2,6-Difluorobenzonitrile

Doyle Britton

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431, USA

Correspondence e-mail: britton@chem.umn.edu

2,6-Difluorobenzonitrile packs in slightly puckered molecular sheets (molecules tilted 4.1 (2)° with respect to the sheets). All of the H atoms in the molecule are in contact with N and F atoms in adjacent molecules in the sheet.

Key indicators

Single-crystal X-ray study
$T = 174$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.120
Data-to-parameter ratio = 11.0

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

Comment

3,5-Difluorobenzonitrile (Britton, 2002), hereafter 35D, crystallizes with layers of molecules in which $C-H\cdots N$ and $C-H\cdots F$ interactions play a significant role. The structure of the 2,6 isomer, (I), hereafter 26D, is reported here. Isomer 26D melts about 50 K lower than 35D (303–305 and 357–359 K, respectively), and the question of interest was the extent to which the $C-H\cdots N$ and $C-H\cdots F$ interactions differ.

(I)

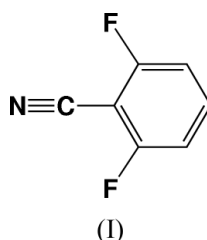Fig. 1 shows the atom labeling. The bond lengths and angles are all normal. The ring angles at atoms C2, C4 and C6 are larger than 120°, and those at C1, C3 and C5 are smaller, in reasonable agreement with the substituent effects described by Domenicano (1992).

The packing of the molecules is shown in Fig. 2. The molecules lie in layers parallel to (100) and are tilted 4.1 (2)° with respect to the layers. All three H atoms are in contact with N and F atoms in adjacent molecules in the layer. The metric details of these contacts are given in Table 1, where they are compared with similar contacts in 35D. As in 35D, the arrangement is close to ideal, in that every H atom interacts with either an N or an F atom, and every N and F atom interacts with an H atom. The $H\cdots X$ distances are about the same in both isomers and about what would be expected for
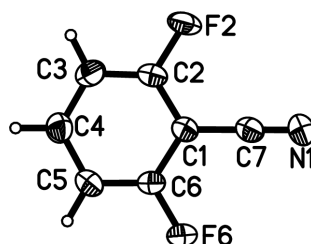
Figure 1
The $F_2H_3C_6CN$ molecule. Displacement ellipsoids are shown at the 50% probability level.
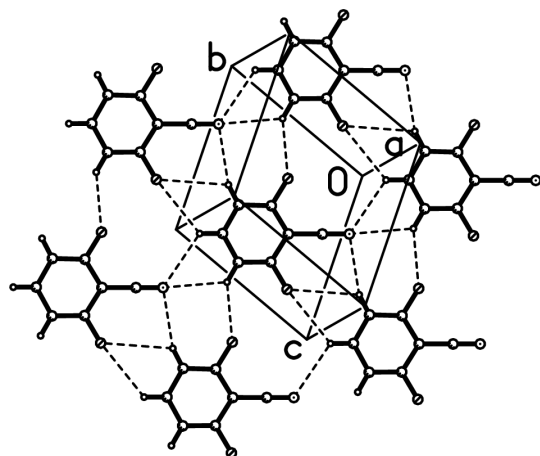
Figure 2
The packing in $F_2H_3C_6CN$. The view is perpendicular to the mean plane of the layer [parallel to (100), 4.1° away from the molecular plane]. The H···N and H···F contacts are shown as dashed lines.

van der Waals contacts. The H···F distances are also similar to those found by Thalladi *et al.* (1998) in the packing of fluorobenzenes.

With no particular differences in the H···X distances, the question now is why the melting points are so different. The molecular volumes are identical, within experimental error, 153.46 (6) and 153.4 (2) Å^3, respectively for 26D and 35D. However, the molecular areas differ by about 2% [48.98 (2) Å^2 for 26D and 48.03 (6) for 35D]. The average interlayer distances then differ in the opposite order, 3.131 (1) and 3.194 (4) Å. If the tilting of the molecules is ignored, the layers have $p1$ and $p2$ symmetry, respectively. The layer in 26D is polar with no CN···CN interactions. The next layer has the opposite polarity, which could account for the slightly shorter interlayer distance. The layer in 25D is non-polar with anti-parallel CN···NC interactions. It is possible that this difference in the CN interactions, rather than differences in the C—H···X interactions, accounts for the difference in the melting points.

Experimental

The compound was obtained from Lancaster Synthesis Inc. Crystals suitable for diffraction were grown by sublimation.

Crystal data

$C_7H_3F_2N$	$Z = 2$
$M_r = 139.10$	$D_x = 1.505$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.8164$ (17) Å	Cell parameters from 1641
$b = 7.2165$ (18) Å	reflections
$c = 7.2951$ (18) Å	$\theta = 3.2–27.4°$
$\alpha = 111.40$ (1)°	$\mu = 0.13$ mm^{-1}
$\beta = 104.57$ (1)°	$T = 174$ (2) K
$\gamma = 101.06$ (1)°	Block cut from needle, colorless
$V = 306.93$ (13) Å^3	$0.50 \times 0.50 \times 0.45$ mm

Data collection

Bruker SMART area-detector	1040 reflections with $I > 2\sigma(I)$
diffractometer	$R_{int} = 0.028$
ω scans	$\theta_{max} = 26.0°$
Absorption correction: none	$h = -8 \rightarrow 8$
1769 measured reflections	$k = -7 \rightarrow 8$
1144 independent reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.061P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.071P]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
1144 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
104 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXTL*
	Extinction coefficient: 1.22 (9)

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
26D						
H3	N1^i	0.95 (2)	160 (1)	2.63 (2)	99 (1)	3.537 (2)
H4	N1^{ii}	0.97 (2)	124 (1)	2.75 (2)	124 (1)	3.393 (2)
H5	N1^{ii}	0.97 (2)	125 (1)	2.71 (2)	175 (1)	3.352 (2)
H3	F6^i	0.95 (2)	122 (1)	3.07 (2)	125 (1)	3.659 (2)
H4	F6^i	0.97 (2)	128 (1)	2.95 (2)	170 (1)	3.624 (2)
H5	F2^{iii}	0.97 (2)	145 (1)	2.57 (2)	142 (1)	3.403 (2)
35D						
H2	N1	0.97 (2)	151 (1)	2.65 (2)	134 (1)	3.523 (2)
H4	F3	0.92 (2)	141 (1)	2.67 (2)	148 (1)	3.431 (3)
H4′	F3′	0.92 (2)	141 (1)	2.67 (2)	148 (1)	3.431 (3)

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

When the data collection was about 60% complete, the crystal shattered, indicating a phase change had taken place. Since there were enough data for an acceptable determination, another crystal was not used.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Britton, D. (2002). *Acta Cryst*, E**58**, o840–o841.
Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin USA.
Domenicano, A. (1992). *Accurate Molecular Structures*, edited by A. Domenicano & I. Hargittai, pp. 437–468. Oxford University Press.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1 Siemens Analytical X- ray Instruments Inc., Madison, Wisconsin, USA.
Thalladi, V. R., Weiss, H.-C., Bläser, D., Boese, R., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 8702–8710.