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3,5-Difluorobenzonitrile

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Key indicators

Single-crystal X-ray study
T = 172 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.120
Data-to-parameter ratio = 13.3

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

The title compound, $C_7H_3F_2N$, packs with slightly puckered molecular sheets [molecules tilted by 8.1 (1)° with respect to the sheets]. Two of the H atoms in the molecule are in contact with N atoms in adjacent molecules, while the remaining H atom is in contact with two F atoms in adjacent molecules.

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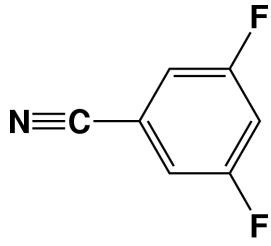
Comment

The melting point of 3,5-difluorobenzonitrile, (I), is 357–359 K, over 80 K higher than those of benzonitrile (260 K) and pentafluorobenzonitrile (275 K). This suggested that the solid compound might be a good place to look for C—H···F hydrogen bonds. The structure of (I) is reported here.



(I)

Fig. 1 shows the atom labeling. The bond lengths and angles are all normal. The ring angles at C1 and C3 are larger than 120° and those at C2 and C4 smaller, in reasonable agreement with the substituent effects described by Domenicano (1992).

The packing of the molecules is shown in Fig. 2. The molecules lie in a layer parallel to $(10\bar{2})$ and are tilted by 8.1 (1)° with respect to the layers. The perpendicular distance between molecules in adjacent layers is 3.434 (1) Å. Atoms H2 and H4 are in contact with N and F atoms in adjacent molecules. The metric details of these contacts are given in Table 1. In one sense, the arrangement is close to ideal; every H atom inter-

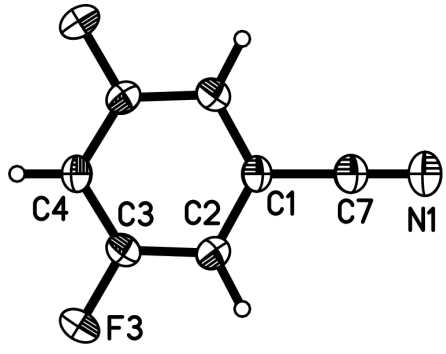


Figure 1
The title molecule, with displacement ellipsoids shown at the 50% probability level.

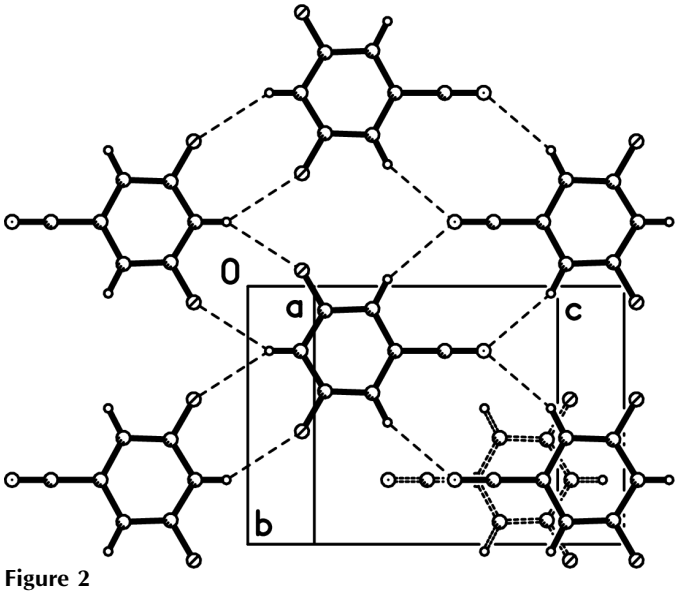


Figure 2
The packing in (I). The view is perpendicular to the molecular plane, 8.1° away from the overall plane, which is parallel to $(10\bar{2})$. The H···N and H···F contacts are shown as dashed lines. A molecule from the next layer is shown in the lower right hand corner.

acts with either an N or an F atom and every N and F atom interacts with an H atom. However, the H···*X* distances are about what would be expected for van der Waals contacts.

Recent reviews (Howard *et al.*, 1996; Dunitz & Taylor, 1997) have shown that short H···F distances are rare, even with good donor groups, such as OH and NH, and are extremely rare when the donor group is CH. On the other hand, Thalladi *et al.* (1998) have shown in the packing of fluorobenzenes that, even if the H···F contact distances are not especially short, the contacts are energetically strong enough to lead to packing patterns that are similar to those in compounds where the CH interacts with O or N atoms in adjacent molecules. The situation in 3,5-difluorobenzene appears to be similar to the results of Thalladi *et al.* (1998). Although the contact distances are, again, not especially short, they are energetically strong enough to lead to the unexpectedly high melting point.

Experimental

Crystal data

$C_7H_3F_2N$
M_r = 139.10
Monoclinic, $P2_1/m$
a = 3.730 (4) Å
b = 7.486 (4) Å
c = 11.019 (5) Å
β = 94.34 (7)°
V = 306.8 (4) Å^3
Z = 2
D_x = 1.506 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 22–27°
μ = 0.13 mm^{-1}
T = 172 (2) K
Prism, colorless
0.50 × 0.35 × 0.30 mm
Crystal source: commercial (Aldrich Chemical Co.)

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2908 measured reflections
784 independent reflections
654 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 27.9°
$h = -4 \rightarrow 4$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 70 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.120
S = 1.06
784 reflections
59 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.057P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Distances and angles (Å, °) in the C—H···*X*—C contacts.

H	*X*	C—H	C—H···*X*	H···*X*	H···*X*═C	C···*X*
H2	N1^{i}	0.97	151	2.65	134	3.523 (2)
H4	F3^{ii}	0.92	141	2.67	148	3.431 (3)
H4	F3^{iii}	0.92	141	2.67	148	3.431 (3)

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$; (iii) $-x, -1/2+y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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