

## 2-Allenyl-2*H*-benzotriazole

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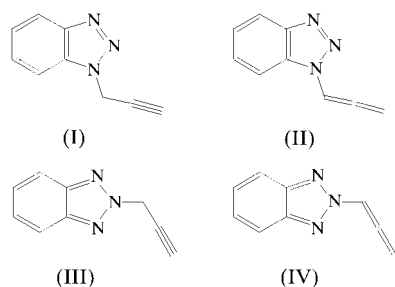
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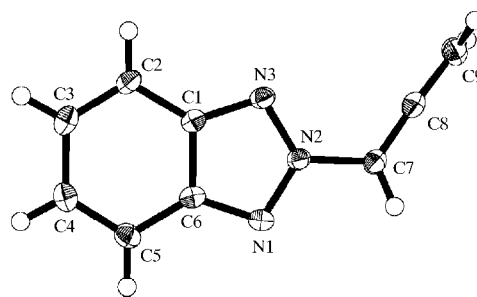
In the title compound, C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>, the allenyl form of the side chain (–CH=C=CH<sub>2</sub>) is found in preference to the propargyl form (–CH<sub>2</sub>–C≡CH). The bond distances between the C atoms in the side chain are 1.303 (3) and 1.289 (3) Å.

### Comment

1-Propargylbenzotriazole, (I), is a useful starting material for producing the versatile pyrrole derivatives (Katrintzky *et al.*, 1992, 1994). During the synthesis of (I) from benzotriazole and propargyl bromide under basic conditions, a regioisomer, 2-allenyl-2*H*-benzotriazole, (IV), containing a tautomeric form of the propargyl moiety, was obtained as a by-product (Katrintzky *et al.*, 1996). In this paper, the molecular structure and intermolecular interactions of the title compound, (IV), in the solid state are reported.

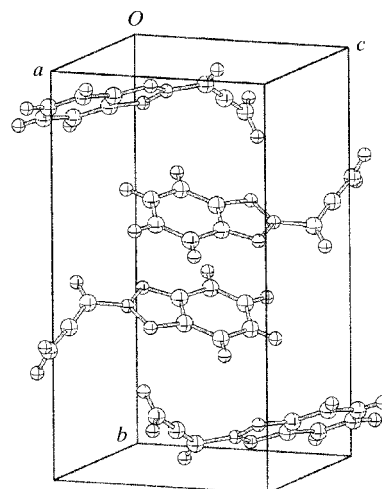


The molecular structure of (IV) is shown in Fig. 1. The C7=C8 and C8=C9 bond lengths are quite similar [1.303 (3) and 1.289 (3) Å, respectively; Table 1], reflecting the allenic structure. The C7=C8=C9 angle is almost linear [176.57 (19)°] and the N2–C7=C8 angle is 122.41 (17)°, which indicates that the hybridization of C7 is *sp*<sup>2</sup> rather than *sp*<sup>3</sup>. From these data, it can be concluded that the formation of the allenyl structure, (IV), in preference to the propargyl structure, (III), is demonstrated in the crystal.

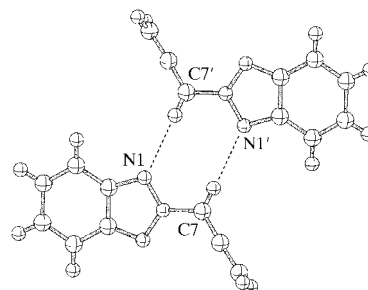


**Figure 1**  
A view of the molecular structure of (IV). Displacement ellipsoids are shown at the 50% probability level.

In the crystal-packing diagram (Fig. 2), the two molecular planes are partially overlapped and display  $\pi$ – $\pi$  stacking. The distance between benzotriazole rings related by a center of symmetry is 3.343 (2) Å. The formation of a weak associated dimer, which contains a pair of intermolecular C7–H···N1' hydrogen-bonding interactions at a C···N distance of 3.395 (2) Å, is also observed (Fig. 3 and Table 2). The formation of this hydrogen-bonding dimer is a consequence of the apparent polarization of the H atom attached to atom C7,



**Figure 2**  
Packing diagram for the crystal structure of (IV).



**Figure 3**  
The ditopic weak interaction involving C–H···N hydrogen bonding.

this polarization being a result of the  $sp^2$  character of the C atom (Jeffrey & Saenger, 1991).

The relative stability of the isomers (I)–(IV) was estimated by density functional theory (DFT) using *GAUSSIAN98* (Frisch *et al.*, 1998). At the B3LYP/6-31G\*\* calculation level, both the allenyl forms, (II) and (IV), are more stable (by 27.4 and 34.3 kJ mol<sup>-1</sup>) than the corresponding propargyl isomers, (I) and (III), respectively. This result is consistent with the predominance of structure (IV) over (III) in the crystal.

## Experimental

Compound (IV) was synthesized according to the procedure reported by Katrintzky *et al.* (1992, 1996). Crystals of (IV) were obtained by slow evaporation from a saturated dichloromethane solution.

### Crystal data

C <sub>9</sub> H <sub>7</sub> N <sub>3</sub>	Mo $K\alpha$ radiation
$M_r = 157.17$	Cell parameters from 7469 reflections
Monoclinic, $P2_1/c$	$\theta = 3.0\text{--}27.5^\circ$
$a = 6.8755$ (7) Å	$\mu = 0.09$ mm <sup>-1</sup>
$b = 14.5505$ (2) Å	$T = 123.1$ K
$c = 7.8520$ (1) Å	Prism, colorless
$\beta = 96.898$ (6)°	$0.80 \times 0.40 \times 0.40$ mm
$V = 779.84$ (8) Å <sup>3</sup>	
$Z = 4$	
$D_x = 1.339$ Mg m <sup>-3</sup>	

### Data collection

Rigaku R-AXIS RAPID diffractometer	$R_{\text{int}} = 0.030$
$\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$
7031 measured reflections	$h = -8 \rightarrow 8$
1785 independent reflections	$k = -18 \rightarrow 16$
1584 reflections with $F^2 > 2\sigma F^2$	$l = -10 \rightarrow 10$

**Table 1**

Selected geometric parameters (Å, °).

N1–N2	1.335 (2)	C2–C3	1.364 (3)
N1–C6	1.346 (2)	C3–C4	1.426 (3)
N2–N3	1.329 (2)	C4–C5	1.362 (3)
N2–C7	1.416 (2)	C5–C6	1.405 (3)
N3–C1	1.346 (2)	C7–C8	1.303 (3)
C1–C2	1.408 (2)	C8–C9	1.289 (3)
C1–C6	1.414 (2)		
N2–N1–C6	102.63 (14)	C2–C3–C4	122.11 (18)
N1–N2–N3	117.62 (15)	C3–C4–C5	121.98 (18)
N1–N2–C7	119.45 (15)	C4–C5–C6	116.60 (18)
N3–N2–C7	122.91 (15)	N1–C6–C1	108.31 (16)
N2–N3–C1	102.28 (14)	N1–C6–C5	129.96 (17)
N3–C1–C2	130.10 (17)	C1–C6–C5	121.73 (18)
N3–C1–C6	109.16 (16)	N2–C7–C8	122.41 (17)
C2–C1–C6	120.73 (18)	C7–C8–C9	176.57 (19)
C1–C2–C3	116.85 (17)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$C7\text{--}H5\cdots N1^i$	0.92	2.48	3.395 (2)	178

Symmetry code: (i)  $1 - x, -y, 1 - z$ .

### Refinement

Refinement on $F$	H-atom parameters constrained
$R = 0.051$	$w = 1/(0.004F_o^2 + 3\sigma^2F_o + 0.5)$
$wR = 0.087$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.27$ e Å <sup>-3</sup>
1589 reflections	$\Delta\rho_{\text{min}} = -0.42$ e Å <sup>-3</sup>
116 parameters	

All H atoms were located in difference Fourier maps and were constrained to ride on their parent atoms ( $C\text{--}H = 0.92\text{--}0.95$  Å), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2001); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2000); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1116). Services for accessing these data are described at the back of the journal.

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