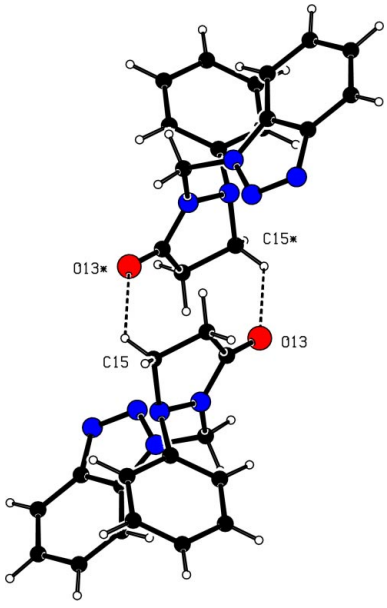


Figure 2
A view of the $R_2^2(10)$ dimer. The molecule labelled with an asterisk (*) is at $(1-x, 2-y, -z)$.

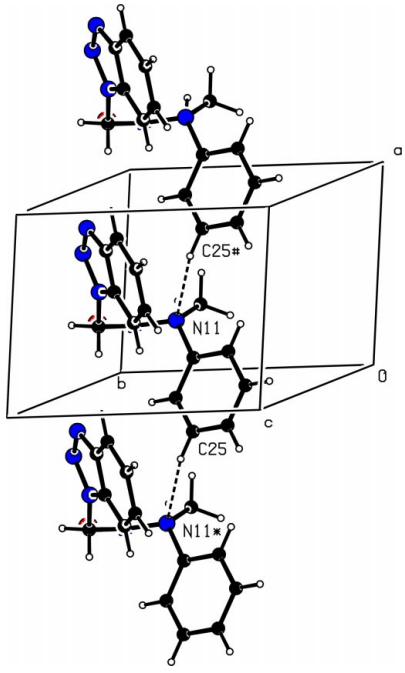


Figure 3
A view of the $C(5)$ chains running along the a axis. The molecule labelled with an asterisk (*) is at $(x-1, y, z)$ and that labelled with a hash (#) is at $(1+x, y, z)$.

0.05 Å. A search of the Cambridge Structural Database (Version of April 2002; Allen, 2002), for all organic N1-substituted 1,2,3-benzotriazole compounds, excluding metal complexes, 50 in all, revealed bond lengths with a similar pattern of values as seen in (I). The conformation of the pyrazolidine ring is a half-chair, with a local pseudo-twofold axis running through N12 and the midpoint of the C14—C15 bond.

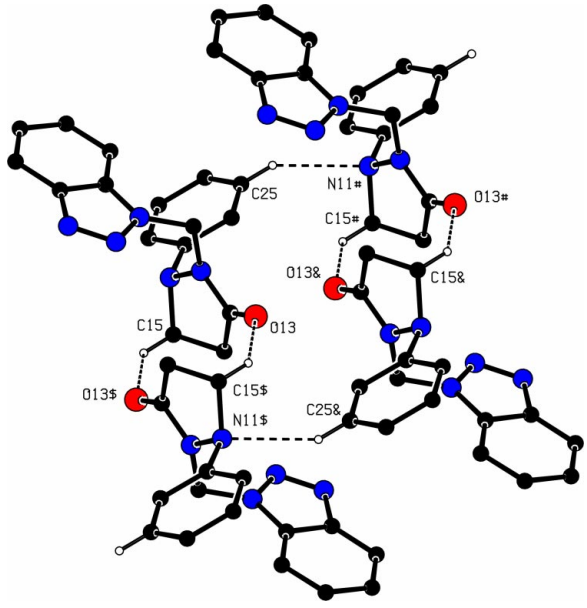


Figure 4
The $R_4^4(22)$ ring formed by the combination of the two hydrogen bonds. The molecule labelled with a dollar sign ($) is at $(1-x, 2-y, -z)$, that labelled with a hash (#) is at $(x-1, y, z)$ and that labelled with an ampersand (&) is at $(-x, 2-y, -z)$. The unit-cell outline and H atoms not involved in the hydrogen bonding have been omitted for clarity.

The bonds and angles of the benzotriazole moiety, along with selected torsion angles for the side chains, are given in Table 1.

The C—H···O bond links the molecules into dimers consisting of an $R_2^2(10)$ ring (Bernstein *et al.*, 1995) (Fig. 2). The bond C15—H15*B*···O13^{i} and the bond related to it by the centre of symmetry at ($\frac{1}{2}$, 1, 0), C15^{i}—H15*B*^{i}···O13, form the dimer (see Table 2 for symmetry codes). The C25—H25···N1^{ii} bond links the molecules into a $C(5)$ chain, which runs parallel to the a axis (Fig. 3). These two interactions combine to form a molecular ladder in which the rungs are the C—H···O bonds and the uprights are formed by the C—H···N bonds, forming in the process an $R_4^4(22)$ ring (Fig. 4). Fig. 5 shows a stereoview of the ladder structure.

There is a π–π-stacking interaction in the structure, involving the benzotriazole moiety. This can be described in terms of two centroid-to-centroid distances, where $Cg1$ is the centroid of the triazole ring and $Cg2$ is the centroid of the

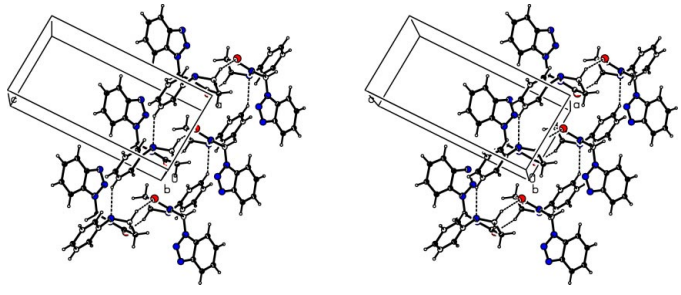


Figure 5
Stereoview of the the molecular ladder.

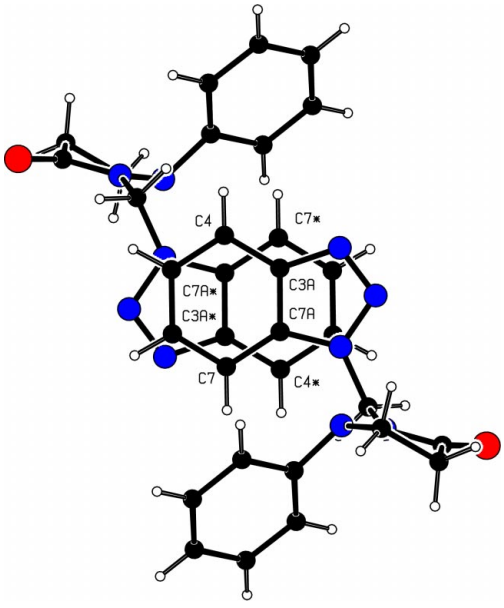


Figure 6
The π–π stacking of the benzotriazole moiety, viewed perpendicular to the moiety.

fused benzene ring. The relevant distances are $Cg2\cdots Cg1(1-x,\ 2-y,\ 1-z)$ = 3.5819 (17) Å and $Cg2\cdots Cg2(1-x, 2-y, 1-z)$ = 3.6393 (18) Å. In Fig. 6, the molecules are viewed perpendicular to the mean plane of the benzotriazole moiety. This shows clearly that the C3*A*═C7*A* double bond lies parallel to the C4···C7 direction, above the centre of the benzene ring of the overlapping benzotriazole moiety.

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

Experimental

A mixture of 1-phenyl-3-pyrazolidinone (1.0 g, 6.17 mmol), benzotriazole (0.74 g, 6.21 mmol), aqueous formaldehyde (0.65 g, 37% *w*/*w*, 8 mmol) and *p*-toluenesulfonic acid (30 mg) in toluene (50 ml) was refluxed, using a Dean–Stark apparatus, for about 1 h. After cooling, the mixture was washed with aqueous NaOH solution (5%, 50 ml) followed by H_2O, and dried with Na_2SO_4. The solvent was removed under vacuum and the residue washed with methanol to give the pure product as a white solid (87% yield; m.p. 385 K). Crystals suitable for X-ray diffraction were collected from a DMF solution. Found: C 66.68, H 6.19, N 17.24%; calculated for $C_{16}H_{15}N_5O$: C 66.65, H 6.21, N 17.27%.

Crystal data

$C_{16}H_{15}N_5O$
M_r = 293.33
Triclinic, $P\overline{1}$
a = 6.4009 (2) Å
b = 8.3596 (3) Å
c = 13.2794 (5) Å
α = 92.778 (1)°
β = 94.382 (1)°
γ = 95.039 (3)°
V = 704.66 (4) Å^3
Z = 2
D_x = 1.382 Mg m^{-3}
Mo Kα radiation
Cell parameters from 3036 reflections
θ = 3.0–27.5°
μ = 0.09 mm^{-1}
T = 120 (1) K
Tablet, colourless
0.36 × 0.26 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
9646 measured reflections
3036 independent reflections
2538 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.110
S = 1.06
3036 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.1652P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.3579 (15)	C3*A*—C4	1.4066 (18)
N1—C7*A*	1.3608 (15)	C4—C5	1.377 (2)
N2—N3	1.3038 (16)	C5—C6	1.405 (2)
N3—C3*A*	1.3821 (16)	C6—C7	1.3777 (18)
C3*A*—C7*A*	1.388 (2)	C7—C7*A*	1.4026 (17)
N2—N1—C7*A*	110.17 (10)	C4—C5—C6	122.17 (12)
N3—N2—N1	108.80 (10)	C7—C6—C5	122.17 (12)
N2—N3—C3*A*	108.13 (11)	C6—C7—C7*A*	115.51 (13)
N3—C3*A*—C7*A*	108.50 (11)	N1—C7*A*—C3*A*	104.40 (11)
C7*A*—C3*A*—C4	120.88 (12)	C3*A*—C7*A*—C7	122.89 (12)
C5—C4—C3*A*	116.38 (13)		
N2—N1—C1—N12	84.60 (13)	N1—C1—N12—N11	48.05 (14)
N1—C1—N12—C13	−121.06 (13)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*B*···O13^{i}	0.99	2.58	3.3084 (16)	130
C25—H25···N11^{ii}	0.95	2.51	3.3530 (17)	149

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

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. MM, AS and JC thank the Ministerio de Educación, Cultura y Deportes (Programa de Cooperación con Iberoamérica, AECI) of Spain for financial support of part of this work. AQ thanks the Ministerio de Educación, for funding in support of his stay in Dundee.

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