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2,6-Dibromo-4-fluorobenzonitrile

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Key indicators

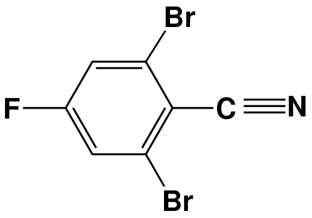
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.005 Å
R factor = 0.036
wR factor = 0.089
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_7H_2Br_2FN$, packs in approximately planar sheets with molecules held together in pairs by CN$\cdots$Br intermolecular Lewis acid–base interactions across a center of symmetry. The CN$\cdots$Br arrangement is approximately linear at the Br atom and bent at the N atom, with an N$\cdots$Br distance of 3.11 Å. The molecular pairs form sheets through C—H$\cdots$N hydrogen bonds, with H$\cdots$N distances of 2.55 Å, and C—H$\cdots$F hydrogen bonds with H$\cdots$F distances of 2.68 Å.

Comment

In the structures of 4-X-2,6-dibromobenzonitriles, the types of intermolecular interaction vary greatly depending on X. When X is Br (Carter & Britton, 1972), there are CN$\cdots$Br contacts with the CN group interacting equally with the 2- or 6-Br atoms on adjacent molecules, with the 4-Br atoms making normal contacts with 2- and 6-Br atoms on different adjacent molecules. When X is Cl (Britton, 2000), the crystal is isostructural with the crystal where X is Br. When X is I (Gleason & Britton, 1978), the shortest contact distance is CN$\cdots$I, as a consequence of the stronger Lewis acidity of I compared with Br. There is one CN$\cdots$Br contact and one Br$\cdots$I contact, but neither is especially short.



(I)

When X is CH_3 (Gleason & Britton, 1976) or H (Britton *et al.*, 2000), there are no CN$\cdots$Br contacts. Rather, there are short Br$\cdots$Br contacts between adjacent molecules. In addition, when X is H, the CN is involved in a weak C—H$\cdots$NC hydrogen bond.

The absence of CN$\cdots$Br interactions when X is H or CH_3 suggests that electron-withdrawing groups are necessary in the 4-position for Br to be a strong enough Lewis acid to form the CN$\cdots$Br interactions. To test this idea, we have prepared 2,6-dibromo-4-fluorobenzonitrile, (I), and determined its crystal packing.

Fig. 1 shows the atom labeling and the anisotropic displacement ellipsoids. The bond lengths and angles are all normal.

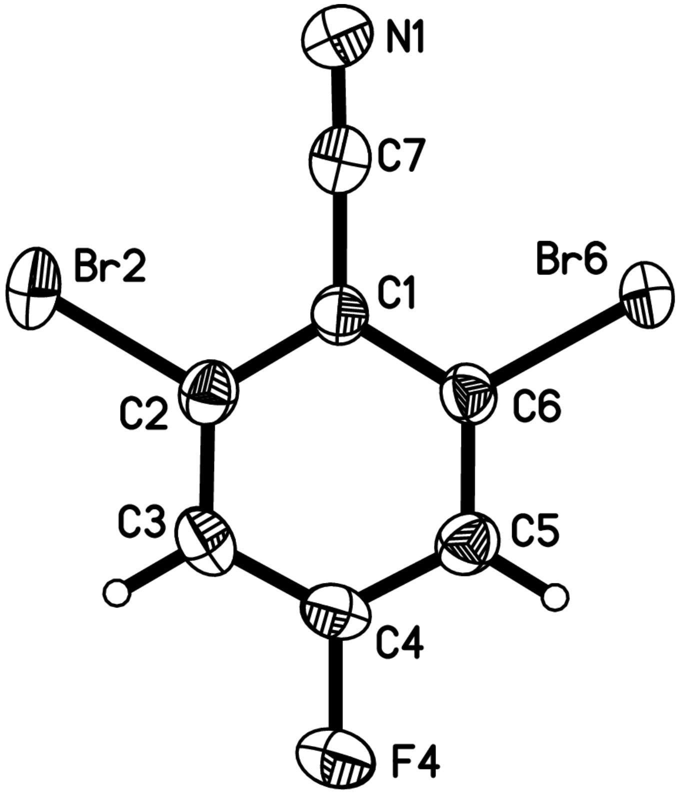


Figure 1
The $C_6H_2Br_2F(CN)$ molecule. Displacement ellipsoids are shown at the 50% probability level.

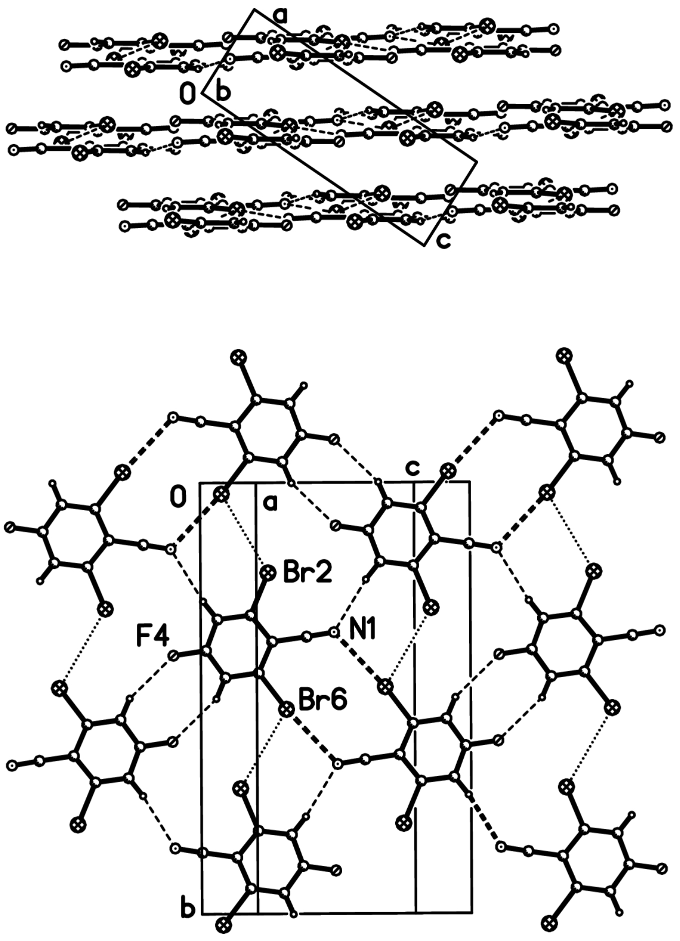


Figure 2
The packing of $C_6H_2Br_2F(CN)$. Top: view along *b*. Bottom: view normal to ($\bar{1}02$); only the central layer from the top view is shown. CN···Br interactions are shown with heavy dashes, N···H and F···H interactions are shown with light dashes, and Br···Br interactions are shown with dots.

The packing of the molecules in the crystal is shown in Fig. 2. The molecules lie in slightly puckered layers. The metric details of the N···Br and Br···Br contacts within the layer are given in Table 1, those for the H···N and H···F contacts in Table 2. With F in the 4-position, there is a short N···Br contact similar to those when Cl or Br is present, but the second N···Br contact is replaced by an H···N contact, that is, a C—H···N hydrogen bond. It appears that C—H···F hydrogen bonds are also present. Both of these weak hydrogen bonds would appear to be the consequence of the presence of the F atom increasing the fractional positive charge on both H atoms. For discussions of C—H···F interactions, see Howard *et al.* (1996), Dunitz & Taylor (1997) and Thalladi *et al.* (1998). For a more wide-ranging discussion of C—H···*X* interactions, see Desiraju & Steiner (1999).

Experimental

2,6-Dibromo-4-fluoroaniline (0.873 g, 3.25 mmol), prepared by bromination of 4-fluoroaniline in acetic acid (Pavlath & Olah, 1956), was added to concentrated HCl (26.25 ml, 322 mmol) and the mixture was stirred in an ice bath at 273 K. A solution of $NaNO_2$ (1.794 g, 26.0 mmol) in water (35 ml) was also cooled to 273 K and then added dropwise to the acidic aniline solution, which then changed from colorless to yellow with a precipitate. The supernatant solution gave a positive test with KI-starch paper. Then $KCu(CN)_2$ (4.024 g, 26.0 mmol) was added and the mixture turned dark green. The mixture was stirred for 2 h, then neutralized with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (13 × 20 ml). The organic extracts were combined, dried over anhydrous $MgSO_4$, gravity filtered, and the solvent was removed by rotary evaporation. The residue was purified on a silica-gel column using CH_2Cl_2, which eluted a green residue, shown by TLC with hexanes to contain three products. Rechromatography on silica gel using hexanes removed two of the three products. Elution with CH_2Cl_2 removed the third product (m.p. 376–377 K), which proved to be 2,6-dibromo-4-fluorobenzonitrile (0.052 g, 0.186 mmol, 6%). IR (CH_2Cl_2 film) 2348 cm^{-1}; ^1H NMR (acetone-d_6): δ 7.72 (*d*, J = 7.9 Hz, 2 H).

Crystal data

$C_7H_2Br_2FN$
$M_r = 278.92$
Monoclinic, $P2_1/c$
$a = 4.0352\ (10)$ Å
$b = 17.710\ (4)$ Å
$c = 11.007\ (3)$ Å
$\beta = 92.31\ (1)^\circ$
$V = 785.9\ (3)$ Å^3
$Z = 4$
$D_x = 2.357$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 904 reflections
$\theta = 3.0$–27.4°
$\mu = 10.26$ mm^{-1}
$T = 123\ (2)$ K
Prism, yellow
0.20 × 0.15 × 0.05 mm

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Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min} = 0.17$, $T_{\max} = 0.60$
6999 measured reflections
1792 independent reflections
1325 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.059$
$\theta_{\max} = 27.5°$
$h = -5 \rightarrow 5$
$k = -22 \rightarrow 23$
$l = -14 \rightarrow 13$
126 standard reflections
frequency: 600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.089$
$S = 0.95$
1792 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.94$ e Å^{-3}

Table 1

Distances and angles (Å,°) in the non-hydrogen $X\cdots Y$ contacts.

X	Y	C$X\cdots Y$	X···Y	$X\cdots$YC
N1	Br6$^{\rm i}$	123.1 (3)	3.110 (4)	173.3 (4)
Br6	Br2$^{\rm ii}$	112.9 (4)	3.827 (1)	125.7 (4)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 2

Intermolecular hydrogen contacts C—H$\cdots X$—C (Å,°).

H	X	C···H	H···X	C···X	C—H···X	H···X—C
H3	N1$^{\rm i}$	0.95	2.55	3.480 (5)	165	130
H5	F4$^{\rm ii}$	0.95	2.68	3.544 (5)	152	138

Symmetry codes: (i) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x - 1, 1 - y, -z$.

Both H atoms (H3 and H5) were placed in geometrically calculated positions and included in the refinement in the riding-model approximation, with $U_{\rm iso} = 1.2U_{\rm eq}$ of the carrier C atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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