

2,4,6-Trifluorobenzonitrile

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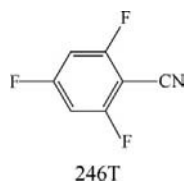
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The title compound, $C_7H_2F_3N$, contains three crystallographically independent molecules in the crystal structure; two of these molecules have symmetry m and the third has symmetry mm . Each independent molecule forms a planar or approximately planar layer with its own kind. There are three different types of interlayer contacts, two of which are similar to each other, while the third is distinctly different. The packing within the layers is similar to that found in 2,5- and 3,6-difluorobenzonitrile, with weak $C-H\cdots N$ interactions holding the molecules in the layers. The remarkable feature of this structure is the presence of more than one type of interlayer interaction.

Comment

3,5-Difluorobenzonitrile (hereafter 35D; Britton, 2002) and 2,6-difluorobenzonitrile (hereafter 26D; Britton, 2004) both pack in slightly puckered molecular sheets held together by weak $C-H\cdots N$ and very weak $C-H\cdots F$ hydrogen bonds. The structure determination of the title compound (hereafter 246T) was undertaken to see the effect of replacing one more H atoms with an F atom, with the expectation that the $C-H\cdots N$ interactions would be slightly stronger (shorter).



There are two half molecules and one quarter molecule in the asymmetric unit ($Z' = \frac{3}{4}$). Molecules 1 and 2 are normal to a mirror plane, and molecule 3 is on the intersection of two mirror planes. The Z value can be described, in the notation of Zorky (1996), as $20(m^2mm^1)$. The atom labeling and anisotropic displacement parameters for all three molecules are shown in Fig. 1. The bond lengths and angles are all normal. The ring angles at C11, C13 and analogous atoms are less than 120° , and those at C12, C14 and analogous atoms are greater,

in reasonable agreement with the substituent effects described by Domenicano (1992).

The molecules are arranged in layers normal to c . Each of the three types of molecules form layers with its own kind. The stacking of these layers is shown in Fig. 2; the unique layers are indicated by the labeling of the N atoms. Layer 3 is exactly planar. Molecules in layer 2 are tilted $2.9(1)^\circ$ away from parallel to layer 3. The N28 atoms are $2.862(3) \text{ \AA}$ from the plane of layer 3, and the F24 atoms are $3.181(2) \text{ \AA}$ away. A molecule in layer 1 is tilted $8.7(1)^\circ$ away from the plane of layer 3 and 11.6° away from the mean plane of a molecule in layer 2.

The molecules in the layers form $C-H\cdots N$ hydrogen bonds. The metric data for these bonds are given in Table 1, where they are compared with similar bonds in 35D and 26D. The $H\cdots N$ distances in molecules 2 and 3 are shorter than those in 35D and 26D, but the $H\cdots N$ distance in molecule 1 is not. This would appear to be a consequence of the deviation from planarity in the layer.

The stacking of the layers is shown in Fig. 3. The overlaps between layers 1 and 2 and between layers 2 and 3 are about

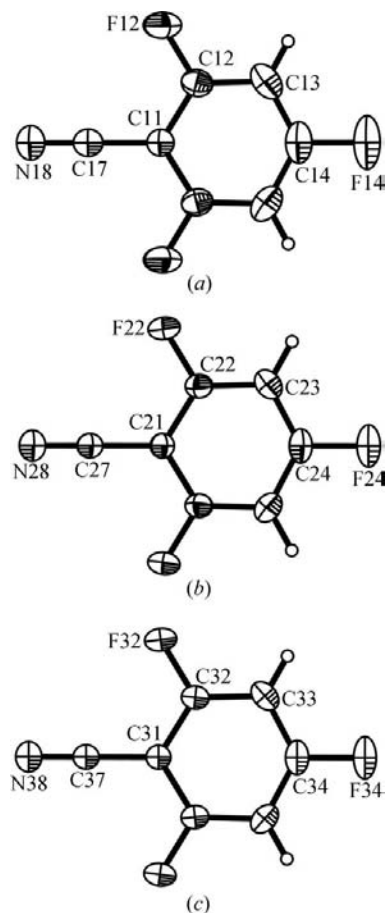


Figure 1

Individual views of the molecular structures of the three independent molecules of the title compound. All of the molecules contain a mirror plane perpendicular to the plane of the molecule; in (c) the molecule also lies on a mirror plane. Only the crystallographically independent atoms are labeled. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius.

the same, with no overlap between the rings and F atoms in one ring above the ring in the next layer. When layer 1

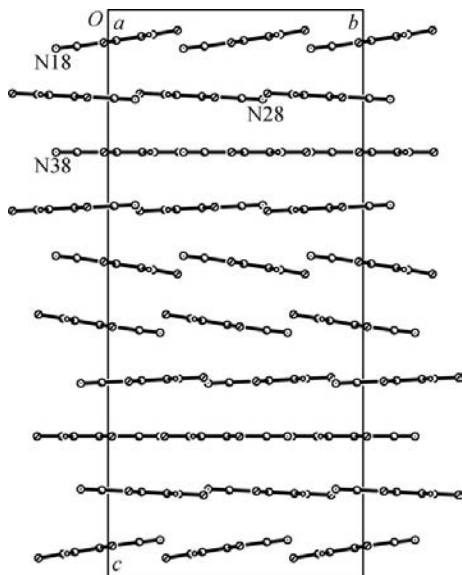


Figure 2
The crystal packing viewed along the *a* axis. One atom in each of the three independent layers is labeled.

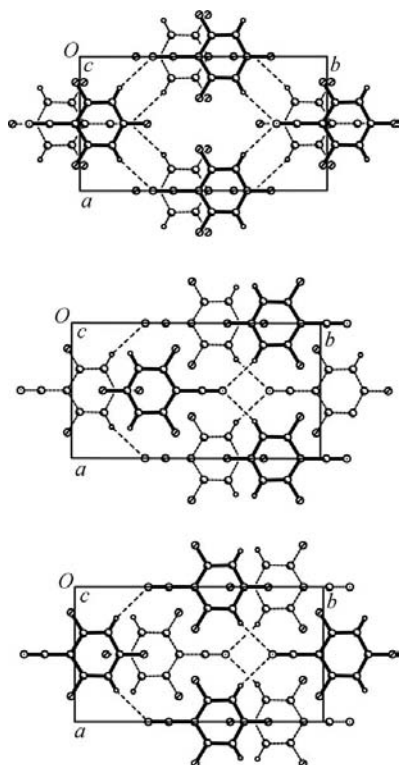


Figure 3
The layers and their interactions with adjacent layers. In every case, the C—H...N interactions are shown with dashed lines. Top: layer 1, shown with solid bonds, and layer 1', shown with dashed bonds, related to layer 1 by an inversion center at $(\frac{1}{2}, \frac{1}{2}, 0)$. Center: layer 2, shown with solid bonds, and layer 1, shown with dashed bonds. Bottom: layer 3, shown with solid bonds, and layer 2, shown with dashed bonds. Note that the overlap 1–1' is distinctly different from that of 2–1 and 3–2, which are similar to each other.

overlaps with layer 1', the rings do overlap, and the CN group in one molecule lies above the ring in the next layer. The two intralayer packing modes must have about the same energy, otherwise a structure with one of these modes exclusively ought to be favored.

Given the two distinctly different packing modes in the same structure, it seems likely that polymorphs might exist. Crystals were grown from acetone, benzene, CH₂Cl₂, CHCl₃, CCl₄ and acetonitrile. However, the crystals were all poor; in the two cases where a unit cell could be determined, it was the known cell.

Experimental

The title compound was obtained from Lancaster Synthesis Inc. Attempts were made to recrystallize the compound from a number of solvents but none gave acceptable crystals. Crystals from the original sample were used for the data collection.

Crystal data

$C_7H_2F_3N$	$V = 3198.0 (7) \text{ \AA}^3$
$M_r = 157.10$	$Z = 20$
Orthorhombic, $Cmcm$	Mo $K\alpha$ radiation
$a = 7.5228 (10) \text{ \AA}$	$\mu = 0.16 \text{ mm}^{-1}$
$b = 13.8222 (18) \text{ \AA}$	$T = 173 (2) \text{ K}$
$c = 30.755 (4) \text{ \AA}$	$0.5 \times 0.5 \times 0.4 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector diffractometer	18050 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003; Blessing, 1995)	2004 independent reflections
$T_{\min} = 0.93, T_{\max} = 0.94$	1721 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	165 parameters
$wR(F^2) = 0.127$	All H-atom parameters refined
$S = 1.12$	$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
2004 reflections	$\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$

Table 1

Distances and angles ($\text{\AA}, ^\circ$) in C—H...N≡C interactions.

Compound	H	N	C—H	C—H...N	H...N	H...N≡C	C...N
35D	H2	N1	0.967 (18)	151.4 (12)	2.645 (18)	134.2 (3)	3.523 (2)
26D	H3	N1	0.95 (2)	159.8 (16)	2.63 (2)	98.9 (4)	3.537 (2)
26D	H4	N1	0.97 (2)	124.5 (16)	2.75 (2)	124.2 (5)	3.393 (2)
26D	H5	N1	0.96 (2)	124.4 (17)	2.708 (18)	175.2 (5)	3.352 (2)
246T	H13	N18 ⁱ	0.905 (19)	151.5 (15)	2.663 (19)	131.8 (4)	3.484 (2)
246T	H23	N28 ⁱⁱ	0.970 (18)	161.0 (13)	2.468 (16)	135.7 (4)	3.3977 (19)
246T	H33	N38 ⁱ	0.91 (3)	164 (2)	2.50 (3)	135.7 (6)	3.385 (3)

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

The crystals had a strong tendency to twin. When a single crystal was eventually found, the solution and refinement were straightforward. The H-atom positions and isotropic displacement parameters were refined.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3002). Services for accessing these data are described at the back of the journal.

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