Perfluorinated 6-isopropyl-2,4,5-trimethyl-benzonitrile

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.057
wR factor = 0.134
Data-to-parameter ratio = 12.5

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

In the title compound, 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzonitrile, $C_{13}F_{17}N$, the benzene ring is puckered due to steric repulsion between substituents.

Comment

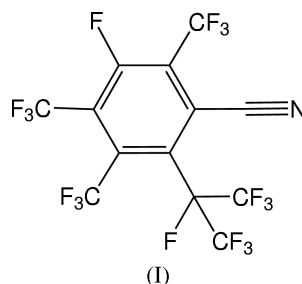The title compound, (I), was obtained as a by-product during our studies concerning fluoride-ion induced perfluoro-alkylation reactions of highly fluorinated aromatic systems (Chambers & Sargent, 1981; Brooke, 1997; Richmond, 2001).

(I)

The molecule of (I) (Fig. 1) is sterically overcrowded, resulting in some very short intramolecular non-bonded distances, *viz*. F1···F2 = 2.467 (4) Å, F1···F8 = 2.503 (4) Å, F6···F10 = 2.503 (4) Å, F9···F12 = 2.430 (4) Å, F11···F12 = 2.547 (4) Å, C7···F4 = 2.681 (4) Å, C7···F15 = 2.606 (4) Å and C7···F18 = 2.962 (4) Å, *cf*. the standard van der Waals contact distances (Rowland & Taylor, 1996) F···F = 2.90 Å and C···F = 3.22 Å. As a result, the substituents tilt out of the benzene plane and induce some puckering of the ring itself. Thus atoms C1, C2, C3 and C4 of the ring are coplanar within 0.012 (2) Å, but C5 and C6 deviate from the plane by −0.102 (6) and 0.052 (6) Å, respectively. The deviations of the substituent atoms are −0.196 (6) (C7), −0.467 (7) (N), −0.073 (7) (C8), −0.035 (6) (F1), 0.119 (7) (C9), −0.69 (1) (C10) and 0.35 (1) Å (C11).

The C—F bond distances in the trifluoromethyl groups range from 1.316 (4) to 1.342 (4) Å, with an average of 1.330 (7) Å.

Experimental

A mixture containing tetrafluorophthalonitrile (5.0 g, 25 mmol) and dried KF (2.2 g, 100 mmol) in anhydrous DMF (25 ml) was heated to 323 K under dry N_2 with a cold-finger condenser attached, containing acetone/CO_2. Me_3SiCF_3 (14 g, 100 ml) in anhydrous DMF (5 ml) was added slowly to the reaction vessel *via* a syringe. The mixture was stirred at 323 K for 6 h. The deep red solution was transferred to an autoclave (160 ml) under dry N_2. Hexafluoropropene (15 g, 90 mmol)
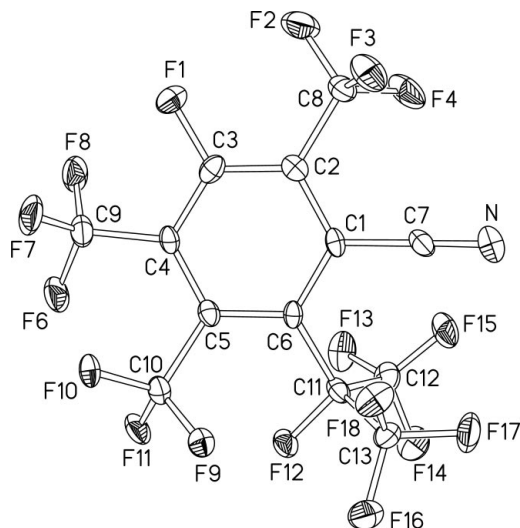
Figure 1
Molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level.

was transferred into the autoclave under vacuum. The autoclave was sealed and heated to 358 K over a period of 48 h, and then opened in a vacuum. 7.0 g (41 mmol) of hexafluoropropene was recovered. Continuous extraction into perfluoromethylcyclohexane followed by evaporation of the solvent on a rotary evaporator gave a very small quantity of (I) as a white solid. Analysis found: C 31.6, N 2.8%; $C_{13}F_{17}N$ requires: C 31.4, N 2.8%. The ^{19}F NMR data (field strength 376 MHz) are listed in Table 2. The very broad peak at -55.0 p.p.m. can be interpreted as a poorly resolved multiplet of the $C10F_3$ group, resulting from unusual rotation of this group and the adjacent perfluoroisopropyl group.

Crystal data

$C_{13}F_{17}N$	$D_x = 2.157$ Mg m^{-3}
$M_r = 493.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 692 reflections
$a = 9.521$ (1) Å	$\theta = 10.2–21.4°$
$b = 9.410$ (1) Å	$\mu = 0.28$ mm^{-1}
$c = 17.426$ (2) Å	$T = 100$ (2) K
$\beta = 103.44$ (1)°	Needle, colourless
$V = 1518.5$ (3) Å^3	$0.55 \times 0.08 \times 0.02$ mm
$Z = 4$	

Data collection

Bruker SMART 1K CCD area detector diffractometer	1972 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.106$
Absorption correction: none	$\theta_{max} = 27.5°$
10 711 measured reflections	$h = -12 \rightarrow 12$
3497 independent reflections	$k = -12 \rightarrow 12$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 0.8197P]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
3497 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

N—C7	1.148 (5)	C3—C4	1.386 (5)
F1—C3	1.336 (4)	C4—C5	1.400 (5)
F12—C11	1.377 (4)	C4—C9	1.532 (5)
C1—C2	1.403 (5)	C5—C6	1.405 (5)
C1—C6	1.407 (5)	C5—C10	1.542 (5)
C1—C7	1.443 (5)	C6—C11	1.539 (5)
C2—C3	1.384 (5)	C11—C12	1.559 (5)
C2—C8	1.520 (5)	C11—C13	1.578 (5)

Table 2
^{19}F NMR spectrum of (I).

δ (p.p.m.)	Intensity	Multiplicity	Coupling (Hz)	Assignment
-55.0	3	br m	–	$C10F_3$
-56.5	3	dq	$^4J_{FF}$ 28, $^5J_{FF}$ 4	$C9F_3$
-57.2	3	d	$^4J_{FF}$ 28	$C8F_3$
-69.2	6	br s	–	$C12F_3$, $C13F_3$
-100.6	1	sept	$^4J_{FF}$ 28	F1
-163.5	1	q	$^3J_{FF}$ 54	F12

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supporting information

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3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5- tris(trifluoromethyl)benzonitrile

Crystal data

$C_{13}F_{17}N$	$F(000) = 952$
$M_r = 493.14$	$D_x = 2.157$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point = 351–352 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.521$ (1) Å	Cell parameters from 692 reflections
$b = 9.410$ (1) Å	$\theta = 10.2$–21.4°
$c = 17.426$ (2) Å	$\mu = 0.28$ mm^{-1}
$\beta = 103.44$ (1)°	$T = 100$ K
$V = 1518.5$ (3) Å^3	Needle, colourless
$Z = 4$	$0.55 \times 0.08 \times 0.02$ mm

Data collection

Bruker SMART 1K CCD area detector diffractometer	3497 independent reflections
Radiation source: fine-focus sealed tube	1972 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.106$
Detector resolution: 8 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
ω scans	$h = -12 \rightarrow 12$
	$k = -12 \rightarrow 12$
10711 measured reflections	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.057$	
$wR(F^2) = 0.134$	
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.8197P]$ where $P = (F_o^2 + 2F_c^2)/3$
3497 reflections	
280 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.34$ e Å^{-3}
	$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Experimental. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of 4 sets of exposures; each set had a different φ and/or 2θ angles and each exposure (50 s) covered 0.3° in ω. Crystal decay was monitored by repeating 50 initial frames at the end of data collection and comparing 78 duplicate reflections. Crystal to detector distance 4.53 cm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
N	0.2327 (4)	0.6948 (3)	0.2402 (2)	0.0301 (8)
F1	0.0004 (2)	0.2198 (2)	0.04015 (13)	0.0293 (5)
F2	−0.1394 (3)	0.4289 (3)	0.06439 (15)	0.0451 (7)
F3	−0.0544 (2)	0.4634 (2)	0.18788 (13)	0.0328 (6)
F4	−0.0287 (3)	0.6210 (2)	0.10331 (15)	0.0378 (6)
F6	0.3691 (3)	0.0630 (2)	0.00157 (14)	0.0346 (6)
F7	0.2104 (3)	−0.0262 (2)	0.05958 (15)	0.0378 (6)
F8	0.1453 (3)	0.1025 (2)	−0.04488 (13)	0.0352 (6)
F9	0.5879 (2)	0.2270 (2)	0.21283 (12)	0.0229 (5)
F10	0.4727 (2)	0.0556 (2)	0.14733 (13)	0.0269 (5)
F11	0.6071 (2)	0.1887 (2)	0.09313 (13)	0.0265 (5)
F12	0.6279 (2)	0.4431 (2)	0.14449 (13)	0.0245 (5)
F13	0.4826 (3)	0.6219 (2)	0.04560 (13)	0.0341 (6)
F14	0.6437 (3)	0.7132 (2)	0.13983 (15)	0.0361 (6)
F15	0.4183 (2)	0.7475 (2)	0.13403 (14)	0.0312 (6)
F16	0.7056 (2)	0.4894 (2)	0.28607 (14)	0.0331 (6)
F17	0.5644 (3)	0.6689 (2)	0.28107 (14)	0.0350 (6)
F18	0.4884 (2)	0.4594 (2)	0.29882 (12)	0.0296 (5)
C1	0.2450 (4)	0.4827 (3)	0.1475 (2)	0.0162 (8)
C2	0.1146 (4)	0.4156 (4)	0.1118 (2)	0.0170 (8)
C3	0.1224 (4)	0.2883 (4)	0.0732 (2)	0.0200 (8)
C4	0.2527 (4)	0.2237 (3)	0.0719 (2)	0.0171 (8)
C5	0.3818 (4)	0.2856 (4)	0.1133 (2)	0.0168 (8)
C6	0.3790 (4)	0.4234 (3)	0.14396 (19)	0.0151 (7)
C7	0.2380 (4)	0.6051 (4)	0.1964 (2)	0.0208 (8)
C8	−0.0287 (4)	0.4813 (4)	0.1170 (2)	0.0222 (8)
C9	0.2446 (5)	0.0883 (4)	0.0222 (2)	0.0275 (9)
C10	0.5157 (4)	0.1899 (4)	0.1405 (2)	0.0213 (8)
C11	0.5182 (4)	0.5116 (4)	0.1689 (2)	0.0190 (8)
C12	0.5138 (4)	0.6530 (4)	0.1218 (2)	0.0266 (9)
C13	0.5710 (4)	0.5318 (4)	0.2610 (2)	0.0237 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N	0.035 (2)	0.0232 (18)	0.034 (2)	0.0063 (15)	0.0119 (17)	−0.0049 (16)
F1	0.0223 (12)	0.0271 (12)	0.0356 (13)	−0.0059 (10)	0.0006 (10)	−0.0036 (10)
F2	0.0204 (13)	0.0660 (18)	0.0457 (16)	0.0075 (13)	0.0008 (11)	−0.0243 (14)
F3	0.0349 (14)	0.0364 (13)	0.0333 (13)	0.0077 (11)	0.0203 (11)	0.0024 (11)
F4	0.0336 (14)	0.0247 (13)	0.0593 (16)	0.0148 (11)	0.0195 (13)	0.0154 (12)
F6	0.0398 (14)	0.0270 (12)	0.0359 (14)	0.0090 (11)	0.0068 (11)	−0.0134 (11)

F7	0.0464 (15)	0.0125 (11)	0.0490 (16)	−0.0040 (11)	−0.0006 (13)	−0.0004 (11)
F8	0.0422 (15)	0.0261 (12)	0.0304 (13)	0.0048 (11)	−0.0055 (11)	−0.0113 (10)
F9	0.0234 (12)	0.0182 (10)	0.0257 (12)	0.0015 (9)	0.0032 (10)	−0.0006 (9)
F10	0.0303 (12)	0.0093 (10)	0.0394 (13)	0.0016 (9)	0.0046 (11)	0.0007 (9)
F11	0.0258 (12)	0.0227 (11)	0.0345 (13)	0.0081 (9)	0.0139 (11)	−0.0028 (10)
F12	0.0203 (11)	0.0196 (11)	0.0374 (13)	−0.0004 (9)	0.0141 (10)	−0.0035 (10)
F13	0.0563 (17)	0.0223 (12)	0.0271 (13)	−0.0038 (11)	0.0164 (12)	0.0038 (10)
F14	0.0347 (14)	0.0210 (12)	0.0550 (16)	−0.0124 (11)	0.0150 (13)	0.0042 (11)
F15	0.0383 (14)	0.0141 (10)	0.0448 (14)	0.0046 (10)	0.0171 (12)	0.0042 (10)
F16	0.0243 (13)	0.0316 (13)	0.0392 (14)	−0.0022 (11)	−0.0008 (11)	−0.0010 (11)
F17	0.0472 (15)	0.0201 (11)	0.0350 (13)	−0.0004 (11)	0.0038 (12)	−0.0110 (10)
F18	0.0304 (13)	0.0354 (13)	0.0226 (12)	−0.0097 (10)	0.0055 (10)	0.0012 (10)
C1	0.024 (2)	0.0104 (16)	0.0165 (18)	0.0027 (15)	0.0086 (15)	0.0012 (14)
C2	0.0191 (19)	0.0186 (18)	0.0152 (18)	0.0021 (16)	0.0077 (15)	0.0042 (15)
C3	0.024 (2)	0.0170 (18)	0.0179 (19)	−0.0049 (16)	0.0018 (16)	0.0017 (15)
C4	0.023 (2)	0.0099 (16)	0.0183 (18)	0.0032 (15)	0.0045 (16)	0.0024 (14)
C5	0.0195 (19)	0.0149 (17)	0.0187 (18)	0.0014 (15)	0.0097 (16)	−0.0006 (15)
C6	0.0224 (19)	0.0092 (16)	0.0140 (17)	0.0003 (14)	0.0049 (15)	0.0010 (14)
C7	0.019 (2)	0.0181 (19)	0.027 (2)	0.0051 (16)	0.0091 (17)	0.0005 (16)
C8	0.019 (2)	0.024 (2)	0.025 (2)	0.0027 (16)	0.0078 (17)	−0.0010 (16)
C9	0.032 (2)	0.0166 (19)	0.032 (2)	0.0031 (18)	0.0027 (19)	−0.0042 (17)
C10	0.023 (2)	0.0144 (18)	0.027 (2)	0.0022 (16)	0.0060 (18)	−0.0006 (16)
C11	0.0172 (19)	0.0155 (18)	0.027 (2)	0.0027 (15)	0.0110 (16)	0.0006 (15)
C12	0.029 (2)	0.0190 (19)	0.035 (2)	−0.0054 (17)	0.0128 (19)	−0.0008 (18)
C13	0.019 (2)	0.0181 (19)	0.031 (2)	−0.0025 (16)	−0.0003 (17)	−0.0023 (17)

Geometric parameters (Å, º)

N—C7	1.148 (5)	F17—C13	1.342 (4)
F1—C3	1.336 (4)	F18—C13	1.326 (4)
F2—C8	1.321 (4)	C1—C2	1.403 (5)
F3—C8	1.325 (4)	C1—C6	1.407 (5)
F4—C8	1.336 (4)	C1—C7	1.443 (5)
F6—C9	1.337 (5)	C2—C3	1.384 (5)
F7—C9	1.337 (4)	C2—C8	1.520 (5)
F8—C9	1.329 (5)	C3—C4	1.386 (5)
F9—C10	1.335 (4)	C4—C5	1.400 (5)
F10—C10	1.342 (4)	C4—C9	1.532 (5)
F11—C10	1.332 (4)	C5—C6	1.405 (5)
F12—C11	1.377 (4)	C5—C10	1.542 (5)
F13—C12	1.324 (5)	C6—C11	1.539 (5)
F14—C12	1.329 (5)	C11—C12	1.559 (5)
F15—C12	1.325 (4)	C11—C13	1.578 (5)
F16—C13	1.316 (4)		
C2—C1—C6	121.3 (3)	F8—C9—C4	110.2 (3)
C2—C1—C7	117.6 (3)	F6—C9—C4	111.7 (3)
C6—C1—C7	120.6 (3)	F7—C9—C4	112.4 (3)

C3—C2—C1	117.6 (3)	F11—C10—F9	108.6 (3)
C3—C2—C8	122.1 (3)	F11—C10—F10	107.7 (3)
C1—C2—C8	120.3 (3)	F9—C10—F10	105.3 (3)
F1—C3—C2	119.2 (3)	F11—C10—C5	115.3 (3)
F1—C3—C4	118.2 (3)	F9—C10—C5	110.2 (3)
C2—C3—C4	122.4 (3)	F10—C10—C5	109.3 (3)
C3—C4—C5	119.4 (3)	F12—C11—C6	109.0 (3)
C3—C4—C9	116.5 (3)	F12—C11—C12	99.6 (3)
C5—C4—C9	124.0 (3)	C6—C11—C12	113.3 (3)
C4—C5—C6	119.2 (3)	F12—C11—C13	106.6 (3)
C4—C5—C10	118.7 (3)	C6—C11—C13	113.7 (3)
C6—C5—C10	120.6 (3)	C12—C11—C13	113.4 (3)
C5—C6—C1	118.7 (3)	F13—C12—F15	107.9 (3)
C5—C6—C11	120.9 (3)	F13—C12—F14	108.1 (3)
C1—C6—C11	120.2 (3)	F15—C12—F14	108.2 (3)
N—C7—C1	174.4 (4)	F13—C12—C11	108.2 (3)
F2—C8—F3	108.0 (3)	F15—C12—C11	115.0 (3)
F2—C8—F4	106.1 (3)	F14—C12—C11	109.2 (3)
F3—C8—F4	107.4 (3)	F16—C13—F18	108.9 (3)
F2—C8—C2	112.9 (3)	F16—C13—F17	107.8 (3)
F3—C8—C2	111.5 (3)	F18—C13—F17	107.2 (3)
F4—C8—C2	110.7 (3)	F16—C13—C11	110.9 (3)
F8—C9—F6	106.0 (3)	F18—C13—C11	111.0 (3)
F8—C9—F7	107.8 (3)	F17—C13—C11	110.9 (3)
F6—C9—F7	108.6 (3)		
C3—C2—C8—F2	−17.8 (5)	C5—C6—C11—F12	9.3 (4)
C3—C4—C9—F7	−79.9 (4)	F12—C11—C12—F14	−56.6 (4)
C4—C5—C10—F11	96.9 (4)	F12—C11—C13—F16	5.3 (4)