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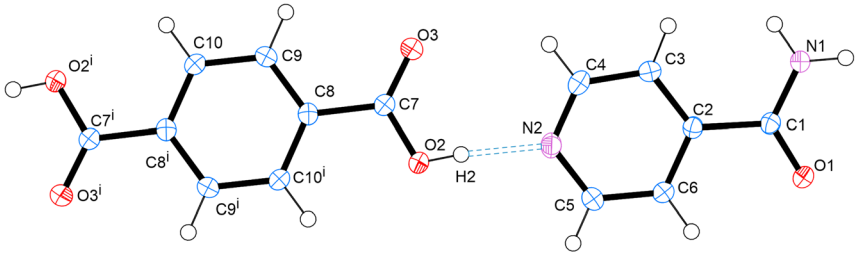
The crystal structure of the co-crystal isonicotinamide · terephthalic acid, $C_8H_6O_4 \cdot 2(C_6H_6N_2O)$



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Abstract

$C_8H_6O_4 \cdot 2(C_6H_6N_2O)$, monoclinic, $C2/c$ (no. 15), a = 20.8371(8) Å, b = 5.2243(2) Å, c = 19.1062(7) Å, β = 118.8350(10)°, V = 1822.01(12) Å^3, Z = 4, $R_{gt}(F)$ = 0.0392, w$R_{ref}(F^2)$ = 0.1143, T = 173 K.

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A part of the molecular 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.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.23 × 0.23 × 0.16 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	70443, 2192, 0.072
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2039
$N(param)_{refined}$:	145
Programs:	Bruker,[1] SHELX,[2,3] WinGX/ORTEP,[4,5] PLATON[6]

1 Source of materials

Isonicotinamide and terephthalic acid were commercially sourced and not purified any further. 0.0204 g of isonicotinamide (0.167 mmol) and 0.0162 g terephthalic acid (0.0975 mmol) were dissolved in 1 ml of AP grade methanol while stirring at 50 °C. 200 µl of AP grade dimethyl sulphoxide was then added to the solution, which was then heated to 100 °C while stirring in a polytop vial. The solution was left to evaporate at room temperature, with the cap being left slightly open. Colourless block crystals formed after 10 days.

2 Experimental details

First the non-hydrogen atoms were refined isotropically, then anisotropically by full matrix least-squares calculations based on F^2. C-bound hydrogen atoms were placed at idealized positions and were allowed to ride on their respective parent atoms with thermal displacement parameters 1.2 times of the parent C atom. The coordinates and isotropic displacement parameters of the N-bound and O-bound H atoms involved in hydrogen bonding interactions were allowed to refine isotropically. Diagrams and publication material were generated using ORTEP-3,[4] WinGX[5] and PLATON.[6]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.71011 (6)	0.0511 (2)	0.92254 (6)	0.0177 (2)
C2	0.68410 (6)	0.2670 (2)	0.86261 (6)	0.0174 (2)
C3	0.61103 (6)	0.3308 (2)	0.81364 (6)	0.0226 (2)
H3	0.573074	0.239098	0.816682	0.027*
C4	0.59482 (6)	0.5317 (2)	0.76020 (7)	0.0247 (3)
H4	0.544891	0.576115	0.72693	0.03*
C5	0.71612 (6)	0.6034 (2)	0.80038 (7)	0.0240 (3)
H5	0.752816	0.698156	0.795769	0.029*
C6	0.73743 (6)	0.4066 (2)	0.85563 (6)	0.0213 (2)
H6	0.787858	0.367601	0.888323	0.026*
C7	0.54169 (6)	1.0976 (2)	0.61722 (6)	0.0190 (2)
C8	0.52041 (5)	1.3060 (2)	0.55635 (6)	0.0190 (2)
C9	0.44791 (6)	1.3868 (2)	0.51581 (7)	0.0233 (2)
H9	0.412388	1.309382	0.526659	0.028*
C10	0.42753 (6)	1.5807 (2)	0.45947 (7)	0.0229 (2)
H10	0.377997	1.636165	0.431691	0.027*
N1	0.66025 (5)	−0.08271 (18)	0.93140 (6)	0.0208 (2)
N2	0.64600 (5)	0.66505 (18)	0.75337 (5)	0.0226 (2)
O1	0.77626 (4)	0.00541 (16)	0.95997 (5)	0.0241 (2)
O2	0.61088 (4)	1.03262 (17)	0.64992 (5)	0.0257 (2)
O3	0.49838 (4)	0.99942 (16)	0.63526 (5)	0.0249 (2)
H1A	0.6766 (8)	−0.215 (3)	0.9659 (9)	0.03*
H1B	0.6108 (9)	−0.049 (3)	0.9062 (9)	0.03*
H2	0.6223 (9)	0.898 (3)	0.6887 (10)	0.037*

3 Comment

Isonicotinamide is an isomer of niacinamide, differing in the position of the carbamide substituent. Isonicotinamide, like niacinamide, is thought to be very useful in co-crystallization because the pyridine nitrogen easily acts as an acceptor for hydrogen bonds, especially when paired with good hydrogen bond donors, such as carboxylic acids and alcohols. Isonicotinamide has been co-crystallized with many carboxylic acids, making use of the robust carboxylic acid···pyridine hydrogen bond.[7] Isonicotinamide in its pure form crystallizes in the $P2_1/c$ space group.[8]

Terephthalic acid, a dicarboxylic acid is used in the synthesis of metal organic frameworks as a linker between metal centres. It is also commonly used to prepare co-crystals with N-heterocyclic molecules.[9] It is also frequently used in the development of saturated polyesters.[10] Terephthalic acid is also useful when preparing coordination polymers.[11] Terephthalic acid in its pure form crystallizes in the $P\bar{1}$ space group.[12]

The asymmetric unit of isonicotinamide · terephthalic contains one molecule of isonicotinamide and half a molecule of terephthalic acid, and crystallizes in the monoclinic *C*2/*c* space group. The complete molecule is generated by symmetry. There is an O2–H2···N2 hydrogen bond, formed between the hydrogen of the carboxyl group and the pyridine nitrogen atom. Being in the *C*2/*c* space group the crystal structure has a glide plane along the c axis. The isonicotinamide molecule is bonded to another isonicotinamide molecule through N1–H1A···O1 hydrogen bonds, forming an R(8) ring, and two terephthalic acid molecules via O2–H2···N2 and N1–H1B···O3 hydrogen bonds. Terephthalic acid is bonded to four isonicotinamide molecules via two N1–H1B···O3 hydrogen bonds and two O2–H2···N2 hydrogen bonds.

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