Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-(Trifluoromethyl)benzonitrile

Stepan Boitsov, Jon Songstad and Karl W. Törnroos*

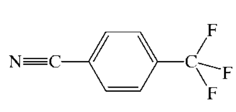
Department of Chemistry, University of Bergen, Allégaten 41, 5007 Bergen, Norway
Correspondence e-mail: karl.tornroos@kj.uib.no

Received 8 November 2001
Accepted 14 November 2001
Online 16 January 2002

4-(Trifluoromethyl)benzonitrile, $C_8H_4F_3N$, at 123 K contains molecules linked together through one C—H···F bond and two C—H···N hydrogen bonds into sheets that are further crosslinked to form a dense two-dimensional network without $\pi\cdots\pi$ ring interactions. The aromatic ring is slightly deformed due to the two *para*-related electronegative groups.

Comment

Most aromatic compounds which contain a trifluoromethyl group are known to have higher melting points, in some cases significantly higher, than the corresponding methyl-substituted compounds. The latter, however, despite their lower molecular weight, generally have higher boiling points. Apparently, forces exist in the crystalline state between molecules containing a CF_3 group which are stronger than in the corresponding methyl-substituted compounds, but which are absent in the liquid state. Intermolecular C—H···F—C contacts are known to be rather weak and are only infrequently reported. However, the structures of several fluoro-substituted aromatic compounds have been published by Thalladi *et al.* (1998). Furthermore, the presence of such contacts has repeatedly been suggested to be the cause of the preferential *gauche* conformation of 2-fluoroethanol and related compounds (Huang & Hedberg, 1989; Dixon & Smart, 1991). A contradicting view, however, has been forwarded by Bakke *et al.* (1994) and the ability of 2,4-difluorotoluene to act as both a hydrogen-bond donor and acceptor has been the subject of some controversy (Evans & Seddon, 1997). Detailed discussions on F···H interactions have recently been published (Shimoni *et al.*, 1994, 1995; Howard *et al.*, 1996; Plenio, 1997; Desiraju & Steiner, 1999; Hiyama, 2000). The present work on the title compound, (I), provides evidence in support of the presence of such contacts.



(I)

The molecular structure of (I) is shown in Fig. 1, and the bond lengths and angles are listed in Table 1. The two *ipso* bond angles at C1 and C4 are, as expected, larger than 120° but are also equal, reflecting the rather similar Hammett σ_p values of the two polar substituents, −0.66 (CN) and −0.54 (CF_3) (Hine, 1962). The C1—C2 and C1—C6 bonds are only slightly longer than the remaining four C—C bonds. The C2—C3 and C5—C6 bonds are not significantly shortened, as anticipated for a compound containing two electronegative substituents *para* to each other (Colapietro *et al.*, 1984). The C7—C1—C2 and C7—C1—C6 bond angles are equal, but the cyano group is bent out of the plane of the aromatic ring, atoms C7 and N deviating by −0.0165 (17) and −0.033 (2) Å, respectively. The trifluoromethyl C8 atom does not depart from the ring plane but is slightly tilted towards atom C3. The C4—C8—F and C—F—C bond angles, as well as the C—F bond lengths, are essentially equal and as expected (Schultz *et al.*, 1981).

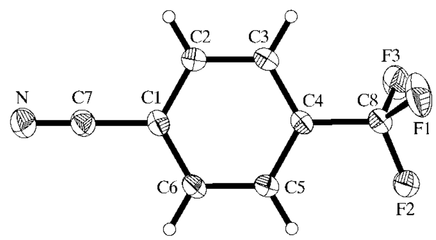


Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

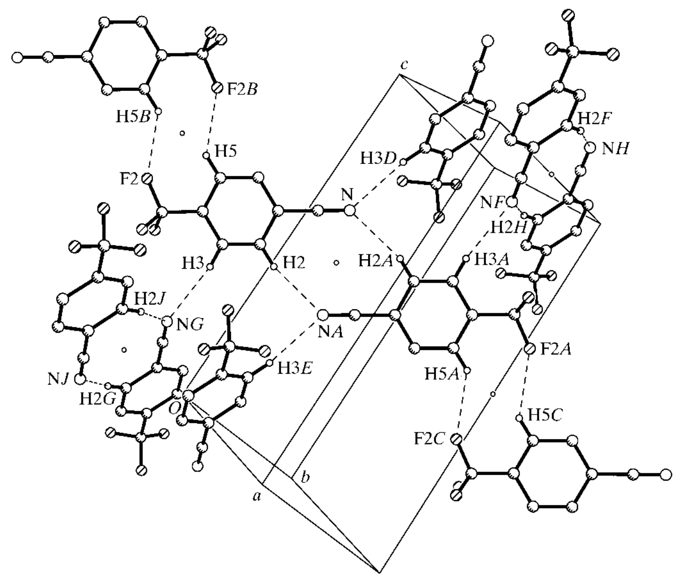


Figure 2
The packing structure of (I) with a ten-membered hydrogen-bonded ring of a [2$\bar{1}$0] sheet centred around the inversion centre at ($\frac{1}{2}$,0,$\frac{1}{2}$) (all $\bar{1}$ are indicated with small circles) and crosslinked along [001] with two [$\bar{2}$10] sheets. H atoms not participating in the hydrogen bonding have been omitted. Atoms labelled with the suffix *A* lie at positions ($1-x, -y, 1-z$), *B* at ($-x, -2-y, 1-z$), *C* at ($1+x, 2+y, z$), *D* at ($x+\frac{1}{2}, -y-\frac{1}{2}, z+\frac{1}{2}$), *E* at ($\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$), *F* at ($\frac{3}{2}-x, y+\frac{1}{2}, \frac{3}{2}-z$), *G* at ($x-\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$), *H* at ($x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$) and *J* at ($\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$).

  DOI: 10.1107/S0108270101019540

Atoms F1 and F3 are located *gauche* to the plane of the phenyl ring, with C3—C4—C8—F torsion angles of 67.91 (12) and −51.71 (13)°, respectively, whereas atom F2 lies close to the phenyl ring plane at a distance of −0.1812 (18) Å, with an F2—C8—C4—C3 torsion angle of −171.86 (9)°. As a result, the intramolecular F2···H5 distance is fairly small (2.40 Å), but the C4—C8—F2 bond angle and the geometry around atom C5 do not suggest any interaction (Sheppard, 1965).

The aromatic ring itself is essentially planar, but a slight tendency towards a boat conformation can be detected, as atoms C1 and C4 depart from the plane by −0.0055 (7) and −0.0051 (7) Å, respectively.

An approximate view of the molecular interactions down [110] is given in Fig. 2, and the intermolecular bond distances and angles are summarized in Table 2. The intermolecular bonds connect the molecules into sheets alternating between directions [$\bar{2}$10] and [2$\bar{1}$0] along [001]. Within the sheets, there are two types of centrosymmetric ten-membered rings, the first created through N···H2 and H2···N intermolecular bonds, the second through F2···H5 and H5···F2 intermolecular bonds. The N atom becomes bifurcated, as a second hydrogen bond crosslinks the sheets along [001] *via* alternating N···H3 and H3···N bonds. The N atom deviates by −0.046 (1) Å from the plane formed by atoms C7, H2($3-x$, $2-y$, $1-z$) and H3($\frac{1}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$). The angle formed with the aromatic ring plane is 17.86 (5)°.

There are two types of stacking arrangements within the sheets involving three ring layers, *A* (x, y, z), *B* ($2-x, 1-y, 1-z$) and *C* ($3-x, 1-y, 1-z$). In the first type, the antiparallel rings in *A* and *B* are shifted in relation to one another by about one ring radius normal to the C7···C8 vector. The ring centroid-to-centroid distance, $Cg_A\cdots Cg_B$, is 4.00 (3) Å. Whereas the smallest distance between ring atoms is 3.618 (2) Å for $C6_A\cdots C4_B$, the overall shortest stacking distance in the structure occurs between these layers for $F2_A\cdots C7_B$, at 3.427 (2) Å.

The second arrangement relates the antiparallel rings in layers *B* and *C*, which are shifted by about one ring diameter parallel to the C7···C8 vector. Consequently, the $Cg_B\cdots Cg_C$ distance is longer, at 4.84 (3) Å. The shortest distances between rings in layers *B* and *C* are 3.521 (3) and 3.581 (2) Å for $C1_B\cdots C1_C$ and $C4_B\cdots N_C$, respectively. Hence, there is no π–π stacking overlap between the aromatic rings in the structure of (I).

Due to the numerous contacts which are slightly but significantly smaller than the sum of the van der Waals radii (2.67 and 2.75 Å for F···H and N···H, respectively; Bondi, 1964), the molecules are closely packed, resulting in a crystal density of 1.5497 (2) Mg m^{-3}, higher than for *e.g.* 1,4-dicyanobenzene (1.285 Mg m^{-3}; Colapietro *et al.*, 1984). The latter structure also exhibits a bifurcated N atom but with longer N···H distances, of 2.61 and 2.72 Å. Instead, the molecules are linked through antiparallel contacts between neighbouring cyano groups, with a shortest N···N distance of 3.65 Å. No such short interactions appear in the packing structure of (I), the shortest N···N($3-x$, $2-y$, $1-z$) contact being 3.887 (2) Å.

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.3978 (13)	C4—C8	1.5050 (13)
C1—C6	1.3975 (14)	C5—C6	1.3911 (14)
C1—C7	1.4500 (13)	C7—N	1.1482 (14)
C2—C3	1.3902 (14)	C8—F1	1.3388 (13)
C3—C4	1.3935 (14)	C8—F2	1.3390 (12)
C4—C5	1.3922 (13)	C8—F3	1.3370 (12)
C2—C1—C6	121.10 (9)	C1—C6—C5	119.14 (9)
C2—C1—C7	119.35 (9)	N—C7—C1	179.59 (12)
C6—C1—C7	119.54 (9)	F1—C8—F2	106.41 (9)
C1—C2—C3	119.47 (9)	F1—C8—F3	106.23 (8)
C2—C3—C4	119.36 (9)	F2—C8—F3	106.41 (9)
C3—C4—C4	121.23 (9)	F1—C8—C4	112.33 (9)
C3—C4—C8	118.52 (8)	F2—C8—C4	112.74 (8)
C5—C4—C8	120.25 (9)	F3—C8—C4	112.22 (8)
C4—C5—C6	119.69 (9)		

Table 2
Geometry of short contacts (Å,°).

ΣvdW(H+*A*) is the sum of the van der Waals radii for H and *A*.

C—H···*A*	C—H	H···*A*	ΣvdW(H+*A*)	C···*A*	C—H···*A*
C2—H2···N^{i}	0.95	2.56	2.75	3.4603 (15)	158
C3—H3···N^{ii}	0.95	2.59	2.75	3.5263 (14)	170
C5—H5···F2^{iii}	0.95	2.50	2.67	3.2706 (12)	138

Symmetry codes: (i) $3-x, 2-y, 1-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $2-x, -y, 1-z$.

Experimental

4-(Trifluoromethyl)benzonitrile (Aldrich, 99%, m.p. 312–314 K) was dissolved in a minimum amount of cyclohexane at room temperature. After filtration, a similar volume of hexane was added and the solution was left at 275 K overnight, yielding crystals of (I) suitable for X-ray analysis.

Crystal data

$C_8H_4F_3N$
M_r = 171.12
Monoclinic, $P2_1/n$
a = 8.2189 (6) Å
b = 6.0621 (3) Å
c = 15.0977 (10) Å
β = 102.835 (3)°
V = 733.43 (8) Å^3
Z = 4
D_x = 1.550 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 4972 reflections
θ = 2.6–31.5°
μ = 0.15 mm^{-1}
T = 123 (2) K
Block, colourless
0.45 × 0.33 × 0.25 mm

Data collection

Bruker SMART 2K CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997*a*)
T_{min} = 0.947, T_{max} = 0.988
12 772 measured reflections
2417 independent reflections
1835 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 31.5°
$h = -12 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.115
S = 1.08
2417 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.0443P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

H atoms were refined as riding, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). 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, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Sheldrick, 1997*a*); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1086). Services for accessing these data are described at the back of the journal.

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