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A new polymorph of 1-(4-nitrophenyl)-1H-benzimidazole ($C_{13}H_9N_3O_2$)

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Abstract

$C_{13}H_9N_3O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 3.7375(1)$ Å, $b = 27.9680(6)$ Å, $c = 10.2595(2)$ Å, $\beta = 95.5120(10)^\circ$, $V = 1067.47(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0370$, $wR_{ref}(F^2) = 0.0975$, $T = 100$ K.

CCDC no.: 1565535

The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized according to literature [5]. Colourless, block crystals were obtained by slow evaporation of its dichloromethane solution.

Table 1: Data collection and handling.

Crystal:	Block, colourless
Size:	$0.35 \times 0.22 \times 0.14$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	28.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16,686, 2678, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2340
$N(\text{param})_{\text{refined}}$:	163
Programs:	Bruker programs [1], SHELX [2, 3], Mercury [4]

Experimental details

Crystal evaluation and data collection were done on a Bruker Smart APEX2 diffractometer [1]. The structure was solved by the direct method using the SHELXS [2] program. The visual crystal structure information was performed using MERCURY [4] system software. All C–H_{aromatic} bond distances were restrained to 0.95 Å with $U_{\text{iso}}(\text{H}_{\text{aromatic}}) = 1.2U_{\text{eq}}$ of the parent atom.

Discussion

N-substituted azoles bearing imidazole or benzimidazole have generated attention as common heterocyclic moieties in various pharmaceutical compounds [6]. Their mode of synthesis includes incorporating an azole ring into the framework of a pharmaceutical candidate compound [7, 8] and following advanced protocols to achieve more stereo- and regio-selective control of the product [9]. A greener route to *N*-substituted azoles is to alkylate/arylate the azole nitrogen with appropriate electrophiles, such as alkyl halides [1, 10, 11]. This involves basic deprotonation of the N atom in a suitable aprotic solvent and subsequent nucleophilic displacement of the halide from the alkyl halide. Polymorphs of *N*-substituted azoles are rare [12–14]. However, solid state structural study of the different crystalline forms of available compounds is important especially, due to the variety of the biological and pharmacological activities of different polymorphs [15].

The title compound crystallizes in the $P2_1/c$ space group and is a polymorph of the $C2/c$ -type structure

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.5825 (3)	0.23558 (3)	−0.28700 (10)	0.0359 (3)
O2	0.4120 (3)	0.29322 (3)	−0.41760 (9)	0.0307 (2)
N1	0.5643 (3)	0.27807 (4)	−0.31499 (10)	0.0190 (2)
N2	1.1115 (3)	0.40974 (3)	0.06625 (9)	0.0142 (2)
N3	1.3137 (3)	0.48000 (3)	0.15102 (10)	0.0168 (2)
C1	0.7257 (3)	0.31238 (4)	−0.21878 (11)	0.0150 (2)
C6	0.9016 (3)	0.29518 (4)	−0.10301 (11)	0.0157 (2)
H6	0.928437	0.261777	−0.088348	0.019*
C5	1.0370 (3)	0.32772 (4)	−0.00933 (11)	0.0148 (2)
H5	1.161927	0.316828	0.070135	0.018*
C4	0.9892 (3)	0.37661 (4)	−0.03204 (10)	0.0137 (2)
C8	1.0857 (3)	0.40654 (4)	0.20120 (11)	0.0141 (2)
C9	1.2102 (3)	0.45074 (4)	0.25120 (11)	0.0153 (2)
C10	1.2101 (3)	0.46071 (4)	0.38404 (12)	0.0188 (2)
H10	1.290473	0.490731	0.418927	0.023*
C11	1.0890 (3)	0.42547 (4)	0.46370 (11)	0.0199 (2)
H11	1.089811	0.431278	0.554958	0.024*
C2	0.6871 (3)	0.36085 (4)	−0.24519 (11)	0.0159 (2)
H2	0.572419	0.371569	−0.326602	0.019*
C3	0.8191 (3)	0.39332 (4)	−0.15052 (11)	0.0151 (2)
H3	0.794037	0.426691	−0.166046	0.018*
C13	0.9582 (3)	0.37116 (4)	0.27998 (11)	0.0168 (2)
H13	0.870739	0.341494	0.244845	0.020*
C12	0.9652 (3)	0.38140 (4)	0.41247 (11)	0.0189 (2)
H12	0.884150	0.357961	0.469864	0.023*
C7	1.2482 (3)	0.45461 (4)	0.04498 (11)	0.0158 (2)
H7	1.290807	0.465953	−0.039429	0.019*

(CCDC number: 1565535; CSD refcode: **PESNEJ**) [16]. The new polymorph reported herein consists of one molecule in the asymmetric unit compared to the former which has two. Though the magnitude of the *b* axis in the new polymorph (27.9680(6) Å) is significantly larger than that of the former (7.1422(8) Å), the other unit cell dimensions of the new polymorph are much smaller than those of **PESNEJ**. Hence, the new polymorph has a lower unit cell volume (1067.47(4) Å³) and a higher packing coefficient (0.738) than the former (cell volume = 1067.47(4) Å³; packing coefficient = 0.719). The molecular geometries of the two polymorphs are similar based on the root mean square deviation values (0.0576–0.0680 Å) obtained from the molecular overlays. This is an indication that intermolecular interactions are solely responsible for the formation of the different polymorphs. In the title compound, intermolecular C–H⋯N hydrogen bonds with the *R*₂²(6) graph set descriptor were found between the H7 and N3 atoms of neighbouring benzimidazolyl moieties (C7⋯N3 = 3.271(2) Å, H7⋯N3 = 2.471(1) Å, C7–H7⋯N3 = 142°, symmetry code: 3–*x*, 1–*y*, –*z*). Furthermore, intermolecular

π⋯π interactions were observed in the title structure between the neighbouring benzimidazolyl units (π_{benzimidazolyl}⋯π_{benzimidazolyl} = 3.737 Å, symmetry code: 1+*x*, *y*, *z*). Interestingly, these two types of intermolecular interactions were not observed in the literature known C2/*c*-type structure.

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