

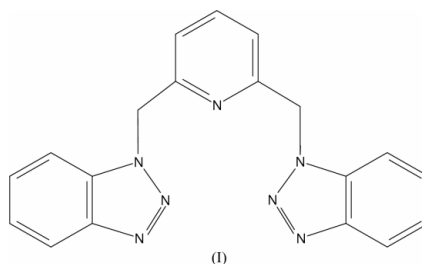
2,6-Bis(*N,N'*-benzotriazol-1-ylmethyl)pyridineS. Selvanayagam,^a
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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.036
wR factor = 0.100
Data-to-parameter ratio = 12.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.In the title molecule, C₁₉H₁₅N₇, the dihedral angle between the two benzotriazole moieties is 72.49 (6)° and those between the pyridine and the two benzotriazole moieties are 70.26 (6) and 57.70 (7)°. The crystal structure is stabilized by intermolecular C—H···N and C—H··· π interactions.

Comment

Benzotriazole derivatives exhibit a high degree of analgesic, anti-inflammatory (Calvino *et al.*, 1980), diuretic and anti-hypertensive activities (Boido *et al.*, 1991). Also, these derivatives comprise an important class of corrosion inhibitors, typically used as trace additives in industrial chemical mixtures, such as coolants, de-icers, surface coatings, cutting fluids and hydraulic fluids (Pillard *et al.*, 2001). Recent studies have shown that benzotriazole derivatives are a major component of aircraft de-icing fluids responsible for toxicity to bacteria (Gruden *et al.*, 2001; Pillard *et al.*, 2001). In this paper, we report the structure of the title compound, (I), a benzotriazole derivative.

The molecular structure of (I) and atom-numbering scheme are shown in Fig. 1. The C—C and C—N bond lengths in the pyridine ring are comparable to the reported mean values of 1.379 and 1.337 Å, respectively (Allen *et al.*, 1987). The bond lengths and angles observed in the two benzotriazole ring systems agree with each other and are comparable with those reported for the benzotriazole moiety (Fayos & Garcia-Blanco, 1972; Smith *et al.*, 2001). Atoms N4 and N7 are in a planar configuration. As in previous reports (Fayos & Garcia-Blanco, 1972; Peeters *et al.*, 1993; Smith *et al.*, 2001), the exocyclic angles around atoms N4 and N7 (Table 1) show considerable asymmetry, with the C—N—C angles [129.2 (2) and 130.6 (1)°] being much wider than the C—N—N angles [120.1 (1) and 118.8 (1)°]. One of the benzotriazole ring systems (N2/N3/N4/C7—C12) is planar within 0.026 (2) Å, while the other is planar within 0.021 (1) Å. The conformation of the attachment of the two benzotriazole rings to the pyridine ring is described by the torsion angles N1—C5—C6—N4 [43.1 (2)°] and C2—C1—C13—N7 [97.5 (2)°], *i.e.* they adopt a *syn-anti* conformation with respect to one another. The

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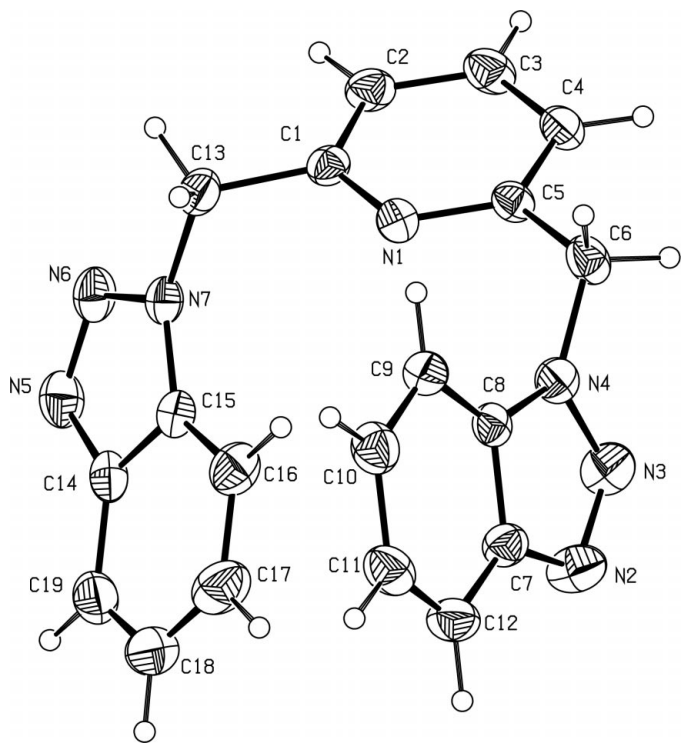


Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

dihedral angle between the two benzotriazole rings is $72.49(6)^\circ$ and the two benzene rings adopt a displaced T-shaped structure (face-to-edge), with their centroids separated by $5.133(1) \text{ \AA}$. In the crystal, symmetry-related molecules are linked by weak $\text{C9-H9} \cdots \text{N6}(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$ intermolecular hydrogen bonds to form infinite one-dimensional chains along the b axis (Fig. 2). Along the chain, the molecules are also linked by intermolecular $\text{C-H} \cdots \pi$ contacts, so that H13A is 2.56 \AA from the ring centroid of the pyridine ring at $(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$, with an angle of 138° for $\text{C13-H13A} \cdots$ centroid. The short intermolecular contacts observed in the structure are listed in Table 2.

Experimental

To a solution of benzotriazole (0.02 mol) in acetonitrile (50 ml), NaOH solution (10 ml, 25%) was added and the solution stirred for 10 min. Then 2,6-bis(bromomethyl)pyridine (0.01 mol) in acetonitrile (10 ml) was added in one portion and the solution stirred for 28 h at room temperature. After completion of the reaction, the reaction mixture was evaporated in a vacuum, extracted with CHCl_3 ($4 \times 50 \text{ ml}$), washed with brine ($2 \times 50 \text{ ml}$) and dried (MgSO_4). The solvent was evaporated in a vacuum. The crude product was purified by column chromatography on neutral alumina, using ethyl acetate-hexane (1:4) as the eluting solvent. The compound was recrystallized from an ethyl acetate-hexane mixture (1:1). The melting point of the compound was $392\text{--}394 \text{ K}$.

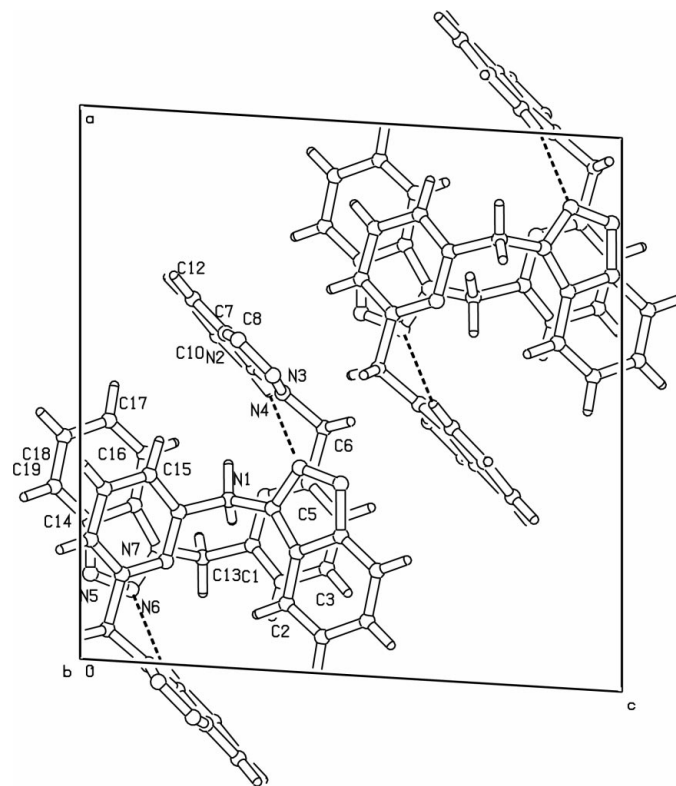


Figure 2

The packing of the title compound, viewed down the b axis.

Crystal data

$\text{C}_{19}\text{H}_{15}\text{N}_7$
 $M_r = 341.38$
 Monoclinic, $P2_1/n$
 $a = 14.5526(12) \text{ \AA}$
 $b = 7.9438(9) \text{ \AA}$
 $c = 14.2666(8) \text{ \AA}$
 $\beta = 93.480(6)^\circ$
 $V = 1646.2(2) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.377 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 19.7\text{--}28.2^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Block, colourless
 $0.30 \times 0.25 \times 0.20 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: none
 3025 measured reflections
 2901 independent reflections
 2104 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 25.0^\circ$
 $h = -17 \rightarrow 17$
 $k = 0 \rightarrow 9$
 $l = 0 \rightarrow 16$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.100$
 $S = 1.03$
 2901 reflections
 236 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.2138P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0058(9)

Table 1
Selected geometric parameters (Å, °).

N2—N3	1.307 (2)	C7—C12	1.397 (2)
N2—C7	1.373 (2)	C8—C9	1.389 (2)
N3—N4	1.354 (2)	C9—C10	1.368 (2)
N4—C8	1.358 (2)	C10—C11	1.406 (3)
N4—C6	1.4496 (19)	C11—C12	1.357 (3)
N5—N6	1.299 (2)	C14—C15	1.389 (2)
N5—C14	1.371 (2)	C14—C19	1.396 (2)
N6—N7	1.3538 (18)	C15—C16	1.391 (2)
N7—C15	1.3603 (19)	C16—C17	1.365 (3)
N7—C13	1.457 (2)	C17—C18	1.404 (3)
C7—C8	1.386 (2)	C18—C19	1.357 (3)
N3—N4—C6	120.1 (1)	N6—N7—C13	118.8 (1)
C8—N4—C6	129.2 (2)	C15—N7—C13	130.6 (1)
C8—N4—C6—C5	−99.05 (17)	C15—N7—C13—C1	78.5 (2)
N1—C5—C6—N4	43.1 (2)	C2—C1—C13—N7	97.54 (18)

Table 2
Short-contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C16—H16 \cdots N1	0.93	2.78	3.385 (2)	124
C6—H6A \cdots N3 ⁱ	0.97	2.78	3.734 (2)	170
C13—H13B \cdots N3 ⁱⁱ	0.97	2.82	3.718 (2)	154
C9—H9 \cdots N6 ⁱⁱ	0.93	2.49	3.405 (2)	166

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

The H atoms were positioned geometrically and were treated as riding on their parent C atoms, with aromatic C—H distances of 0.93 Å and methylene C—H distances of 0.97 Å.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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