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The crystal structure of 2,6-dibromo-4-fluoroaniline, $C_6H_4Br_2FN$

<https://doi.org/10.1515/ncrs-2020-0557>

Received November 1, 2020; accepted December 18, 2020;
published online February 12, 2021

Abstract

$C_6H_4Br_2FN$, monoclinic, $P2_1/c$ (no. 14), $a = 17.0332(5)$ Å, $b = 4.34070(10)$ Å, $c = 21.9732(5)$ Å, $\beta = 109.6910(10)^\circ$, $V = 1529.61(7)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0256$, $wR_{ref}(F^2) = 0.0518$, $T = 200$ K.

CCDC no.: 2051174

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

The compound was obtained commercially (fluorochem). Crystals suitable for the diffraction study were obtained

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.21 \times 0.18 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	10.5 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	15088, 3804, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3015
$N(\text{param})_{\text{refined}}$:	197
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

upon free evaporation of a solution of the compound in *iso*-propanol at ambient conditions.

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 $U(H)$ set to $1.2U_{eq}(C)$.

All nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Comment

Aniline and its derivatives are interesting bonding partners for a variety of transition metals and elements from the p-block of the periodic system. They can act as neutral

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br11	−0.09740 (2)	−0.14506 (8)	0.33547 (2)	0.05053 (9)
Br12	0.23647 (2)	0.05025 (8)	0.34592 (2)	0.04825 (9)
F1	0.11577 (13)	0.5142 (5)	0.51079 (9)	0.0657 (6)
N1	0.05672 (17)	−0.2031 (6)	0.29229 (12)	0.0344 (5)
H711	0.022 (2)	−0.336 (8)	0.2865 (14)	0.044 (9)*
H712	0.098 (2)	−0.270 (8)	0.2857 (14)	0.043 (9)*
C11	0.07181 (15)	−0.0322 (6)	0.34800 (11)	0.0266 (5)
C12	0.01018 (16)	0.0269 (6)	0.37509 (13)	0.0323 (6)
C13	0.02379 (18)	0.2072 (7)	0.42957 (13)	0.0414 (7)
H13	−0.019161	0.240583	0.447380	0.050*
C14	0.10081 (19)	0.3359 (7)	0.45697 (13)	0.0404 (7)
C15	0.16419 (17)	0.2959 (6)	0.43266 (12)	0.0334 (6)
H15	0.216981	0.390918	0.452101	0.040*
C16	0.14815 (15)	0.1115 (6)	0.37868 (11)	0.0272 (5)
Br21	0.56899 (2)	0.06654 (7)	0.09784 (2)	0.04293 (8)
Br22	0.31655 (2)	−0.00840 (8)	0.21211 (2)	0.04674 (9)
F2	0.29327 (11)	0.6756 (4)	0.01434 (8)	0.0541 (5)
N2	0.48768 (15)	−0.1316 (5)	0.19718 (11)	0.0306 (5)
H721	0.5264 (17)	−0.217 (7)	0.1891 (12)	0.030 (8)*
H722	0.4658 (19)	−0.259 (8)	0.2182 (14)	0.049 (9)*
C21	0.43669 (15)	0.0555 (5)	0.14931 (11)	0.0238 (5)
C22	0.46300 (14)	0.1805 (6)	0.10076 (11)	0.0257 (5)
C23	0.41531 (17)	0.3843 (6)	0.05493 (12)	0.0313 (6)
H23	0.434693	0.463714	0.022265	0.038*
C24	0.33944 (17)	0.4684 (6)	0.05794 (12)	0.0340 (6)
C25	0.30873 (16)	0.3540 (6)	0.10353 (13)	0.0335 (6)
H25	0.255354	0.413293	0.104236	0.040*
C26	0.35802 (15)	0.1494 (6)	0.14845 (11)	0.0281 (5)

or – upon deprotonation – as anionic monodentate ligands. Upon variation of the substituents on the aromatic system, a seemingly endless series of symmetric as well as asymmetric aniline derivatives featuring different steric pretenses and acidities of the amine-group are available. In continuation of our interest in the structural variety of halogenated derivatives of benzene [7–18] we determined the molecular and crystal structure of the title compound.

The structure shows the presence of a three-fold halogenated derivative of aniline bearing two bromine atoms in *ortho* position to the amine group as well as a fluorine atom in *para* position to the protic substituent. The asymmetric unit contains two complete molecules. C–Br bond lengths of 1.892(2) and 1.897(3) Å in the first molecule and 1.894(2) Å as well as 1.895(2) Å are uniform and in good agreement with values apparent for other brominated derivatives of benzene whose metrical parameters have been deposited with the Cambridge Structural Database [19]. A similar statement holds true for the C–F bond lengths of 1.364(3) and 1.356(3) Å as well as C–N bond lengths of 1.379(3) and 1.380(3) Å. C–C angles cover

ranges of 115.1(2)–123.9(2)° in the first molecule and 115.5(2)–123.2(2)° with the smallest angle invariably on the carbon atom bearing the amino group as substituent and the largest angle on one of the two brominated carbon atoms (with the second largest angle on the remaining brominated carbon atoms in both molecules). The least-squares planes as defined by the respective carbon atoms of the aromatic systems enclose an angle of 76.36(7)°.

In the crystal, classical hydrogen bonds of the N–H···N are observed next to C–H···F contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. While the cooperative donor···acceptor pairs for the classical hydrogen bonds are neatly reserved for each of the two molecules present in the asymmetric unit and its pertaining symmetry-generated equivalents the C–H···F contacts are exclusively supported by the two hydrogen atoms of one of the two molecules as donors with the fluorine atoms on the two different molecules as acceptors. In terms of graph-set analysis [20, 21], the classical hydrogen bonds necessitate a *C*₁¹(2)*C*₁¹(2) descriptor on the unary level while the C–H···F contacts require *DR*₂²(8) descriptor on the same level. It is pertinent to point out that one could discuss the existence of classical intramolecular hydrogen bonds of the N–H···Br type, however, these are characterized by pronounced deviations of the D–H···A angles and are, therefore, only listed in the pertaining table for completeness. The latter problem also holds true for two potential F···*π* interactions. *π*-Stacking is not a strong stabilizing factor in the crystal structure with the shortest distance between two centers of gravity measured at 4.3405(15) Å which is in agreement with the length of one of the unit cell's axes. In total, the molecules are connected to a three-dimensional network.

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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