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The crystal structure of the co-crystal: 2-hydroxybenzoic acid – *N'*-(butan-2-ylidene) pyridine-4-carbohydrazide, $C_{10}H_{13}N_3O \cdot C_7H_6O_3$

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Abstract

$C_{10}H_{13}N_3O \cdot C_7H_6O_3$, monoclinic, $P2_1/n$ (no. 14), $a = 7.4038(9)$ Å, $b = 30.448(3)$ Å, $c = 7.6744(8)$ Å, $\beta = 112.013(3)^\circ$, $V = 1603.9(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0492$, $wR_{ref}(F^2) = 0.1384$, $T = 173$ K.

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The asymmetric unit of the title 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

All reagents used were commercially available and used without further purification. An amount of 0.220 g of isonicotinic acid hydrazide (1.60 mmol), 0.220 g of 2-hydroxy-

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.43 × 0.34 × 0.31 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.10 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture Photon, ω
θ_{max} , completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	77005, 3868, 0.034
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3459
$N(param)_{refined}$:	217
Programs:	Bruker [1], SHELX [2], WinGX [3], PLATON [4]

benzoic acid (1.59 mmol) and 3.0 mL of 2-butanone were added into a screw-top dram vial (with rubber septum) and stirred at 300 rpm at 60 °C for 10 min. The vial was closed, and the solution was allowed to reflux in the vial at 60 °C for 24 h. The solution was then left slightly open to allow slow evaporation at room temperature. Colourless block crystals were observed after three days.

Experimental details

The collection method involved ω -scans of width 0.5°. Data reduction was carried out using SAINT-Plus version 6.02.6 software, and SADABS was used to process empirical absorption corrections [1]. The crystal structure was solved through direct methods using SHELXS-97 [2]. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms with $d(C-H) = 0.95$ Å and

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.47422 (19)	0.69710 (4)	0.79314 (18)	0.0183 (3)
C2	0.4466 (2)	0.71769 (5)	0.6233 (2)	0.0232 (3)
H2	0.4381	0.7488	0.6132	0.028*
C3	0.4316 (2)	0.69213 (5)	0.4685 (2)	0.0262 (3)
H3	0.4147	0.7064	0.3534	0.031*
C4	0.4657 (2)	0.62846 (5)	0.6387 (2)	0.0267 (3)
H4	0.4704	0.5973	0.644	0.032*
C5	0.4857 (2)	0.65154 (5)	0.8007 (2)	0.0228 (3)
H5	0.5069	0.6364	0.915	0.027*
C6	0.5103 (2)	0.72181 (4)	0.97278 (18)	0.0188 (3)
C7	0.4555 (2)	0.82709 (5)	1.1042 (2)	0.0218 (3)
C8	0.4302 (3)	0.85230 (5)	0.9284 (2)	0.0322 (4)
H8A	0.4336	0.8839	0.9544	0.048*
H8B	0.5358	0.8448	0.886	0.048*
H8C	0.3048	0.8447	0.8302	0.048*
C9	0.4893 (2)	0.85415 (5)	1.2773 (2)	0.0267 (3)
H9A	0.3772	0.8743	1.2516	0.032*
H9B	0.6064	0.8725	1.3007	0.032*
C10	0.5164 (3)	0.82882 (6)	1.4547 (2)	0.0327 (4)
H10A	0.5372	0.8494	1.5586	0.049*
H10B	0.3998	0.8112	1.4357	0.049*
H10C	0.6297	0.8094	1.4849	0.049*
C11	0.2919 (2)	0.52453 (5)	0.0505 (2)	0.0222 (3)
C12	0.2453 (2)	0.48062 (5)	0.0713 (2)	0.0272 (3)
C13	0.1844 (2)	0.45300 (5)	−0.0850 (3)	0.0344 (4)
H13	0.1503	0.4234	−0.0727	0.041*
C14	0.1737 (3)	0.46848 (6)	−0.2571 (2)	0.0362 (4)
H14	0.1321	0.4493	−0.3625	0.043*
C15	0.2225 (2)	0.51151 (5)	−0.2795 (2)	0.0313 (3)
H15	0.2161	0.5218	−0.3986	0.038*
C16	0.2807 (2)	0.53909 (5)	−0.1255 (2)	0.0250 (3)
H16	0.3138	0.5687	−0.1398	0.03*
C17	0.3518 (2)	0.55441 (5)	0.2134 (2)	0.0248 (3)
N1	0.42658 (18)	0.76138 (4)	0.95584 (16)	0.0222 (3)
H1A	0.3544	0.7721	0.8451	0.027*
N2	0.43990 (19)	0.64817 (4)	0.47484 (18)	0.0267 (3)
N3	0.45845 (18)	0.78518 (4)	1.12194 (17)	0.0226 (3)
O1	0.61992 (16)	0.70594 (3)	1.12281 (14)	0.0255 (2)
O2	0.38141 (18)	0.59551 (3)	0.17611 (15)	0.0307 (3)
H2A	0.415	0.6104	0.2753	0.046*
O3	0.3705 (2)	0.54221 (4)	0.37140 (16)	0.0391 (3)
O4	0.2580 (2)	0.46347 (4)	0.23750 (18)	0.0404 (3)
H4A	0.2961	0.4829	0.321	0.061*

$U_{iso}(H) = 1.2U_{eq}(C)$. Diagrams and publication material were generated using WinGX [3] and PLATON [4].

Comment

Isoniazid, a synthetic derivative of nicotinic acid [5] is a drug that has been used for many years as a first-line anti-tuberculosis (TB) drug. However, bacterial strains

targeted by isoniazid have developed resistance over the years, thus leading to the urgent need to develop novel drugs. There are several ways in which novel anti-TB drugs can be derived. However, one method that stands out is by making modifications to existing drugs so that they can no longer be deactivated by mycobacteria [6]. Therefore, the compound being reported in this article is a modification of isoniazid.

As shown in the figure, the asymmetric unit contains one molecule of *N'*-(butan-2-ylidene)pyridine-4-carbohydrazide and one molecule of 2-hydroxybenzoic acid (salicylic acid). All bond lengths and angles are as expected [7]. Each carbohydrazide moiety is hydrogen bonded by a $O2-H2a \cdots N2$ hydrogen bond to a salicylic acid molecule to form a co-crystal. As is expected from similar co-crystals reported in the literature [8], this co-crystal is formed through a robust carboxylic acid $\cdots$ pyridine heterosynthon. The phenol group on the salicylic acid molecule forms an expected intramolecular $S(6)$ hydrogen bond [9], between the H4a donor and the O3 acceptor. Each carbohydrazide moiety is also hydrogen bonded via its $N1-H$ donor to the carbonyl oxygen (O1) acceptor of an adjacent carbohydrazide moiety (not shown in the figure). These hydrogen bonding interactions within the packing form a one dimensional (1D) ribbon along the *a*-axis. The plane of the salicylic acid is slightly offset from the plane of the pyridine ring by an acute angle of 22° . However, the pyridine rings of the carbohydrazide moiety as well as the benzene rings of salicylic acid lie parallel to each other respectively, and the packing is thus stabilized by π -stacking of these rings along the *a*-axis.

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