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Polymorph β of 1*H*-benzotriazole

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A new polymorph of 1*H*-benzotriazole, $C_6H_5N_3$, with a melting point of 372 K and a crystal density of 1.33 Mg m^{-3}, has been obtained by recrystallization from acetone. The triclinic unit cell contains ten molecules joined by N—H···N hydrogen bonds into a discrete large supramolecular macrocycle.

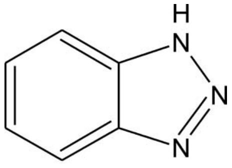
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.105
Data-to-parameter ratio = 12.2

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

Comment

The title compound, (I), is a white crystalline substance that is used as a corrosion inhibitor, an antifreeze agent, an ultraviolet light stabilizer for plastics and as an antifoggant in photography. It is also an excellent and widely used auxilliary in chemical synthesis (Katritzky & Rogovoy, 2003). To our knowledge, despite its many uses and large industrial production, no systematic studies of its polymorphism have been carried out. A monoclinic polymorph of (I) has been reported (Escande *et al.*, 1974). These crystals, obtained by zone melting, were found to be monoclinic in space group $P2_1$, with four molecules in the asymmetric unit. This form of (I), the α polymorph, consists of 1*H*-tautomers. Three out of the four symmetry-independent molecules are connected into polymeric chains *via* N—H···N hydrogen bonds, whereas the fourth molecule is attached to the chain *via* N—H···N and C—H···N interactions.



(I)

Recently, we recrystallized (I) from polar and non-polar solvents and checked the resulting crystalline samples by X-ray powder diffractometry. Depending on the solvent used for crystallization, two types of diffractograms were recorded, pointing to possible polymorphism of (I). The powder diffractogram of the α form reported by Escande *et al.* (1974), generated by *MERCURY* (Bruno *et al.*, 2002), corresponded well with the diffractograms of samples obtained from ethanol, 2-propanol, ethyl acetate, nitromethane and xylene. The second form was obtained by recrystallization of (I) from acetone, toluene and benzene. The melting point of all samples was the same at 372 K. Happily, we were able to obtain single crystals of the β form of (I) by slow evaporation of an acetone solution. In this paper, we report the crystal structure of the β form and compare it with the α polymorph reported earlier.

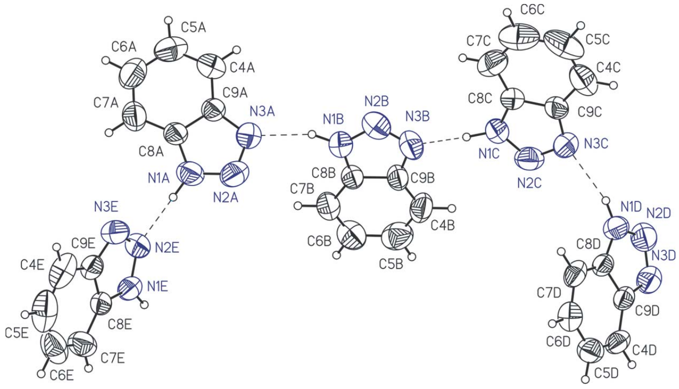


Figure 1
View of the asymmetric unit of (I), shown with 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

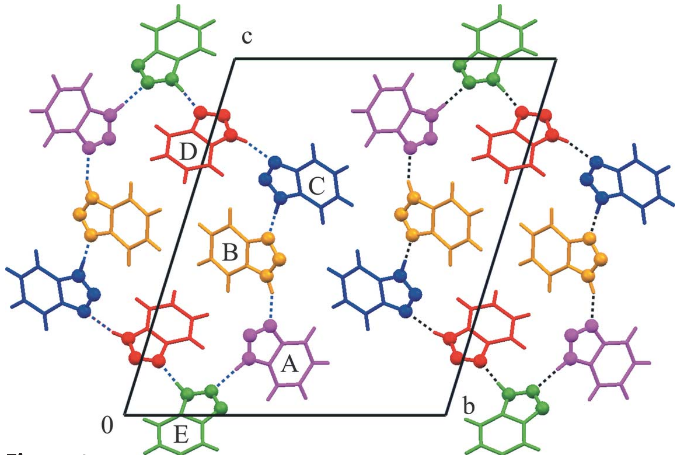


Figure 2
The crystal structure of (I). N atoms are shown as large circles. Dashed lines indicate hydrogen bonds.

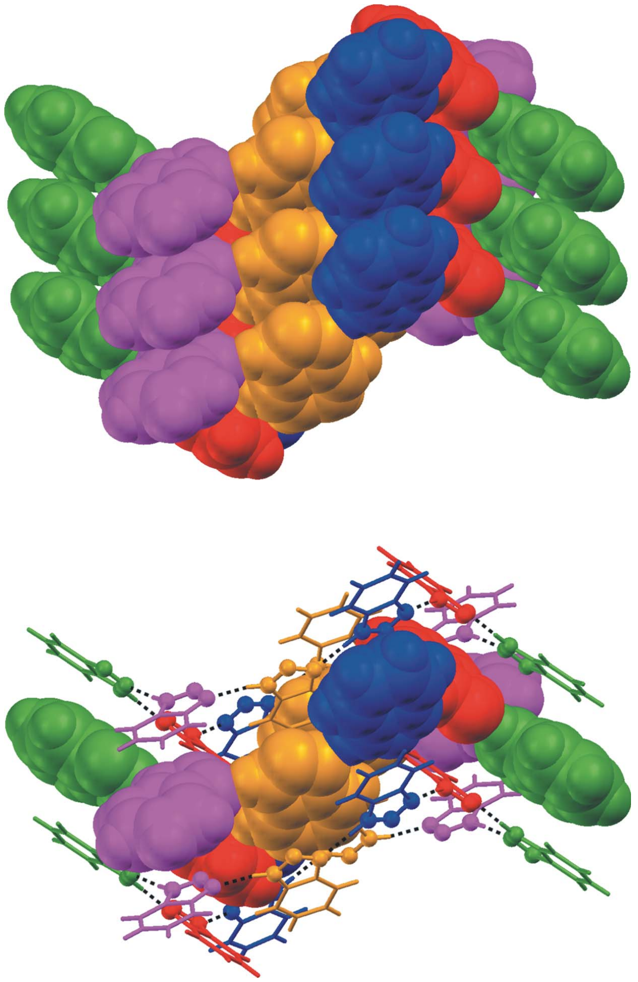


Figure 3
Packing diagrams for (I), showing how the macrocycles stack, as well as the twisted relationship between the individual molecules comprising the macrocycle.

Needle-shaped crystals of the β form are triclinic, in space group $P\overline{1}$. The asymmetric unit, consisting of five molecules of (I), is shown in Fig. 1. As was found in the α polymorph, all molecules are in the 1*H*-tautomeric form. They are joined into an unusual supramolecular macrocycle *via* N—H$\cdots$N hydrogen bonds, forming discrete hydrogen-bonded molecular assemblies in the crystal structure (Fig. 2 and Table 1). Molecules *A*, *B*, *C* and *D* accept hydrogen bonds through atom N3, whereas in the case of molecule *E*, atom N2 acts as the acceptor. Adjacent molecules *B* and *C* in the macroocycle are nearly coplanar [dihedral angle = 11.41 (8)°], *C* and *D* are strongly twisted [70.74 (5)°], and *D* and *E* are slightly twisted [17.51 (7)°], whereas molecule *A* is considerably twisted relative to its two neighbours, *B* and *E*, within the macrocyclic ring [58.72 (5) and 61.51 (5)°, respectively]. In addition to hydrogen bonding, the structure of the β polymorph is stabilized by π–π stacking interactions (Fig. 3). The molecules forming the macrocycle are arranged into five symmetry-independent stacks with the stack axes parallel to [100]. Distances between the neighbouring molecules along the stacks range from 3.355 (8) to 3.611 (8) Å. π–π stacking interactions were also observed in the α polymorph, where the four symmetry-independent molecules formed stacks parallel to the [001] direction, with a translational parameter of 4.130 (5) Å.

Experimental

The title compound was purchased from Aldrich.

Crystal data

$C_6H_5N_3$
M_r = 119.13
Triclinic, $P\overline{1}$
a = 4.2422 (11) Å
b = 17.827 (6) Å
c = 20.685 (7) Å
α = 72.63 (3)°
β = 87.15 (2)°
γ = 86.23 (3)°
V = 1489.0 (8) Å^3
Z = 10
D_x = 1.329 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1854 reflections
θ = 3–25°
μ = 0.09 mm^{-1}
T = 294 (2) K
Needle, colorless
0.50 × 0.15 × 0.03 mm

Data collection

Kuma KM4CCD κ geometry diffractometer
ω scans
Absorption correction: none
11571 measured reflections
5181 independent reflections
2688 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037
$\theta_{\max}$ = 25.0°
$h = -5 \rightarrow 4$
$k = -21 \rightarrow 21$
$l = -24 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.105$
$S = 0.92$
5181 reflections
426 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.11$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···N2E	0.93 (3)	1.99 (3)	2.916 (3)	174 (2)
N1B—H1B···N3A	0.96 (3)	1.93 (3)	2.831 (3)	157 (2)
N1C—H1C···N3B	1.02 (3)	1.83 (3)	2.854 (3)	178 (2)
N1D—H1D···N3C	0.90 (3)	2.08 (3)	2.954 (3)	164 (2)
N1E—H1E···N3D^{i}	0.96 (3)	1.88 (3)	2.841 (3)	176 (2)

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

All H atoms were located in electron-density difference maps. H atoms bonded to C atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{eq}(H) = 1.2U_{eq}(C)$. Positional parameters and isotropic displacement parameters of H atoms of the NH groups were allowed to refine.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: Stereochemical Workstation Operation Manual (Siemens, 1989) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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