Heterocyclic Polyfluoro-compounds. Part 30.[1] Perfluoroalkylation of Trifluoro-1,2,4-triazine

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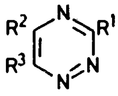
Reaction of trifluoro-1,2,4-triazine with hexafluoropropene and caesium fluoride in the absence of solvent leads to successive replacement of fluorine by perfluoroisopropyl groups to give 5-mono-, 3,5- and possibly 3,6-di-, and tri-substituted derivatives. Similarly, perfluoro-2-azapropene yields 5- and some 6-, 3,6-bis-, and tris-perfluorodimethylamino-derivatives.

Pyrolysis of trifluoro-1,2,4-triazine at 500 °C/42 h yields trifluoro-1,3,5-triazine (32%); of perfluoro(tri-isopropyl-1,2,4-triazine) at 560 °C/0.26 s yields perfluoroisobutyronitrile and perfluoro-2,5-dimethylhex-3-yne; and of perfluoro(trisdimethylamino-1,2,4-triazine) at 620 °C/2.4 s yields *N,N*-bis(trifluoromethyl)cyanamide and perfluorobis(dimethylamino)acetylene.

TRIFLUORO-1,2,4-TRIAZINE, readily prepared by the vapour-phase fluorination of trichloro-1,2,4-triazine with potassium fluoride,[2] is a versatile and reactive compound, undergoing Diels-Alder addition with olefins,[3] and nucleophilic displacement of fluorine. Here we describe its successful perfluoroalkylation, and the pyrolysis of its trisheptafluoroisopropyl and bistrifluoromethylamino-derivatives.

Introduction of perfluoroisopropyl groups into trifluoro-1,2,4-triazine proceeded smoothly with hexafluoropropene and caesium fluoride in the absence of solvent and the trisubstituted derivative (1) (52%) was formed at 110 °C over 2 h. When the reaction was carried out at 125 °C for 25 min, and the products were rapidly quenched, the 5-substituted derivative (2) (11%), and 3,5-disubstituted derivative (3) (10%) were also formed. ^{19}F N.m.r. spectroscopic examination of the triazine (3) indicated the presence of small amounts of a 3,6-disubstituted derivative (4).

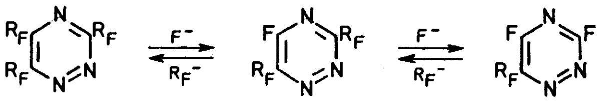


(1) $R^1 = R^2 = R^3 = (CF_3)_2CF$
(2) $R^1 = R^3 = F;\ R^2 = (CF_3)_2CF$
(3) $R^1 = R^2 = (CF_3)_2CF;\ R^3 = F$
(4) $R^1 = R^3 = (CF_3)_2CF;\ R^2 = F$
(5) $R^1 = R^3 = (CF_3)_2N;\ R^2 = F$
(6) $R^1 = R^2 = R^3 = (CF_3)_2N$
(7) $R^1 = R^3 = F;\ R^2 = (CF_3)_2N$
(8) $R^1 = R^2 = F;\ R^3 = (CF_3)_2N$
(9) $R^1 = R^2 = R^3 = CF_3CF{=}C(CF_3)$

Trifluoro-1,2,4-triazine also underwent easy substitution by the bistrifluoromethylamino-anion, from perfluoro-2-azapropene and caesium fluoride.[4] At 110 °C for 9 h, the 3,6-di- (5), (35%) and tri-substituted derivative (6), (37%) were obtained. Reactions which were rapidly quenched after a shorter reaction period also yielded the mono-substituted derivative (7), and small amounts of a compound identified spectroscopically as the 6-substituted derivative (8).

Attempts at perfluoroalkylation with perfluorocyclobutyl anions, from hexafluorocyclobutene and fluoride ion,[5] and perfluorobut-2-en-2-yl anions, from hexafluorobut-2-yne and fluoride ion,[6] were less successful. Hexafluorocyclobutene and caesium fluoride with trifluoro-1,2,4-triazine yielded small amounts of a mixture which contained by mass spectrometry, mono-, di-, and tri-substituted compounds. Hexafluorobut-2-yne and caesium fluoride yielded trace amounts of a compound which may have been the trisubstituted compound (9).

In trifluoro-1,2,4-triazine, the expected order of nucleophilic displacement of fluorine is 5-F > 3-F > 6-F, if the activating influence[7] of the ring nitrogen atoms (*para*-N > *ortho*-N) and fluorines (*m*- and *o*-F > *p*-F) is considered. The major mono-substituted derivatives (2) and (7) thus follow the expected pattern, but for the bis(trifluoromethyl)amino-derivative substantial amounts of the unexpected 6-derivative were formed. Introduction of a perfluoroalkyl substituent into the 5-position activates the 6-position to further attack,[8] but the second substituent is still expected to occupy the 3-position, which is activated by two *ortho*-nitrogens. The major di-isopropyl-derivative (3) was thus expected, but some 3,6-derivative appeared to be present, and the 3,6-derivative was the sole bis(dimethylamino)-derivative (5) detected. The trisubstituted compounds (1) and (6) were readily formed. The presence of the unexpected isomers can most easily be rationalised in terms of reversible attack by the anions, $(CF_3)_2CF^-$ and $(CF_3)_2N^-$, on the triazine ring, with the latter ion more easily lost. In the trisubstituted compounds, the 5-substituent would first be lost, followed by the 3-substituent (Scheme 1). Displacement of a perfluoroisopropyl group by fluoride ion has been reported for the pyridine[9] and pyridazine[10] systems.

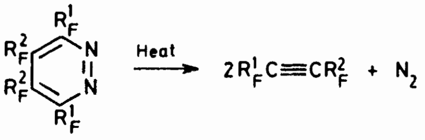


$R_F = (CF_3)_2CF$ or $(CF_3)_2N$

SCHEME 1

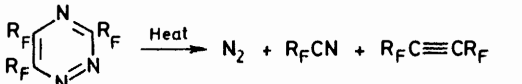
Certain fluorinated pyridazines with aromatic substituents undergo thermal fragmentation to form acetylenes in good yield (Scheme 2),[11] but when perfluoroalkyl substituents are present rearrangement to pyrimidines rather than fragmentation is favoured.[12] Perfluoroalkyl-1,2,4-triazines might thus, by analogy, undergo either fragmentation or rearrangement.

Static pyrolysis of trifluoro-1,2,4-triazine (500 °C/42 h) gave trifluoro-1,3,5-triazine in moderate yield (32%), but nitrogen (64%) and perfluoro-2-azapropene (12%) were also formed, and the symmetrical triazine may well have been formed *via* a fragmentation pathway involving FCN trimerisation. The tri-isopropyltriazine (1) underwent clean fragmentation upon flow pyrolysis (560 °C/0.26 s), and the trisdimethylaminotriazine (6) underwent analogous cleavage to give the nitrile $(CF_3)_2NCN$ (95%) and the acetylene $(CF_3)_2NC{\equiv}CN(CF_3)_2$ (34%) under conditions which appeared to be too severe since further fragmentation occurred to give perfluoro-2-azapropene (620 °C/2.4 s) (see Scheme 3). As a method of preparing fluoroalkylacetylenes, the route has promise.



$R_F^1 = R_F^2 = C_6F_5$; $R_F^1 = C_6F_5$, $R_F^2 = C_2F_5$ or $(CF_3)_2CF$;
or $R_F^1 = 4\text{-}C_5F_4N$, $R_F^2 = (CF_3)_2CF$

SCHEME 2



$R_F = (CF_3)_2CF$ or $(CF_3)_2N$

SCHEME 3

Chambers and his co-workers have recently described unsuccessful attempts to prepare trifluoro-1,2,4-triazine, using potassium fluoride in autoclaves.[13] They successfully prepared the tri-isopropyl-compound (1) from trichloro-1,2,4-triazine, potassium fluoride, and hexafluoropropene in sulpholan, and described its pyrolysis.

EXPERIMENTAL

Volatile materials were manipulated in a Pyrex vacuum system, and techniques similar to those described earlier were employed. External trifluoroacetic acid was used as reference for ^{19}F n.m.r. chemical shifts.

Trifluoro-1,2,4-triazine was obtained by fluorination of trichloro-1,2,4-triazine over potassium fluoride in a flow reactor at 450 °C.[2]

Perfluoroalkylation of Trifluoro-1,2,4-*triazine*.—(*a*) *With hexafluoropropene*. To anhydrous caesium fluoride (4 g), cooled to −196 °C in a Pyrex ampoule (50 ml), was added trifluoro-1,2,4-triazine[2] (0.37 g, 2.7 mmol) and hexafluoropropene (1.83 g, 12.6 mmol). The ampoule was then sealed and heated at 110 °C for 2 h. The volatile products were fractionated *in vacuo* to give hexafluoropropene (1.08 g, 7.2 mmol) and perfluoro(tri-isopropyl-1,2,4-triazine) (0.82 g, 1.4 mmol, 52%) (Found: C, 24.9; F, 68.7; N, 7.0%; *M*, 585. Calc. for $C_{12}F_{21}N_3$: C, 24.6; F, 68.2; N, 7.2%; *M*, 585), as a yellow oil, $\lambda_{max.}$ (hexane) 253 (ε 3 300), 292 (82), and 398 nm (395) and an i.r. spectrum similar to that described.[13]

Similarly, caesium fluoride (14.1 g), trifluoro-1,2,4-triazine (3.29 g, 24.4 mmol) and hexafluoropropene (7.0 g, 47 mmol), heated at 125 °C for 25 min in a 300 ml ampoule, rapidly cooled, and volatile material fractionated *in vacuo*, gave recovered hexafluoropropene (3.9 g, 26 mmol), and a fraction which was separated by g.l.c. (4m Kel-F No 10 oil on Celite at 83 °C) to give in order of elution, *perfluoro*-(5-*isopropyl*-1,2,4-*triazine*) (0.77 g, 2.7 mmol, 11%) (Found: C, 25.2; F, 60.1; N, 14.7%; *M*, 285. $C_6F_9N_3$ requires C, 25.3; F, 60.0; N, 14.7%; *M*, 285), as a pale yellow moisture-sensitive oil, $\nu_{max.}$ (vapour) 1 560w, 1 541w, 1 432s, 1 410m, 1 309s, 1 260s, 1 210w, 1 191w, 1 162w, 1 094w, 1 029m, 988m, 888m, 808w, 756w, and 737m cm^{-1}; *perfluoro*-(3,5-*di-isopropyl*-1,2,4-*triazine*) (1.04 g, 2.4 mmol, 10%) (Found: C, 24.7; F, 66.0; N, 9.9%; *M*, 435. $C_9F_{15}N_3$ requires C, 24.8; F, 65.5; N, 9.7%; *M*, 435), as a yellow, moisture-sensitive oil, $\nu_{max.}$ 1 532w, 1 431m, 1 413m, 1 308s, 1 270s, 1 255s, 1 208w, 1 189m, 1 172w, 1 160w, 1 092w, 1 028m, 986m, 962w, 886w, 862w, 800w, 757w, and 722m cm^{-1}, and perfluoro(tri-isopropyl-1,2,4-triazine) (1.52 g, 2.6 mmol, 11%). Careful examination of the g.l.c. trace indicated the presence of small amounts of a compound isomeric with perfluoro-(3,5-di-isopropyl-1,2,4-triazine). This could not be separated pure from the 3,5-di-isopropyl-compound, but its ^{19}F n.m.r. spectrum (see below) indicated that it was perfluoro-(3,6-di-isopropyl-1,2,4-triazine).

(*b*) *With perfluoro*-2-*azapropene*. Similarly, caesium fluoride (4.1 g), trifluoro-1,2,4-triazine (1.00 g, 7.4 mmol), and perfluoro-2-azapropene (3.6 g, 27 mmol), heated in a Pyrex ampoule (88 ml) at 110 °C for 9 h, gave volatile material which was fractionated *in vacuo* to give perfluoro-2-azapropene, perfluoro-(4-methyl-2,4-diazapent-2-ene),[4] and a fraction which was separated by g.l.c. (7.5 m SE 30 at 75 °C) to give *perfluoro*-(3,6-*bisdimethylamino*-1,2,4-*triazine*) (1.04 g, 2.6 mmol, 35%) (Found: C, 21.3; F, 61.6; N, 17.4%; *M*, 401. $C_7F_{13}N_5$ requires C, 21.0; F, 61.6; N, 17.5%; *M*, 401), as a pale yellow oil which reacted vigorously with water, $\nu_{max.}$ (liq. film) 1 584w, 1 536m, 1 433s, 1 334s, 1 323s, 1 268s, 1 202s, 1 111w, 1 072s, 992s, 971s, 893w, 866w, 810w, 777m, 732m, 720w, and 693m cm^{-1}, and *perfluoro*(*trisdimethylamino*-1,2,4-*triazine*) (1.44 g, 2.7 mmol, 37%) (Found: C, 20.4; F, 64.0; N, 15.6%; *M*, 534. $C_9F_{18}N_6$ requires C, 20.2; F, 64.0; N, 15.7%; *M*, 534), as a yellow, water-stable oil, $\nu_{max.}$ (liq. film) 1 547m, 1 526s, 1 448s, 1 418s, 1 320s, 1 283s, 1 221s, 1 190s, 1 070s, 984s, 945m, 882w, 826m, 775s, 769m, 750m, 732s, 726s, 718s, 687w, 660m, and 650m cm^{-1}.

Caesium fluoride (14.4 g), trifluoro-1,2,4-triazine (1.70 g, 12.6 mmol), and perfluoro-2-azapropene (4.5 g, 34 mmol), heated in a Pyrex ampoule (300 ml) at 110 °C for 3 h, gave, after rapid quenching and fractionation *in vacuo*, perfluoro-2-azapropene and perfluoro-(4-methyl-2,4-diazapent-2-ene), and a fraction, a sample of which was separated by g.l.c. (4m Kel-F No 10 oil at 87 °C) and shown to contain *perfluoro*-(5-*dimethylamino*-1,2,4-*triazine*) (0.32 g, 1.2 mmol, 10%) (Found: *M*, 267.999 6. $C_5F_8N_4$ requires *M*, 267.999 4) as moisture-sensitive colourless needles, m.p. 20 °C, in addition to the above bis- (1.68 g, 4.2 mmol, 33%) and tris-dimethylamino-compounds (0.85 g, 1.6 mmol, 13%).

Careful separation of the product from a similar reaction carried out at 105 °C for 55 min yielded a small sample of a compound identified spectroscopically as *perfluoro-*(6-*dimethylamino-*1,2,4-*triazine*) (4%) (Found: *M*, 268.000 1. $C_5F_8N_4$ requires *M*, 267.999 4) as a pale yellow oil, and a small shoulder on the peak due to perfluoro-(3,6-bisdimethylamino-1,2,4-triazine) may have been due to the presence of an isomeric bisdimethylamino-compound.

(*c*) *With hexafluorocyclobutene.* A reaction in which caesium fluoride (16.4 g), trifluoro-1,2,4-triazine (1.49 g, 11.0 mmol) and hexafluorocyclobutene (6.48 g, 40.0 mmol) were heated in a Pyrex ampoule (300 ml) at 80 °C for 4 h, gave a small amount (0.40 g) of a moisture-sensitive yellow oil, which g.l.c.-coupled mass spectrometry indicated to be a mixture of mono- (*M*, 297), di- (*M*, 459), and tri-substituted (*M*, 621) triazines, and hydrolysis products with F replaced by OH (*M*, 295 and 457) of the first two compounds.

(*d*) *With hexafluorobut-*2-*yne.* A reaction in which caesium fluoride (2.7 g), trifluoro-1,2,4-triazine (0.57 g, 4.2 mmol), and hexafluorobut-2-yne (2.74 g, 16.9 mmol) were heated in a Pyrex ampoule (75 ml) at 165 °C for 4 h yielded a small amount of a liquid (50 mg), which mass spectrometry indicated to contain a perfluoro[tris(1-methylprop-1-enyl)-1,2,4-triazine] (*M*, 621).

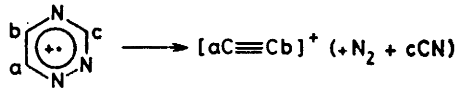
Pyrolysis of 1,2,4-*Triazines.*—(*a*) *Trifluoro-*1,2,4-*triazine.* Trifluoro-1,2,4-triazine (0.57 g, 4.2 mmol), sealed in a Pyrex ampoule (75 ml) and heated at 500 °C for 42 h, gave nitrogen (2.7 mmol, 64%) and after fractionation of the volatile product by trap-to-trap distillation *in vacuo*, silicon tetrafluoride, perfluoro-2-azapropene (0.5 mmol, 12%), unidentified material, and a fraction (0.23 g) which condensed at −78 °C, and was shown by i.r. spectroscopy to consist of trifluoro-1,3,5-triazine [14] (0.18 g, 1.3 mmol, 32%), and less-volatile material (0.05 g).

(*b*) *Perfluoro*(*tri-isopropyl-*1,2,4-*triazine*). The title triazine (0.830 g, 1.42 mmol), passed through a silica tube (heated length 500 mm × 11 mm i.d.) packed with silica chips (reaction volume 36 ml) and heated to 560 °C, at a pressure of 0.2 Torr over 45 min (contact time *ca.* 0.26 s) gave after fractionation of the product *in vacuo* perfluoroisobutyronitrile [15] (0.275 g, 1.41 mmol, 100%) (Found: C, 24.6; F, 67.7; N, 7.0. Calc. for C_4F_7N: C, 24.7; F, 68.2; N, 7.2%), δ_F (neat liq.) −0.6 (CF_3, ^3J 10 Hz) and −104.1 p.p.m. (CF) and $\nu_{max.}$ (vapour) 2 267 cm^{-1} (C≡N str), and perfluoro-2,5-dimethylhex-3-yne * (0.44 g, 1.24 mmol, 88%) (Found: C, 26.8; F, 73.0%; *M*, 362. Calc. for C_8F_{14}: C, 26.5; F, 73.5%; *M*, 362), δ_F −0.8 (CF_3) and −99.8 p.p.m. (CF, complex symmetrical multiplet, $|^3J + {}^6J| = 9$ Hz).

(*c*) *Perfluoro*(*trisdimethylamino-*1,2,4-*triazine*). In a similar manner, the title triazine (0.520 g, 0.97 mmol), heated at 620 °C/0.80 Torr over 1.25 h (contact time *ca.* 2.4 s), gave *NN*-bis(trifluoromethyl)cyanamide (0.164 g, 0.92 mmol, 95%), identified by i.r. spectroscopy [17] and mass spectrometry (*M*, 178), perfluoro(bisdimethylaminoacetylene) (0.108 g, 0.33 mmol, 34%), identified by i.r. and ^{19}F n.m.r. spectroscopy [18] and mass spectrometry (*M*, 328), and a mixture containing silicon tetrafluoride and perfluoro-2-azapropene.

*The Structure of the Perfluoroalkyl-*1,2,4-*Triazines.*—The structural assignments of the various 1,2,4-triazines described above rest largely upon spectroscopic, particularly ^{19}F n.m.r., grounds.

In their mass spectra, the perfluoroisopropyl substituted triazines all showed a molecular ion which decreased in intensity with increasing alkylation, and ions corresponding to loss of F and N_2 fragments. The base peak corresponded to CF_3^+ for the 5-isopropyl- and tri-isopropyl-derivatives, but to $C_4F_5^+$ for the 3,5-di-isopropyl compound. However, the spectra did not indicate which isomer was formed with any great certainty. The dimethylamino-compounds also showed molecular ions which diminished in intensity with increasing substitution, with the base peak corresponding to CF_3^+ in each case. Here, the fragmentation pattern was somewhat more helpful, in that an acetylenic fragment $[aC{\equiv}Cb]^+$ corresponding to the fragmentation:



was prominent [$(CF_3)_2NC{\equiv}CF$ for the 5- (24.4%) and 6-dimethylamino-(43.7%), and 3,6-bisdimethylamino-triazine (82.0%), and $(CF_3)_2NC{\equiv}CN(CF_3)_2$ for the trisdimethylaminotriazine (85.4%)], but ambiguity as to whether a substituent was in the 5- or 6-position remained.

The ^{19}F n.m.r. spectral data for the parent trifluoro-1,2,4-triazine,[2] for 6-chlorodifluoro-1,2,4-triazine,[2] and for the substituted triazines prepared here, all determined for the neat liquids, are shown in the Table. The parent trifluoro-1,2,4-triazine shows three somewhat broad multiplets. In pyridines, ring fluorine atoms adjacent to the ring nitrogen atom are deshielded,[19] and this is enhanced in pyrimidines,[20] where 2-fluorine atoms between the nitrogens are more deshielded than 4,6-fluorine atoms. On this basis the chemical shift assignment shown follows, and this is supported by the magnitudes of the coupling constants. In six-membered N-heterocycles, ^3J is usually around 20 Hz, but ^5J is larger, being 25.4 Hz in pentafluoropyridine,[19] 26.0 Hz in tetrafluoropyrimidine,[20] and up to 50 Hz in pyrazines.[21] The observed coupling constants are in line, and the small value for ^4J is also shown by fluoropyrimidines.[20] Introduction of a chlorine atom at C-6 causes the

^{19}F N.m.r. spectral data for derivatives of trifluoro-1,2,4-triazine

	Chemical shifts (p.p.m.) [a]			Coupling constants (Hz) [b]		
Substituent [c]	δ_3	δ_5	δ_6	$\lvert J_{35}\rvert$	$\lvert J_{36}\rvert$	$\lvert J_{56}\rvert$
	15.9	4.6	−24.9	<3	35	24
6-Cl	18.3	16.5		<4		
5-$(CF_3)_2CF$	14.6	2.8	−11.5		37	44
		−108.8				
3,5-$(CF_3)_2CF$	1.6	2.2	−2.7			44
	−109.5	−112.8				
3,6-$(CF_3)_2CF$ [d]	~2.3	15.8	~2.3			38
	−110.2		−111.5			
3,5,6-$(CF_3)_2CF$	2.1	3.7	3.5			156
	−111.3	−106.9	−106.9			
5-$(CF_3)_2N$	13.7	20.7	−17.4		35	7
6-$(CF_3)_2N$	22.2	11.0	20.0	<4		3
3,6-$(CF_3)_2N$	21.2	8.8	20.7			4
3,5,6-$(CF_3)_3N$	21.1	20.2	21.4			2

[a] Positive values to low field of external trifluoroacetic acid. [b] For the $(CF_3)_2CF$ substituted compounds, J_{56} refers to the coupling constant involving the tertiary fluorine of the $(CF_3)_2CF$ group. [c] Other than fluorine. [d] *Ca.* 10% in a mixture with the 3,5-isomer.

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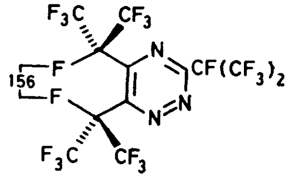
* Perfluoro-2,5-dimethylhex-3-yne has been described, but without physical properties.[16] The description (ref. 13) of the CF-absorption as a septet is clearly in error, although the CF_3-absorption does resemble a doublet upon casual inspection.

expected low-field shift of the 5-fluorine absorption in particular, and also ^{4}J is small in magnitude. In pentafluoropyridine, introduction of a $(CF_3)_2CF$ substituent causes substantial deshielding of *ortho* and to a lesser extent *para*-fluorine nuclei, but *meta*-fluorines are less affected.[22] By analogy, the position of mono-substitution then follows, the magnitude of J_{36} supports the assignment, and the magnitude of the four-bond coupling J_{35} indicates that the ring and tertiary fluorines are in close proximity.[23] For the disubstituted derivatives, a ring fluorine absorption to high field of the reference in the major isomer is indicative of a fluorine at C-6, and in the minor isomer, an absorption at 15.8 p.p.m. is indicative of a fluorine at C-5, deshielded by an adjacent $(CF_3)_2CF$ group, and again the long-range coupling J_{56} is substantial. The very large (156 Hz) coupling of tertiary fluorine nuclei in the tri-isopropyl compound indicates that it has the conformation (10), with a large ' through space ' contribution.*



(10)

The position of the bistrifluoromethylamino-substituent in the major and minor mono-substituted compounds follows from the magnitudes of the coupling constants for ring fluorines, and both show small coupling of CF_3 group fluorines to adjacent ring fluorine. The observed substituent shifts for the mono-substituted compounds allow the shifts for the ring fluorines of all three possible disubstituted triazines to be predicted, and the observed shift of 8.8 p.p.m., 2.2 p.p.m. to high field of the 5-fluorine absorption in perfluoro(6-dimethylamino-1,2,4-triazine), is just as expected for introduction of a further substituent *meta* to the 5-fluorine. The alternative 3,5-isomer, which would also fit the mass spectrum, and show coupling of ring fluorine with adjacent CF_3 groups, is predicted to show an absorption at —11 p.p.m.

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* In perfluoro(tetraisopropylpyrimidine), the corresponding five-bond coupling has a magnitude of 120 Hz.[24]