

Polyfluorocarbanion Chemistry. Part III.^{1,2} Reaction of Hexafluoropropene with Pentafluorobenzonitrile †

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Hexafluoropropene reacts with pentafluorobenzonitrile in the presence of caesium fluoride to give two mono- (2- and 4-), two di- (2,4- and 2,5-), and two tri- (2,4,5- and 2,4,6-) (perfluoroisopropyl) derivatives; no solvent is necessary. The 2,4,5-derivative rearranges to the less sterically hindered 2,4,6-derivative when heated with fluoride ion. The ring fluorine atoms in the perfluoroisopropyl derivatives are highly susceptible to nucleophilic displacement; the cyano-group resists hydrolysis.

NUCLEOPHILES attack pentafluorobenzonitrile (I) predominantly in the 4-position; certain nucleophiles (*e.g.* MeO⁻ and PhO⁻) give in addition a small amount of 2-substitution.³ An excess of nucleophile leads to the formation of 2,4-disubstituted and 2,4,6-trisubstituted derivatives. In the early stages of an investigation of the reactions of perfluorocarbanions with perfluoroaromatic compounds, perfluoroisopropyl carbanion (II), generated in the usual way from an excess of hexafluoropropene and caesium fluoride,⁴ but in the absence of solvent at 70°, gave a trisubstituted derivative, (C₃F₇)₃C₆F₂CN as the major product from pentafluorobenzonitrile. Related results were obtained by other workers, who found that generation of the carbanion (II) from the olefin *via* potassium fluoride in tetramethylene

anionically produced hexafluoropropene oligomers,⁶ and a mixture of perfluoroisopropyl derivatives of (I) (Table 1). This mixture could not be separated by distillation, and a very polar column (trixyllyl phosphate) was necessary to give complete separation by preparative g.l.c.; the most highly substituted compounds were eluted first, possibly because the perfluoroisopropyl groups offset the dipole moment of the cyano-group. Five derivatives were thus obtained: the 4- and 2-monosubstituted derivatives, (III) and (IV), the 2,4-disubstituted derivative (V), and the 2,4,5- and 2,4,6-trisubstituted derivatives (VII) and (VIII) [note: R = CF(CF₃)₂ throughout this paper]. These products accounted for 91% of the pentafluorobenzonitrile employed, and after the 4-derivative (III) the 2,4,6-derivative (VIII) was the most abundant.

TABLE I
Reaction of hexafluoropropene (II) with pentafluorobenzonitrile (I)^a

Ratio C ₃ F ₆ : (I)	Solvent	Temp. (°C)	Overall yield (%) ^b	(II) recovered (%) ^c	Oligomers of (II) (%) ^e	(I) recovered (%) ^b	(IV) (%) ^b	(III) (%) ^b	(V) (%) ^b	(VI) (%) ^b	(VII) (%) ^b	(VIII) (%) ^b	
1:1 ^d	None	20	91	11	5	49	3	21	6	0	2	10	
1:1		70	88	3	7	43	3	18	5	1	6	12	
1:1		90	77	0	2	26	2	18	6	2	4	19	
1:1		140	65	0	1	20	2	10	5	1	3	24	
2:1		70	94	4	22	32	2	17	6	2	8	27	
3:1		70	89	2	31	15	2	13	5	3	12	39	
1:1	MeCN	70	87	1	5	42	2	20	5	2	5	11	
1:1		O: $\overset{\text{C}}{\text{[CH}_2\text{]}_3\text{NMe}}$	70	72	0	23	31	1	25	8	0	4	3
1:1			$\text{[CH}_2\text{]}_4\text{SO}_2$	70	80	0	11	33	1	28	8	1	4

^a All reactions were carried out for 20 h with continuous shaking. ^b Based on (I) loaded. ^c Based on C₃F₆ loaded. ^d 72 h. All yields calculated from g.l.c. with adequate calibration.

sulphone at 125° gave a moderate yield (30%) of the 4-perfluoroisopropyl derivative (III), together with products of cyano-group displacement.⁵ Our results, now reported in full, agree with the formation of (III) as an initial product but loss of the cyano-group was not observed.

RESULTS AND DISCUSSION

At 20° and in the absence of solvent use of a 1:1 ratio of hexafluoropropene and pentafluorobenzonitrile resulted in 49% recovery of (I) and gave a small amount of

† Presented in part at the S.C.I. Fluorine Chemistry Symposium, University of Birmingham, March 1968, and in the Tilden Lecture, University College, London, November 1968.

¹ Part II, C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, preceding paper.

² W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Comm.*, 1970, 371, contains reference to part of this work.

³ J. M. Birchall, R. N. Haszeldine, and M. E. Jones, *J. Chem. Soc. (C)*, 1971, 1343, and references therein.

Several subsequent experiments also yielded a second disubstituted derivative, believed to be the 2,5-isomer (VI), although the possibility that it is the 2,6-isomer cannot be completely ruled out.

Similar experiments at 70, 90, and 140° showed that the overall yield, and the yields of the 4- and 2,4,5-derivatives, (III) and (VII), fell, whereas the yield of the 2,4,6-derivative (VIII) increased until it became the major product of the highest temperature.

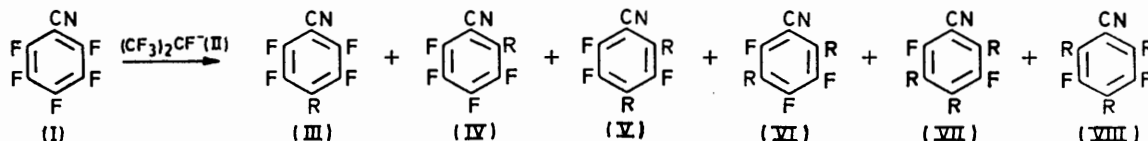
Since use of the three solvents acetonitrile, *N*-methylpyrrolidone, and tetramethylene sulphone gave, at 70°, inferior overall yields and yields of the trisubstituted derivatives, further reactions employing solvents were

⁴ W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, 1966, **82**, 3091; R. D. Chambers, R. A. Storey, and W. K. R. Musgrave, *Chem. Comm.*, 1966, 384 and subsequent papers.

⁵ R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.

⁶ W. Brunskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, *Chem. Comm.*, 1970, 1444, and references therein.

not attempted. Of the various perfluoroaromatic compounds which have so far been employed in these investigations,^{1,7} only the benzonitrile (I) reacted in the absence of solvent. It was observed that the disubstituted deriva-



tives were only very sparingly soluble in the three solvents employed, whereas the precursor benzonitrile appeared to be an effective solvent.

Table 1 shows that when an equimolar ratio of reactants is employed, the yield of the trisubstituted derivatives (VII) and (VIII) accounts for the majority of the hexafluoropropene, thus leaving a considerable amount of unchanged benzonitrile (I). Replacement of a ring fluorine atom by one and two perfluoroisopropyl groups must thus markedly activate the ring to further nucleophilic attack.

Increasing the ratio of hexafluoropropene to pentafluorobenzonitrile from 1 : 1 to 3 : 1 leads to an increase in yield of the trisubstituted derivatives and of the hexafluoropropene oligomers, with corresponding reduction in the recovery of benzonitrile and the yield of the 4-derivative.

The 2,4,6-Isomer (VIII).—Carbanionic attack on pentafluorobenzonitrile occurs at positions 4 and 2, since stabilisation of the intermediate σ -complex depends predominantly on the possibility of locating the negative charge on carbon carrying the cyano-group, *e.g.* (IX). Intermediate carbanions which rely only on stabilisation by α -fluorine, *e.g.* (XI), are less preferred.⁸ Disubstitution of pentafluorobenzonitrile should thus give the 2,4- or 2,6-isomer predominantly [*e.g. via* (XII)]. Formation of the 2,5- as well as the 2,4-compound reveals that the α -perfluoroisopropyl group, which cannot

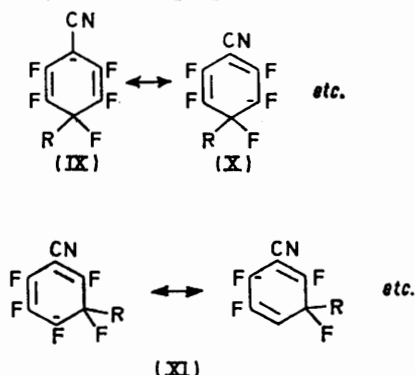


exhibit the destabilising p -electron repulsion effect shown by α -fluorine, is comparable to cyano in carbanion-stabilising power; the 3,4- and 2,3-isomers were not

⁷ W. T. Flowers, R. N. Haszeldine, and J. E. G. Kemp, *Chem. Comm.*, 1969, 203.

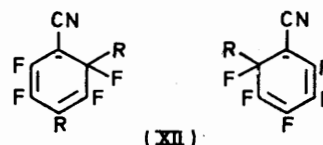
⁸ C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *Chem. Comm.*, 1970, 662, and references therein.

⁹ C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1971, 2750.

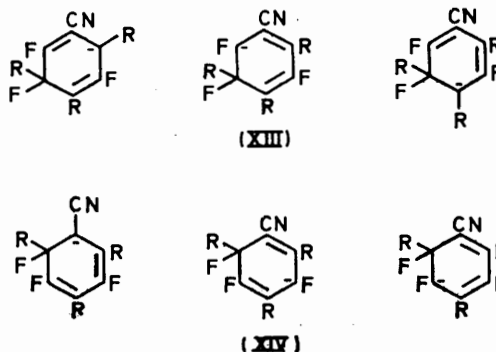
observed, and steric crowding probably inhibits formation of the latter.

The ratio of (VII) to (VIII) is *ca.* 1 : 3; it seems reasonable to assume that the latter is thermodynamically the

most stable of all the six possible isomers of $(C_3F_7)_3-C_6F_2CN$.



The 2,4,5-Isomer (VII).—The formation of an appreciable quantity of this isomer despite the large steric factor involved when two perfluoroisopropyl groups are on adjacent ring carbons (*cf.* related derivatives of tetrafluoropyrimidine,⁹ pentafluoropyridine,^{1,10} and tetrafluoropyridazine^{8,11}) suggested that this may be a product of kinetic control. Assuming the major precursor of the 2,4,5-isomer to be the 2,4-compound (V), consideration of the intermediate carbanions (XIII) and (XIV) shows

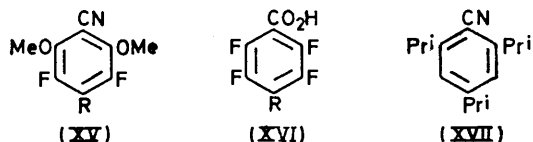


that (XIII) involves the cyano-group in the stabilisation only *via* its general $-I$ effect and not *via* its $-M$ effect, and that stabilisation relies upon the two perfluoroisopropyl groups and one less effective α -fluorine. However, in (XIV) stabilisation is achieved by the powerful cyano group exerting both $-I$ and $-M$ effects and the two α -fluorines add further to the overall stabilisation of the precursor to what is considered to be the thermodynamically most stable isomer. The effectiveness of the α -perfluoroisopropyl groups in the stabilisation of the product of kinetic control, the 2,4,5-isomer, is noteworthy. There thus appear to be two distinctions between heptafluoroisopropyl carbanion attack on pentafluoropyridine^{1,10} and pentafluorobenzonitrile: (i) in the case of the former no monosubstituted compound was detected; (ii) with the benzonitrile, attack on the 2,4-disubstituted compound at the 6-position predominates¹⁰ R. D. Chambers, R. P. Corbally, and W. K. R. Musgrave, *J.C.S. Perkin I*, 1972, 1281.
¹¹ R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1971, 532.

over attack at the 5-position, whereas the reverse is found with the pyridine. Both these distinctions indicate that a cyano-group is superior to a ring nitrogen in stabilising the negative charge resulting from attack at the *ortho*-position.

That the ratio of 2,4,6- to 2,4,5-isomer increases from 2 : 1 at 70° (20 h) to 8 : 1 at 140° (20 h) shows that the 2,4,6-derivative is distinctly the more stable isomer. Reaction at 20° for a longer time (72 h) gave a 5 : 1 ratio implying that the initially formed 2,4,5-isomer (VII) rearranged into the thermodynamically more stable 2,4,6-isomer (VIII). Separate study of the pure 2,4,5-isomer showed that its rearrangement at 170° (20 h) in the presence of fluoride ion was almost complete; 81% of the product was the 2,4,6-isomer, and 2% unchanged 2,4,5-isomer and small amounts of other components accounted for the rest.

Reactions of Derivatives.—The 4-derivative (III) reacted readily with sodium methoxide to give the 2,6-dimethoxy-derivative (XV) in good yield; both the methoxy-groups entered the ring *ortho* to the cyano-group rather than *ortho* to the perfluoroisopropyl group indicating once again the greater activating effect of the cyano-group. The nitrile (III) was readily hydrolysed to the corresponding acid (XVI), but under a wide



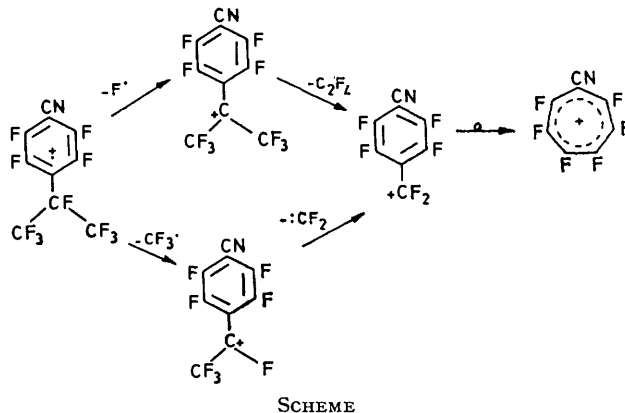
variety of conditions acids could not be obtained from either of the trisubstituted derivatives (VII) and (VIII). The 2,4,6-derivative (VIII) withstood treatment with concentrated sulphuric, phosphoric, or trifluoroperoxyacetic acid at 100° for several hours; hydrolysis occurred under alkaline conditions, but afforded oils which could not be purified satisfactorily. The hydrocarbon analogue of (VIII), 2,4,6-tri-isopropylbenzonitrile (XVII) may be hydrolysed to the corresponding amide under forcing alkaline conditions,¹² but the amide is completely resistant to further hydrolysis. Since the perfluoroisopropyl group is considerably more bulky than the isopropyl group, the resistance to hydrolysis of (VII) and (VIII) is not surprising.

U.v. Spectra.—Increasing substitution by perfluoroisopropyl groups leads to a red shift in the shorter wavelength band, from 223 nm in the 4-derivative (III) to 232 nm in the 2,4,6-derivative (VIII) (Table 3). In the 2,4,6-derivative there was a marked reduction in the intensity of the longest wavelength band, probably owing to the cyano-group being forced out of the plane of the ring by the two adjacent perfluoroisopropyl groups.

Mass Spectra.—All the derivatives gave intense molecular ions but the orientation of the substituents in the various isomers could not be deduced from the fragmentation patterns, apart from the observation that in the spectrum of the sterically hindered 2,4,5-trisubstituted derivative (VII) the intensities of several of the most

abundant ions were considerably different from those of the other derivatives. Two general observations were made: (i) no loss of CN• from the parent ion or of FCN from any of the fragment ions occurred, and the vast majority of the fragment ions still contained the nitrogen atom; (ii) in contrast to the perfluoroisopropylpyridines¹ and pyrimidines,⁹ CF₃⁺ was not the most abundant ion.

In each of the six derivatives the following metastable transitions were observed: $M^{+\bullet} \rightarrow (M - CF_3)^+ + CF_3^{\bullet}$; $(M - CF_3)^+ \rightarrow (M - C_2F_5)^+ + CF_2^{\bullet}$; $(M - F)^+ \rightarrow (M - C_2F_6)^+ + C_2F_4^{\bullet}$. These transitions, together with the fact that in the majority of the spectra $(M - C_2F_6)^+$ is the most abundant ion, support a fragmentation scheme of the type shown.



¹⁹F N.m.r. Spectra.—As in the case of the heteroaromatic substrates employed,^{1,9} the orientation of substituents was determined by a detailed consideration in these laboratories of the chemical shifts of the remaining ring fluorines. When the chemical shifts of the ring fluorines in pentafluorobenzonitrile (I) (2,6- 53.1; 3,5- 79.8; 4- 64.1 p.p.m.) are compared with those of the six

TABLE 2

Effect of introducing perfluoroisopropyl groups on ¹⁹ F chemical shifts			
<i>ortho</i>	(I) → (IV)	-28.6 p.p.m.	Average -28.8 ± 4.9 p.p.m.
	(I) → (III)	-21.2	
	(III) → (V)	-33.4	
	(IV) → (V)	-26.0	
	(V) → (VII)	-24.6	
	(V) → (VIII)	-36.0	
<i>meta</i>	(I) → (IV)	+1.9	-2.2 ± 5.0
	(I) → (III)	-4.7	
	(III) → (V)	+2.9	
	(IV) → (V)	-5.4	
	(V) → (VII)	+2.2	
<i>para</i>	(I) → (IV)	-10.6	-13.1 ± 2.5
	(III) → (V)	-11.4	
	(V) → (VIII)	-14.8	
	(V) → (VIII)	-13.2	

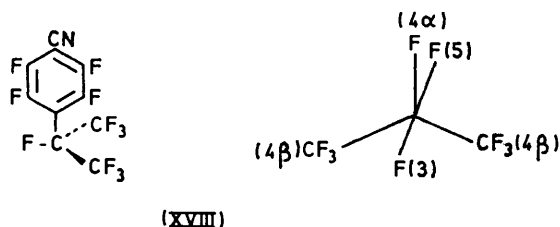
perfluoroisopropyl derivatives, the effect of introducing a perfluoroisopropyl group on the remaining ring fluorines is seen to be as in Table 2. The three ranges are distinct, and are in good agreement with the values for the insertion of a CF₃ group into hexafluorobenzene, *viz.* *ortho*

¹² A. Newton, *J. Amer. Chem. Soc.*, 1943, **65**, 2441.

—22.9, *meta* —2.3, *para* —15.0.¹³ The values for *meta*-substitution, which show the widest deviation, may be divided into three sub-groups: (i) +1.9, +2.9, and +2.2 p.p.m., when the cyano-group is not between the new perfluoroisopropyl substituent and the ring fluorine, (ii) —4.7 and —5.4 p.p.m. when the cyano-group is between the new perfluoroisopropyl group and the ring fluorine, and (iii) —10.6 p.p.m. in the case of the sterically hindered 2,4,5-derivative (VII).

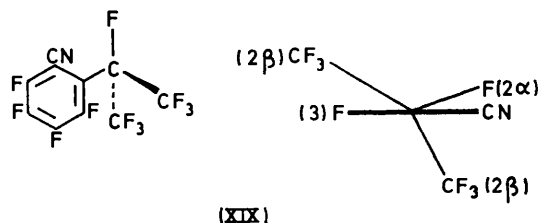
The chemical shifts of the β -fluorines of the substituent group fall in a very close range, though those in the 2-substituent are usually to low field of those in the 4-substituent, the exception again being the 2,4,5-derivative (VII). The range for the α -fluorines is considerably greater; in this case the chemical shift difference between the 2- and 4-substituents is constant at 9 p.p.m., except for the 2,4,5-derivative (VII) for which the value is —5 p.p.m.

In compounds where it is adjacent to two ring fluorines, the bulky perfluoroisopropyl group can rotate at the normal n.m.r. operating temperature (35°) but only with the same difficulty; the bands of both α - and β -fluorines are broadened, the former especially so. At low temperatures the α -fluorine couples (90 Hz) to only one ring fluorine showing that the substituent is in the preferred conformation (XVIII), and rotation is practically non-



existent. On raising the temperature, coupling (45 Hz) to both ring fluorines is observed, but even at 160° the band system only approaches a sharp triplet of heptets which would be expected if rotation is completely unhindered, and which is actually observed in the corresponding pyridine derivative.¹

When the perfluoroisopropyl group is adjacent to the cyano-group then the former has the preferred conformation (XIX) even at 35°: the coupling constants of the α - and the β -fluorines to the adjacent ring fluorine are, in the case of the 2-derivative (IV), 5.6 and 28 Hz, respectively, in contrast to the values of 45 and 14 Hz for the 4-derivative. The through-space component of the



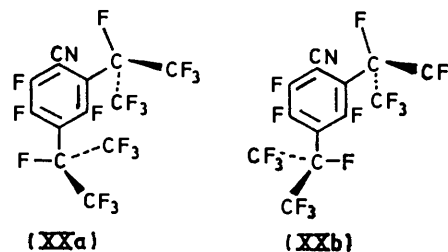
α -coupling constant is lost in conformation (XIX) and thus the overall value is markedly reduced, whereas the

two CF_3 groups are kept in close proximity to the ring fluorine and thus the coupling to them is increased.

In the case of the 2,4-derivative (V), the —40° spectrum reveals the presence of the two conformational isomers [Table 3, (XXa and b)] in the ratio 2 : 1; other workers¹⁴ have shown that perfluoro-2,4-di-isopropylpyridine similarly exists in two conformations at this temperature. The reason for the predominance of (XXa) over (XXb) is probably the fact that, in the absence of rotation, a ring fluorine is sterically less influenced by a β -fluorine than by an α -fluorine, because the latter is more nearly in the same plane; thus the 3-fluorine in (XXa) is not as crowded as it is in (XXb). This deduction is supported by the relative magnitudes of the coupling constants observed for the two isomers (Table 3). It will be seen

TABLE 3

¹⁹F N.m.r. spectra of conformational isomers of perfluoro-2,4-di-isopropylbenzonitrile (V) at —40°



(i) Chemical shifts

Band	Chemical shift (p.p.m.)	Intensity	Description	Assignment (XXa)	Assignment (XXb)
1	—2.0	36	sharp m	2 β , 4 β	2 β , 4 β
2	25.2	2	br unresolved m	3	
3	28.2	1	br unresolved m		3
4	41.6	1	br q		5
5	43.8	2	br d of d	5	
6	49.6	2	sharp q	6	
7	50.6	1	br q		6
8	92.6	1	br unresolved m		2 α
9	93.2	2	br unresolved m	2 α	
10	101.3	2	br d	4 α	
11	101.7	1	br d		4 α

(ii) Moduli of spin-spin coupling constants (Hz)

	(XXa)	(XXb)	(XXa)	(XXb)
$J_{2\alpha, 2\beta}$	5.6	5.1	$J_{3, 6}$	10
$J_{2\alpha, 3}$	<3	<3	$J_{4\alpha, 4\beta}$	5.6
$J_{2\beta, 3}$	24	28	$J_{4\alpha, 5}$	89
$J_{3, 4\alpha}$	<3	104	$J_{4\beta, 5}$	<2
$J_{3, 4\beta}$	26	<2	$J_{5, 6}$	19
				21

that $J_{3, 4\alpha}$ (104 Hz) for (XXb) is greater than $J_{4\alpha, 5}$ (89 Hz) for (XXa), indicating slightly greater spatial proximity for the respective atoms, and hence a higher ground state energy for (XXb) than for (XXa). The average coupling (96 Hz) between the 4 α -fluorine and the ring fluorine for the two isomers is, as expected, approximately twice that observed (47 Hz) for cases when free rotation of the iso- C_3F_7 group exists; for the 4 β -fluorines the respective values are 23 and 14 Hz. However the —40° values for $J_{2\alpha, 3}$ (0) and $J_{2\beta, 3}$ (26 Hz) are almost identical with the average 35° values (2.4 and 26 Hz, respectively), which is

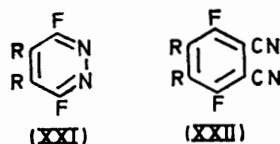
¹³ I. J. Lawrenson, *J. Chem. Soc.*, 1965, 1117.

¹⁴ R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, 1970, **26**, 71.

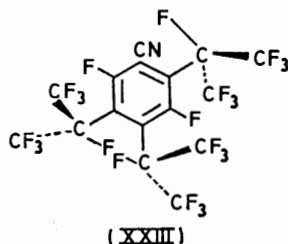
in agreement with the previous observation that the 2-isopropyl group is in fixed conformation even at the latter temperature. The downfield shift (8.8 p.p.m.) for the 2 α -fluorine in comparison with the 4 α -fluorine is probably due to the through-space deshielding effect of the cyano-group; a similar chemical shift difference (9.6 p.p.m.) was observed between the respective fluorines in the 2,4,6-derivative (VIII).

The 35° spectrum of the 2,4,6-derivative showed that the 2- and 6-iso-C₃F₇ groups were in the same fixed conformation as the 2-iso-C₃F₇ group in both the 2- and the 2,4-derivative, (IV) and (V), respectively; at the same temperature it appeared that the 4-iso-C₃F₇ group suffered restricted rotation, but no variable temperature studies were carried out.

The 2,4,5-derivative (VII) has two iso-C₃F₇ groups adjacent to each other, each being also adjacent to a ring fluorine; the same arrangement of substituents also occurs in the 2,4,5-derivative of pyridine,¹ the 4,5-derivative of the pyridazine (XXI),^{10,11} and the 4,5-derivative of the phthalonitrile (XXII).¹⁵ The steric



interaction of the adjacent iso-C₃F₇ groups produces a number of effects common to all four compounds: (i) the chemical shift of the α -fluorines is 89.3 ± 1.5 p.p.m., compared with 103.0 ± 1.3 , 93.5 ± 0.9 , and 108.6 ± 1.1 p.p.m., when the iso-C₃F₇ group is adjacent to two ring fluorines, one ring fluorine and a cyano-group, and one ring fluorine and a ring nitrogen, respectively; (ii) a similar downfield shift occurs for the β -fluorines, the chemical shifts for the four categories detailed in (i) above being -5.2 ± 0.5 p.p.m. compared with -1.9 ± 0.1 , -2.8 ± 0.6 , and -1.7 ± 0.7 p.p.m., respectively; (iii) the coupling between the α - and the ring fluorines (*ca.* 7 Hz) is smaller and that between the β - and the ring fluorines (*ca.* 33 Hz) is larger than that for an iso-C₃F₇ group adjacent to a cyano-group, indicating that the conformations of the iso-C₃F₇ groups are as shown in (XXIII); (iv) although the two adjacent iso-C₃F₇ groups



[in (VII) and in perfluoro-(2,4,5-tri-isopropylpyridine)] are not chemically equivalent, the chemical shifts of both the α - and the β -fluorines in the respective groups are the same.

* For details of Supplementary Publications, see Notice to Authors No. 7, in *J.C.S. Perkin I*, 1974, Index issue.

EXPERIMENTAL

The general preparative and analytical techniques have been described previously.^{1,11} Pentafluorobenzonitrile was prepared by the standard method.^{3,16} G.l.c. columns were adequately calibrated to determine product yields. ¹⁹F N.m.r. data for compounds (III)—(VIII) and mass spectral data for compounds (III)—(VIII) are available as Supplementary Publication No. SUP 21323 (3 pp.).*

Reaction of Pentafluorobenzonitrile with Hexafluoropropene.—(i) *Without solvent.* Caesium fluoride (*ca.* 0.5 g) in a Pyrex tube (*ca.* 300 ml) was heated *in vacuo* for *ca.* 15 min. Pentafluorobenzonitrile (5.8 g, 30 mmol) and hexafluoropropene (4.5 g, 30 mmol) were added, and the tube was sealed then heated at 70° for 20 h in a thermostatically controlled water-bath, with continuous end-over-end rotation. The gaseous material present (0.1 g) was shown by i.r. spectroscopy to be unchanged hexafluoropropene (3%). The liquid products (9.4 g) were shown by analytical g.l.c. (8 m trixylyl phosphate; 140°) to consist of hexafluoropropene dimers and trimers and seven aromatic compounds. The products of several similar reactions were combined, the hexafluoropropene dimers and trimers were removed by distillation, and the aromatic compounds were separated by preparative g.l.c. (8 m 25% trixylyl phosphate on Celite; 125°) to give, in order of increasing retention time: (i) perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII); (ii) perfluoro-(2,4,5-tri-isopropylbenzonitrile) (VII); (iii) perfluoro-(di-isopropylbenzonitrile), probably the 2,5-isomer (VI); (iv) perfluoro-(2,4-di-isopropylbenzonitrile) (V); (v) perfluoro-(4-isopropylbenzonitrile) (III); (vi) perfluoro-(2-isopropylbenzonitrile) (IV); and (vii) pentafluorobenzonitrile (I).

Several similar reactions were carried out with various reactant ratios and conditions (Table 1).

(ii) *With solvent.* When a solvent (10 ml) was employed, this was removed by washing the liquid contents of the Carius tube with water (50 ml) and separating the lower fluorocarbon layer. The procedure was otherwise identical with that described above.

Reaction of Perfluoro-(2,4,5-tri-isopropylbenzonitrile) (VII) with Caesium Fluoride.—Perfluoro-(2,4,5-tri-isopropylbenzonitrile) (0.64 g, 1 mmol), dried caesium fluoride (*ca.* 0.5 g), and tetramethylene sulphone (2 ml) in a 25 ml Pyrex evacuated tube, heated for 20 h at 170° with continuous shaking, gave no gaseous product. The liquid and solid products were dissolved in acetone (10 ml); the resultant solution was analysed by g.l.c. (8 m trixylyl phosphate; 140°) and by comparison with pure samples shown to contain perfluoro-(2,4,5-tri-isopropylbenzonitrile) (2%), and perfluoro-(2,4,6-tri-isopropylbenzonitrile) (81%), together with several unidentified components. The acetone solution was poured into water (50 ml) and the solid which precipitated was filtered off and dried by washing with ether; yield 0.50 g; m.p. 90—120°. The product was recrystallised (chloroform) to give perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII) (0.40 g, 63%), m.p. 129—130°.

Reaction of Perfluoro-(4-isopropylbenzonitrile) (III) with Sodium Methoxide.—Perfluoro-(4-isopropylbenzonitrile) (III) (1.03 g, 3 mmol) was added to sodium (0.14 g, 6 mg atom) in dry methanol (5 ml) and the mixture refluxed for 1 h then poured into water (50 ml). The lower layer was

¹⁵ C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, in preparation.

¹⁶ L. J. Belf, M. W. Buxton, and G. Fuller, *J. Chem. Soc.*, 1965, 3372.

TABLE 4
 B.p., analytical, and u.v. data

Fluorobenzonitrile (IV) 2-(iso-C ₃ F ₇)	B.p. (°C) [mmHg]	Formula	Found (%)			Required (%)			λ _{max.} /nm (ε) *
			C	N	I	C	N	F	
(IV) 2-(iso-C ₃ F ₇)	200—201 [754]	C ₁₀ F ₁₁ N							224 (9670) 231 (9900) 281 (2850)
(III) 4-(iso-C ₃ F ₇)	192—193 [754] †	C ₁₀ F ₁₁ N	35.1	4.4	61.1	35.0	4.1	60.9	223 (17,400) 231 (17,400) 297 (3170)
(V) 2,4-(iso-C ₃ F ₇) ₂	(57—58) ‡	C ₁₃ F ₁₇ N	31.9	2.9	65.0	31.7	2.8	65.5	226 (12,300) 233 (11,850) 288 (3760) 295 (4080)
(VI) 2,5-(iso-C ₃ F ₇) ₂ ?	(55—57) ‡	C ₁₃ F ₁₇ N							
(VII) 2,4,5-(iso-C ₃ F ₇) ₃	(77—78) ‡	C ₁₅ F ₂₃ N	30.0	2.2	67.9	29.9	2.2	67.9	228 (11,700) 233 (11,600) 306 (6850)
(VIII) 2,4,6-(iso-C ₃ F ₇) ₃	(129—130) ‡	C ₁₅ F ₂₃ N	29.8	2.8	67.7	29.9	2.2	67.9	232 (11,950) 239 (11,600) 283 (1170)

* In hexane solution. † Lit.,⁵ 191—192° [760]. ‡ M.p.

separated; distillation gave 3,5-difluoro-4-heptafluoroisopropyl-2,6-dimethoxybenzonitrile (XV) (0.85 g, 77%) (Found: C, 39.3; H, 1.7; F, 46.5; N, 4.1%; *M*⁺, 367. C₁₂H₉F₉NO₂ requires C, 39.2; H, 1.7; F, 46.6; N, 3.8%; *M*, 367) as a viscous liquid, b.p. 148—150° at 15 mmHg.

Hydrolysis of Perfluoro-(4-isopropylbenzonitrile) (III).—Perfluoro-(4-isopropylbenzonitrile) (III) (2.06 g, 5 mmol) was heated at ca. 100°, with stirring, with conc. sulphuric acid (5 ml). The mixture was cooled, water (5 ml) was added, then the mixture was heated under reflux for 5 h, cooled, and poured into ice-water (50 ml). Extraction with ether (2 × 25 ml) followed by removal of the solvent gave a white solid, recrystallised [from light petroleum (b.p. 60—80°)] to give perfluoro-(4-isopropylbenzoic acid) (XVI) (1.58 g, 71%) (Found: C, 33.3; H, 0.5; F, 57.4%; *M*, 362. Calc. for C₁₀HF₁₁O₂: C, 33.2; H, 0.3; F, 57.7%; *M*, 362) as a crystalline solid, m.p. 110—111° (lit.,⁵ 95° [S-benzylisothiuronium salt, m.p. 165—166° (from aqueous ethanol)]).

Attempted Hydrolysis of Perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII).—Perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII) (1.3 g, 2 mmol) failed to react with conc. sulphuric acid (10 ml) at ca. 100° with stirring during 2 h.

Similar results were obtained with conc. phosphoric acid and trifluoroperoxyacetic acid in an open system, and with conc. sulphuric acid and conc. phosphoric acid in a sealed

tube. Heating the nitrile under reflux in dilute sodium hydroxide solution for 5 h gave only a sticky yellow oil which could not be purified. Use of aqueous 50% sodium hydroxide, ethanolic sodium hydroxide, and n-butanolic potassium hydroxide also gave unidentified oils.

Perfluoro-(2,4,5-tri-isopropylbenzonitrile) (VII) likewise gave unchanged material with conc. sulphuric acid and a yellow oil with sodium hydroxide solution.

Reaction of Perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII) with Sodium Methoxide.—Perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII) (1.3 g, 2 mmol), heated under reflux with sodium (0.1 g, 4 mg atom) in dry methanol (10 ml) for 2 h, gave a water-insoluble yellow oil (0.8 g) which could not be purified.

Reaction of Perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII) with Lithium Aluminium Hydride.—Perfluoro-(2,4,6-tri-isopropylbenzonitrile) (VIII) (1.3 g, 2 mmol) was stirred with lithium aluminium hydride (0.2 g, 5 mmol) in dry tetrahydrofuran (10 ml) at 0° for 2 h. The yellow-green mixture was poured into water (100 ml) but the yellow oil which separated (0.7 g) could not be purified.

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