extract was dried over magnesium sulfate and the solvent was removed on the rotary evaporator. The residue was twice dissolved in 10 ml. of petroleum ether (b.p. 30–40°) and the petroleum ether removed on the rotary evaporator. Attempts to distill a portion of the residue at reduced pressure led to decomposition. The remainder of the residue was heated at ~50° under reduced pressure for 5 min. and gave 1.5 g. of 4-methyl-3-penten-1-yl tosylate.

This compound could not be obtained in crystalline form. The purity was established by examination of the nuclear magnetic resonance spectroscopy. The n.m.r. spectrum (Figure 1) shows only one minor absorption due to an impurity at 0.9 p.p.m. The absence of other absorptions which could be ascribed to impurities and the location of the resonance suggests that it may be due to a high-boiling hydrocarbon. An equivalent quantity of petroleum ether was evaporated to dryness (1 hr. at ~50° and 20 mm.) on the rotary evaporator and the flask rinsed with 1 ml. of ethanol-free chloroform. The n.m.r. spectrum of the chloroform solution showed an absorption at 0.9 p.p.m. (The same absorption was detected in the n.m.r. spectrum of *cis*-3-penten-1-yl tosylate.)

The high reactivity of 4-methyl-3-penten-1-yl tosylate made the measurement of the rate of solvolysis somewhat difficult. (The half-life is less than 1 min. at 50° in 98% formic acid.) However, the absence of any detectable deviation from linearity in the rate of solvolysis further substantiates its purity.

Nuclear Magnetic Resonance Spectroscopy. Studies of 1,1,4,4-Tetrafluoro-1,3-alkadienes[1]

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1,1,4,4-Tetrafluoro-1,3-butadiene is indicated by dipole moment studies to exist in the s-trans conformation. The $^{19}F-^{19}F$ spin–spin coupling constants for this compound are surprisingly similar to those of bis-4,5-(difluoromethylene)cyclohexene and perfluoro-1,2-dimethylenecyclobutane, both of which substances have their double bonds held in s-cis configurations. The results are related to the mechanism of transmission of fluorine–fluorine spin–spin interactions and are inconsistent with a predominance of a "through-space" mechanism of coupling.

Introduction

The conformational *s-cis–s-trans* equilibria of 1,3-butadienes have been investigated by a number of techniques. Detailed studies of the infrared and Raman spectra and extensive calorimetric measurements have indicated that 1,3-butadiene exists predominantly (at least 96%) in the *s-trans* form at room temperature.[2–5] Substituted butadienes have received less attention. Microwave studies of 2,3-dimethyl-1,3-butadiene, isoprene, and fluoroprene provide no evidence for the presence of more than a few per cent of the *s-cis* form.[6,7] 2,3-Di-*t*-butyl-1,3-butadiene has been reported to exist in a non-*transoid* conformation as a result of steric interactions of the bulky *t*-butyl groups.[8]

From the intensities of ultraviolet absorptions, it has been concluded that the double bonds in 2,4-dimethyl-1,3-pentadiene and 2-chloro-4-methyl-1,3-pentadiene deviate some 50° from planar, while with 1,1,-4,4-tetrachloro-1,3-butadiene the favored conformation is >70° from planar.[9] Infrared and Raman studies indicate that chloroprene, 2,3-dichloro-1,3-butadiene, and isoprene exist predominantly in the *s-trans* form while hexachloro-1,3-butadiene has a preferred nonplanar conformation.[10] From analysis of the infrared and Raman spectra and the polarization ratios of the stronger Raman lines of hexafluoro-1,3-butadiene, Nielsen and Albright concluded that "the spectral data are inconsistent with the assumption of molecular symmetry C_{2h} (*trans* form) but can be interpreted satisfactorily on the basis of symmetry C_{2v} (*cis* form)."[11]

The report by Anderson, Putnam, and Sharkey[12] that the 40-Mc.p.s. fluorine nuclear magnetic resonance of 1,1,4,4-tetrafluoro-1,3-butadiene (I) exhibits a broad (~160 c.p.s.) but unresolvable band which at temperatures of −80 to −120° sharpens somewhat suggests the possibility that conformational equilibrium between the *s-trans* form (Ia) and *s-cis* form (Ib) might be only slowly established, the broad band being the result of slow exchange of the fluorine nuclei between magnetically nonequivalent environments in Ia

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[1] Supported in part by the Office of Naval Research and the National Science Foundation.

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[4] M. Batuev, A. Onishchenko, A. Matveeva, and N. I. Aronova, *Proc. Acad. Sci. USSR*, **135**, 543 (1960).

[5] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta. Chem. Scand.*, **12**, 1221 (1958).

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[8] H. Wynberg, A. DeGroot, and D. W. Davies, *Tetrahedron Letters*, 1083 (1963).

[9] E. A. Braude, *Experientia*, **11**, 457 (1955).

[10] G. J. Szasz and H. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953).

[11] J. C. Albright and J. R. Nielsen, *J. Chem. Phys.*, **26**, 370 (1957).

[12] J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961).

Table I. N.m.r. Parameters for 1,1,4,4-Tetrafluoro-1,3-butadiene Derivatives[a]

1,1,4,4-Tetrafluoro-1,3-butadiene	Bis-4,5-(difluoromethylene) cyclohexene	Perfluoro-1,2-dimethylenecyclobutene
$\Delta\nu_{AB} = 1.461$	$\Delta\nu_{AB} = 1.756$	$\Delta\nu_{AB} = 1.391$
$J_{AA} = +35.7 \pm 0.2$	$J_{AA} = +31.4 \pm 0.2$	$J_{AA} = +23.2 \pm 0.2$
$J_{AB} = +36.6 \pm 0.2$	$J_{AB} = +39.0 \pm 0.2$	$J_{AB} = +14.7 \pm 0.2$
$J_{AB'} = +8.0 \pm 0.2$	$J_{AB'} = +4.8 \pm 0.2$	$J_{AB'} = +6.7 \pm 0.2$
$J_{BB'} = +4.8 \pm 0.2$	$J_{BB'} = +3.3 \pm 0.2$	$J_{BB'} = +7.6 \pm 0.2$
$J_{HH} = 10.8 \pm 0.2$	$J_{H_{v1}F_a} + J_{H_{v2}F_a} = 2.0$	
	$J_{H_{v1}F_b} + J_{H_{v2}F_b} = 0.2$	
	$J_{H_{m3}F_b} + J_{H_{m4}F_b} = 3.2$	
	$J_{H_{m3}F_a} + J_{H_{m4}F_a} = 1.3$	

[a] $\Delta\nu_{AB}$ values in p.p.m.; J values in c.p.s.

and Ib, and the sharpening at low temperature being the result of "freezing" the molecule into the *s-trans* and/or the *s-cis* form.

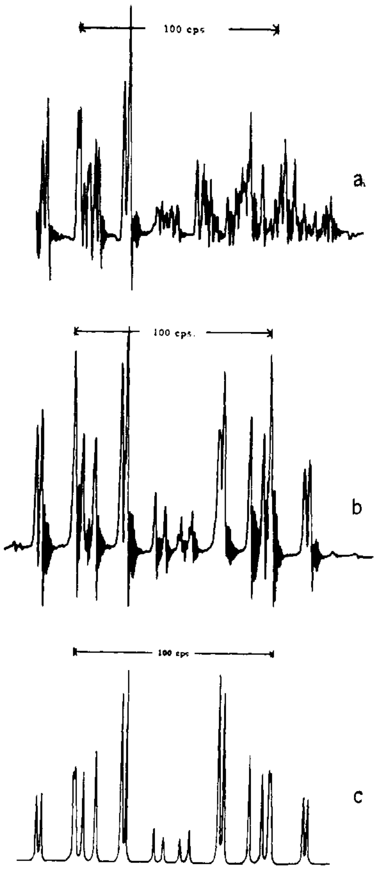
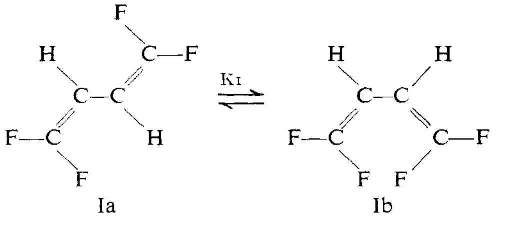


Figure 1. Fluorine nuclear magnetic resonance spectrum at 56.4 Mc.p.s. of (a) 1,1,4,4-tetrafluoro-1,3-butadiene, (b) $^{19}F-\{^1H\}$ spectrum, and (c) calculated $^{19}F-\{^1H\}$ spectrum.

We report here a determination of the favored conformation of 1,1,4,4-tetrafluoro-1,3-butadiene and studies of ^{19}F nuclear magnetic resonance spectra of some 1,1,4,4-tetrafluoroalkadienes.



Results

The ^{19}F nuclear magnetic resonance spectrum of 1,1,4,4-tetrafluoro-1,3-butadiene, I (Figure 1a), at room temperature under conditions of good resolution, is very complex and a complete analysis was only made of the AA'BB'-type spectrum obtained by decoupling the protons by double resonance.[13] The decoupled spectrum (designated as $^{19}F-\{^1H\}$[14]) is shown in Figure 1b. Average line positions determined from ten independent spectra were used in the analysis which involved the iterative technique of Swalen and Reilly.[15] The n.m.r. parameters are summarized in Table I. The H-H coupling constant for I was obtained from the ^{13}C satellites of the $^1H-\{^{19}F\}$ spectrum.

The ^{19}F n.m.r. spectrum of bis-4,5-(difluoromethylene)cyclohexene (II), prepared by the addition of tetrafluoro-1,2,3-butatriene[16] to 1,3-butadiene, is shown in Figure 2. Both the methylene (H_m) and vinyl (H_v) hydrogens were coupled to the fluorine; consequently, a completely decoupled fluorine spectrum could not easily be obtained. However, only the low-field fluorines were coupled to the vinyl hydrogens. The high-field half of the ^{19}F n.m.r. spectrum with the

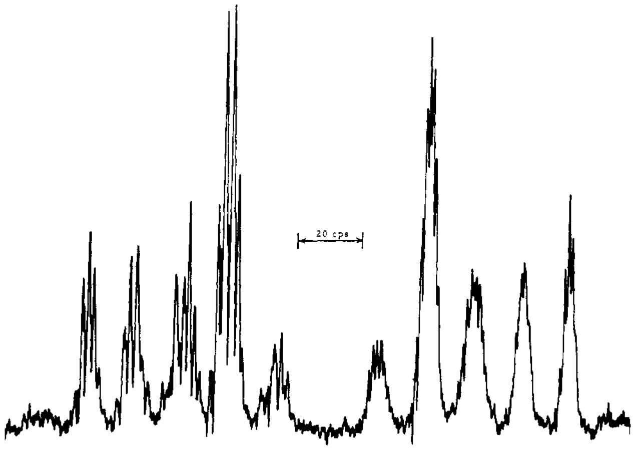


Figure 2. Fluorine nuclear magnetic resonance spectrum at 56.4 Mc.p.s. of bis-4,5-(difluoromethylene)cyclohexene.

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(13) *Cf.* J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., 1959, pp. 160, 161, 229, 230.

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(15) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(16) E. L. Martin and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 5256 (1959).

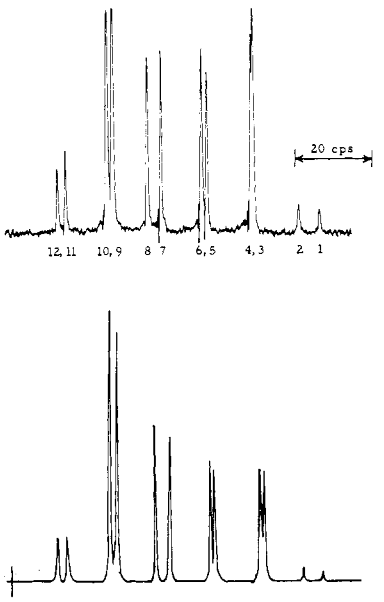

Figure 3. High-field half of the 56.4-Mc.p.s. ^{19}F-{^{1}H} nuclear magnetic resonance spectrum of bis-4,5-(difluoromethylene)cyclohexene: (a) observed, (b) calculated.

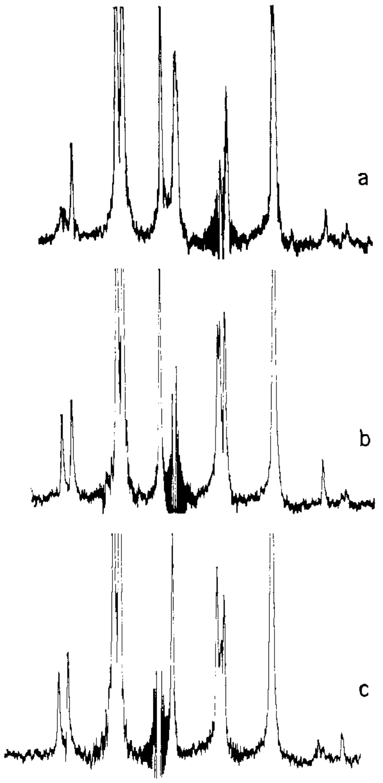

Figure 4. High-field portion of the 56.4-Mc.p.s. ^{19}F-{^{1}H$_{\mathrm{m}}$} nuclear magnetic resonance spectrum of bis-4,5-(difluoromethylene)cyclohexene with fluorine-fluorine decoupling: (a) line 6 irradiated, (b) line 7 irradiated, (c) line 8 irradiated.

methylene hydrogens decoupled (Figure 3) was used for analysis of the ^{19}F chemical shifts and coupling constants. This double-irradiation spectrum was obtained by sweeping the frequency at constant field using the audio side-band phase detection field-lock method.[17] The experimental energy levels and the n.m.r. parameters were determined by the iterative technique. The results are summarized in Table I; the observed and calculated spectra are compared in Figure 3. Fluorine double-irradiation "tickling" experiments were used to confirm the transition assignments. Irradiation of line 6 with a weak radiofrequency field causes line 12 to decrease in intensity and split while line 7 is slightly enhanced but still broadened (Figure 4a). The small intensity changes are due to the nuclear Overhauser effect which results when the population of one state is decreased and another increased upon double irradiation.[18]

Freeman and Anderson have described the expected effects of weakly irradiating one transition in a multiplet and give the following rules. (1) Any transition with an energy level in common with the transition irradiated will split into a doublet. (2) If the other two energy levels which are not common for the irradiated and perturbed transitions have the same F_z value then the doublet will be well resolved; if the F_z values differ by 2 then the doublet will be poorly resolved.[19]

Using the Freeman-Anderson tickling rules, the location of transitions 12 and 7 in the energy level diagram is easily assigned. The spectra obtained on weak irradiation of lines 7 and 8 (Figure 4b and 4c) were interpreted similarly. These experiments permit a unique set of transition assignments.

The ^{1}H and ^{19}F coupling constants of II were determined from the ^{19}F n.m.r. spectra. The methinyl proton-fluorine coupling constants ($J_{\mathrm{H_vF}}$) were determined from the ^{19}F spectrum observed upon decoupling the methylene protons. The methylene proton-fluorine coupling constants ($J_{\mathrm{H_mF}}$) were determined from the ^{19}F spectrum with the methinyl protons decoupled. The fine-structure pattern for spectra such as these has been shown[20] to be indistinguishable with either equal and unequal H-F coupling constants when the line width of a component of the observed pattern, $\delta_{1/2}$, is greater than

$$\frac{(J_{\mathrm{HF}} - J_{\mathrm{HF'}})^2}{2(J_{\mathrm{FF}} - J_{\mathrm{HH}})}$$

For these spectra, $\delta_{1/2} \approx 0.5$ c.p.s., $J_{\mathrm{FF}} = 35$ or 4 c.p.s., and $J_{\mathrm{HH}} \approx 10$ c.p.s. (for methinyl proton) or 15 c.p.s. (for methylene protons). Both J_{FF} values are consistent with any sum of J_{HF} and $J_{\mathrm{HF'}}$ equal to the observed line separations.

The ring fluorines and the vinylic fluorines in perfluoro-1,2-dimethylenecyclobutane (III)[21] were strongly coupled (~8 c.p.s.), and fluorine-fluorine decoupling was accomplished by a previously unreported technique, devised and kindly carried out for us by Drs. S. L. Manatt and D. D. Elleman. The center-band frequency was first adjusted to precisely the ring-fluorine resonance frequency; the field was then locked on the hexafluorobenzene resonance (internal) using the audio side-band phase-detection, field-lock system; the vinylic-fluorine resonances were observed by frequency sweep using audio side-band detection (Figure 5). In field-sweep spectra, it is currently im-

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(17) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2349 (1962).

(18) R. Kaiser, *ibid.*, **39**, 2435 (1963).

(19) R. Freeman and W. A. Anderson, *ibid.*, **37**, 2053 (1962).

(20) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

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Table II. Dipole Moment of 1,1,4,4-Tetrafluoro-1,3-butadiene[a]

Concn., mole fraction in CCl_4	P_2	R_2	n^4D	d^4	ϵ_{soln}	Concn., moles/ml. $\times 10^4$	Δ, $\times 10^3$
0.0232	25.69	27.70	1.4683	1.6113	2.267	2.44	2.29
0.0345	25.68	20.62	1.4637	1.6080	2.265	3.62	13.2
0.0685	26.10	20.58	1.4581	1.5945	2.257	7.19	21.4
0.1072	26.24	20.63	1.4519	1.5180	2.247	11.21	28.4

[a] $P_2^\circ = 25.06$ ml., $P_\infty = 25.47$ ml., $\mu = 0.4$ D.

possible to obtain homonuclear decoupling over such a large frequency range since both resonances are swept simultaneously. The line positions were determined by measuring the frequency of the audio side band used for observation.

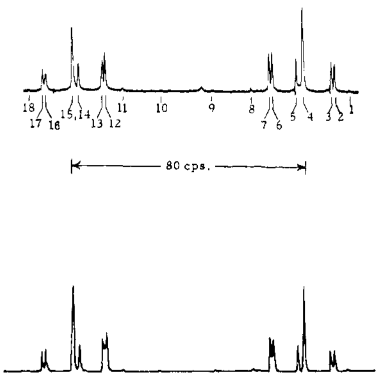

Figure 5. Fluorine, $^{19}F_v$–{$^{19}F_r$}, nuclear magnetic resonance spectrum at 56.4 Mc.p.s. of perfluoro-1,2-dimethylenecyclobutane: (a) observed, (b) calculated.

The experimental energy levels and n.m.r. parameters were determined by the iterative technique. The calculated chemical shifts and coupling constants are given in Table I; the calculated spectrum is shown in Figure 5. Another audio side band was used to perform the double-irradiation tickling experiments. Irradiation of line 2 perturbs line 10, 13, and 15; line 10 (and 15?) appears as broad doublet while line 13 is a sharp doublet. Irradiation of line 14 perturbs lines 1, 8, and 18; line 1 nearly disappears, line 18 becomes a low-intensity, inverted doublet, and line 8 is very broadened. Using the Freeman–Anderson rules, these observations are as expected for the given assignments.

Attempts to decouple the perfluoromethyl fluorines from the vinylic fluorines to permit analysis of the spectrum of perfluoro-2,3-dimethyl-1,3-butadiene[22] were unsuccessful. The fluorine resonances are separated by only ~400 c.p.s. (at 56.4 Mc.) and are very strongly coupled (the half-width of the CF_3 resonance is ~40 c.p.s.).

The dipole moment of I has been measured in carbon tetrachloride solution at 4°. The data are summarized in Table II. Both the density and dielectric constant of the solution were nonlinear in concentration. Calculation of the dipole moment by the Guggenheim method or by extrapolation of the solute polarization to zero concentration yielded a dipole moment of 0.4 D.[23] The molar refraction of II obtained ($R_2 = 20.6$ ml./mole) agrees reasonably well with the value calculated by summing the bond refractions ($R_2 = 19.8$ ml./mole).[24] Since a small difference between two large numbers is used as a multiplicative factor in calculating the dipole moment, the uncertainty in the dipole moment is on the order of ±0.4 D.

Discussion

The ^{19}F n.m.r. spectrum of I at 56.4 Mc.p.s. consists of a dense pattern of sharp lines which upon proton decoupling simplifies to that of a very tightly coupled AA′BB′ system. No significant change was observed in the decoupled fluorine spectrum down to −80°. In Figure 6 the ^{19}F–^{19}F coupling constants are plotted as a function of temperature. Similar variations of F–F coupling constants of fluoroalkenes with temperature have been reported.[25] The broadness in the previously reported spectra may be partially due to the greater complexity at 40 Mc.p.s. but must also be due to poorer resolution. No evidence for a slowly established *cis–trans* equilibrium was obtained. Furthermore, the lack of any very appreciable temperature

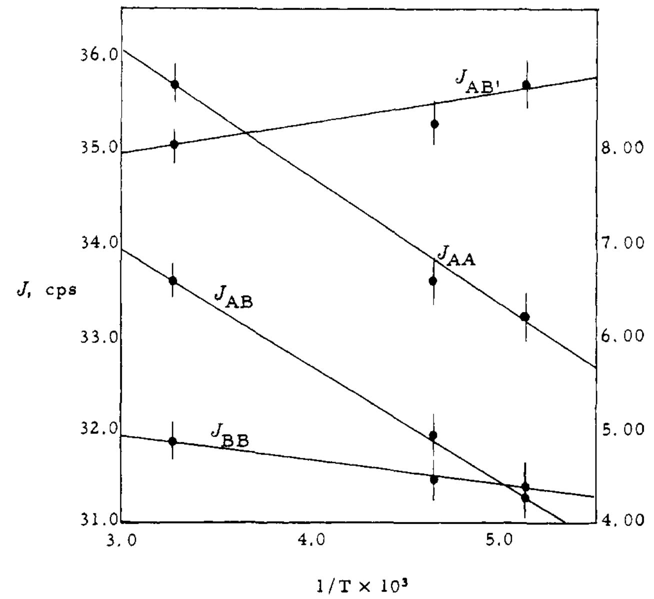

Figure 6. Temperature dependence of F–F coupling constants in 1,1,4,4-tetrafluoro-1,3-butadiene, J_{AA} and J_{AB} left scale, $J_{AB'}$ and J_{BB} right scale.

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(22) W. Mahler, *J. Am. Chem. Soc.*, **84**, 4600 (1962).

(23) See J. W. Smith, "Electric Dipole Moments," Butterworth and Co. (Publishers) Ltd., London, 1955.

(24) E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

(25) W. S. Brey, Jr., and K. C. Ramey, *J. Chem. Phys.*, **39**, 844 (1963).

dependence of the coupling constants suggests that the equilibrium constant, K_I, is very large or very small.

The measured small dipole moment of I is not consistent with the cisoid conformation. The expected dipole moment for the cisoid conformation in which the angle between the axes of the C=C double bonds is 120° (*trans* = 0°) is 2.3 D. (based on the dipole moment of $CH_2{=}CF_2$[26]). If we assume $\mu = 0$ D. for Ia and $\mu = 2.3$ D. for Ib, the equilibrium mixture which corresponds to $\mu = 0.4$ D. contains 17% Ib. However, because of the inaccuracy of the dipole determination this value probably represents an upper limit.

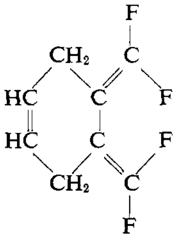
A microwave study of I by Beaudet[27] supports this conclusion. The intensities of pure rotational transitions are proportional to the square of the dipole moment and because the dipole moment of Ia is zero by symmetry, an observable microwave spectrum is expected only for Ib. Hence a qualitative examination of I for a pure rotational absorption should in itself confirm the presence or absence of appreciable concentrations of Ib. No pure rotational absorption was found under conditions where 3% of Ib should have easily been detected.

To check the possibility that a change in preferred conformation may occur between the condensed phase (on which the n.m.r. studies were done) and the gas phase (on which the microwave studies were done) the infrared spectrum of I in the gas and condensed phase was determined. No significant difference was detected between the gas at 2 mm., pure liquid, or carbon disulfide solutions. If a change in preferred conformation had occurred, a marked change in the infrared spectra would have been expected because of the difference in symmetries of the *s-cis* and *s-trans* forms.

Preliminary results from infrared and Raman studies of I provide additional evidence for the *s-trans* conformation.[28] The infrared spectrum of I shows a doublet in the C–H stretch region and a doublet in the C=C stretch region. However, the Raman spectrum of I shows only a single C–H stretch and a single C=C stretch; the Raman frequencies are different from the infrared frequencies. The absence of correspondence in the infrared and Raman frequencies favors the C_{2h} symmetry of the *s-trans* form (Ia).

Before completion of the dipole moment, microwave, and infrared studies, the very large magnitude (36 c.p.s.) of one of the five-bond fluorine–fluorine coupling constants led us to believe that I exists predominantly in the cisoid form, Ib. This suggestion rested upon the supposition that long-range F–F coupling occurs mainly *via* through-space interactions which are thought to be negligible at F–F distances of greater than 2.7 Å.[29] Since the mechanisms of F–F coupling are not on a sufficiently firm basis to permit a definite conclusion, we decided to use what appeared to be a much firmer empirical observation, the sensitivity of long-range coupling constants to the spatial relationship of the two spin-coupled nuclei. Long-range H–H,[30] H–F,[31] and F–F[32] coupling constants have all been shown to be sensitive to the geometrical relationship of the two spin-coupled nuclei in a variety of compounds.

Evidence based on the spatial sensitivity of long-range F–F coupling constants was sought from model compounds with similar geometrical relationship between the fluorines to those of Ia and Ib. Structurally rigid molecules containing a *transoid* 1,1,4,4-tetrafluoro-1,3-butadiene fragment are difficult to devise because only the 2,3-positions are available for substitution which would lock the molecule into the desired shape. Structures locked in the cisoid relationship are much more easily obtained, and we have examined two such molecules containing *cis*-1,1,4,4-tetrafluoro-1,3-butadiene systems: bis-4,5-(difluoromethylene)cyclohexene (II) and perfluoro-1,2-dimethylenecyclobutane (III).[21] The similarity of the long-range, five-bond coupling constants for I, II, and III was originally thought to be very strong evidence in favor of the cisoid conformation (Ib) of 1,1,4,4-tetrafluoro-1,3-butadiene. This has now been shown to be incorrect by the dipole and spectral data.[27,28] As a result, the assumption of a spatial dependence of the long-range F–F coupling constants in these fluoroalkadienes is apparently not justified, and quite obviously the notion that the large five-bond F–F coupling occurs *via* a through-space interaction is also incorrect.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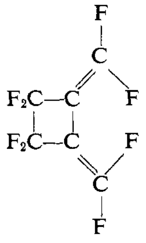
III

Theoretical calculation of F–F coupling constants[33] is much more complicated than calculation of H–H coupling constants[34] because the additional electrons in p-type orbitals must be included and both one-electron orbital and two-electron spin and orbital interactions may make significant and sometimes comparable contributions to nuclear spin coupling.[33] None of the attempts at theoretical calculations of F–F coupling constants have achieved any substantial degree of success.[35]

Empirical rationalizations of F–F coupling constant data have been offered. Consideration of the available data led Petrakis and Sederholm[29] to propose that F–F couplings do not occur through the bonding electrons but by a through-space mechanism involving

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(26) A. Roberts and W. F. Edgell, *J. Chem. Phys.*, **17**, 742 (1949).

(27) R. A. Beaudet, *J. Am. Chem. Soc.*, **87**, 1390 (1965). We are greatly indebted to Dr. Beaudet for providing us with this information in advance of publication.

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(29) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); S. Ng, and C. H. Sederholm *ibid.*, **40**, 2090 (1964).

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(32) *Cf.* ref. 29; ref. 25; G. V. D. Tiers, *J. Chem. Phys.*, **35**, 2263 (1961); H. M. Beisner, L. C. Brown, and D. Williams, *J. Mol. Spectry.*, **7**, 385 (1961).

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(34) N. F. Ramsey and E. M. Purcell, *Phys. Rev.*, **85**, 143 (1952); N. F. Ramsey, *ibid.*, **91**, 303 (1953).

(35) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); J. A. Pople, *Mol. Phys.*, **1**, 216 (1958); G. A. Williams and H. S. Gutowsky, *J. Chem. Phys.*, **30**, 717 (1959).

nonbonded F–F interactions. In support of this idea it was shown (with the aid of a number of somewhat *ad hoc* assumptions) that a reasonably smooth correlation between magnitudes of F–F coupling constants and F–F distances could be obtained. No justification for this correlation is apparent from the present work.

For the three fluoroalkadienes, the five-bond coupling constants, J_{AA}, $J_{AB'}$, and J_{BB} in I, and $J_{AB'}$ and J_{BB} in II and III, are all between fluorines at distances much longer than the supposed minimums necessary to produce a through-space interaction and must therefore arise from through-bond interactions. To be sure, the interactions occur through an unsaturated system and are expected to be larger than those for the corresponding saturated system; nonetheless, through-bond interactions of fluorines are clearly not negligible.

Since II and III exist in cisoid conformations, the resultant *cis–cis* F–F distance is expected to be nearly as small as will be ever observed for nongeminal fluorines in a stable molecule since models show that the "inside" fluorines must be tightly held against one another. The coupling between these fluorines should therefore approach the maximum observable from a through-space interaction. If this F–F distance ($\sim$1.5 Å. using standard bond lengths and bond angles) is less than or equal to that of geminal fluorines, one would predict on the basis of Sederholm's correlation that $J_{FF} > 200$ c.p.s. The observed values are an order of magnitude smaller.

For Ia, no contributions to the coupling constants from through-space interactions would be expected since all of the F–F distances are greater than $\sim$4.0 Å. The similarity of the coupling constants in Ia and II suggests that no significant through-space interaction contributes to the coupling in II. Since II should be a nearly ideal situation for the occurrence of such interactions, serious doubt is cast onto the necessity of invoking through-space coupling in other systems. The mechanism of long-range spin–spin coupling appears to be much more complicated than a simple distance *vs.* J_{FF} correlation would suggest. Further studies, both theoretical and experimental, are clearly necessary.

Experimental

Proton nuclear magnetic resonance spectra were obtained at 60 Mc.p.s., using a Varian Associates Model A-60 for the room temperature spectra and a Varian Associates V-4300 B spectrometer with 12-in. magnet, superstabilizer, field homogeneity control coils, and Model V-3421 integrator and base-line stabilizer for variable temperature work.

Fluorine nuclear magnetic resonance spectra were obtained at 56.4 Mc.p.s. using the same Varian Associates V-4300 B spectrometer. Proton decoupling was achieved using a Nuclear Magnetic Resonance Specialties Model SD-60 spin decoupler. Frequency sweep spectra were obtained using the Varian Associates V-4300 B spectrometer at the Jet Propulsion Laboratory which was equipped with a phase-sensitive lock-in detector for field stabilization.[17] A variable-frequency, audio side band provided the exciting radio-frequency signal for observation. Drs. S. L. Manatt and D. D. Elleman kindly assisted with these measurements.

Measurements of line positions in the field-sweep spectra were accomplished by the usual audio side band method using a Hewlett–Packard Model 200 AB audio-oscillator and Model 521-C frequency counter. In the frequency-sweep spectra, the line positions were measured by determining the frequency of the radio-frequency field using a Hewlett–Packard Model 524-C frequency counter.

1,1,4,4-Tetrafluoro-1,3-butadiene (*I*) was provided by H. N. Jacobson of du Pont. Vapor phase chromatography using columns packed with diisobutyl maleate, diisodecyl phthalate, silver nitrate, silver nitrate–ethylene glycol, Fluorolube, and Kel-F No. 3 indicated the material was more than 99% pure.

Bis-4,5-(difluoromethylene)cyclohexene (*II*). 1,1,4,4-Tetrafluoro-1,2,3-butatriene, prepared by the procedure of Martin and Sharkey,[16] was swept with a stream of deoxygenated nitrogen as it was generated through a series of two Dry Ice–acetone cooled traps each of which contained approximately 10 g. of 1,3-butadiene. After 1 day at −70°, the traps were warmed to −10 to −20° for 2 days, then to −5° for 2 days, and then to 25° for 1 day. The product was purified by preparative v.p.c. on the Megachrom using 12-ft. Carbowax columns at 85°. The infrared spectrum of II was consistent with the assigned structure. The absorptions were assigned as follows: $C{=}CF_2$ (stretch) 1740, $C{-}F$ (stretch) 1260 and 1268, $C{=}C$ (stretch) 1657, $={C}{-}H$ (stretch) 3030, and $-CH_2-$ (stretch) 2970 and 2875 cm.$^{-1}$. The ultraviolet spectrum of II in cyclohexane showed a single absorption maximum at 216 mμ. The ^1H n.m.r. spectrum had resonances at 5.56 and 2.68 p.p.m. in the ratio of 1:2.

Because the compound is unstable, good combustion analyses could not be obtained. Quantitative hydrogen analysis[36] by n.m.r. of a freshly purified sample gave better agreement with the value calculated for this compound.

Anal. Calcd. for $C_8H_6F_4$: C, 53.9; H, 3.37. Found: C, 52.9; H, 7.62 (combustion), 3.5 (n.m.r.).

Tetrafluoroallene. A generous sample of 1,3-dibromo-1,1,3,3-tetrafluoropropane was kindly provided by Dr. L. Morantz and was dehydrobrominated to tetrafluoroallene.[21]

Perfluoro-1,2-dimethylenecyclobutane. Approximately 5 g. of tetrafluoroallene and 0.05 g. of hydroquinone were sealed in a heavy-wall glass tube and heated at 40° for 20 hr. The tube was cooled and opened; the contents were distilled to give 1.0 g. of perfluoro-1,2-dimethylenecyclobutane, b.p. 57–63° (lit.[21] 63°). The infrared spectrum was identical with that reported.

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(36) R. B. Williams, "Conference on Molecular Spectroscopy, London," Pergamon Press Inc., New York, N. Y., 1959.