Some Characteristics of the Fluorine Nuclear Magnetic Resonance of Alicyclic Fluorocarbons

V. W. GASH AND D. J. BAUER

Central Research Department, Monsanto Company, St. Louis, Missouri

Received May 31, 1966

A fluorine nmr study of several alicyclic fluorocarbons has shown some general correlations between chemical shifts and fluorine environment. Other aspects of the nmr data relative to the characteristics of these ring compounds are presented.

During some recent work in fluorocarbon chemistry, the need arose for additional information on the fluorine nmr spectroscopy of such compounds, particularly its application to the solution of structural problems associated with alicyclic molecules.

The only significant catalog of fluorine nmr data is a recent one[1] listing the chemical shifts of a number of fluorine compounds including some alicyclic molecules. Although useful, part of the data is accurate, some is approximate, and many key structures are not represented.

The present work involved a limited fluorine nmr study of alicyclic fluorocarbon rings which were available from a synthesis program and was designed to derive correlations useful in structural analyses of similar compounds. The precise measurement of F^{19} spectra of a number of alicyclic fluorocarbons is reported herein. Some correlations are evident between chemical shifts and fluorine environment in these ring compounds. Also presented is some additional evidence relating chemical shift to ring size and perhaps relevant to ring strain and conformational mobility of these alicyclic rings. It was also found that the multiplicity of the shifts of some of these simple ring systems either requires as an explanation through-space coupling or appreciable through-bond coupling of fluorines situated four bonds apart.

Experimental Section

After consideration of methods and standards for recording of spectral data, the most reliable procedure appeared to be that of Tiers.[2]

Infinite dilution in trichlorofluoromethane (which fulfills all of the requirements of a good internal reference[3]) was chosen by Tiers as the standard state for measurement of fluorine chemical shifts based on the φ scale defined as follows

$$\varphi_{(\mathrm{CFCl_3})} = \pm 0.0000 \text{ ppm}$$

$$\varphi_{\mathrm{compd}} = 10^6 \frac{(H_{(\mathrm{S})} - H_{(\mathrm{CFCl_3})})}{H_{(\mathrm{CFCl_3})}}$$

$$\varphi = \varphi^* \text{ (infinite dilution)}$$

The data presented in ref 2 showed φ^* a linear function of volume per cent of solute and, for practical purposes, the difference between φ and φ^* is less than experimental error in dilute solutions. We have adopted this experimental technique in our work using 10% solutions.

All chemical shifts were determined on a Varian HR-60 spectrometer (56.444 Mc) except those of structures **2** and **6** (Table I) which were determined on a newly acquired Varian A56/60 (56.466 Mc). The latter instrument was also used for measuring all line widths, fluorine ratios, and coupling constants. The A56-60 was operated in a straightforward manner.

Chemical shifts were measured on the HR-60 as follows. The signals were phase detected by passing them through a Varian V-3521 integrator for baseline stabilization. Spectra were recorded on a high-response Mosely autograph recorder. Resolution ranged from 0.5 to 1.0 cps throughout the spectra collection period. The amplitude was adjusted so that at least the third 2-kc integrator side band of each shift appeared in the spectrum. A precisely measured modulation was then applied through the linear sweep coils, usually of the order of 200–300 cps, which produced secondary side bands on all the integrator side bands as well as on all the shifts. By this technique, a side band of a shift and one of the reference were brought into close proximity, thereby minimizing the usual errors involved in the measurement of a large chemical shift.

All chemical shifts (φ^*) reported in Table I are reproducible to ± 0.1 ppm except those of structures **3** and **8**. These spectra showed an additional uncertainty of about ± 0.1 ppm owing to line broadness and unsymmetrical multiplicity, respectively. Accuracy of the coupling constants is estimated as ± 0.1 cps. The materials which were used in this investigation are listed in Table II.

Results

A tabular summary of the nmr data on the compounds studied is given in Table I.

The spectra of the saturated perfluorocyclobutane and-pentane consisted of one sharp singlet at 134.6 and 132.9 ppm, respectively, indicating all fluorines to be equivalent (in the same average environment) in the respective structures. A value of 138 ppm has been reported[4] for the neat perfluorocyclobutane. Perfluorocyclohexane exhibited one broad singlet, which is a result of two fluorine environments only partially averaged by an intermediate rate of ring inversion (see below).

The following assignments were evident in the analogous series of monounsaturated perfluorinated ring systems. The cyclobutene system showed two types of fluorines with a population ratio of nearly 2:1 and the assignments are unambiguous on this basis alone.

Perfluorocyclopentene exhibited three groups of nonequivalent fluorines. Assignment a was made on the basis of fluorine population. Assignments b and c were made by comparison to structure **4**, which clearly predicts the olefinic fluorines to resonate at a higher field than the *gem*-fluorines.[5]

Assignment c (vinyl fluorines) in the perfluorocyclohexene ring is unambiguous. Assignments a and b were made with certainty based on the resonance of like groups in the ring systems (structures **1–5**) preceding it in Table I. All of the chemical

---

[1] J. J. Burke and T. R. Krugh, "A Table of F^{19} Chemical Shifts for a Variety of Compounds," Mellon Institute, Pittsburgh, Pa.

[2] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[3] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillian Co., New York, N. Y., 1959.

[4] N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

[5] Burke and Krugh[1] list φ^* values of +117.8, +129.7, and +151.1 for this structure assigning the fluorines as in Table I. Although their values were calculated from data obtained on the neat liquid with an external C_4F_8 reference, they are in fairly good agreement.

TABLE I

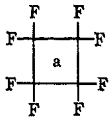
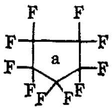
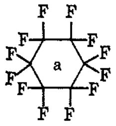
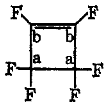
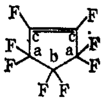
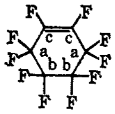
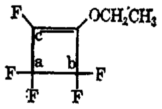
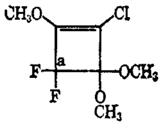
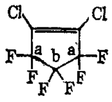
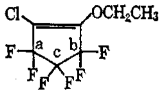
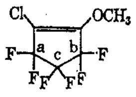
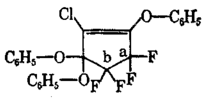
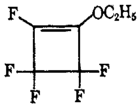
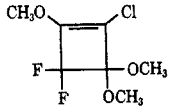
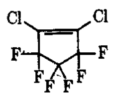
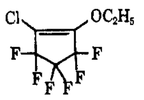
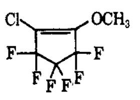
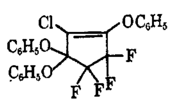
Structure	Assignment	φ^*	Multiplicity	J (FF), cps	Line width at 0.5 height, cps ($T = \pm 1°$)	Measured fluorine ratio
 1	a	+134.6	Singlet		≤0.8 (30) ≤0.8 (−70)	
 2	a	+132.9	Singlet		≤0.7 (30) ≤0.8 (−70)	
 3	a	+133.0	Singlet		49 ± 5 (25) 38 ± 5 (30)	
 4	a	+120.3	Multiplet			1.96
	b	+130.4	Multiplet			1.00
 5	a	+117.8	Multiplet			1.98
	b	+130.2	Multiplet			1.01
	c	+150.2	Multiplet			1.00
 6	a	+119.0	Multiplet			2.03
	b	+133.8	Multiplet			2.05
	c	+151.9	Multiplet			1.00
 7	a	+162.6	Singlet		≤0.8 (30)	
 8	a or b	+116.9	Multiplet			2.03
	b or a	+119.6	Multiplet			2.09
	c	+143.0	Multiplet			1.00
 9	a	+116.8	Singlet		1.3 (30)	
 10	a	+114.4	Triplet	3.1		2.03
	b	+130.4	Pentet	3.1		1.00
 11	a or b	+112.1	Pseudo-pentet			1.04
	b or a	+115.4	Pseudo-pentet			1.00
	c	+130.4	Pseudo-pentet			1.01
 12	a or b	+112.2	Pseudo-pentet			1.00
	b or a	+114.9	Pseudo-pentet			1.02
	c	+130.3	Pseudo-pentet			1.02
 13	a	+116.5	Triplet	4.6		1.00
	b	+124.3	Triplet	4.6		0.98

TABLE II

Compd	Structure	Bp, °C (mm)	Source
Perfluorocyclobutane (1)[a]		−6	Penninsular
Perfluorocyclopentane (2)		26–28	Synthesized[b]
Perfluorocyclohexane (3)		50–52[c]	Imperial Smelting, Ltd.
Perfluorocyclobutene (4)[a]		5–6	Penninsular
Perfluorocyclopentene (5)		33–35	Synthesized[d]
Perfluorocyclohexene (6)		53	Imperial Smelting, Ltd.
Hexafluorobenzene (7)		81	Imperial Smelting, Ltd.
1-Ethoxy-2,3,3,4,4-pentafluoro-1-cyclobutene (8)		66 (200)	Synthesized[e]
1-Chloro-3,3-difluoro-2,4,4-trimethoxy-1-cyclobutene (9)		80 (12)	Synthesized[f]
1,2-Dichloro-3,3,4,4,5,5-hexafluoro-1-cyclopentene (10)		90	Penninsular
1-Chloro-2-ethoxy-3,3,4,4,5,5-hexafluoro-1-cyclopentene (11)		55 (25)	Synthesized[g,i]
1-Chloro-2-methoxy-3,3,4,4,5,5-hexafluoro-1-cyclopentene (12)		63 (55)	Synthesized[h]
1-Chloro-3,3,4,4-tetrafluoro-2,5,5-triphenoxy-1-cyclopentene (13)		Mp 58–59[c]	Synthesized[j]

[a] The nmr measurements were made on the 10% (v/v) solution in a sealed Varian tube. [b] This fluorocarbon was prepared by conventional fluorination of cyclopentane with cobalt trifluoride at 305°: R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 292 (1947). Amine treatment gave material of 85% purity. Compounds 2 and 5 were prepared at the Monsanto Research Corp. Laboratory, Boston, Mass. [c] Solid compounds made up on a 10% (w/v) basis in CCl_3F. [d] The procedure of Maynard was used to convert octachlorocyclopentene to the fluorocarbon: J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963). [e–h] These compounds have been reported previously: J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 4480 (1950); J. D. Park, C. M. Snow, and J. R. Lacher, *ibid.*, **73**, 2342 (1951); R. A. Shepard, H. Lessoff, J. D. Domijan, D. B. Hilton, and T. F. Finnegan, *J. Org. Chem.*, **23**, 2011 (1958); A. L. Henne and K. A. Latif, *J. Ind. Chem. Soc.*, **30**, 809 (1953), respectively. [i] The proton nmr resonance of compound 11 in 30 volume % carbon tetrachloride showed a quartet ($\delta = -4.56$ ppm) and a triplet ($\delta = -1.44$ ppm) referenced to TMS internal standard, thus confirming its structure. [j] *Anal.* Calcd for $C_{23}H_{15}ClF_4O$ (450.9): C, 61.26; H, 3.35; Cl, 7.86; F, 16.86. Found: C, 61.15; H, 3.46; Cl, 7.86; F, 16.61.

shifts of the three monounsaturated systems were complex multiplets.

Hexafluorobenzene (**7**, included to obtain a precise φ^* value for an all vinyl fluoro environment) and 1-chloro-3,3-difluoro-2,4,4-trimethoxy-1-cyclobutene (**9**) each exhibited only one singlet indicating all fluorines to be equivalent in the respective structures.

In 1-ethoxy-2,3,3,4,4-pentafluoro-1-cyclobutene (**8**) the olefinic fluorine c was assigned to $\varphi^* = +143.0$ on the basis of fluorine count and its high upfield position. Each of the remaining shifts (a,b) corresponds to one of the two sets of *gem*-fluorines in the molecule. The available evidence precludes a definite assignment of these closely related fluorines.

Two shifts were detected in the spectrum of 1,2-dichloro-3,3,4,4,5,5-hexafluoro-1-cyclopentene (**10**) with a ratio of nearly 2:1. The shift assignments are unambiguous on the basis of this ratio.

The spectra of the closely related 1-chloro-2-ethoxy-3,3,4,4,5,5-hexafluoro-1-cyclopentene (**11**) and the 2-methoxy derivative **12** each showed the presence of three types of nonequivalent fluorines in very nearly a 1:1:1 ratio. The highest φ^* values are readily assignable to the *gem*-fluorines in the 4 positions (*cf.* structures **5** and **10**). Each of the remaining two shifts in each structure are assignable to one set of *gem*-fluorines in the 3 and 5 positions.

The spectrum of 1-chloro-3,3,4,4-tetrafluoro-2,5,5-triphenoxy-1-cyclopentene (**13**) showed this structure to contain two nonequivalent pairs of fluorine atoms (two triplets with a fluorine ratio of nearly 1:1). The φ^* values of the *gem*-fluorines in the 3,5 positions of structures **5**, **10**, **11**, and **12** were relatively invariant even though the olefinic substituents were fairly diversified. The φ^* value of +116.5, which is in the same range, was therefore assigned to the 3 position in this structure.

Discussion

Chemical Shifts.—The general correlations possible between chemical shifts and fluorine environment are evident in the greater chemical shift of vinyl fluorines ($\varphi^* = 162.6–130.4$) relative to insulated *gem*-difluoro groups (*i.e.*, situated between other CF_2 groups) ($\varphi^* = 134.6–130.2$) and the latter appear in the upper part of the range for all types of *gem*-difluoro groups. This upfield displacement of vinyl fluorines was noted by earlier workers[6–9] particularly in the acyclic series where shielding is in the order $CF > CF_2 > CF_3$.

Muller, *et al.*,[6] report δ values (relative to CF_3COOH) of $CF_3 = -14–16$; $CF_2 = 35–55$; $CF = 107–113$. The more positive shifts imply a higher electron density around the F^{19} nucleus in vinyl fluorines than in *gem*-difluoro groups. The electronegative group (F in *gem*-difluoro) must cause deshielding by electron withdrawal from the common carbon atom. A donating group should conversely cause increased shielding and evidence for this is the very high chemical shift shown by the $>CHF$ group in undecafluorocyclohexane. The

---

[6] N. Muller, P. C. Lauterbur, and C. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1807 (1957).

[7] H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

[8] A. Saika and C. P. Slichter, *ibid.*, **22**, 26 (1954).

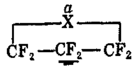
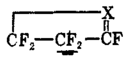
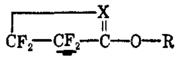
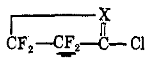
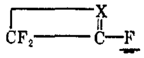
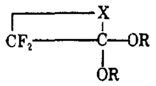
[9] S. K. Alley, Jr., and R. L. Scott, *J. Chem. Eng. Data*, **8**, 117 (1963).

φ^* calculated from the data of Feeney and Sutcliffe[10] ($\varphi^* = \varphi^*_R + \varphi_S$) was 255 ppm. Such interpretation also rationalizes the downfield shift observed for a *gem*-difluoro group (φ^* = 112.1 to 120.3) adjacent to a vinylic grouping which is functioning as an electron-withdrawing group.

Finally, the shift position of a *gem*-difluoro group adjacent to a ring ketal grouping, but isolated from a vinylic grouping is shown by **13** of Table I. The rationale of this chemical shift at 124.3 ppm is not readily apparent considering that a highly electronegative and low-bulk group (F) was displaced with a less electronegative group of high bulk resulting in a deshielding of the CF_2 group at position 4. The proposal of Pople[11] that the local field associated with the π-electron system in molecules containing six-membered aromatic rings is sometimes important in determining chemical shifts of neighboring nuclei could qualitatively explain the fluorine shielding observed in this compound. Waugh and Fessenden[12] as well as Curtin and Dayagi[13] have logically utilized this concept to explain anomalous proton shielding in polymethylene benzenes and *cis*-1,2-diarylcyclopentanes, respectively. Further observations of this type of structure are necessary.

These correlations of shifts relative to groups are summarized in Table III.

TABLE III

Group	Observations	Range of φ^* found
 $\overset{X^a}{CF_2{-}\underline{CF_2}{-}CF_2}$ 1	8	134.6–130.2
 $CF_2{-}\underline{CF_2}{-}\overset{X}{\overset{\Vert}{C}}F$ 2	4	120.3–116.9
 $CF_2{-}\underline{CF_2}{-}\overset{X}{\overset{\Vert}{C}}{-}O{-}R$ 3	4	119.6–112.1
 $CF_2{-}\underline{CF_2}{-}\overset{X}{\overset{\Vert}{C}}{-}Cl$ 4	3	115.4–112.1
 $CF_2{-}\overset{X}{\overset{\Vert}{C}}{-}\underline{F}$ 5	4	151.9–130.4
 $CF_2{-}\overset{X}{\overset{\vert}{\underset{OR}{\underset{\vert}{C}}}}{-}OR$ 6	2	124.3, 116.8

[a] X is a ring-closing function.

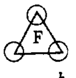
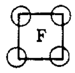
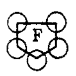
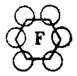
Although the CF_2 shifts in groups 2–4 (Table III) are listed separately, too few observations are recorded here to make any definitive conclusions regarding the effect of vinyl substituents (F, Cl, OMe, OEt, OC_6H_5) upon the shift position of the adjacent CF_2 group and the fluorine atom in the other vinyl position.

It has been suggested[14] that changes in bonding properties such as ring strain will affect chemical shift values. The limited data so far available indicate this may be factual provided *like* structures are compared as shown in Table IV with the shifts relevant to the circled fluorine atoms. The chemical shift evidence indicates the order of ring strain in saturated alicyclics to be 3 > 4 > 5 ~ 6 and 6 > 5 within the monounsaturated alicyclics. The conformational mobility of the four- to six-membered alicyclic fluorocarbons is also evident in the line widths *vs.* temperature study discussed below. The six-membered ring exhibits a broad singlet at room temperature which has been previously resolved by Tiers.[15] Conversely, the four- and five-membered ring systems failed to show any line broadening to −70°. The Stuart and Briegleb models also indicate a more flexible five-membered ring in the fluorocarbon alicyclic series than the sterically crowded (1,3-fluorine interaction) cyclohexane ring.

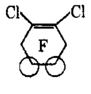
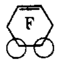
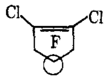
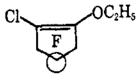
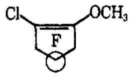
TABLE IV

CHEMICAL SHIFT *vs.* RING STRAIN

I. Saturated Alicyclics, φ^{*a}

			
$\geq 151^b$	134.6	132.9	133.0

II. Monounsaturated Alicyclics, φ^*

			
132.3	133.8		
			
130.4	129.9	130.4	130.2

[a] The φ^* values refer to chemical shift values of the circled fluorines. [b] See ref 14.

Recently we have had the occasion to study[16] the properties of some fluids based on four- to six-membered rings as connecting groups. Comparative data on related structures based on low temperature viscosities indicate desirable fluid properties in the order 5 > 4 ≫ 6.

Line Widths.—The broad resonance peak of perfluorocyclohexane (49 cps at 25° and 38 cps at 30°) is attributable to ring inversion of the nonplanar ring system. At these temperatures, ring inversion is only rapid enough to partially average the shielding values of the A- and B-type fluorine atoms. Tiers[15] has previously shown this compound to be nonplanar by resolution of its F^{19} resonance into an AB-type spectrum at −66° ($\Delta\delta$ = 18.2 ppm).

The perfluorocyclobutane ring system exhibited a sharp singlet (0.8 cps from 30 to −70°). The failure to resolve this singlet into an AB-type spectrum or even to broaden the singlet indicates a very high ring inversion frequency or a planar ring.[17] Our finding that the singlet of the perfluorocyclopentane ring, known to be nonplanar, did not broaden under the same temperature interval does not allow a definite conclusion to be made between these two possibilities.

A temperature study of the highly substituted ring **13** 1-chloro-3,3,4,4-tetrafluoro-2,5,5-triphenoxy-1-cyclo-

---

[10] J. Feeney and L. H. Sutcliffe, *Trans. Faraday Soc.*, **56**, 1559 (1960).

[11] J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

[12] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[13] D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42**, 867 (1964).

[14] E. G. Brame, Jr., *Anal. Chem.*, **34**, 591 (1962).

[15] G. V. D. Tiers, *Proc. Chem. Soc.*, 389 (1960).

[16] Unpublished data.

[17] H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.*, **18**, 569 (1950).

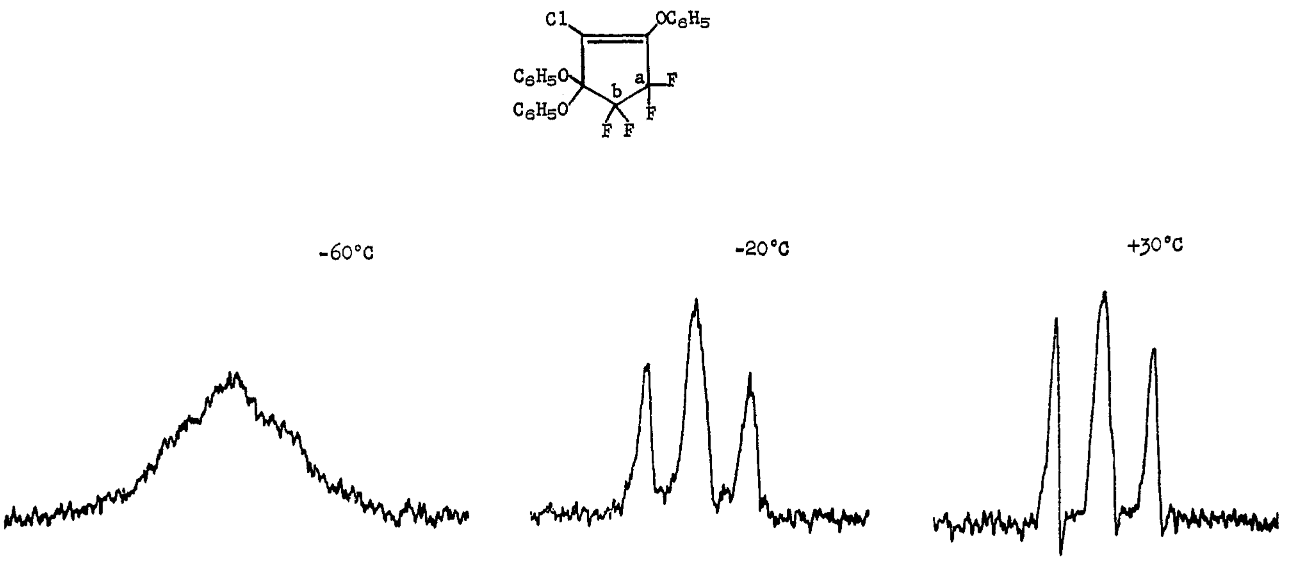


Figure 1.—F^{19} spectra of the "a" fluorine atoms in 1-chloro-3,3,4,4-tetrafluoro-2,5,5-triphenoxy-1-cyclopentene at three different temperatures.

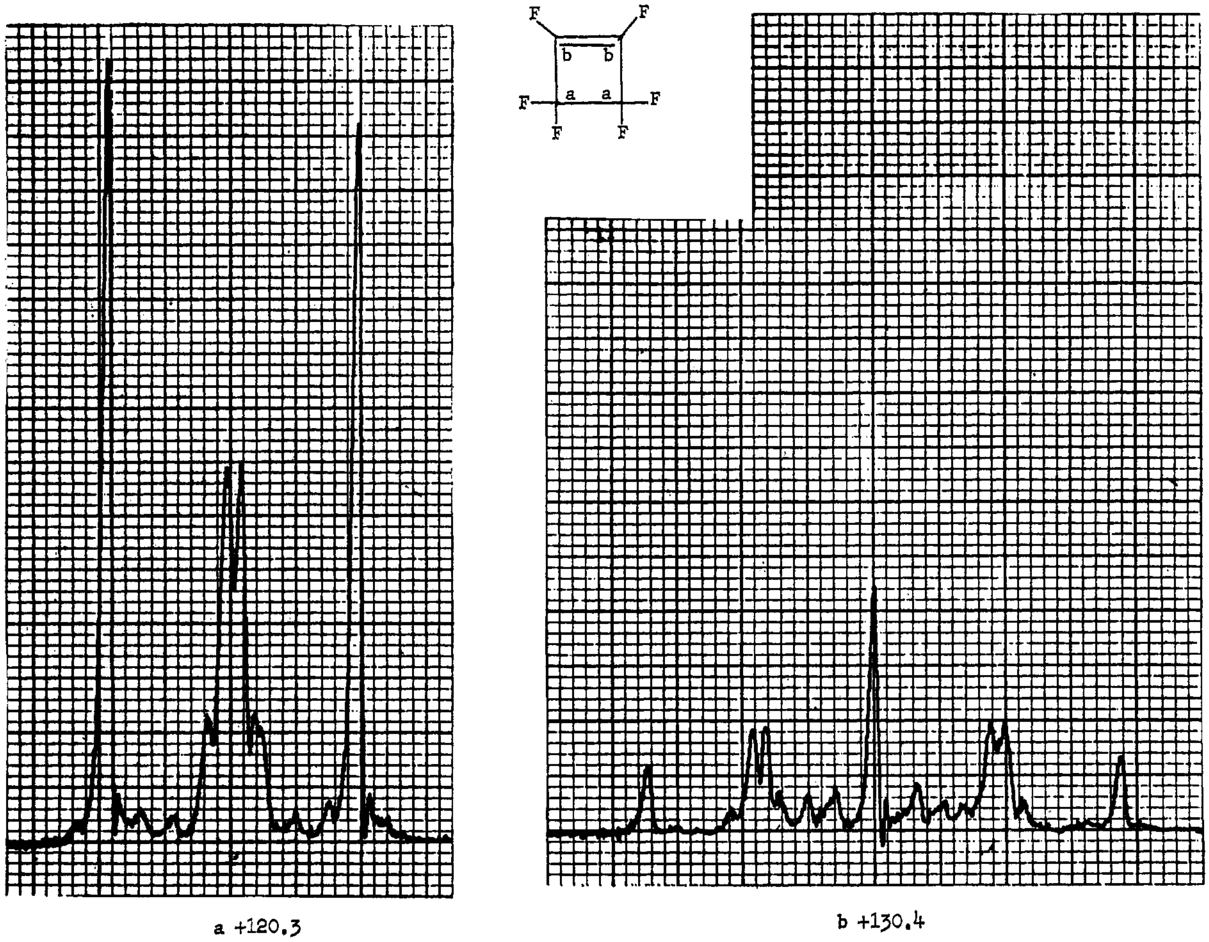


Figure 2.—F^{19} spectrum of perfluorocyclobutene.

pentene, is shown by Figure 1. The triplet at 116.5 ppm assigned to the "a" fluorines (see Table I) is well defined at 30°, broadens at −20°, and finally coalesces into a broad band at −60°. The resolution at all three temperature measurements was maintained at <1 cps. The progressive broadening with lower temperature is clear evidence of the noncoplanarity of this ring system. The broad band is interpreted as representing an intermediate ring innersion rate at which the environments of the geminal fluorines are only partially averaged (*i.e.*, between an inversion rate resulting in an A_2X_2 case and one resulting in an ABXY case).

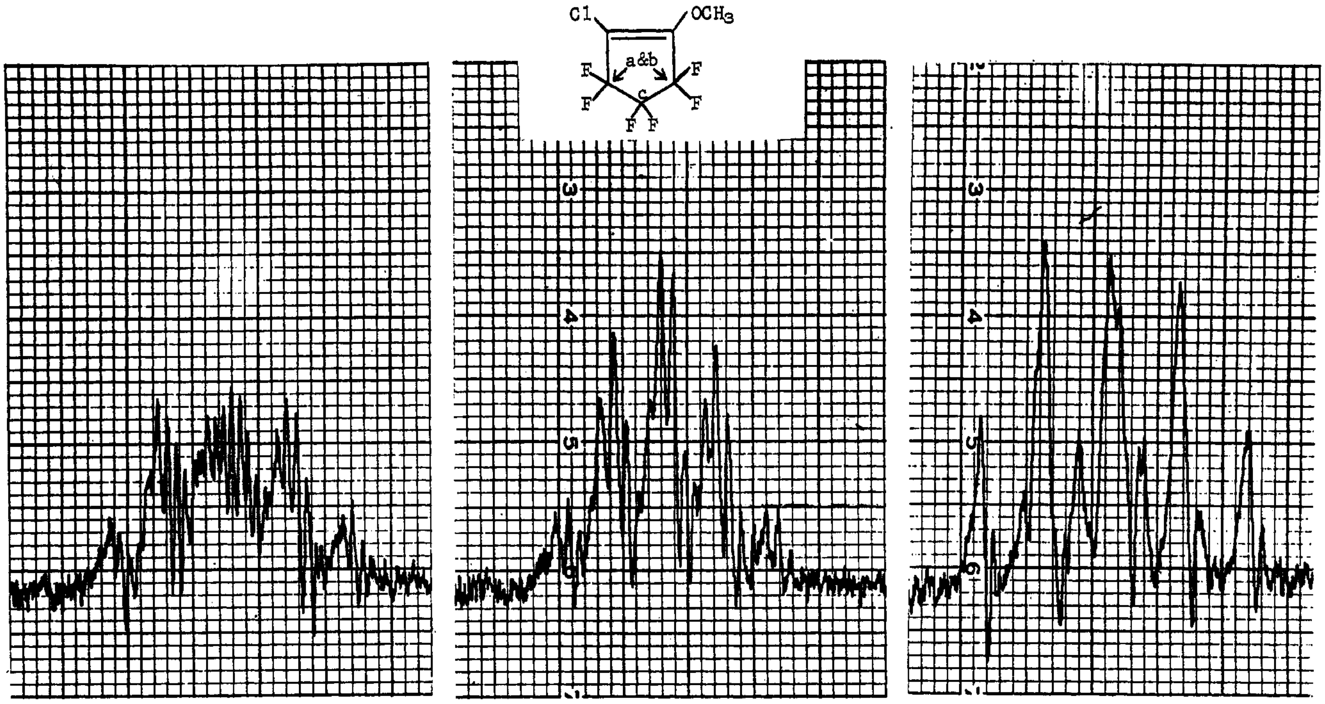
Multiplicity of Chemical Shifts.—Petrakis and Sederholm,[18] Roberts, *et al.*,[19] and Ng and Sederholm[20] have suggested that a major contribution to coupling con-

---

[18] L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961).

[19] D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

[20] S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964).



a +112.2 b +114.9 c +130.3

Figure 3.—F^{19} spectrum of 1-chloro-2-methoxy-3,3,4,4,5,5-hexafluoro-1-cyclopentene.

stants between fluorine nuclei separated by more than three bonds is a result of through-space coupling rather than through-bond coupling. Petrakis and Sederholm and also Ng and Sederholm base their conclusion on the sensitivity of coupling constants to internuclear distances between interacting nuclei. While Boden, Feeney, and Sutcliffe[21] have recently questioned the proposed[18,20] relationship between fluorine spatial separation and the magnitude of the coupling constant, they do concur in the interaction of spatially close fluorine nuclei. The multiplicity observed in several of the ring compounds of Table I appears to substantiate the existence of through-space coupling. The measured coupling constants, **10** and **13**, are small as expected for fluorines on adjacent carbon atoms. The complex multiplicity of such simple ring compounds as **4**, **5**, **6**, **8**, **11**, and **12** (Table I) would appear to reinforce the opinion that through-space cross-ring coupling is significant for fluorine nuclei. Cross-ring H^1–F^{19} coupling has been reported[22] in some four-membered ring systems. The multiplicity observed for two of these simple compounds is illustrated in Figures 2 and 3.

The simple A_2X_4 spectrum (triplet and pentet) of structure **10** and the simple A_2X_2 spectrum (two triplets) of structure **13** indicate the nonplanar nature of these ring systems. A rigid ring would be expected to exhibit discretely different *cis* and *trans* coupling which would result in more complex spectra than those observed. Inversion of the ring system is rapid enough to average the *cis* and *trans* coupling to a single observed value.

Acknowledgment.—The authors wish to express appreciation to Dr. J. W. Dale and Dr. G. J. O'Neill for those preparations carried out at the Monsanto Research Corp. Laboratory, Boston, Mass.

---

[21] N. Boden, I. Feeney, and L. H. Sutcliffe, *J. Chem. Soc.*, 1965, 3482.

[22] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 331–334.