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The crystal structure of *para*-trifluoromethyl-aniline hemihydrate, $C_{14}H_{14}F_6N_2O$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.52 × 0.32 × 0.29 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.14 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12771, 1906, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1330
$N(\text{param})_{\text{refined}}$:	146
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

<https://doi.org/10.1515/ncrs-2020-0512>

Received July 3, 2020; accepted November 19, 2020;

published online February 15, 2021

Abstract

$C_{14}H_{14}F_6N_2O$, orthorhombic, *Pbcn* (no. 60), $a = 17.7552(12)$ Å, $b = 10.7574(9)$ Å, $c = 8.0207(7)$ Å, $V = 1532.0(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0415$, $wR_{\text{ref}}(F^2) = 0.1154$, $T = 200$ K.

CCDC no.: 2045357

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.

Source of material

The compound was obtained commercially (Fluka). Crystals were taken directly from the crystalline product.

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.500000	0.49124 (17)	0.750000	0.0573 (5)
N1	0.57698 (7)	0.34368 (15)	0.4965 (2)	0.0520 (4)
C1	0.89510 (9)	0.39375 (17)	0.5090 (2)	0.0564 (4)
C11	0.65549 (7)	0.35450 (12)	0.49763 (16)	0.0366 (3)
C12	0.69036 (7)	0.45499 (12)	0.41937 (18)	0.0374 (3)
H12	0.660770	0.515151	0.362563	0.045*
C13	0.76765 (7)	0.46730 (12)	0.42416 (18)	0.0383 (3)
H13	0.791011	0.535818	0.370226	0.046*
C14	0.81141 (7)	0.38059 (13)	0.50697 (17)	0.0386 (3)
C15	0.77703 (8)	0.28104 (13)	0.58534 (19)	0.0445 (4)
H15	0.806777	0.221108	0.642183	0.053*
C16	0.70005 (8)	0.26853 (12)	0.58129 (19)	0.0434 (4)
H16	0.676985	0.200246	0.636369	0.052*
H1	0.5234 (10)	0.4423 (11)	0.6858 (19)	0.081 (7)*
H1A	0.5533 (10)	0.3855 (17)	0.416 (2)	0.064 (6)*
H1B	0.5623 (10)	0.2714 (19)	0.510 (2)	0.060 (6)*
F1 ^a	0.9293 (2)	0.3371 (5)	0.6340 (6)	0.0993 (13)
F2 ^a	0.91733 (18)	0.5102 (2)	0.5155 (7)	0.1009 (15)
F3 ^a	0.9292 (2)	0.3455 (4)	0.3779 (4)	0.0863 (11)
F4 ^b	0.9165 (7)	0.389 (2)	0.6614 (12)	0.142 (6)
F5 ^b	0.9194 (6)	0.4923 (17)	0.439 (3)	0.181 (8)
F6 ^b	0.9244 (7)	0.302 (2)	0.430 (3)	0.171 (8)

^aOccupancy: 0.742(11). ^bOccupancy: 0.258(11).

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Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

Both nitrogen-bound H atoms as well as the hydrogen atom of the water molecule were located on a difference Fourier map and refined freely. The fluorine atoms of the trifluoromethyl group show rotational disorder with the major component being present in 74.2% of cases.

Comment

Aniline, pyridine and their respective core-substituted derivatives are important synthons in preparative chemistry as the pattern of additional functional groups introduced to the aromatic system allows for a broad range of physicochemical properties and their respective fine-tuning. Therefore, many of the more common members of these two classes of compounds are commercially available and their basic physical properties have been tabulated. In this context it is particularly striking if a reagent that is known to be a liquid at ambient conditions presents itself as a solid in excess of 20 °C beyond its melting point after prolonged storage at ambient temperatures. To establish the nature of the crystalline material that presented itself in a vial of the title compound a diffraction study was conducted as this was seen as a possible extension of our continued interest in the structural aspects of anilines and pyridines [7–16]. Structural data about the title compound acting as a ligand towards iridium [17] or boron [18] as well as forming part of a rotaxane compound [19] is available.

While the structure confirms the presence of the title compound it simultaneously shows the presence of half a molecule of water (one molecule of water on a mirror plane), thus denoting the crystalline material as the title compound's hemihydrate. The C–N bond length of 1.3988(18) Å is in good agreement with numerical values apparent for other aniline derivatives deposited with the Cambridge Structural Database [20]. Intracyclic C–C–C angles cover a narrow range of 118.70(12)–120.84(13)°.

In the crystal, classical hydrogen bonds of the O–H···N and the N–H···O type are apparent that are supported by both hydrogen atoms on the water molecule but only one of the hydrogen atoms of the amino group. These intermolecular interactions present themselves as a cooperative set of hydrogen bonds and give rise to cyclic D···A patterns. In terms of graph-set analysis [21, 22], the descriptor for these hydrogen bonds is *DD* on the unary and *R*₄⁴(8) on the binary level. In total, the entities present in the crystal are connected to infinite chains along the crystallographic *c* axis. π -stacking is not a prominent feature in the crystal structure of the title compound with the shortest distance between two centers of gravity measured at 4.7797(9) Å.

The hydrogen bonding pattern supported by the presence of half a molecule of water per molecule of the title compound (supposedly absorbed from the atmosphere through a small crevice in the lid over years of storage) explains the significant increase for the melting point in comparison to the anhydrous material. The results of this study strengthen the notion that even simple organic compounds that enjoy a – supposedly! – infinite shelf-life and are impervious to decomposition can undergo chemical alterations over prolonged periods of time.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The corresponding author thanks the National Research Foundation for financial support.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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