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The crystal structure of 4-(trifluoromethyl)nicotinic acid, $C_7H_4F_3NO_2$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.20 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.18 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.2°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8642, 1327, 0.060
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 968
$N(\text{param})_{\text{refined}}$:	123
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2564(3)	0.24552(14)	0.6831(3)	0.0226(5)
C2	0.4344(3)	0.30516(14)	0.7697(3)	0.0212(5)
C3	0.4464(3)	0.39823(14)	0.7541(3)	0.0237(5)
C4	0.6210(4)	0.44297(15)	0.8461(3)	0.0281(6)
H4	0.633039	0.506139	0.836468	0.034*
C5	0.7774(4)	0.39415(15)	0.9522(3)	0.0282(6)
H5	0.896206	0.425157	1.015853	0.034*
C6	0.6021(3)	0.26272(14)	0.8778(3)	0.0237(5)
H6	0.597746	0.199304	0.887286	0.028*
C7	0.2776(4)	0.45240(15)	0.6375(3)	0.0307(6)
F1	0.1061(2)	0.46464(9)	0.70817(18)	0.0385(4)
F2	0.3486(2)	0.53504(8)	0.6096(2)	0.0458(5)
F3	0.2174(2)	0.41500(9)	0.48051(17)	0.0383(4)
N1	0.7683(3)	0.30548(12)	0.9687(2)	0.0264(5)
O1	0.0700(3)	0.28262(11)	0.6696(2)	0.0339(5)
O2	0.2894(3)	0.17027(10)	0.6368(2)	0.0307(4)
H1	-0.031(6)	0.249(2)	0.597(5)	0.091(12)*

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Abstract

$C_7H_4F_3NO_2$, monoclinic, $P2_1/c$ (no. 14), $a = 6.4488(11)$ Å, $b = 14.922(2)$ Å, $c = 7.7868(12)$ Å, $\beta = 100.941(5)^\circ$, $V = 735.7(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0431$, $wR_{\text{ref}}(F^2) = 0.1158$, $T = 150(2)$ K.

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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.

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Source of material

Both the starting materials, 4-(trifluoromethyl)nicotinic acid and THF, are commercial and used without further purification. 1.91 g 4-(trifluoromethyl)nicotinic acid (1 mmol) was added to 25 mL THF at room temperature. After stirring for 15 min, the solution was filtered and sat quietly. Colorless crystals were obtained, yield 88.6% (based on 4-(trifluoromethyl)nicotinic acid).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C, N and O atoms were

positioned with idealized geometry and refined isotropic ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $1.2U_{\text{eq}}(\text{N})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, respectively), for all H atoms) using a riding model with C—H = 0.950 Å and O—H = 0.925 Å).

Comment

The research on nicotinic acid derivatives becomes a growing area of scientific interest due to the bioactivity of them. In 1953, Wright and coworker already reported the crystal structure of nicotinic acid [5]. Thereafter, many crystal structures of nicotinic acid derivatives, especially halogeno-substituted derivatives, have been reported, such as F-, Cl-, Br-, I-substituted nicotinic acid derivatives [6–8]. Anilinic nicotinic acids have aroused interest for a long time and a number of crystal structures have been reported successively [9–13]. Some other substituted nicotinic acid derivatives although have been made [14–17]. However, to the best of our knowledge, the trifluoromethyl-substituted nicotinic acid have not been reported until now.

As shown in the figure, 4-(trifluoromethyl)nicotinic acid crystallizes in monoclinic, $P2_1/c$ group with one molecule in the asymmetric unit. All of the C and N atoms are nearly co-planar. All bond lengths and angles of the title compound are comparable with its analogues [5–18]. The classical hydrogen bond, O—H...N, generates a one-dimensional structure by a head-to-tail mode. There are at least two kinds of non-classical hydrogen bonds: C—H...O and C—H...F, which link one-dimensional chains mentioned above to a two-dimensional structure.

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References

1. Bruker. SAINT v8.37A. Bruker AXS Inc, Madison, WI, USA (2015).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected. *Acta Crystallogr. A* **71** (2015) 59–75.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
5. Wright, W. B.; King, G. S. D.: The crystal structure of nicotinic acid. *Acta Crystallogr.* **6** (1953) 305–317.
6. de Souza, M. V. N.; Wardella, S. M. S. V.; Howieb, R. A.: 2-Chloropyridine-3-carboxylic acid. *Acta Crystallogr.* **E61** (2005) o1347–o1349.
7. Howie, R. A.; Goncalves, R. S.; de Souza, M. V. N.; Tiekink, E. R. T.; Wardell, J. L.: 2-Bromo-pyridine-3-carboxylic acid. *Acta Crystallogr.* **E66** (2010) o486.
8. Lu, J. Y.; Babb, A. M.: A simultaneous reduction, substitution, and self-assembly reaction under hydrothermal conditions afforded the first diiodopyridine copper(I) coordination polymer. *Inorg. Chem.* **41** (2002) 1339–1341.
9. Braga, D.; Chelazzi, L.; Grepioni, F.; Nanna, S.; Rubini, K.; Curzi, M.; Gialfreda, S.; Saxell, H. E.; Bratz, M.; Chiodo, T.: Imazamox: a quest for polymorphic modifications of a chiral and racemic herbicide. *Cryst. Growth Des.* **14** (2014) 1430–1437.
10. Long, S.; Li, T.: Controlled formation of the acid-pyridine heterosynthon over the acid-acid homosynthon in 2-anilinic nicotinic acids. *Cryst. Growth Des.* **9** (2009) 4993–4997.
11. Nath, N. K.; Kumar, S. S.; Nangia, A.: Neutral and zwitterionic polymorphs of 2-(*p*-tolylamino)nicotinic acid. *Cryst. Growth Des.* **11** (2011) 4594–4605.
12. Kalra, A.; Zhang, M.; Parkin, S.; Li, T.: Crystal packing and crystallization tendency from the melt of 2-((2-ethylphenyl)amino) nicotinic acid. *Z. Kristallogr. CM* **233** (2018) 9–16.
13. Peng, S.; Yu, F.; Xu, D.; Li, C.; Parkin, S. R.; Li, T.; Zhang, M.; Long, S.: Structural isomerization of 2-anilinic nicotinic acid leads to a new synthon in 6-anilinic nicotinic acids. *Cryst. Growth Des.* **18** (2018) 4849–4859.
14. Mazur, L.; Koziol, A. E.; Modzelewska-Banachiewicz, B.: 2-(4-Phenyl-5-(2-pyridyl)-4*H*-1,2,4-triazol-3-yl)nicotinic acid: a case of solvent-dependent polymorphism. *Acta Crystallogr.* **C64** (2008) o574–o577.
15. Mansor, S.; Yehye, W. A.; Ariffin, A.; Rahman, N. A.; Ng, S. W.: 2-(3,5-Di-*tert*-butyl-4-hydroxy-benzyl-sulfan-yl)nicotinic acid. *Acta Crystallogr.* **E64** (2008) o1778.
16. Basavoju, S.; Reddy, C. M.; Desiraju, G. R.: 2-(Methyl-sulfanyl)-nicotinic acid. *Acta Crystallogr.* **E61** (2005) o822–o823.
17. Ma, M.; Li, C.; Li, X.; Wen, K.; Liu, Y. A.: Efficient synthesis of 6-aryl-2-chloronicotinic acids *via* Pd catalyzed regioselective suzuki coupling of 2,6-dichloronicotinic acid. *J. Heterocycl. Chem.* **45** (2008) 1847–1849.
18. You, G.-R.; Rao, G.-W.: Crystal structure of 8-(trifluoromethyl)imidazo[1,2-*a*]pyridine-3-carbaldehyde, C₉H₅F₃N₂O. *Z. Kristallogr. NCS* **233** (2018) 1081–1082.