Analysis of the Nuclear Magnetic Resonance Spectrum of Hexafluoro-1,3-butadiene[1,2]

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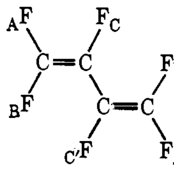
Abstract: The analysis of the complex fluorine-19 nuclear magnetic resonance (nmr) spectrum of hexafluoro-1,3-butadiene (**1**) at 56.4 MHz has been carried out. The following spin–spin coupling constants, J_{ij} in hertz, and chemical shifts, φ_i in parts per million relative to internal fluorotrichloromethane, were found: $J_{AB} = +50.74$, $J_{AC} = +31.91$, $J_{BC} = -118.58$, $J_{AB'} = +2.45$, $J_{AC'} = +2.41$, $J_{BC'} = +14.19$, $J_{AA'} = +4.80$, $J_{BB'} = +11.31$, $J_{CC'} = -30.30$; φ_A +93.8586, φ_B +107.9558, φ_C +179.6853. The relative magnitudes of J_{AB}, J_{AC}, and J_{BC} are rather similar to those reported for a large number of trifluorovinyl systems so the analysis was based on the previously determined signs for these three coupling constants. Because of the strongly coupled nature of the AA'BB'CC' spin system, no spectral assignments involving sign combinations for the other six couplings different from that given above could be found which would fit even approximately the experimental spectrum. The signs of all the long-range $^5J_{FF}$ in **1** are positive, and the magnitudes are somewhat smaller than the analogous couplings in three other 1,1,4,4-tetrafluoro-1,3-alkadienes recently studied by Servis and Roberts. Available nmr data on other fluorobutadienes are discussed. Speculations regarding the mechanisms of the $^5J_{FF}$ couplings in **1** and other fluorobutadienes are presented. It is suggested that the two trifluorovinyl groups of **1** may not be coplanar.

Only a few studies of the signs and magnitudes of fluorine–fluorine nmr coupling constants in fluorine-substituted 1,3-butadienes have been reported.[4–10] The characterization of the spin–spin coupling parameters of these systems is important to a better understanding of the mechanisms of fluorine–fluorine spin–spin couplings and of the molecular and electronic structures of substituted 1,3-butadienes. In light of the difficulties in theoretical calculations of spin–spin couplings involving fluorine[11] and the paucity of exhaustive structural studies of highly fluorine-substituted 1,3-butadienes, we have begun a systematic study of certain of these molecules employing both microwave and nmr spectroscopy. We report here an analysis of the fluorine nmr spectrum of hexafluoro-1,3-butadiene (**1**).



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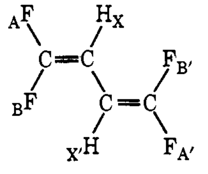

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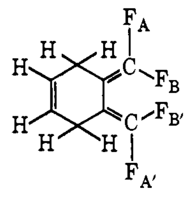

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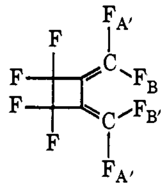

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Recently, Servis and Roberts[4] reported the analysis of the fluorine nmr spectra of three 1,1,4,4-tetrafluoro-1,3-alkadienes: 1,1,4,4,-tetrafluoro-1,3-butadiene (**2**), bis-4,5-(difluoromethylene)cyclohexene (**3**), and perfluoro-1,2-dimethylenecyclobutane (**4**). From the assumed molecular geometries and from the magnitudes of the long-range five-bond fluorine–fluorine coupling constants, $^5J_{FF}$, in these molecules they concluded that the existence of large "through-space" contributions[12] to the couplings between sterically proximate fluorine nuclei is unlikely in **2**, **3**, and **4**. In our mind, there were still several questions yet unanswered about the nmr parameters of these latter 1,1,4,4-tetrafluoro-1,3-alkadiene molecules. First, what is the assignment of the large $^5J_{FF}$ coupling in these systems? Second, what are the mechanisms of transmission of the $^5J_{FF}$ couplings. Third, are the same coupling mechanisms operative in both *cis*- and *trans*-dienes? Fourth, can anything be learned about the conformation of the 1,1,4,4-tetrafluoro-1,3-butadiene system from the $^5J_{FF}$ couplings?

Recent nmr results on two of the three 1,4-dichlorotetrafluoro-1,3-butadienes[6] (**5** and **6**) raised several

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[2] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 2, 1968, Abstract No. I-1.

[3] Author to whom correspondence should be addressed.

[4] K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1339 (1965).

[5] A. A. Bothner-By and R. K. Harris, *ibid.*, **87**, 3451 (1965).

[6] P. L. Bladon, D. W. A. Sharp, and J. M. Winfield, *Spectrochim. Acta*, **22**, 343 (1966).

[7] C. G. Moreland and W. S. Brey, *J. Chem. Phys.*, **45**, 803 (1966).

[8] T. N. Nuckerby, E. F. Mooney, and R. Stephens, *Tetrahedron*, **23**, 709 (1967).

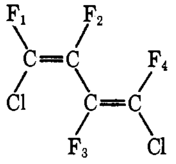
[9] A. A. Bothner-By and E. Moser, *J. Am. Chem. Soc.*, **90**, 2347 (1968).

[10] A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968).

[11] See, for example, (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956); (b) J. A. Pople, *Mol. Phys.*, **1**, 216 (1958); (c) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (d) G. A. Williams and H. S. Gutowsky, *ibid.*, **30**, 717 (1959); (e) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964); (f) A. H. Cowley, W. D. White, and S. L. Manatt, *J. Am. Chem. Soc.*, **89**, 6433 (1967).

[12] The concept of the "through-space" mechanism for fluorine–fluorine coupling has been advanced by Sederholm. See, for example, (a) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); (b) S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964). According to this mechanism, the coupling between nuclei would result from direct overlap of orbitals of the two fluorine atoms which do not form formal chemical bonds.

additional questions. What is the sign of $^3J_{FF}$ between fluorines in the 2 and 3 positions in these molecules? Are the signs of the $^5J_{FF}$ couplings in these derivatives the same as in **2**, **3**, and **4**? What types of substituent effects on the coupling constants might be expected in the trifluorovinyl group on attachment of a second trifluorovinyl group? What are the geometries of **5** and **6**? We hoped that the analysis of the nmr spectrum of hexafluoro-1,3-butadiene (**1**) would contribute to the partial or complete resolution of some of these questions.



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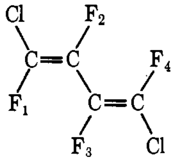

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Experimental Section

The spectra were recorded with a Varian A-56/60 spectrometer whose fluorine-19 50-Hz sweep width was determined to be exceedingly linear over its entire range and which was calibrated to ±0.02 Hz at the time the spectra were recorded. The temperature of the magnet cooling water was controlled through a Varian V-6021 water-to-"Freon"-to-water heat exchanger to which had been added an additional knife heater controlled by a mercury thermoswitch; control of the cooling water temperature of the order of ±0.1° could be maintained for days. The copper heat exchanger on the back of the magnet enclosure and the solenoid valve temperature controller supplied with the A-56/60 were removed. The operation of the latter value significantly reduced the reproducibility in highly accurate work. It was determined that the slow drift of the system over a 250-sec sweep time, as measured on the 50-Hz sweep width, was undetectable provided the room air temperature was stable. However, drifts of the order of 0.05–0.2 Hz were evident with sweep times of 2500 and 5000 sec.

The output of a Hewlett-Packard 5100A frequency synthesizer was substituted for the fluorine frequency off-set crystal oscillator of the A-56/60. For very accurate work, the slight temperature drifts of these crystals can give rise to measurable loss of reproducibility even at 250-sec sweep times. The spectra of the three 150–300-Hz-wide regions of **1** were recorded by stepping the synthesizer in increments such that there were at least three lines overlapped between two adjacent 50-Hz sweep widths. The relative positions of the lines for each spectral region were determined by matching and averaging of the positions of the overlapping lines. Then the sweep calibration was applied. Also, in this manner the spacings between several widely separated groups of lines in each spectral region were checked by recording one group and then, without interrupting the sweep, switching the synthesizer so that another group, some 150–200 Hz away, was recorded. These results agreed to ±0.03 Hz with those obtained by the matching and averaging procedure. The line positions of a particular group were then adjusted by this amount. It was found that the average line positions from multiple recordings of one of the spectral regions agreed to ±0.01 Hz. The chemical shifts between hexafluorobenzene, fluorotrichloromethane, and certain lines in each of the spectral regions of **1** were determined to about ±0.02 Hz by the method described above. In this manner, accurate chemical shift differences of many kilohertz can be measured very easily.

The spectrum of **1** proved to be significantly temperature dependent. The sample was placed in the probe, whose normal temperature is 30.2°, and allowed 20 min to come to temperature equilibrium before spectra were recorded. In many cases spectra recorded with a 250-sec sweep time did not exhibit complete resolution of many closely spaced multiplet groups. These latter regions were scanned with sweep times of 1000–5000 sec. In some cases, lines closer together than 0.3 Hz could not be satisfactorily resolved. The relative spacing of these unresolved lines were estimated from their composite line widths by comparison with the line width of singlets. Weak lines were scanned under higher power levels and slow sweep times.

Careful attention was made to position the chart paper such that pen recorded a vertical trace parallel with the vertical chart lines. Measurement of the horizontal chart graduation with an accurate millimeter scale confirmed that from sheet to sheet of paper there was negligible variation. With all the precautions discussed here, it was demonstrated that triplet traces at a 250-sec sweep time and 50-Hz sweep width of one of the regions gave measurements, for all but the weaker lines, reproducible to ±0.01 chart divisions. We estimate the confidence level from only one measurement to be ±0.02 chart division. Thus, because of the large number of lines in the spectrum of **1**, only one complete set of traces was completely measured although several groups of lines in each region were measured in duplicate or triplicate, and the spacings between the outer lines of each region were accurately determined. We estimate that most of the line position measurements for **1** at 30.2° are accurate to about ±0.02 Hz. Several of the weaker lines could only be measured to about ±0.05 Hz either because of low signal-to-noise ratio or because of the presence of adjacent strong lines. A total of 194 lines was measured and assigned. These ranged in relative intensity, as estimated from calculated spectra, from about 2.2 down to about 0.034.

The sample of hexafluoro-1,3-butadiene (**1**) was obtained from Peninsular Chemresearch Inc. This material was bled into a vacuum line, degassed, and sealed into a 4.96-mm o.d. Pyrex nmr tube along with about 5% degassed hexafluorobenzene and 5% fluorotrichloromethane. The nmr spectrum of this sample indicated no detectable impurities.

Some Comments on the AA′BB′CC′ Spin System

Although there have been calculations of a few six-spin systems of the AA′BB′CC′ type,[13] the general properties of this type of spin system have not been discussed in detail as have the properties of the AA′BB′ system.[14] The latter spin system can be considered to be a lower homolog of the AA′BB′CC′ problem. There are a number of molecules, such as 1,2-difluorobenzene, 1,1,4,4-tetrafluoro-1,3-butadiene, *trans,trans*-1,4-difluoro-1,3-butadiene, *cis,cis*-1,4-difluoro-1,3-butadiene, and 2,3-difluoro-1,3-butadiene, which exemplify the AA′BB′CC′ spin system and whose nmr spectra have not been completely analyzed. We discuss here some of the general features of the AA′BB′CC′ problem and present the basic symmetry wave functions and corresponding matrix elements of the Hamiltonian which are essential to some of the discussion presented in the next section.

The AA′BB′CC′ spin system can be considered to have C_{2h} symmetry. This problem is distinct from the $A_2B_2C_2$ problem. With some modification, the discussion presented below can be expanded to the description of this latter system, the AA′BB′C_2 and AA′A′′A′′′BB′ spin systems. The 64 symmetry spin functions can be constructed from the products of each of the group symmetry functions by well-known procedures.[15] Table I presents these basic product functions using a simplified notation where a 1 corresponds to $\alpha\alpha$, 0 to $1/\sqrt{2}(\alpha\beta + \beta\alpha)$, $\bar{0}$ to $1/\sqrt{2}(\alpha\beta - \beta\alpha)$, and -1 to $\beta\beta$.[16] Thus, in this notation the functions $\alpha\alpha\ 1/\sqrt{2}(\alpha\beta + \beta\alpha)\beta\beta$ and $1/\sqrt{2}(\alpha\beta - \beta\alpha)\ 1/\sqrt{2}(\alpha\beta + \beta\alpha)\beta\beta$ would be written 1 0 −1 and $\bar{0}$ 0 −1, respectively. The first number corresponds to the group function for the AA′ set, the second to the BB′

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(13) See, for example, (a) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, 12, 76 (1964); (b) F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, 42, 3900 (1965); (c) D. Kummer and J. D. Baldeschwieler, *J. Phys. Chem.*, 67, 98 (1963).

(14) See, for example, D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, 38, 470 (1963); 40, 1909 (1964).

(15) (a) E. B. Wilson, *ibid.*, 27, 60 (1957); (b) P. L. Corio, "Structure of High-Resolution NMR Spectra," Academic Press, New York, N. Y., 1966.

(16) See, for example, R. G. Jones, R. C. Hirst, and H. J. Bernstein, *Can. J. Chem.*, 43, 683 (1965).

Table I. Basic Product Functions for AA′BB′CC′ Spin System[a]

	Symmetry			Symmetry	
F_z	A_1	B_1	F_z	A_1	B_1
+3	$1\ 1\ 1$		−1	$1-1-1$	
				$\bar{0}\ \bar{0}-1$	
+2	$1\ 1\ 0$	$1\ 1\ \bar{0}$		$0\ 0-1$	$\bar{0}\ 0-1$
	$1\ 0\ 1$	$1\ \bar{0}\ 1$		$-1\ 1-1$	$0\ \bar{0}-1$
	$0\ 1\ 1$	$\bar{0}\ 1\ 1$		$\bar{0}-1\ \bar{0}$	$\bar{0}-1\ 0$
				$0-1\ 0$	$0-1\ \bar{0}$
+1	$1\ 1-1$			$-1\ \bar{0}\ \bar{0}$	$-1\ \bar{0}\ 0$
	$1\ 0\ 0$			$-1\ 0\ 0$	$-1\ 0\ \bar{0}$
	$1\ \bar{0}\ \bar{0}$			$-1-1\ 1$	
	$0\ 1\ 0$	$1\ 0\ \bar{0}$			
	$\bar{0}\ 1\ \bar{0}$	$1\ \bar{0}\ 0$	−2	$0-1-1$	$\bar{0}-1-1$
	$1-1\ 1$	$0\ 1\ \bar{0}$		$-1\ 0-1$	$-1\ \bar{0}-1$
	$0\ 0\ 1$	$\bar{0}\ 1\ 0$		$-1-1\ 0$	$-1-1\ \bar{0}$
	$\bar{0}\ \bar{0}\ 1$	$0\ \bar{0}\ 1$			
	$-1\ 1\ 1$	$\bar{0}\ 0\ 1$	−3	$-1-1-1$	
0	$1\ 0-1$	$1\ \bar{0}-1$			
	$0\ 1-1$	$\bar{0}\ 1-1$			
	$1-1\ 0$	$1-1\ \bar{0}$			
	$0\ 0\ 0$	$\bar{0}\ \bar{0}\ \bar{0}$			
	$0\ \bar{0}\ \bar{0}$	$\bar{0}\ 0\ 0$			
	$\bar{0}\ 0\ \bar{0}$	$0\ \bar{0}\ 0$			
	$\bar{0}\ \bar{0}\ 0$	$0\ 0\ \bar{0}$			
	$-1\ 1\ 0$	$-1\ 1\ \bar{0}$			
	$0-1\ 0$	$\bar{0}-1\ 1$			
	$-1\ 0\ 1$	$-1\ \bar{0}\ 1$			

[a] For notation, see text.

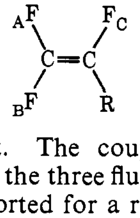
set, and the last to the CC′ set. Sixty-four symmetry product functions can be formed, where A_1 and B_1 designate the corresponding symmetries:[15,16] $A_1(AA') \times A_1(BB') \times A_1(CC')$, $A_1 \times B_1 \times B_1$, $B_1 \times B_1 \times A_1$, and $B_1 \times A_1 \times B_1$ yield 36 symmetric A_1 functions, and $A_1 \times A_1 \times B_1$, $A_1 \times B_1 \times A_1$, $B_1 \times A_1 \times A_1$, and $B_1 \times B_1 \times B_1$ yield 28 antisymmetric B_1 functions. Because functions of different total F_z and different symmetry do not mix, A_1 blocks (in order of F_z) of 1 × 1, 3 × 3, 9 × 9, 10 × 10, 9 × 9, 3 × 3, and 1 × 1 result. B_1 blocks of 3 × 3, 6 × 6, 10 × 10, 6 × 6, and 3 × 3 result. The matrix elements of the Hamiltonian for each of these blocks are given in Table II. These were computed in the usual manner.[17] We have found it convenient to employ sums and differences similar to the N, L, K, and M parameters adopted in the detailed treatment of the AA′BB′ spin system,[14] *i.e.*, $N_{AB} = J_{AB} + J_{AB'}$, $L_{AB} = J_{AB} - J_{AB'}$, $K_{AB} = J_{AA'} + J_{BB'}$, $M_{AB} = J_{AA'} - J_{BB'}$, etc. (see Table II).

From Table II it is evident that for the general AA′BB′CC′ problem it is not possible to derive any simple explicit expressions for energies or transitions. Simplification to an AA′BB′XX′ system[15a,17] in the case of the A_1 elements reduces the 3 × 3 blocks to a 1 × 1 and a 2 × 2, the 9 × 9 blocks each to two 1 × 1's, a 2 × 2, and a 5 × 5, and the 10 × 10 block to two 2 × 2's and a 6 × 6. For the B_1 elements, the 3 × 3's reduce to a 1 × 1 and a 2 × 2, the 6 × 6's each to a 2 × 2 and a 4 × 4, and the 10 × 10 to two 2 × 2's and a 6 × 6. In this approximation it is possible to obtain explicit expressions for a few of the energies and transitions. Since the AA′XX′YY′ simplification neglects even more off-diagonal matrix elements, more explicit energies and intensities are available. It was felt that consideration of this approximation would be useful in the assignment of the particular spectrum of interest. For this problem the Hamiltonian matrix is diagonal except for 12 easily diagonalized 2 × 2 blocks, an A_1 4 × 4 block between the 000, $0\bar{0}\bar{0}$, $\bar{0}0\bar{0}$, and $\bar{0}\bar{0}0$ functions, and a B_1 4 × 4 block between the $\bar{0}\bar{0}\bar{0}$, $00\bar{0}$, $00\bar{0}$, and $\bar{0}00$ functions.

Using the basic product functions of Table I it is possible to derive the number and nature of the permitted transitions[17] for each pair of nuclei in the AA′BB′CC′, AA′BB′XX′, or AA′XX′YY′ system. There should be a total of 72 single spin-flip transitions per pair of nuclei. The symmetric transitions consist of 1 between the $F_z = 2$ and 3 states, 5 between the $F_z = 1$ and 2 states, 14 between the $F_z = 0$ and 1 states, 14 between the $F_z = -1$ and 0, 5 between the $F_z = -2$ and −1, and 1 between the −3 and −2 states. The antisymmetric states have 4 transitions between the $F_z = 1$ and 2 states, 14 between the $F_z = 0$ and 1 states, 14 between the $F_z = -1$ and 0 states, and 4 between the $F_z = -2$ and −1 states. Thus there will be a total of 216 A_1 and B_1 transitions of this type for the general AA′BB′CC′ problem. Also, a total of 120 so-called mixed A_1 and 60 mixed B_1 transitions, which involve the simultaneous turning of more than one spin but with $\Delta F_z = +1$, are predicted. All of these latter transitions should be very weak except in an AA′BB′CC′ spectrum where the chemical shifts are comparable in magnitude to the couplings. It is possible to derive information on the relative intensities of a number of the AA′BB′CC′ transitions by consideration of the AA XX′YY′ approximate wave functions which, except for the 4 × 4 blocks and twelve 2 × 2 blocks which are easily diagonalized, are just the basic product symmetry functions. Some of these are given for the AA′ region in Table III along with the transition origins and the intensities calculated from the final parameters for **1**. The parameters used to calculate the eigenvectors of the 2 × 2 blocks were in this case the final iterated ones, but parameters within ±3 Hz of the correct ones yield only slightly different intensities. The reasonably good agreements exhibited indicate that intensities derived from the AA′XX′YY′ product functions for such a strongly mixed system can be useful.

Spectral Assignment and Analysis

The fluorine-19 spectrum of hexafluoro-1,3-butadiene (**1**) is complex. It consists of three regions approximately 130, 270, and 240 Hz wide which are rich in narrow lines. These are shown in Figures 1a, 2a, and 3a. Available data on the chemical shifts of the three fluorine-19 nuclei in a trifluorovinyl group[18] indicate that, in every case thus far reported, the order of shielding is $\varphi_A < \varphi_B < \varphi_C$ with φ_C approximately 70 to 80 ppm upfield from φ_B. Initially for **1**, we made



the same assignment. The coupling constants J_{AB}, J_{AC}, and J_{BC}, between the three fluorine-19 nuclei in this group, have been reported for a relatively wide variety of substituents and in general $|J_{BC}| > |J_{AB}| > |J_{AC}|$. In addition it has been demonstrated that the

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(17) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(18) See ref 7.

Table II. Matrix Elements for AA′BB′CC′ Spin System[a]

Symmetric

$F_z = +3$	(1 1 1)	$\omega_A + \omega_B + \omega_C + \frac{1}{2}(N_{AB} + N_{AC} + N_{BC})$

$F_z = +2$	(1 1 0)	$\omega_A + \omega_B + \frac{1}{2}N_{AB}$		
	(1 0 1)	$\frac{1}{2}N_{BC}$	$\omega_A + \omega_C + \frac{1}{2}N_{AC}$	
	(0 1 1)	$\frac{1}{2}N_{AC}$	$\frac{1}{2}N_{AB}$	$\omega_B + \omega_C + \frac{1}{2}N_{BC}$

$F_z = +1$	(1 1 −1)	$\omega_A + \omega_B - \omega_C + \frac{1}{2}(N_{AB} - N_{AC} - N_{BC})$								
	(1 0 0)	$\frac{1}{2}N_{BC}$	ω_A							
	(1 $\bar{0}$ $\bar{0}$)	$-\frac{1}{2}L_{BC}$	$\frac{1}{2}L_{BC}$	$\omega_A - K_{BC}$						
	(0 1 0)	$\frac{1}{2}N_{AC}$	$\frac{1}{2}N_{AB}$	0	ω_B					
	($\bar{0}$ 1 $\bar{0}$)	$-\frac{1}{2}L_{AC}$	0	$\frac{1}{2}L_{AB}$	$\frac{1}{2}L_{AC}$	$\omega_B - K_{AC}$				
	(1 −1 1)	0	$\frac{1}{2}N_{BC}$	$-\frac{1}{2}L_{BC}$	0	0	$\omega_A - \omega_B + \omega_C + \frac{1}{2}(-N_{AB} + N_{AC} - N_{BC})$			
	(0 0 1)	0	$\frac{1}{2}N_{AC}$	0	$\frac{1}{2}N_{BC}$	0	$\frac{1}{2}N_{AB}$	ω_C		
	($\bar{0}$ $\bar{0}$ 1)	0	0	$\frac{1}{2}L_{AC}$	0	$\frac{1}{2}L_{BC}$	$-\frac{1}{2}L_{AB}$	$\frac{1}{2}L_{AB}$	$\omega_C - K_{AB}$	
	(−1 1 1)	0	0	0	$\frac{1}{2}N_{AC}$	$-\frac{1}{2}L_{AC}$	0	$\frac{1}{2}N_{AB}$	$-\frac{1}{2}L_{AB}$	$-\omega_A + \omega_B + \omega_C + \frac{1}{2}(-N_{AB} - N_{AC} + N_{BC})$

$F_z = 0$	(1 0 −1)	$\omega_A - \omega_C - \frac{1}{2}N_{AC}$									
	(0 1 −1)	$\frac{1}{2}N_{AB}$	$\omega_B - \omega_C - \frac{1}{2}N_{BC}$								
	(1 −1 0)	$\frac{1}{2}N_{BC}$	0	$\omega_A - \omega_B - \frac{1}{2}N_{AB}$							
	(0 0 0)	$\frac{1}{2}N_{AC}$	$\frac{1}{2}N_{BC}$	$\frac{1}{2}N_{AB}$	0						
	(0 $\bar{0}$ $\bar{0}$)	0	$-\frac{1}{2}L_{BC}$	0	$\frac{1}{2}L_{BC}$	$-K_{BC}$					
	($\bar{0}$ 0 $\bar{0}$)	$-\frac{1}{2}L_{AC}$	0	0	$\frac{1}{2}L_{AC}$	$\frac{1}{2}L_{AB}$	$-K_{AC}$				
	($\bar{0}$ $\bar{0}$ 0)	0	0	$-\frac{1}{2}L_{AB}$	$\frac{1}{2}L_{AB}$	$\frac{1}{2}L_{AC}$	$\frac{1}{2}L_{BC}$	$-K_{AB}$			
	(−1 1 0)	0	$\frac{1}{2}N_{AC}$	0	$\frac{1}{2}N_{AB}$	0	0	$-\frac{1}{2}L_{AB}$	$-\omega_A + \omega_B - \frac{1}{2}N_{AB}$		
	(0 −1 1)	0	0	$\frac{1}{2}N_{AC}$	$\frac{1}{2}N_{BC}$	$-\frac{1}{2}L_{BC}$	0	0	0	$-\omega_B + \omega_C - \frac{1}{2}N_{BC}$	
	(−1 0 1)	0	0	0	$\frac{1}{2}N_{AC}$	0	$-\frac{1}{2}L_{AC}$	0	$\frac{1}{2}N_{BC}$	$\frac{1}{2}N_{AB}$	$-\omega_A + \omega_C - \frac{1}{2}N_{AC}$

Antisymmetric

$F_z = +2$	(1 1 $\bar{0}$)	$\omega_A + \omega_B + \frac{1}{2}N_{AB} - J_C$		
	(1 $\bar{0}$ 1)	$\frac{1}{2}L_{BC}$	$\omega_A + \omega_C + \frac{1}{2}N_{AC} - J_B$	
	($\bar{0}$ 1 1)	$\frac{1}{2}L_{AC}$	$\frac{1}{2}L_{AB}$	$\omega_B + \omega_C + \frac{1}{2}N_{BC} - J_C$

$F_z = +1$	(1 0 $\bar{0}$)	$\omega_A - J_C$					
	(1 $\bar{0}$ 0)	$\frac{1}{2}L_{BC}$	$\omega_A - J_B$				
	(0 1 $\bar{0}$)	$\frac{1}{2}N_{AB}$	0	$\omega_B - J_C$			
	($\bar{0}$ 1 0)	0	$\frac{1}{2}L_{AB}$	$\frac{1}{2}L_{AC}$	$\omega_B - J_A$		
	(0 $\bar{0}$ 1)	0	$\frac{1}{2}N_{AC}$	$\frac{1}{2}L_{BC}$	0	$\omega_C - J_B$	
	($\bar{0}$ 0 1)	$\frac{1}{2}L_{AC}$	0	0	$\frac{1}{2}N_{BC}$	$\frac{1}{2}L_{AB}$	$\omega_C - J_A$

$F_z = 0$	(1 0 −1)	$\omega_A - \omega_C - \frac{1}{2}N_{AC} - J_B$									
	($\bar{0}$ 1 −1)	$\frac{1}{2}L_{AB}$	$\omega_B - \omega_C - \frac{1}{2}N_{BC} - J_A$								
	(1 −1 $\bar{0}$)	$\frac{1}{2}L_{BC}$	0	$\omega_A - \omega_B - \frac{1}{2}N_{AB} - J_C$							
	($\bar{0}$ $\bar{0}$ $\bar{0}$)	$-\frac{1}{2}L_{AC}$	$-\frac{1}{2}L_{BC}$	$-\frac{1}{2}L_{AB}$	$\frac{1}{2}(K_{AB} + K_{AC} + K_{BC})$						
	($\bar{0}$ 0 0)	0	$\frac{1}{2}N_{BC}$	0	$\frac{1}{2}L_{BC}$	$-J_A$					
	(0 $\bar{0}$ 0)	$\frac{1}{2}N_{AC}$	0	0	$\frac{1}{2}L_{AC}$	$\frac{1}{2}L_{AB}$	$-J_B$				
	(0 0 $\bar{0}$)	0	0	$\frac{1}{2}N_{AB}$	$\frac{1}{2}L_{AB}$	$\frac{1}{2}L_{AC}$	$\frac{1}{2}L_{BC}$	$-J_C$			
	−(1 1 $\bar{0}$)	0	$\frac{1}{2}L_{AC}$	0	$\frac{1}{2}L_{AB}$	0	0	$\frac{1}{2}N_{AB}$	$-\omega_A + \omega_B - \frac{1}{2}N_{AB} - J_C$		
	($\bar{0}$ −1 1)	0	0	$\frac{1}{2}L_{AC}$	$-\frac{1}{2}L_{BC}$	$\frac{1}{2}N_{BC}$	0	0	0	$-\omega_B + \omega_C + \frac{1}{2}N_{BC} - J_A$	
	(−1 $\bar{0}$ 1)	0	0	0	$-\frac{1}{2}L_{AC}$	0	$\frac{1}{2}N_{AC}$	0	$\frac{1}{2}L_{BC}$	$\frac{1}{2}L_{AB}$	$-\omega_A + \omega_C - \frac{1}{2}N_{AC} - J_B$

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[a] ω_i's are chemical shifts; $N_{ij} = J_{ij} + J_{ij}'$; $L_{ij} = J_{ij} - J_{ij}'$; $K_{ij} = J_{ij} + J_{ij}'$; $M_{ij} = J_{ij} - J_{ij}'$; states given in parentheses in notation of Table I; from each diagonal element $\frac{1}{8}(K_{AB} + K_{AC} + K_{BC})$ has been subtracted; elements only given for $F_z = +3, +2, +1$, and 0 states because those for −3, −2, and −1 states can be formed by trivial sign changes of the diagonal elements of the corresponding +3, +2, and +1 states; because of symmetry each block is given in triangular form.

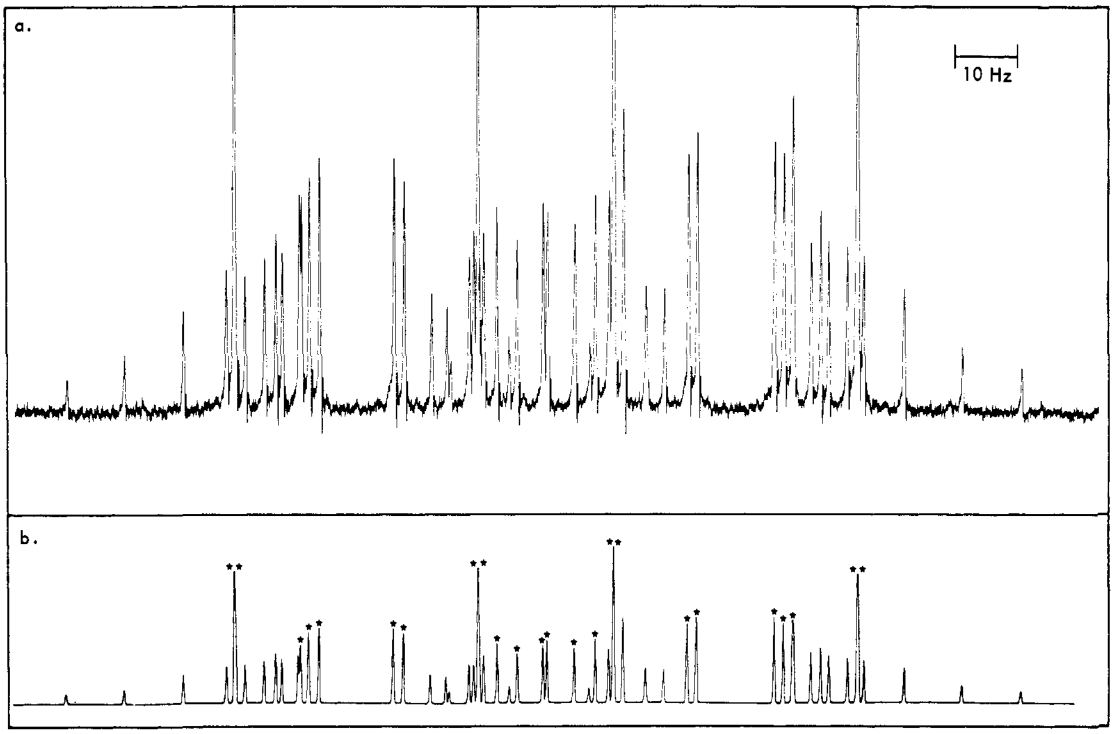

Figure 1. Comparison of experimental (a) and calculated (b) spectra of the AA′ nuclei of **1**. This A-56/60 spectrum was recorded on an external recorder with a sweep width of 500 Hz at a rate of 0.1 Hz/sec. Such conditions accentuate the small nonlinearities of the A-56/60 sweep on comparison of a and b but allow presentation of any spectral region of **1** on one continuous record. As described in the text, the starred transitions represent those initially assigned based on calculated intensities.

Table III. Comparison of Line Intensities in AA′ Region for the AA′XX′YY′ Approximation and Actual AA′BB′CC′ Problem for the F_z ($+2 \rightarrow +3$), ($+1 \rightarrow +2$), and ($0 \rightarrow +1$) Transitions

Symmetric			Antisymmetric		
	Intensities			Intensities	
Origin	AA′XX′YY′	Actual	Origin	AA′XX′YY′	Actual
$011 \longrightarrow 111$	2.001	2.158	$01\bar{0} \longrightarrow 11\bar{0}$	1.767	1.876
$010 \longrightarrow 110$	1.655	1.766	$\bar{0}10 \longrightarrow 11\bar{0}$	0.235	0.259
$\bar{0}1\bar{0} \longrightarrow 110$	0.346	0.368	$0\bar{0}1 \longrightarrow 1\bar{0}1$	1.134	1.197
$001 \longrightarrow 101$	1.315	1.253	$\bar{0}01 \longrightarrow 1\bar{0}1$	0.865	0.817
$\bar{0}\bar{0}1 \longrightarrow 101$	0.684	0.760	$-10\bar{0} \longrightarrow 01\bar{0}$	1.767	1.892
$-111 \longrightarrow 011$	2.001	2.160	$-11\bar{0} \longrightarrow \bar{0}10$	0.235	0.244
$01-1 \longrightarrow 11-1$	2.001	2.110	$-1\bar{0}1 \longrightarrow 0\bar{0}1$	1.133	1.067
$-110 \longrightarrow 010$	1.655	1.750	$-1\bar{0}1 \longrightarrow \bar{0}01$	0.867	0.947
$-110 \longrightarrow \bar{0}1\bar{0}$	0.346	0.386			
$0-11 \longrightarrow 1-11$	1.999	1.871			
$-101 \longrightarrow 001$	1.316	1.377			
$-101 \longrightarrow \bar{0}\bar{0}1$	0.683	0.636			

signs of these three couplings are J_{BC} −, J_{AB} +, and J_{AC} +.[19] These sign relations were used in the initial stages of the analysis. Available evidence relevant to the effects of substituents on the magnitudes of the coupling constants shows that J_{BC} should always be about −110 to −130 Hz regardless of the R group.[18] Wider variations are exhibited for J_{AC} and J_{BC}, but in general[18] J_{AC} is at least 10–50 Hz less than J_{AB}.

With the facts discussed above in mind, the lowest field resonance region of **1** was assigned to the fluorine-19 nuclei (AA′) *trans* to the formal single bond, the next lowest field resonance region to those (BB′) *cis* to the formal single bond, and the highest field resonance region to the fluorine nuclei (CC′) attached at the 2 and 3 positions.

Very prominent in the spectrum of **1** (see Figures 1a, 2a, and 3a) is the presence, in each region, of a subspectral structure very suggestive of the quartets typical of a trifluorovinyl compound.[20] In the low-field spectral region, designated fluorines AA′, the approximate quartet spacings of 34.2 and 53.2 Hz were measured. Similarly, spacings of 53.2 and 102.4 Hz and 34.3 and 102.3 Hz can be measured in the BB′ and CC′ regions, respectively. Recognition of these repetitive spacings, coupled with consideration of the available data for the trifluorovinyl moiety, strongly suggested that the 34.2-Hz spacing is related to $J_{AB} + J_{AB'} = N_{AB}$, the 53.2-Hz

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(19) (a) D. F. Evans, *Mol. Phys.*, **5**, 183 (1962); (b) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 1945 (1962); (c) D. F. Evans, S. L. Manatt, and D. D. Elleman, *J. Chem. Soc.*, **85**, 238 (1963); (d) M. Barfield and J. D. Baldeschwieler, *J. Mol. Spectry.*, **12**, 23 (1964).

(20) See, for example, H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

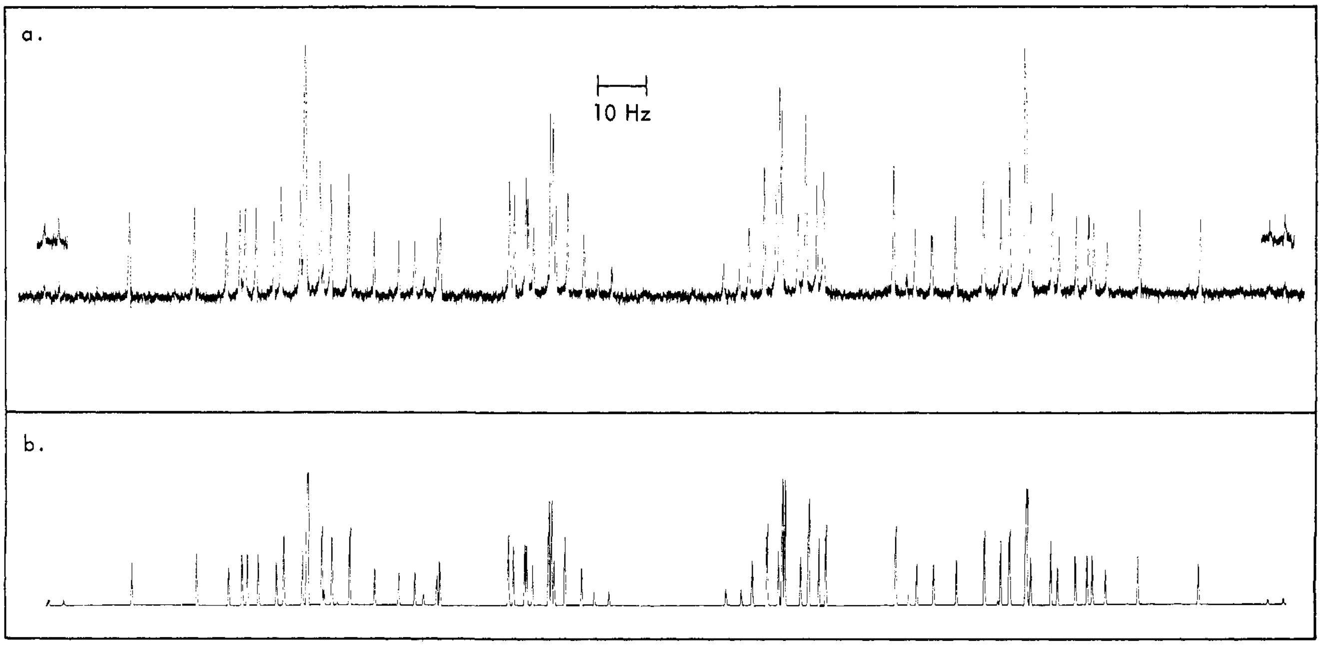


Figure 2. Comparison of experimental (a) and calculated (b) spectra of the BB′ nuclei of **1**. Recorded as described for Figure 1.

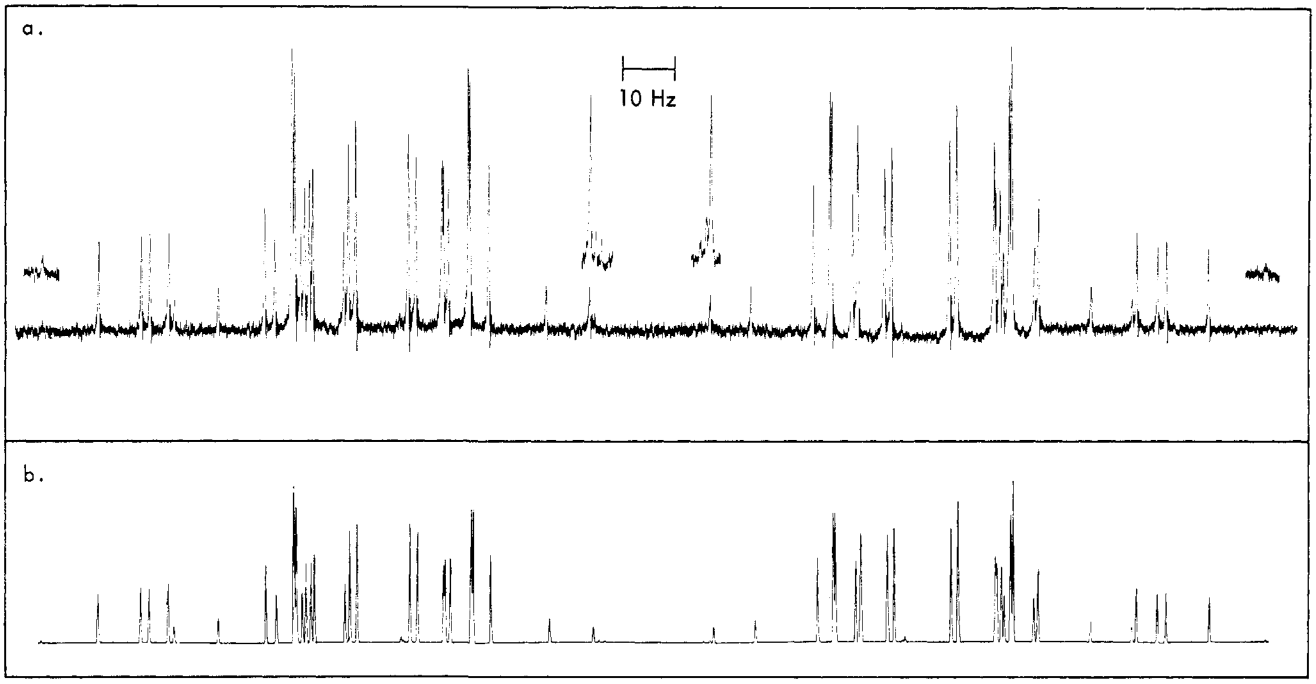
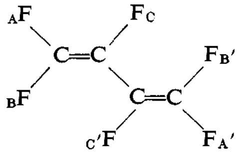


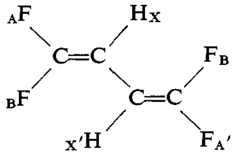
Figure 3. Comparison of experimental (a) and calculated (b) spectra of the CC′ nuclei of **1**. Recorded as described for Figure 1.

spacing to $J_{AC} + J_{AC'} = N_{AC}$, and the 102.3-Hz spacing to $J_{BC} + J_{BC'} = N_{BC}$. The assignments based on chemical shift arguments then appeared to be confirmed by that based on the approximate magnitudes of the coupling constants. Verification that these spacings are related to the parameters N_{AB}, N_{AC}, and N_{BC} can be found by considering the matrix elements of the AA′XX′YY′ problem (obtainable from those for the AA′BB′CC′ problem given in Table II). From Table III the most intense transitions in any region of **1** are expected to be 16 A_1 and 8 B_1 in number. The A_1 set involves one transition with $F_z(2 \rightarrow 3)$, three with $F_z(1 \rightarrow 2)$, four with $F_z(0 \rightarrow 1)$, four with $F_z(-1 \rightarrow 0)$, three with $F_z(-2 \rightarrow 1)$, and one with $F_z(-3 \rightarrow -2)$. To obtain approximate expressions for the frequencies of these lines we adopted the AA′XX′YY′ treatment. Some feeling for the appropriateness of this simplification can be obtained from the approximate values for the $N_{ij}/\Delta\varphi_{ij}$ ratios for a particular problem.[15a] In the case of **1** the ratios $N_{AB}/\Delta\varphi_{AB}$, $N_{AC}/\Delta\varphi_{AC}$, and $N_{BC}/\Delta\varphi_{BC}$ are about 0.07, 0.03, and -0.007, respectively. Usually with a ratio smaller than about $|0.1|$ useful intensities and transitions energies can be derived from the AA′XX′YY′ symmetry functions and the matrix elements. In the present case this approach yielded identification of the 24 strongest lines in each region. As an example, these transitions are indicated for the AA′ region in Figure 1.

With approximate values of the chemical shifts and sums of certain of the couplings in hand, the next order of business concerned the selection of trial magnitudes for the long-range couplings, ${}^4J$ and ${}^5J$, and a trial magnitude for the ${}^3J$ between the nuclei in the CC′ set.

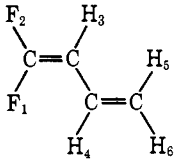


1

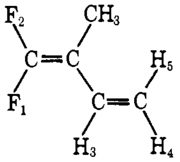


2

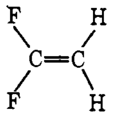
From the analysis of the spectrum of 1,1,4,4-tetrafluoro-1,3-butadiene (**2**),[4] the magnitudes and signs J_{AB} = +36.6 and $J_{AB'}$ = +8.0 Hz were obtained. Although the magnitudes and relative signs of $J_{AA'}$ and $J_{BB'}$ were determined to be +35.7 and +4.8 Hz, the exact assignments of $J_{AA'}$ and $J_{BB'}$ in **2** could not be made.[4] The absolute signs of J_{AB} and $J_{AB'}$ are based on analogy to similar systems and at present appear to be reliable.[19] In the previous analysis of the spectrum of **2**, no detailed discussion regarding a definitive assignment of each of the coupling constants was presented.[4] This point is under active reinvestigation, and we believe that it is possible to clarify this matter somewhat here. It has been demonstrated that in a strongly coupled AA′BB′ system it is possible to establish whether N and K are the same sign.[14] This was confirmed for **2**.[4] As mentioned above, it is not possible to determine the signs of L or M relative to N and K without involving independent information on the relative magnitudes and signs of the couplings and chemical shift assignment for **2**. Strong evidence exists that the largest coupling (+36.6 Hz) in **2**, between the nuclei possessing different chemicals shifts, is the geminal ${}^2J_{FF}$ or J_{AB}. In two 1,1-difluoro-1,3-butadienes (**7** and **8**) whose nmr spectra we have recently investigated,[21] the ${}^2J_{FF}$ couplings are very similar to that in **2**. It is unlikely that the 4,4-difluoro substituents would severely reduce the ${}^2J_{FF}$ to about 8 Hz. This coupling in the simpler molecule **9** is also very similar in magnitude to those in **7** and **8**.[22] However, when an electronegative substituent is appended to the 2 position of a 1,1-difluorovinyl system, the ${}^2J_{FF}$ increases significantly (for example, trifluoroethylene[19,20] (**10**) and 1,2,2-trifluoro-1,3-butadiene[23] (**11**)).



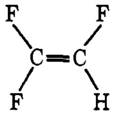
7, ${}^2J_{FF}$ = +31.6 Hz



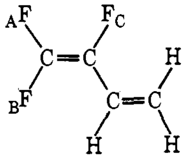
8, ${}^2J_{FF}$ = +35.7 Hz



9, ${}^2J_{FF}$ = +36.4 Hz



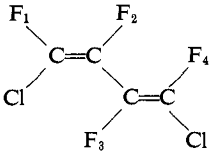
10, ${}^2J_{FF}$ = +87 Hz



11, ${}^2J_{FF}$ = +67.2 Hz

The next point to be established regarding the spectrum of **2** is the chemical shift assignment of the AA′ and BB′ sets. The fluorine nmr parameters for **2** were extracted from the fluorine-19 spectrum resulting from nearly complete decoupling of the protons.[4] It is evident from the published fluorine-19 single resonance spectrum of **2** that the downfield fluorine nuclei are very weakly, if at all, coupled to the protons while the upfield fluorine nuclei are strongly coupled. Small *cis*-${}^3J_{HF}$ couplings have been observed in compounds **7** (0.35 Hz),[21] **9** (+0.7 Hz),[22] and **10** (−3 Hz).[10] Much larger *trans*-${}^3J_{HF}$ couplings appear to be the rule as exemplified in **7** (23.5 Hz),[22] **9** (+33.9 Hz),[22] and **10** (+12 Hz).[19] The firm assignment of the chemical shifts, relative magnitudes of J_{AB} and $J_{AB'}$, and sign of J_{AB} then allow an unequivocal assignment of the sign of L in **2**. However, the sign of M is still indeterminate. At least we can say that the sign of all the ${}^5J_{FF}$ couplings in **2** are positive although the identification of the large ${}^5J_{FF}$ is not possible.

Data are available on ${}^4J_{FF}$ couplings similar to those in **1** which suggest that $J_{AC'}$ and $J_{BC'}$ should be the same sign[19a,c] and that $J_{AC'} < J_{BC'}$.[24] Additional, and perhaps more appropriate, data on the two 1,4-dichlorotetrafluoro-1,3-butadienes **5** and **6** shows a $J_{AC'}$-type coupling of $|3.6|$ Hz (J_{13} in **5**) and two $J_{BC'}$-type couplings of $|14.5|$ Hz (J_{24} in **5**) and +14.2 Hz (J_{13} in **6**).[6] Also from **5** and **6** two values for a J_{BC}-type coupling of −133.8 Hz (J_{34} in **5**) and −132.9 Hz (J_{12} in **6**) have been clearly identified.[6]



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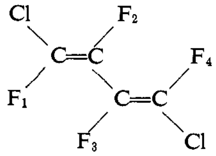

6

Collection of all the data discussed led to consideration of several sets of trial coupling constants for **1** from which spectra were calculated. Initially the following values for six of the nine unique couplings were selected: J_{AB} = +45.0, $J_{AB'}$ = +8.2, J_{AC} = +28.0, $J_{AC'}$ = +6.0, J_{BC} = −120.0, $J_{BC'}$ = +22.7. Trial spectra were calculated using NMRIT[25] and plotted[26] for the following combinations of $J_{AA'}$, $J_{BB'}$, and $J_{CC'}$.

	I	II	III	IV
$J_{AA'}$	+35.0	+35.0	+5.0	+5.0
$J_{BB'}$	+5.0	+5.0	+35.0	+35.0
$J_{CC'}$	−30.0	+30.0	−30.0	−30.0

Aside from the identification of the quartet subspectra in each spectral region from which values of N_{AB}, N_{AC}, and N_{BC} had been taken, the resulting spectra exhibited very little resemblance to the experimental spectra.

At this juncture several different subsequent courses of action were open. Systematic double-resonance experiments could be employed to ascertain the connected transitions. More sets of trial parameters could be tried,

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[21] W. D. Cumming, R. A. Beaudet, and S. L. Manatt, unpublished work.

[22] G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 226 (1963).

[23] S. L. Manatt, unpublished work.

[24] See data summarized in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, pp 908–914.

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

[26] By a program written for the IBM 7090 by S. L. M. This program uses a 20 point approximation to a Gaussian line shape and will accommodate 400 transitions. Details and listings are available, but this routine is rather specific to the S-C 4020 plotters at the Jet Propulsion Laboratory.

Table IV. Final Iterated Parameters for Hexafluoro-1,3-butadiene (**1**)[a]

J_{AB}	J_{AC}	J_{BC}
$+50.737 \pm 0.006$	$+31.911 \pm 0.006$	-118.577 ± 0.006
$J_{AB'}$	$J_{AC'}$	$J_{BC'}$
$+2.449 \pm 0.006$	$+2.409 \pm 0.005$	$+14.195 \pm 0.006$
$J_{AA'}$	$J_{BB'}$	$J_{CC'}$
$+4.800 \pm 0.008$	$+11.313 \pm 0.008$	-30.305 ± 0.008
$\varphi_A^{CCl_3F}$	$\varphi_B^{CCl_3F}$	$\varphi_C^{CCl_3F}$
$+93.8586 \pm 0.0009$	-107.9558 ± 0.0009	$+179.6853 \pm 0.0009$
$\varphi_A^{C_6F_6}$	$\varphi_B^{C_6F_6}$	$\varphi_B^{C_6F_6}$
-73.7340 ± 0.0004	-59.6346 ± 0.0004	$+13.0445 \pm 0.0004$

Sum of squares of residuals, 0.054 (8th iteration)
Sum of squares of energy level errors, 0.0148
Average deviation of observed minus calculated line positions, 0.026 Hz
Maximum deviation for two weak lines, +0.092 and +0.074 Hz

[a] Coupling constants in hertz and chemical shifts in parts per million from internal CCl_3F and internal C_6F_6; estimates of error and other parameters given are those usually calculated in NMRIT (see ref 25); results were obtained from iteration and 194 transitions.

but with the sums N_{AB}, N_{AC}, and N_{BC} held constant. Alternately, it might be possible to apply recently suggested methods of subspectral analysis[27] to this problem. A careful examination of this latter approach for the AA'BB'XX' problem was carried out. Derivation of the various aa'bb' subspectral transformations for the $F_z(XX) = 1,0,-1$ block led us to the conclusion that the validity of a previous treatment of a related six-spin problem is, in part, in doubt.[27e,h] From the matrix elements of the AA'BB'XX' system it was obvious that a subspectral treatment involving an aa'bb' system with energy levels symmetrically disposed about $F_z(\text{total}) = 0$ would fail because the F_z (total) block of the $F_z(XX) = 0$ states is not 4×4 but rather 6×6 since these states $(01-1,\ 0-11,\ 000,\ \text{and}\ \overline{0}0\overline{0})$ are coupled with the $0\overline{00}$ and $\overline{00}0$ functions. However, for aa'bb' subspectra symmetric about either $F_z(\text{total}) = +1$ or -1 the 4×4 blocks are isolated, and valid transformation equations should be obtainable. These were derived and involve the subspectral parameters ϵ, n, k, l, m, ν_a, and ν_b for the aa'bb' system[27h] expressed in terms of the parameters N_{AB}, N_{AC}, N_{BC}, K_{AA}, etc., of the real AA'BB'XX problem. Although the expressions for n, k, and ϵ are relatively simple, the equations which arise for ν_a, ν_b, l, and m are so cumbersome that this approach does not seem at all useful. Thus, it appears that the rather simple transformation equations previously given for the AA'A''A'''XX' are in error.[27h,28]

Computation of additional trial spectra were next resorted to. Systematic variations of the coupling parameters involving the AA' nuclei were carried out such that the sums N_{AB} and N_{AC} were held constant while the signs and magnitudes of $J_{AA'}$, $J_{BB'}$, and $J_{CC'}$ were varied. After computation of 20 trial spectra, a spectrum was obtained which embodied many of the features of the experimental AA' region. In this spectrum the parameters $J_{AA'}$, $J_{BB'}$, and $J_{CC'}$ had the signs +, +, and −, respectively. Six more trials involving adjustment of J_{BC} and $J_{BC'}$ yielded calculated spectra for the BB' and CC' regions with some resemblance to the experimental. Finally, eight additional trials involving systematic variation of first $J_{AA'}$ and then $J_{BB'}$ and then $J_{CC'}$ over a few cycles with concomitant adjustment of the other six couplings over a range of a few tenths of a cycle gave a spectrum having the same number of observed lines and a distribution of lines similar to the experimental. At this point enough (about 80) of the 170 easily discernible lines could be assigned to link all the 36 A_1 energy levels together and all the 28 B_1 energy levels together. These sets of transitions were processed by the iterative program NMRENIT[29] which yielded a convergent solution for the parameters and a calculated spectrum agreeing exceedingly well with the experimental in every detail. This solution was used to assign the remainder of the lines. The positions of incompletely resolved lines were estimated from line-width considerations. A number of the weak lines predicted by this first iteration were found and measured. Finally, a total of 194 transitions (108 A_1 type and 86 B_1 type) were identified and measured. These were inserted in NMRENIT[29] to give the parameters shown in Table IV after nine iterations. The spectra resulting from the parameters are plotted in Figures 1b, 2c, and 3c. The average deviation between observed and calculated frequencies was ±0.026 Hz with the maximum deviations being +0.092 and +0.074 Hz for two very weak lines. We believe that the coupling constants and chemical shifts for **1** at 30.2° presented in the table are accurate to ±0.01 Hz. This conclusion was based, in part, on the fact that displacement of each line in one-half of one of the spectral regions (about 36 lines) by 0.5 Hz per line and iteration on these incorrect line positions resulted in a error of less than 0.1 Hz in all the couplings to this region and an error of about 0.25 Hz in the chemical shift. It should be emphasized that the spectrum of **1** is temperature dependent, and probably solvent dependent, and the parameters presented here apply for 30.2° and **1** in the mixture described above.

With one iterated solution in hand, the question of uniqueness still remained. In the solution obtained, the magnitudes[7] and relative signs[19] of J_{AB}, J_{AC}, and J_{BC} are exactly characteristic of the trifluorovinyl group. The $J_{AC'}$ and $J_{BC'}$ couplings turn out to be identical in sign[19] and similar in magnitude[24] to analogous couplings in other related molecules. The signs and magnitudes of the parameters $J_{AB'}$, $J_{AA'}$, $J_{BB'}$, and $J_{CC'}$, however, need

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[27] (a) J. A. Pople and T. Schaefer, *Mol. Phys.*, 3, 547 (1961); (b) P. Diehl and J. A. Pople, *ibid.*, 3, 557 (1961); (c) P. Diehl, R. G. Jones, and H. J. Bernstein, *Can. J. Chem.*, 43, 81 (1965); (d) R. G. Jones, R. C. Hirst, and H J. Bernstein, *ibid.*, 43, 683 (1965); (e) P. Diehl, *Helv. Chim. Acta*, 48, 567 (1965); (f) R. G. Jones and S. M. Walker, *Mol. Phys.*, 10, 363 (1966); (g) P. Diehl and P. Weisenhorn, *Helv. Chim. Acta*, 50, 143 (1967); (h) P. Diehl and D. Trautman, *Mol. Phys.*, 11, 531 (1966).

[28] Although this method is not appropriate for the AA'BB'XX' case, it is possibly useful for the AA'XX'YY' problem; see E. Lustig, N. Duy, P. Diehl, and H. Kellerhals, *J. Chem. Phys.*, 48, 5001 (1968).

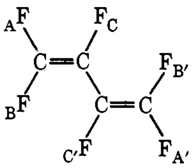
[29] M. T. Bowers, T. I. Chapman, and S. L. Manatt, *ibid.*, in press; this program performs the functions of NMREN-2 and NMRIT in one step.

to be carefully considered relative to reasonableness and the limited data available on analogous couplings. The value for $J_{AB'}$ of +2.44 Hz is slightly different in magnitude but of the same sign as the corresponding coupling of +8.0 Hz in 1,1,4,4-tetrafluoro-1,3-butadiene (**2**).[4] As discussed below, this difference could be the result of a difference in the degree of planarity between **1** and **2**. At any rate the $J_{AB'}$ value in **1** seems to us to be perfectly reasonable. The acceptability of the signs and magnitudes of $J_{AA'}$ and $J_{BB'}$ stem mainly from comparison with the results from the analysis of the spectrum of **2**.[4] However, as was mentioned above, an unambiguous assignment of these $^5J_{FF}$ couplings has yet to be made for **2**. At least these signs are both the same and the same as that of $^2J_{FF}$ which is positive.[19] There are no data available relative to the sign of $J_{CC'}$. Evidence exists that the magnitude of this coupling lies in the range of 20–40 Hz.[6] In light of the moderate uncertainties concerning the parameters $J_{AA'}$, $J_{BB'}$, and $J_{CC'}$, series of spectra were calculated embodying systematic changes of these couplings in such a manner that the sums K_{AB}, K_{AC}, and K_{BC} were constant. Also spectra were calculated with inversions of the signs of L_{AB}, L_{AC}, L_{BC}, M_{AB}, M_{AC}, and M_{BC}. The permutations of the parameter signs and systematic variations of coupling magnitudes gave spectra which in no case approached closely the experimental even as regards line positions. From the results of these test calculations, which suggest the strongly coupled nature of this AA'BB'CC' problem, we conclude that the fit obtained for the spectrum of **1** has a high probability of being unique. Although the reasonability of the resulting signs and magnitudes of the coupling constants for **1** is strong evidence for the latter point, systematic double-resonance experiments could fully verify this conclusion.[29a]

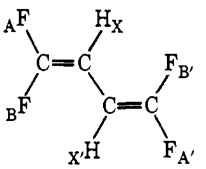
Discussion

A number of questions regarding the nmr parameters and structures of fluorine-substituted 1,3-butadienes were raised in the introductory section. We will now discuss to what extent some of these questions are resolved by the results for **1**.

Comparison of $^5J_{FF}$'s in 1 and 2. The existence of a large (+35.7 Hz) $^5J_{FF}$ coupling between distant fluorine nuclei (either approximately 5.9 or 4.8 Å apart) in tetrafluoro-1,3-butadiene (**2**),[4] which has been demonstrated to be planar,[30, 31] is remarkable. As mentioned above, this $^5J_{FF}$ coupling in **2** could be $J_{AA'}$ or $J_{BB'}$. On the basis of the results for **1**, it would seem that the choice $J_{BB'}$ = +35.7 Hz is the correct one. A reasonable amount of question regarding this conclusion can be raised. Results from a study of the vibrational spectra of **1** could be interpreted either in terms of the existence of two molecular configurations with C_{2v} symmetry or alternately, in terms of a nonplanar configuration with C_2 symmetry.[32] More recently, nmr[10, 33] and infrared[34] investigations of 1,3-butadienes have resulted in the conclusion that a nonplanar skew conformation exists in some butadienes. The nonplanarity appears to result primarily from steric interactions between atoms on the 1 and 3 positions of a butadiene.[35] Consequently, with the exact conformation of **1** in doubt, the assignment of the +35.7-Hz coupling in **2** as $J_{BB'}$ is certainly open to question. The fact that the one large $^5J_{BB'}$ coupling in **1**, which can be unequivocally assigned, is smaller by a factor of 3.3 from that in **2** would seem to signal that there exists significant differences between **1** and **2** in the electronic and structural factors which are paramount to the propagation of these long-range couplings. It might be argued that the differences arise from a substituent effect due to the presence of two fluorine atoms at the 2- and 3-carbon atoms in **1**. To evaluate this possible explanation requires the consideration of the mechanisms of the transmission of the $^5J_{FF}$ couplings. On the basis of current theory,[36] the $^5J_{FF}$ couplings between fluorines 4.8–5.9 Å apart as in **2** must involve the π-electron system. Successful models for long-range proton–proton coupling based on σ–π interaction have been developed[37] which suggest that



1



2

$$J_{NN'}^{\pi} \propto Q_{C-H}Q_{C'-H'}p^2_{NN'}/\Delta E \qquad (1)$$

where $J_{NN'}^{\pi}$ is the contribution to the coupling transmitted *via* the π-electron system, Q_{C-H} and $Q_{C'-H'}$ are the corresponding effective isotropic hyperfine coupling constants for interaction between a π electron in a carbon $p\pi$ atomic orbital and an adjacent σ-bonded proton, $p_{NN'}$ is the mobile π-bond order between carbon atoms bonded to protons H and H', and ΔE is an average triplet excitation energy. Extension of this model to long-range couplings involving fluorines requires some modification. The Q_i's which go into the treatment for the long-range proton–proton couplings are related approximately to the observed proton–electron contact interaction constants, a_H, through the equation[38]

$$a_H = Q_{C-H}\rho_C \qquad (2)$$

where ρ_C is the spin density centered on the carbon atom. In the case of fluorine, however, there are two contributions to a_F such that the corresponding equation is

$$a_F = Q^C{}_{C-F}\rho_C + Q^F{}_{C-F}\rho_F \qquad (3)$$

where $Q^C{}_{C-F}$ is the isotropic hyperfine coupling constant for a σ–π contribution analogous to that important in the proton case, $Q^F{}_{C-F}$ is a hyperfine coupling constant describing a contact contribution stemming from polar-

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(29a) NOTE ADDED IN PROOF. Using a multifrequency synthesizer and digitally swept spectrometer, double resonance experiments on **1** which confirm the assignment reported here have now been carried out by Dr. Bert E. Holder at Lawrence Radiation Laboratory, Livemore, Calif.; to be published.

(30) R. A. Beaudet, *J. Am. Chem. Soc.*, 87, 1390 (1965).

(31) R. M. Conrad and D. A. Dows, *Spectrochim. Acta*, 21, 1039 (1965).

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

(33) A. A. Bothner-By and D. Jang, *J. Am. Chem. Soc.*, 90, 2342 (1968).

(34) K. O. Hartman, G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, 24A, 157 (1968).

(35) Where we mean a substituent in the 1 position which is *cis* to the formal single bond.

(36) See, for example, M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, 1, 149 (1965).

(37) M. Karplus, *J. Chem. Phys.*, 33, 1842 (1960).

(38) H. M. McConnell, *ibid.*, 24, 632 (1956).

ization of the fluorine 1s and 2s electrons by spin density present on a $2p\pi$ orbital centered on the fluorine, and ρ_C and ρ_F are the spin densities in the carbon and fluorine $p\pi$ orbitals, respectively. The generally accepted ability of fluorine to participate in multiple bonding with a conjugated system[39] is responsible for ρ_F. The isotropic carbon-13 contact interactions have been treated similarly.[40] It has been suggested that ρ_F can be related to the C–F double-bond order, p_{C-F}, and ρ_C through the equation

$$\rho_F = Ap_{C-F}\rho_C \qquad (4)$$

where A is a constant of order unity.[41] Substituting (4) into eq 3 for a_F yields

$$a_F = \rho_C(Q^C{}_{C-F} + AQ^F{}_{C-F}p_{C-F}) \qquad (5)$$

The quantity in parentheses in eq 5 represents a composite Q_F which is dependent on p_{C-F}. Thus from the equation

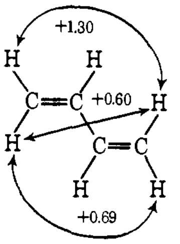
$$J_{FF'}{}^{\pi} \propto Q_FQ_{F'}p_{C-C'}/\Delta E \qquad (6)$$

where Q_F and $Q_{F'}$ represent two composite hyperfine constants, we get

$$J_{FF}{}^{\pi} \propto [Q^C{}_{C-F}Q^C{}_{C'-F'} + AA'Q^F{}_{C-F}Q^F{}_{C'-F'} \times p_{C-F}p_{C'-F'} + Q^C{}_{C-F}A'Q^F{}_{C'-F'}p_{C'-F'} + Q^C{}_{C'-F'}AQ^F{}_{C-F}p_{C-F}]p^2{}_{C-C'}/\Delta E \qquad (7)$$

It would appear from eq 7 that questions regarding the existence of a substituent effect on the $^5J_{FF}$ couplings in **1** and **2** might be answered from a knowledge of the appropriate carbon–fluorine bond orders. There is good evidence from fluorine-19 nmr contact interaction chemical shifts that $Q^C{}_{C-F}$ is negative and $AQ^F{}_{C-F}$ positive.[40] Unfortunately, no appropriate evaluations of p_{C-F} have been made for the molecules **1** and **2**.

Interpretation of experimental data on other types of long-range couplings in 1,3-butadiene should allow some decision regarding the nature of substituent effects which might be indicative of the situation for the fluorine–fluorine case. In the case of 1,3-butadiene (**12**), the $^5J_{HH}$ couplings are as shown.[13a] In **12** the $J_{AA'}$ coupling is the largest. Substitution of a fluorine atom at the 2 position as in 2-fluoro-1,3-butadiene (**13**)[5] would be expected to be a large enough perturbation on the butadiene system to provide information on the magnitudes and signs of any substituent effects on the $^5J_{HH}$ couplings. As can be seen, the changes in **13** indicate that such substituent effects are certainly less than a factor of 25% and not close to the approximately 300% differences between some of the $^5J_{FF}$ couplings in **1** and **2**. An even closer correspondence should exist between $^5J_{FF}$ couplings and $^5J_{HF}$ couplings than between $^5J_{FF}$ couplings and $^5J_{HH}$ couplings. The approximate theoretical model discussed above yields



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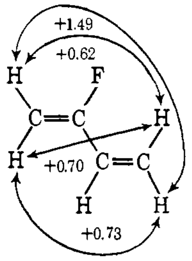

13

$$J_{HF}{}^{\pi} \propto Q_{C-H}(Q^C{}_{C-F} + AQ^F{}_{C'-F}p_{C'-F})p^2{}_{C-C'}/\Delta E \qquad (8)$$

where Q_{C-H} is negative.[42] In 1,1-difluoro-1,3-butadiene (**7**)[21] and 1,1-difluoro-2-methyl-1,3-butadiene (**8**),[21] the larger of the two appropriate $^5J_{HF}$ couplings corresponds not to $J_{BB'}$ but to $J_{AA'}$ in **2**. Unfortunately, again no experimental or theoretical work is available which demonstrates the effect of substituents on $^5J_{HF}$ couplings; an investigation now in progress[23] of the spectrum of 1,1,2-trifluoro-1,3-butadiene (**11**) may yield crucial information on this problem.

Thus, based on the above discussion of the $^5J_{HH}$ couplings, we propose that for now the differences between the $^5J_{FF}$ couplings in **1** and **2** do not arise from a substituent effect due to the presence of fluorine atoms at the 2- and 3-carbon atoms in **1**. Also, it appears likely that the large $^5J_{FF}$ coupling is +35.7 in **2** is $J_{AA'}$, not $J_{BB'}$ as it is in **1**. Strong confirmation of the correctness of the former assignment has now been obtained from comparison of calculated spectra for the full six-spin problem of **2**.[43] We speculate further that the values of the $^5J_{FF}$ couplings in **1** arise because of the importance of a nonplanar skewed geometry. With molecular models based on accepted van der Waals radii it is not possible to construct a planar-*trans* arrangement of the atoms in **1**. The presence of two significant fluorine–fluorine repulsions between two pairs of proximate 1- and 3-fluorine atoms in **1** may cancel any resonance stabilization which would be favored by a near-planar configuration. We propose that the departure from planarity is serious enough in **1** to result in significant reduction in the component of the $^5J_{FF}$ couplings transmitted through the π-electron system. In fact, if the skew conformation of **1** is sufficiently nonplanar, the fluorines involved in the largest $^5J_{FF}$ coupling ($J_{BB'}$) can approach each other most closely before any new repulsions would be expected to arise. On this basis we believe that a substantial contribution to $J_{BB'}$ in **1** may arise from a direct through-space coupling mechansim.[12] This latter mechanism has been recently dismissed as not having any importance,[4] but new evidence warrants a reconsideration of this concept. For example, in order to explain the $^4J_{FF}$ couplings between a CF_3 group in the 1 position on an aromatic ring and a fluorine in the 2 position, it has been proposed that this coupling depends on the dihedral angle (θ) between the C–F bond in the CF_3 group and the C–F bond of the 2-fluorine as shown below.[44]

θ	0°	60°	120°	180°
$^4J_{FF}$, Hz	83.6	11.8	9.2	6.6

Data which appear at present to provide an even more direct confirmation of the existence of significant

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[39] See, for example, L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 314.

[40] A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *J. Chem. Phys.*, 33, 65 (1960); M. Karplus and G. K. Fraenkel, *ibid.*, 35, 1312 (1961).

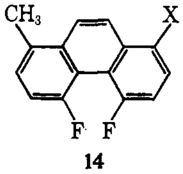
[41] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, 5, 407 (1962).

[42] S. I. Weissman, T. R. Tuttle, and E. de Boer, *J. Phys. Chem.*, 61, 28 (1957).

[43] Unpublished work of S. L. Manatt. Estimates of all the couplings in **2** not measured in ref 4 were obtained from scrutiny of literature and published data. See, for example, ref 5, 19, 20, 21, 23, and 24.

[44] J. Jonas, L. Borowski, and H. S. Gutowsky, *J. Chem. Phys.*, 47, 2625 (1965); J. Jonas, *ibid.*, 47, 4884 (1965).

through-space couplings have recently been found by Servis,[45] Roberts,[46] and in our laboratory.[47]. Servis has found ${}^5J_{FF}$ couplings of the order of 167–170 Hz in various 1-substituted 4,5-difluoro-8-methylphenanthrenes (**14**).[45] Roberts[46] has frozen out the conformers of bis(trifluoromethyl)tetrachloroethane (**15**) at −150° and found that for one conformer (**15a**) there exists a 75-Hz ${}^5J_{FF}$ coupling between proximate fluorine nuclei a and a′. Although the spectrum of heptafluoro-1-naphthol (**16**) is complicated,[47] in the 94.1-MHz spectrum it is possible to identify the four *peri*-fluorine nuclei as two sets of AB quartets which exhibit couplings of approximately 65 Hz. Thus, on the basis of these results, a through-space coupling component could very well account for a substantial part of the $J_{BB'}$ coupling in **1**.



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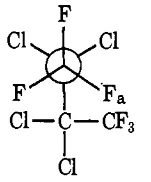
X = $-CH_2Br$, $-CH_2OH$, $-CO_2Et$, $-NH_2$



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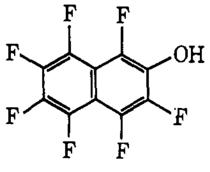


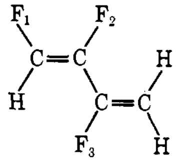
16

It would seem that the couplings reported[4] in **3** and **4** might now be characterized rather well in terms of the arguments and conclusions given above. In these molecules, models demonstrate that the B and B′ fluorines are quite close. In **3** they are closest. In fact, models of **3** indicate that the axes of the pπ orbitals on the 2- and 3-carbon atoms will have to subtend an angle of about 60° to yield a relatively strain-free molecule. This deformation would mean that conjugation, and concomitantly any phenomena propagated by the π-electron system between the ends of the butadiene molecule, would be significantly attenuated.

In the 1,4-dichlorotetrafluorobutadienes **5** and **6** we speculate that the $J_{BB'}$-type couplings are the +31.4- and +23.2-Hz ones and that they are due principally to a through-space mechanism. Obviously, based on the discussion presented above, a skewed geometry is implicated. The other ${}^5J_{FF}$ couplings in the latter molecules arise mainly *via* the residual π-electron mechanism which, as demonstrated in the *trans*-planar **2**, may show a special orientation effect between the *trans,trans* fluorines.

Discussion of ${}^2J_{FF}$, ${}^3J_{FF}$'s, and ${}^4J_{FF}$'s in 1. In Table V most of the available data on the nmr spectra of fluorine-substituted 1,3-butadienes is presented. The data for **1** establishes the signs and confirms the assignments for most of the couplings in the dichlorotetrafluorobutadienes **5** and **6**. Thus, in **5**, J_{14} (5.9 Hz) should be positive in sign and correspond to $J_{AB'}$ (+2.45 Hz) in **1**. The ${}^4J_{FF}$ couplings in **5** and **6** are very similar in magnitude to the corresponding ones in **1** which are all positive in sign. The sign of the J_{23} couplings in **5** and **6** should be negative. In **6**, the 34.4-Hz coupling should be J_{23}, and the 22.7-Hz coupling then corresponds to $J_{BB'}$ in **1**. The increase in magnitude of this coupling in **6** over that in **1** may indicate an even larger contribution of through-space coupling in **6**. This implies that in **6** the B and B′ fluorines approach more closely than in **1** or, alternately, that the skewed conformation is more important in **6**.

The one coupling in **5** and **6** which appears to be unexpected is J_{12} = 11.5 Hz in **5**. In **1** this coupling is +31.91 Hz. Scrutiny of the magnitudes of this ${}^3J_{FF}$ coupling in the trifluorovinyl group for a large number of substituents reveals that it varies from +24 to +66 Hz.[48] However, in *cis*-1,2,3-trifluoro-1,3-butadiene (**17**) J_{12} has been reported as 10.9 Hz[8] and in *cis*-1-phenylperfluoropropene (**18**) as 9 Hz[49] so the value in **6** may be reasonable. The reasons for this small ${}^3J_{FF}$ in **5**, **17**, and **18** are certainly not clear.



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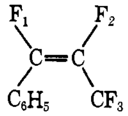

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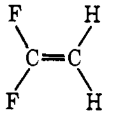
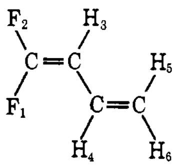
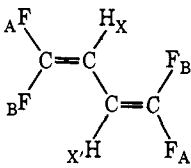
As can be seen from Table V, the ${}^2J_{FF}$ coupling in **1** is similar to those in a number of 1,1-difluorobutadienes. The change of ${}^2J_{FF}$ with substituent in the trifluorovinyl group seems to be qualitatively understandable. In 1,1-difluoroethylene (**9**) ${}^2J_{FF}$ is +36.4 Hz. On substitution of a vinyl group, which results in **7**,[21] this coupling decreases slightly to +31.6 Hz. Substitution of a 4,4-difluorovinyl group to give **2** results in a slight increase to +35.7 Hz. The last two substituents really cause very little change in this ${}^2J_{FF}$ coupling. Attachment of a fluorine atom at the 2 position in **9** to give trifluoroethylene (**10**) results in a significant increase to +87 Hz.



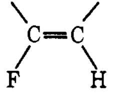
9, ${}^2J_{FF}$ = +36.4 Hz



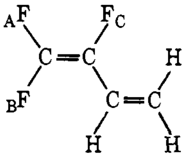
7, ${}^2J_{FF}$ = +31.6 Hz



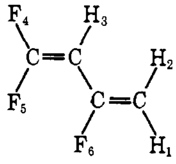
2, ${}^2J_{FF}$ = +35.7 Hz



10, ${}^2J_{FF}$ = +87 Hz



11, ${}^2J_{FF}$ = +67.2 Hz



19, ${}^2J_{FF}$ = +19.5 Hz

Substitution of **9** with a 3-fluorovinyl group to give 1,1,3-trifluoro-1,3-butadiene (**19**) results in a significant decrease to +19.5 Hz.[50] Substitution of a 3,4-difluorovinyl group to give 4-H-pentafluoro-1,3-butadiene (**20**)[7,51] results in a significant increase to +54.7 Hz, while addition of one more fluorine to give **1** yields a coupling of +50.7 Hz.

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(45) K. L. Servis and K. Fang, *J. Am. Chem. Soc.*, **90**, 6712 (1968).

(46) F. J. Weigert and J. D. Roberts, *ibid.*, **90**, 3577 (1968).

(47) E. A. Cohen and S. L. Manatt, unpublished work.

(48) See ref 24, pp 908–916.

(49) S. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962).

(50) D. Koster, private communication.

(51) Configuration not reported in ref 7.

Table V. Summary of Fluoro-1,3-butadiene Nmr Coupling Constant Data[a]

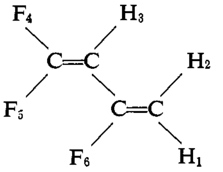
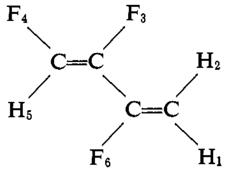
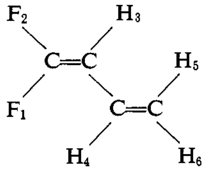
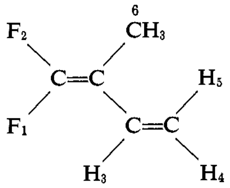
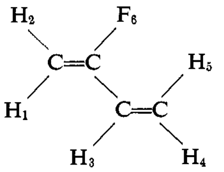
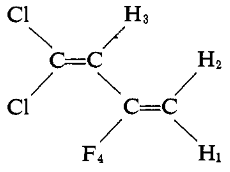
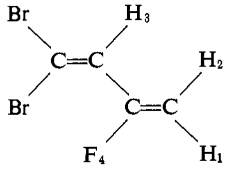
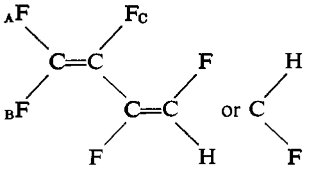
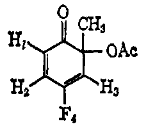
Compound	Ref	Coupling, sign, and magnitude	
1	This work	J_{AB} + 56.86 J_{AC} + 31.91 J_{BC} − 118.57 $J_{AB'}$ + 2.45 $J_{AC'}$ + 2.41	J_{BC}' + 14.19 J_{AA}' + 4.80 $J_{BB'}$ + 11.31 $J_{CC'}$ − 30.30
2	4	J_{AB} + 36.6 $J_{AB'}$ + 8.0 $J_{CC'}$ + 10.8	$J_{AA'}$ + 36.6 or + 4.8 $J_{BB'}$ + 4.8 or + 36.6
3	4	J_{AB} + 39.0 $J_{AB'}$ + 4.8	$J_{AA'}$ + 3.3 or + 31.4 $J_{BB'}$ + 31.4 or + 3.3
4	4	J_{AB} + 14.7 $J_{AB'}$ + 6.7	$J_{AA'}$ + 7.6 or + 23.2 $J_{BB'}$ + 23.2 or + 7.6
 **19**	50	J_{12} − 3.2 J_{13} 0.7 J_{14} 1.0 J_{15} 0.8 J_{16} 17.0 J_{23} 0.0 J_{24} 0.5 J_{25} 0.4	J_{26} 47.0 J_{34} 23.0 J_{35} 2.6 J_{36} 19..2 J_{45} 19.5 J_{46} 27.6 J_{56} 3.1
 **17**	8	J_{12} 3.9 J_{13} 3.9 J_{14} ? J_{15} ? J_{16} 18.1 J_{23} 3.9 J_{24} ? J_{25} ?	J_{26} 48.4 J_{34} 10.9 J_{35} 16.0 J_{36} 35.9 J_{45} 71.5 J_{46} 10.9 J_{56} 3.3
 **7**	21	J_{12} + 31.6 J_{13} + 23.8 J_{14} + 1.1 J_{15} − 0.2 J_{16} − 1.9 J_{23} ± 1.6 J_{24} ± 1.2 J_{25} ± 0.5	J_{26} ± 1.6 J_{34} + 10.8 J_{35} − 0.8 J_{36} − 0.7 J_{45} + 16.7 J_{46} + 10.6 J_{56} + 1.4
 **8**	21	J_{12} + 35.7 J_{13} 1.5 J_{14} 1.7 J_{15} 0.0 J_{16} + 2.8 J_{23} 1.6 J_{24} 1.3 J_{25} 0.6	J_{26} + 3.8 J_{34} + 10.7 J_{35} + 17.2 J_{36} 0.0 J_{45} + 1.3 J_{46} 0.0 J_{56} 0.0
 **13**	5	J_{12} − 2.72 J_{13} − 0.19 J_{14} + 0.73 J_{15} + 0.70 J_{16} + 49.93 J_{23} + 0.09 J_{24} + 1.49 J_{25} + 0.62	J_{26} + 15.76 J_{34} + 11.14 J_{35} + 17.32 J_{36} + 25.15 J_{45} + 1.24 J_{46} + 1.19 J_{56} − 0.19
	10	J_{12} − 3.18 J_{13} + 0.64 J_{14} + 16.28	J_{23} − 0.31 J_{24} + 46.45 J_{34} + 17.04
	10	J_{12} − 3.22 J_{13} + 0.54 J_{14} − 16.08	J_{23} − 0.31 J_{24} + 46.30 J_{34} + 17.33

Table V (*Continued*)

Compound	Ref	Coupling, sign, and magnitude	
 **20**	7	J_{AB} 49 J_{AC} 30 J_{BC} 111	
5	6	J_{12} 11.5 J_{13} 3.6 J_{14} 5.85	J_{23} 34.1 J_{24} 14.5 J_{34} 133.8
6	6	J_{12} − 132.9 J_{13} + 14.2	J_{14} 22.7 or 34.4 J_{23} 34.4 or 22.7
11	22	J_{AB} + 67.2 J_{AC} + 30.2 J_{BC} − 111.6	
	9	J_{12} + 10.39 J_{13} + 0.65 J_{14} + 5.29	J_{23} + 3.14 J_{24} + 7.06 J_{34} + 9.85

[a] Values in hertz. When a sign is not given, only the magnitude was reported.

Thus, substitution of a very electron-attracting group at the 2 position of 1,1-difluoro-1,3-butadiene (**7**) causes a marked increase in $^2J_{FF}$. Substitution of such a group at the 3 position results in a decrease. Similar alternation of direction of substituent effects has been reported for certain proton–proton couplings as a function of the number of bonds the substituent is removed from the group of coupled nuclei.[52,53] It may be that a very electronegative substituent at the 4 position of **5** would result in an increase in $^2J_{FF}$. However, when there are two electronegative substituents at the 4 position little effect results. The presence of electronegative substituents at both the 3 and 4 positions of **7** results in a net decrease in $^2J_{FF}$. The vinyl radical, when bonded to a 1,1-difluoroethylene group to give **7**, appears to act like a weak electron-donating group as preceived by changes in $^2J_{FF}$.

Conclusion

The nmr parameters for hexafluoro-1,3-butadiene and the discussion presented in this report demonstrate that the signs of the three types of long-range $^5J_{FF}$ couplings in fluorobutadiene are positive. The signs of these couplings are the same as has generally been observed for the $^5J_{FF}$ in most fluorobenzenes.[54,55] The signs of these $^5J_{FF}$ couplings were compared above with those of $^5J_{HF}$ and $^5J_{HH}$ couplings. An approximate theoretical model was discussed which, when the appropriate valence bond or molecular orbital calculations on **1** and 1,1,4,4-tetrafluoro-1,3-butadiene (**2**) become available, might be useful for predicting the relative magnitudes of the various $^5J_{FF}$ and $^5J_{HF}$ couplings. The assignment of the large $^5J_{FF}$ coupling in **2** is suggested to correspond to $J_{AA'}$ and to arise from a mechanism involving transmission of spin orientation information through the π-electron system. In contrast, it is proposed that the significant decreases in the magnitudes of the $^5J_{FF}$ couplings in **1** can be attributed to nonplanarity of **1**. This results in an attenuation of the component of the $^5J_{FF}$ couplings transmitted *via* the π-electron route. We speculate that the largest $^5J_{FF}$ coupling in **1** derives from an important contribution from through-space coupling. Recent evidence which reinstates this concept was discussed. The relative magnitudes and assignments of the $^5J_{FF}$ couplings in two *cis*-1,1,4,4-tetrafluoro-1,3-butadienes have been rationalized in terms of a large through-space coupling contribution between proximate fluorine nuclei and attenuated transmission through the π-electron system. The sign of the *trans*-$^3J_{FF}$ coupling between the fluorine nuclei in the 2 and 3 positions in fluorobutadienes has been established as negative. This sign is the same as that of the *trans*-$^3J_{FF}$ coupling across the formal double bond in a trifluorovinyl group. However, the former is about one-quarter the magnitude of the latter.

The discussion and results collected in this paper provide few if any unequivocal answers to many of the questions regarding the conformations of the highly fluorinated butadienes and the mechanisms of fluorine–fluorine couplings, but we hope that some of the important problems which need to be attacked have become more evident. Specifically, there is a need for more theoretical work (or simply calculations) on fluorine–fluorine couplings. Other recent work on 1,3-butadienes is consistent with the existence of more than one conformation in many cases. A nonplanar skew conformation seems to fit the data. However, microwave and/or electron diffraction structure determinations are needed to confirm this proposal. Work in progress[56] has produced the isomeric 4-chloropentafluoro-1,3-butadienes, and we are hopeful that microwave and nmr studies of these molecules may reveal significant information about some of the structural problems concerning the fluorobutadiene series.

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Donor–Acceptor Complexes of the Inorganic π Acceptor, Bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel

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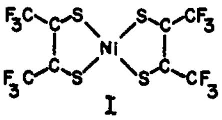
Abstract: Electrically conducting donor–acceptor complexes between the aromatic hydrocarbons perylene and pyrene and the powerful electron acceptor bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel have been prepared. Their crystal structures have been determined from single-crystal X-ray diffraction studies. These 1:1 complexes are found to consist of stacks of alternating organic and inorganic molecules with the stacking axis parallel to the growth axis. The crystals are semiconductors having room-temperature resistivities of the order of 10^5 ohm cm. The activation energy for conduction is anisotropic for the perylene complex with a minimum activation energy along the stacking axis. Absorption bands attributed to an intermolecular charge-transfer transition have maxima in the near-infrared at an energy which is the same as the band-gap energy if the conductivity is assumed to be intrinsic, and if there is no energy barrier for conduction along the stacking axis.

Complexes between electron acceptors and electron donors have been studied extensively.[1] In these complexes, the structure of the individual components remains unchanged but the electrical resistivity of the complex is several orders of magnitude less than that of the isolated components. The absorption spectra of these complexes show new bands where neither of the component molecules absorb, and such bands are attributed to intermolecular charge transfer.[2] Donor–acceptor complexes are described as strong (ionic) or weak (nonionic) depending on the degree of charge transfer in the ground state.[2,3] Both organic molecules and inorganic metal[4] complexes have been used as donors. Acceptors have included organic molecules and simple inorganic molecules such as the halogens.[5] This paper reports the crystal structures and some of the physical properties of donor–acceptor complexes in which the acceptor is the transition metal complex, bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel (nickel thiete) (I),[6] and the donors are the highly conjugated aromatic molecules pyrene and perylene.



I

Experimental Section

Preparation of Complexes. Perylene and pyrene were reagent grade chemicals obtained from the K and K Laboratories. They were purified by recrystallization from benzene and by sublimation, respectively. Nickel thiete was prepared as previously described[6] and recrystallized from pentane. Further purification of these materials for growing crystals to be used for electrical conductivity measurements was done and is described in a later section.

Complexes of both perylene and pyrene with nickel thiete were prepared by mixing benzene solutions containing equimolar amounts of the hydrocarbon and nickel thiete. Large crystals of the perylene complex were grown by allowing a solution of nickel thiete in pentane to diffuse over a period of several days into a solution of perylene in dichloromethane. Large crystals of the pyrene complex could not be grown.

Absorption Spectra. Visible and near-infrared absorption spectra of KBr disk samples were recorded on a Perkin-Elmer Model 621 spectrophotometer. Infrared absorption spectra were recorded on a Perkin-Elmer Model 450 spectrophotometer. To verify that the absorptions were not due to dispersion, blank KBr disks containing only the pure components of the complex were run. No quantitative measurements of absorption intensity were attempted.

Electrical Conductivity and Seebeck Coefficients. The resistance of both single crystals and compressed pellets was measured as a function of temperature. The pellets were pressed with an evacuable KBr die using an applied force of 30,000 lb on a 13-mm piston. A thin layer of silver was pressed on either side of the pellet to ensure good electrical contact.

The resistance of the sample was measured by gluing it to a polystyrene block and attaching thin copper wires to the sample faces using conductive silver paint. The copper wires were soldered to threaded brass rods which were bolted at one end to the polystyrene block and threaded through a Teflon stopper at the other end. The brass rods served as electrical leads to a circuit which consisted of a battery and a shunt resistor in series with the crystal. The voltage drop across the shunt resistor was used to determine the current flow in the circuit from which the resistance of the crystal was calculated. For perylene–nickel thiete the shunt was a precision 10^4-ohm resistor and the voltage drop was measured on the *Y* axis of a Hewlett-Packard XY recorder, Model No. 7001A, which has a 10^6-ohm input impedance. For the pyrene–nickel thiete complex the shunt was a precision 10^8-ohm input resistor to a Cary vibrating reed electrometer, Model 32. The output of the electrometer was measured on the *Y* axis of the same XY

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