[4-(Trifluoromethyl)phenyl]aceto-nitrile

Stepan Boitsov, Jon Songstad and Karl W. Törnroos*

Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway
Correspondence e-mail: karl.tornroos@kj.uib.no

The crystal structure of the title compound, $C_9H_6F_3N$, at 123 K contains molecules linked together via several C—H···F and C—H···N contacts, the strongest of which are 2.58 and 2.65 Å, respectively. Apparently, an F atom in the CF_3 group is able to compete with a cyano N atom for aromatic H atoms but is less prone to interact with the more acidic methylene H atoms. The Ph–CH_2CN torsion angle is $-6.4\,(2)°$ and the planar phenyl ring exhibits a typical deformation of the endo angles at the ipso-C atoms, due to the difference in the electron-withdrawing power of the CF_3 and CH_2CN substituents.

Comment

The molecular structure of 4-(trifluoromethyl)benzonitrile, (I) (Boitsov et al., 2002), has revealed that the molecules are closely packed due to several intermolecular F···H and N···H contacts. A comparison between the F···H contacts (2.50 Å), the N···H contacts (2.56 and 2.59 Å) and the sums of the van der Waals radii (2.67 Å for F···H and 2.75 Å for N···H) indicated that one of the F atoms, located close to the phenyl-ring plane, could readily compete with the cyano N atoms for the H atoms, even though the N···H distances are shorter than in either benzonitrile (2.67 Å; Fauvet et al., 1978) or 1,4-dicyanobenzene (2.61 Å; Colapietro et al., 1984). The F···H interactions (Desiraju & Steiner, 1999) in (I), however, were not sufficiently strong to alter significantly any of the structural parameters of the C—CF_3 fragment (Schultz et al., 1981; Kovacs et al., 1996) of the molecule, but are the probable cause of the fairly high melting point of the compound compared with that of 4-methylbenzonitrile. Furthermore, the close packing of 4-(trifluoromethyl)benzonitrile, (I), gives rise to a relatively high crystal density of 1.550 Mg m^{-3}.

(II)
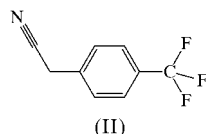
It has been suggested that the strength of F···H interactions may be related to both the acidity of the H atom involved

(Thalladi et al., 1998) and the hybridization of the C atom to which it is bonded (Desiraju & Steiner, 1999). We report herein the molecular structure of [4-(trifluoromethyl)-phenyl]acetonitrile, (II), a compound which contains H atoms linked to both sp^2- and sp^3-hybridized C atoms (Fig. 1). This compound melts at 321 K, significantly higher than the melting point of 4-methylphenylacetonitrile (293 K).

It is clear that the packing structure (Fig. 2) does not resemble reported structures of aryl cyanides, which are based upon parallel layers linked together by antiparallel contacts
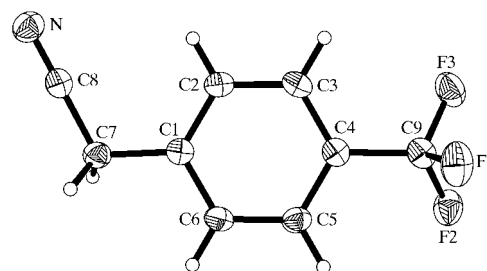

Figure 1
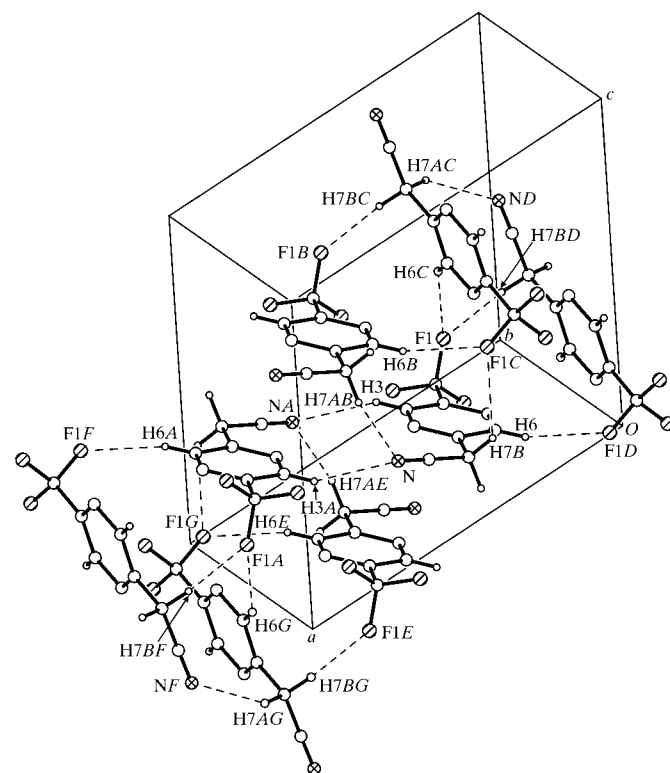The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level.

Figure 2
The packing structure of (II) with a [101] sheet centred around the inversion centre at $(\frac{1}{2}, 1, 0)$. The weak F1···H7B contacts have been included. H atoms (H2 and H5) not participating in hydrogen bonding have been omitted. Atoms labelled with the suffix A lie at positions $(1 - x, 2 - y, -z)$, B at $(x, 1 + y, z)$, C at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, D at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, E at $(1 - x, 1 - y, -z)$, F at $(\frac{1}{2} + x, \frac{5}{2} - y, -\frac{1}{2} + z)$ and G at $(\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$.

organic compounds

between neighbouring cyano groups (Colapietro *et al.*, 1984) or on CH₂···Ar(H···π), CN···Ar (Bond *et al.*, 2001) or Ar···Ar interactions. Molecules of (II) are linked together through four unique contacts (see Table 2), of which three are clearly shorter than the sum of the van der Waals radii (2.67 Å for F···H and 2.75 Å for N···H; Bondi, 1964), *i.e.* F1···H6, N···H7A and N···H3, the fourth, F1···H7B, being a borderline contact, 2.67 Å. The relatively small intermolecular bond angles, 123–146°, are typical for these types of hydrogen-bond interactions, as presented in scatterplots of H···F distances *versus* C—H···F angles by Thalladi *et al.* (1998).

The N···H7A intermolecular contacts connect the molecules into columns along [010] and the N···H3 contacts join two molecules related by an inversion centre. These are further connected *via* F1···H6, and possibly also F1···H7B, contacts into sheets propagating along [101]. As in the structure of 4-(trifluoromethyl)benzonitrile (Boitsov *et al.*, 2002), the N atom participates in bifurcated intermolecular hydrogen-bond interactions. It seems that an F atom (F1) is able to compete with the cyano N atom for the aromatic H atoms but does not favour interactions with the more acidic methylene H atoms (Bordwell, 1988). The shortest distances between the sheets are F2···H3(x, −1 + y, z) and F3···H6($\frac{1}{2}$ + x, $\frac{1}{2}$ − y, $\frac{1}{2}$ + z) of 2.74 and 2.72 Å, respectively. There are no overlaps between the rings in the crystal, and the shortest distance between rings is C5···H5($\frac{1}{2}$ − x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z) of 2.89 Å [ΣvdW(C+H) is 2.90 Å], with the two rings related by an angle of about 99°, as measured over H5—C5···H5.

All bond lengths and angles listed in Table 1 are, in principle, as expected. The *endo* angles C2—C1—C6 and C3—C4—C5 reflect the difference in electron-withdrawing power of the substituents CF₃ and CH₂CN (Colapietro *et al.*, 1984), *cf.* the Hammett σ_p values of −0.54 (CF₃) and ∼−0.2 (CH₂CN), the latter derived from −0.66 (CN) assuming a transmission coefficient of ∼0.3 for a CH₂ group (Hine, 1962).

The phenyl ring is planar within experimental error and is otherwise symmetrical with respect to the bond lengths and angles. The C9—F1 bond, involved in a weak intermolecular interaction with H6, and possibly also H7B, is slightly longer than F2—C9 and F3—C9; *cf.* the suggested elongation of one of the C—F bonds in 2-(trifluoromethyl)phenol (Kovacs *et al.*, 1996). Furthermore, the F1—C9—C4 bond angle is smaller than those of F2—C9—C4 and F3—C9—C4. The two *exo* bond angles around C1 are distinctly different, indicating the effect of the proximity of the CH₂CN group to the plane of the ring; the C2—C1—C7—C8 torsion angle is −6.4 (2)°. [The Cambridge Structural Database (Version 5.21; Allen & Kennard, 1993) presently contains some 30 crystal structures of arylacetonitriles; however, no particular range of torsion angles seems to be favoured.] Similarly, the two *exo* angles around C4 differ, likely due to F3 being closer to the plane of the ring than F2. The distances (Å) of the non-aromatic atoms from the plane of the phenyl ring are as follows: F1 −1.284 (2), F2 0.686 (2), F3 0.429 (2), C7 0.054 (2), C8 −0.055 (2), C9 −0.031 (2) and N −0.150 (3). The pertinent torsion angles are given in Table 1.

Experimental

Crystal data

$C_9H_6F_3N$	$D_x = 1.535$ Mg m⁻³
$M_r = 185.15$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4798
$a = 11.9085$ (15) Å	reflections
$b = 5.5168$ (7) Å	$\theta = 2.3$–28.2°
$c = 12.2376$ (15) Å	$\mu = 0.14$ mm⁻¹
$\beta = 94.67$ (3)°	$T = 123$ (2) K
$V = 801.30$ (17) Å³	Needle, colourless
$Z = 4$	$0.55 \times 0.12 \times 0.10$ mm

Data collection

Bruker AXS SMART 2K CCD diffractometer	1541 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.044$
Absorption correction: numerical (*SHELXTL/PC*; Sheldrick, 2001*a*)	$\theta_{max} = 28.3°$
	$h = -15 \rightarrow 15$
	$k = -7 \rightarrow 7$
$T_{min} = 0.937$, $T_{max} = 0.991$	$l = -16 \rightarrow 16$
11 234 measured reflections	149 standard reflections
1984 independent reflections	intensity decay: none

Table 1
Selected geometric parameters (Å, °).

F1—C9	1.3478 (15)	C2—C3	1.3902 (19)
F2—C9	1.3416 (18)	C3—C4	1.3824 (19)
F3—C9	1.3388 (16)	C4—C5	1.3896 (18)
N—C8	1.1415 (18)	C4—C9	1.4953 (18)
C1—C2	1.3865 (18)	C5—C6	1.3842 (18)
C1—C6	1.3907 (18)	C7—C8	1.4636 (19)
C1—C7	1.5179 (19)		
C2—C1—C6	119.28 (12)	N—C8—C7	179.49 (15)
C2—C1—C7	122.93 (12)	F2—C9—F1	105.52 (12)
C6—C1—C7	117.78 (11)	F3—C9—F1	106.28 (11)
C3—C4—C5	120.43 (12)	F3—C9—F2	106.51 (11)
C3—C4—C9	120.17 (12)	F1—C9—C4	111.86 (11)
C5—C4—C9	119.36 (13)	F2—C9—C4	113.15 (11)
C8—C7—C1	114.81 (11)	F3—C9—C4	112.96 (12)
C2—C1—C7—C8	−6.39 (19)	C3—C4—C9—F3	−23.73 (17)
C3—C4—C9—F1	96.13 (15)	C5—C4—C9—F2	37.26 (16)
C3—C4—C9—F2	−144.86 (12)		

Table 2
Short intermolecular distances and associated bond angles (Å, °).

C—H···A	C—H	H···A	C···A	C—H···A
C3—H3···N^i	0.95	2.70	3.417 (2)	133
C6—H6···F1^{ii}	0.95	2.58	3.376 (2)	141
C7—H7A···N^{iii}	0.99	2.65	3.512 (2)	146
C7—H7B···F1^{iv}	0.99	2.67	3.315 (2)	123

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.125$
$S = 1.00$
1984 reflections
118 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

The H atoms were treated as riding, with C—H(CH) and C—H(CH$_2$) distances of 0.95 and 0.99 Å, respectively. The isotropic displacement parameters of the H atoms were fixed at $1.2U_{eq}$ of their parent atoms. The maximum residual peak is located on the C4—C5 bond, 0.68 Å from C4.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2001*b*); molecular graphics: *SHELXTL/PC* (Sheldrick, 2001*a*); software used to prepare material for publication: *SHELXTL/PC* and *PLATON* (Spek, 2001).

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