

Polymorph β of 1*H*-benzimidazoleSławomir Krawczyk and Maria
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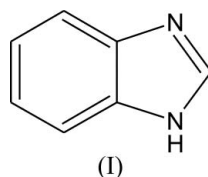
Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.053
 wR factor = 0.116
Data-to-parameter ratio = 12.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

A second orthorhombic polymorph (β) of 1*H*-benzimidazole, $\text{C}_7\text{H}_6\text{N}_2$, metastable at room temperature, has been obtained. It has a melting point of 431 K and a crystal density of 1.27 Mg m^{-3} . At room temperature, the crystals transform into the well known orthorhombic α form, with a melting point of 445 K. In both polymorphs, benzimidazole molecules are connected into polymeric chains *via* $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. However, the mode of aromatic ring interactions differs significantly in the two crystalline forms. In the α form, the molecules show edge-to-face interactions, whereas in the new β form, a sandwich-herringbone arrangement of the aromatic molecules is observed.

Comment

1*H*-Benzimidazole, (I), is a simple heterocyclic aromatic compound used in organic synthesis. It is known as a white substance, slightly soluble in water, with a melting point of 445 K and a crystal density of 1.23 Mg m^{-3} . To the best of our knowledge, the only information that (I) can be dimorphic comes from the work of Domańska & Bogel-Łukasik (2003), who observed a solid–solid first-order phase transition of (I) in differential scanning calorimetry measurements during their solubility studies of benzimidazoles in alcohols.



A new polymorphic form of (I) has been obtained serendipitously during crystallization of 2-benzimidazolecarboxylic acid, (II), from ethanol. Flat needles which precipitated first from the solution had a melting point of 431 K and were

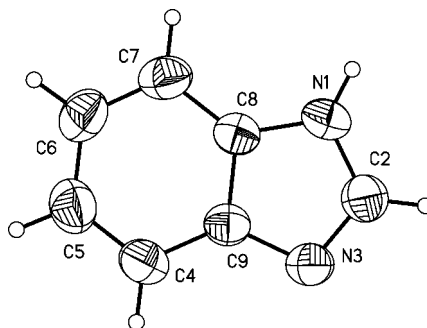


Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids.

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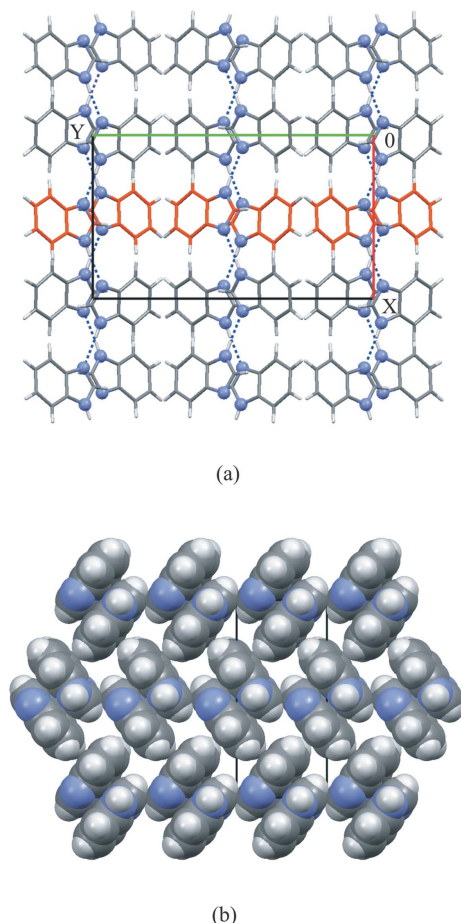


Figure 2

The crystal structure of (I). (a) The packing of the molecules, viewed down the *b* axis, with hydrogen bonds shown as dashed lines and one (100) layer shown in red. (b) The sandwich-herringbone packing of molecules within the (100) layer, viewed along the *a* axis.

identified as a new polymorphic β form of (I) by X-ray crystallography. Further analyses revealed that the sample of (II) was contaminated with (I) by about 10% in weight. To check whether the β form can be obtained from the pure compound, we carried out crystallizations of (I) from water or ethanol solutions. In some cases, regardless of the solvent used, thin plate-like crystals appeared first. However, within a few minutes they disintegrated and transformed into new block-like crystals. The plate-like crystals, when removed immediately from solution, had a melting point of 431 K and the same unit-cell parameters as the crystals of (I) obtained during crystallization of (II). These crystals, when left at room temperature, transformed within one to a few days to the α form, with a melting point of 445 K. Thus, the α form is more stable than the β form at room temperature.

The crystal structure of the α form of (I) was reported by Dik-Edixhoven *et al.* (1973) and Escande & Galigne (1974), and was later redetermined by Stibrany *et al.* (2001). The crystals are orthorhombic, space group $Pna2_1$, with one molecule of (I) in the asymmetric unit. The molecules are connected *via* N–H \cdots N hydrogen bonds into symmetry-equivalent polymeric [011] and $[0\bar{1}1]$ chains with a translational parameter of 9.719 Å. Adjacent molecules along the

chain form a dihedral angle of 78.1°. The aromatic rings of neighbouring molecules related first by an *n*-glide plane perpendicular to the *a* axis, and secondly by a 2_1 axis parallel to the *c* axis, show edge-to-face interactions. The most acidic H atom of (I), H2, is 2.64 Å from the benzene ring centroid [$\pi\cdots\text{H2}^i - \text{C2}^i = 149^\circ$; symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$], whereas atom H4 approaches the benzene ring from the opposite site [$\pi\cdots\text{H4}^{ii} = 2.70 \text{ \AA}$ and $\pi\cdots\text{H4}^{ii} - \text{C4}^{ii} = 148^\circ$; symmetry code: (ii) $1 - x, 1 - y, \frac{1}{2} + z$].

Needle-shaped or plate-like crystals of the β form are also orthorhombic but crystallize in the centrosymmetric space group $Pccn$. The molecule of (I), with the atom-numbering scheme, is shown in Fig. 1. As in the α polymorph, all molecules are linked *via* N–H \cdots N hydrogen bonds (Table 1) into polymeric chains (Fig. 2*a*). The chains are parallel to the [100] direction with a translational parameter of 9.7257 (11) Å. The dihedral angle of 21.74 (5)° between neighbouring molecules along the chain is much smaller than that observed in the α form. Polymeric hydrogen-bonded chains run perpendicular to the (100) layers, in which the molecules of (I) show a sandwich-herringbone type of packing of the aromatic rings (Fig. 2*b*) (Desiraju & Gavezzotti, 1989). The interplanar distance between the two molecules forming a sandwich is 3.418 (8) Å. Except for a C2 \cdots C2($2 - x, 1 - y, 1 - z$) contact of 3.360 (2) Å, there are no other intermolecular contacts shorter than the sum of van der Waals radii within the (100) layer.

Experimental

A sample of compound (II), contaminated with 10% by weight of (I), was dissolved in ethanol at room temperature. Slow evaporation of the solvent gave, in the first crop, crystals melting at 431 K. A single crystal used for X-ray analysis was selected from this crop. The title compound used for crystallization experiments was purchased from Aldrich.

Crystal data

$\text{C}_7\text{H}_6\text{N}_2$	Mo $K\alpha$ radiation
$M_r = 118.14$	Cell parameters from 2816 reflections
Orthorhombic, $Pccn$	$\theta = 4-25^\circ$
$a = 9.7257$ (11) Å	$\mu = 0.08 \text{ mm}^{-1}$
$b = 16.6879$ (17) Å	$T = 295$ (2) K
$c = 7.6056$ (11) Å	Plate, colourless
$V = 1234.4$ (3) Å ³	$0.6 \times 0.2 \times 0.02 \text{ mm}$
$Z = 8$	
$D_x = 1.271 \text{ Mg m}^{-3}$	

Data collection

Kuma KM4 CCD κ -geometry diffractometer	887 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.028$
Absorption correction: none	$\theta_{\text{max}} = 25.0^\circ$
4312 measured reflections	$h = -11 \rightarrow 9$
1091 independent reflections	$k = -19 \rightarrow 14$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1091 reflections	$\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$
88 parameters	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots N3^i$	0.86	2.03	2.884 (2)	172

Symmetry code: (i) $x - \frac{1}{2}, -y + 1, -z + \frac{1}{2}$.

All H atoms were located in electron-density difference maps. The H atoms were positioned with idealized geometry, with C–H = 0.93 Å and N–H = 0.86 Å and refined isotropically using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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* (Version 1.3;

Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

References

- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst. B* **58**, 389–397.
- Desiraju, G. R. & Gavezzotti, A. (1989). *J. Chem. Soc. Chem. Commun.* pp. 621–623.
- Dik-Edixhoven, C. J., Schenk, H. & Van Der Meer, H. (1973). *Cryst. Struct. Commun.* **2**, 23–24.
- Domańska, U. & Bogel-Lukasik, E. (2003). *J. Chem. Eng. Data*, **48**, 951–956.
- Escande, A. & Galigne, J. L. (1974). *Acta Cryst. B* **30**, 1647–1648.
- Oxford Diffraction (2004). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction, Abingdon, Oxfordshire, England.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stibrany, R. T., Potenza, J. A. & Schugar, H. J. (2001). Private communication to the CCDC, refcode BZDMAZ02.