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***p*-Fluorobenzonitrile**

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**Abstract.**  $\text{FC}_6\text{H}_4\text{CN}$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 6.559$  (2),  $b = 12.191$  (3),  $c = 3.869$  (1) Å,  $\alpha = 96.18$  (2),  $\beta = 97.23$  (2),  $\gamma = 90.30$  (3)°,  $Z = 2$ , molecular volume  $152.5$  Å<sup>3</sup>,  $D_o = 1.32$  (floatation in aqueous KI solution),  $D_c = 1.319$  g cm<sup>-3</sup>. Least-squares refinement of diffractometer data (1364 independent reflections, including those with zero intensity) converged at a conventional  $R$  value of 0.084; for the 971 reflections with  $I > 2\sigma(I)$ ,  $R = 0.063$ . The molecule has  $mm2$  symmetry within experimental error; the bond lengths and angles are normal. The packing of the molecules closely resembles that in crystalline terephthalonitrile.

**Introduction.** As part of a study of intermolecular donor–acceptor interactions in crystals we are determining the structures of a variety of halobenzonitriles. When the halogen is Cl, Br or I, we expect to find a nitrile–halogen, donor–acceptor contact that is closer than the contact distance that would be predicted from the usual van der Waals radii. *p*-Iodobenzonitrile (Schlemper & Britton, 1965) and *p*-bromobenzonitrile (Britton, Konert & Lam, 1977) are examples of such a situation. When the halogen is F we would not expect such a contact since the F atom in a molecule is not an electron acceptor. We have determined the crystal structure of *p*-fluorobenzonitrile to see what, if any, unusual features occur in the packing.

*p*-Fluorobenzonitrile, from Aldrich Chemical Co., Inc., was sublimed to provide suitable crystals. A thick needle, elongated along  $c$ , was cut to an equant shape approximately 1 mm on each edge and sealed in epoxy cement to prevent loss of the crystal by sublimation (the melting point is 34°C). Data were collected at room temperature with a four-circle Hilger & Watts automatic diffractometer using Zr-filtered Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å). The cell dimensions were determined from the least-squares fit of 13 crystallographically independent planes. Intensity data were collected for 3406 reflections comprising the complete

Table 1. *Positional parameters* ( $\times 10^4$ )

	$x$	$y$	$z$
C(1)	2539 (2)	3383 (1)	2380 (3)
C(2)	4232 (2)	2757 (1)	1672 (4)
C(3)	4194 (3)	1643 (1)	1871 (5)
C(4)	2465 (3)	1171 (1)	2775 (4)
C(5)	777 (3)	1761 (1)	3487 (5)
C(6)	808 (2)	2878 (1)	3295 (4)
C(7)	2568 (2)	4554 (1)	2161 (4)
N	2583 (2)	5482 (1)	1981 (4)
F	2445 (2)	64 (1)	2975 (4)
H(2)	5391 (27)	3140 (14)	1152 (39)
H(3)	5272 (29)	1184 (13)	1349 (40)
H(5)	-453 (34)	1379 (16)	3909 (48)
H(6)	-300 (27)	3304 (14)	3747 (37)

sphere of reciprocal space out to  $\theta = 27.5^\circ$  plus some duplication. The intensities of two check reflections were measured every 30 reflections; these intensities drifted down and back up by about 10% over the course of the data collection, presumably owing to a drift in the X-ray power supply. These slow fluctuations were corrected for in the subsequent treatment of the data. Equivalent reflections were combined as described previously (Britton, 1974), except that 0.05  $I$  was used rather than 0.04  $I$  in the expression for  $\sigma_1(I)$ , and  $\sigma(I) = \sigma_1(I)$  only was used. All reflections were

used in the subsequent refinement except for the 15 most intense, which appeared to suffer from extinction. Those 112 reflections for which  $I$  was apparently negative were given zero intensity for the refinement. A trial structure was found from Patterson and Fourier maps and refined by full-matrix least squares with anisotropic thermal parameters for the C, N and F atoms, and isotropic thermal parameters for the H atoms. For details of the experimental arrangement and for the calculations and programs used see Chow & Britton (1974). The final positional parameters are given in Table 1.\* A final difference Fourier map was essentially featureless; the greatest excursions from zero were +0.14 and -0.12 e  $\text{\AA}^{-3}$ .

Table 2. Bond lengths ( $\text{\AA}$ )

	Uncorrected	Corrected for rigid-body motion
C(1)–C(2)	1.390 (2)	1.400
C(2)–C(3)	1.370 (2)	1.377
C(3)–C(4)	1.369 (3)	1.378
C(4)–C(5)	1.364 (3)	1.375
C(5)–C(6)	1.372 (2)	1.379
C(6)–C(1)	1.390 (2)	1.400
C(1)–C(7)	1.439 (2)	1.445
C(7)–N	1.141 (2)	1.143
C(4)–F	1.360 (2)	1.364

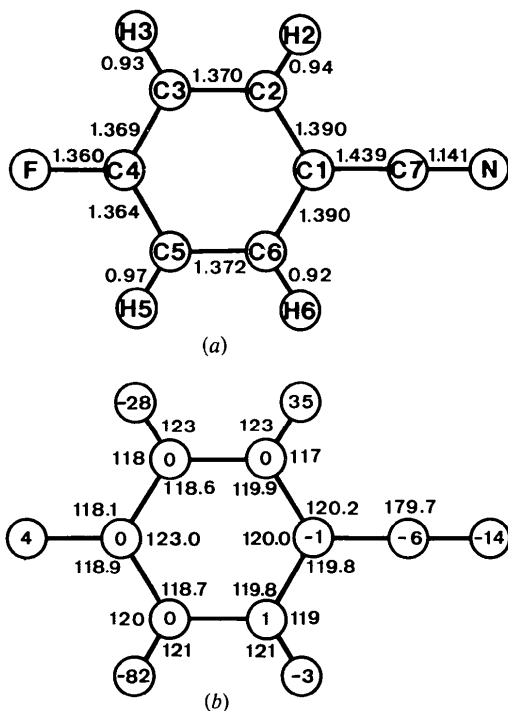


Fig. 1. (a) Bond lengths ( $\text{\AA}$ ) and labelling of the atoms in *p*-fluorobenzonitrile. The e.s.d.'s are 0.02  $\text{\AA}$  for the C–H bond lengths and 0.002–0.003  $\text{\AA}$  for all others. (b) Bond angles ( $^\circ$ ) and deviations from planarity. The e.s.d.'s are  $1^\circ$  for the C–C–H bond angles and 0.2 $^\circ$  for all others. The deviations (in units of 0.001  $\text{\AA}$ ) from the best plane through the ring atoms are given inside the circles.

**Discussion.** The bond distances and angles are given in Fig. 1. A rigid-body analysis was made using the method of Schomaker & Trueblood (1968); the r.m.s. difference between the observed  $B_{ij}$  and those calculated from the rigid-body model is 0.23  $\text{\AA}^2$ . The corrected and uncorrected bond distances are compared in Table 2. The bond distances are all normal within experimental error. The internal angle in the benzene ring opposite the F atom is the largest ring angle and those opposite the H atoms are the smallest, in keeping with the electronegativities of the substituents.

$B_{11}$  and  $B_{33}$  are large for the F atom, 10.1 and 13.1  $\text{\AA}^2$ , respectively, compared with 5–7  $\text{\AA}^2$  for most of the other  $B_{ij}$ . This seems consistent with the packing, however, since the  $a$  and  $c$  distances are determined in part by the contacts between antiparallel CN groups. Owing to the larger sizes of the C and N atoms these contacts leave the F atoms at the other end of the molecules slightly too far apart for good contact. Thus, the F end of each molecule is more free to vibrate in the crystal.

Also shown in Fig. 1 are the deviations from the best plane through the ring atoms. If we give the deviations full credence, the F atom is bent out of the plane of the ring by 0.2 $^\circ$  and the nitrile group by 0.3 $^\circ$ . However, it would require data at higher angles, which in turn would require lower temperatures, to establish this bending beyond question. Both the bending and the uncertainty are similar to those in terephthalonitrile (van Rij & Britton, 1977).

Indeed, the entire crystal structure is similar to that of terephthalonitrile. The packing is shown in Fig. 2; the similarity will be immediately apparent if this figure is compared with the corresponding figure for terephthalonitrile (van Rij & Britton, 1977). In *p*-fluorobenzonitrile the molecules are all parallel or antiparallel to each

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32907 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the authors.

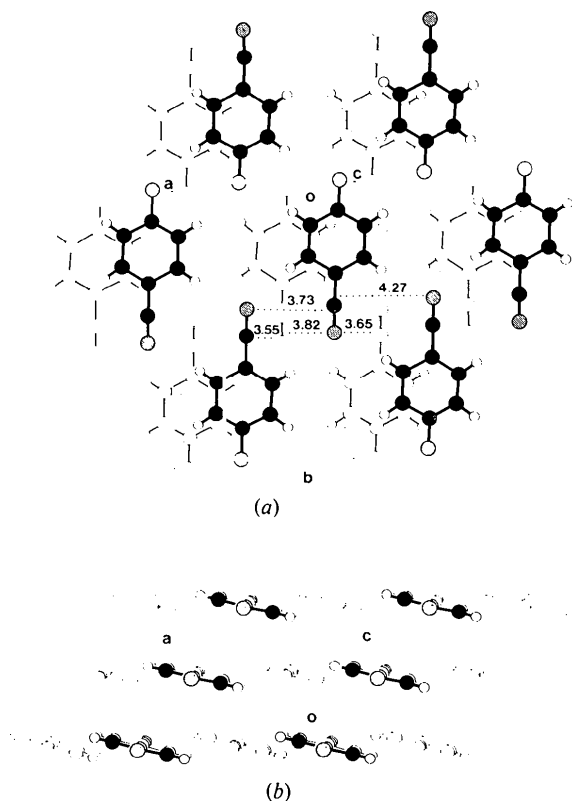


Fig. 2. The packing of *p*-fluorobenzonitrile. (a) View perpendicular to (101). (b) View along **b**. The perpendicular distances (in Å) are shown between some of the parallel and antiparallel nitrile groups.

other and occur in layers that are parallel to (101); the layers are 3.12 Å apart [3.10 Å in *p*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub>]. The individual molecules are tilted 14° out of the plane of the layers [14° in *p*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub>]; the perpendicular distance between molecules is 3.54 Å [3.49 Å in *p*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub>].

In view of the similarity between the two structures the melting point of *p*-FC<sub>6</sub>H<sub>4</sub>CN seems low. If we compare the melting points of *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (−13°C) and *p*-C<sub>6</sub>H<sub>2</sub>F<sub>4</sub> (4°C) with those of *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (−34°C) and *o*-C<sub>6</sub>H<sub>2</sub>F<sub>4</sub> (−42°C), it would appear that the reduction in symmetry from *mmm* to *mm2* is accompanied by a

decrease in the melting point of 20–50°C. If we average the melting points of *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (4°C) and *p*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub> (222°C) and subtract 20–50°C, we predict a melting point for *p*-FC<sub>6</sub>H<sub>4</sub>CN of between 65 and 95°C, compared with the 34°C that is observed. While the comparison is crude it does suggest that a detailed study of the crystal energies of these compounds would be of interest.

In *p*-iodobenzonitrile (Schlemper & Britton, 1965) the C≡N...I arrangement is linear with an N...I distance 0.5 Å less than would be predicted from the van der Waals radii of N and I. In *p*-bromobenzonitrile (Britton, Konnert & Lam, 1977) the C≡N...Br angle is 169°, apparently distorted from 180° by packing forces, and the N...Br distance is 0.2 Å less than would be predicted from the van der Waals radii of N and Br. As we expected, there is no short N...F distance in *p*-fluorobenzonitrile. It is slightly surprising, however, to find that there is no N...F contact at all. In order that the antiparallel nitrile–nitrile contacts can occur in the same manner as in terephthalonitrile, the sideways and endways dipole–dipole interactions between adjacent molecules are all unfavorable. This presumably contributes to the low melting point suggested in the previous paragraph.

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