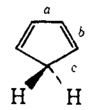
Table I. Observed and Calculated Isotropic Hyperfine Coupling Constants to Protons (in Gauss)

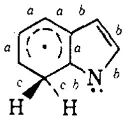
Anion	Proton	Obsd	INDO
2	C-2	45 ± 2	45
	C-3	11 ± 2	8
	C-4		0.5
	C-5	11 ± 2	5
IIIA	C-3		1
	C-4	15 ± 2	9
	C-5	50 ± 2	52
V	C-2		2
	C-4	15 ± 4	11
	C-5	50 ± 2	50
VII	C-2		1
	C-3		1
	C-4	12 ± 2	9
	C-5		5
	C-6	12 ± 2	11
	C-7	40 ± 2	49

were assumed to be the same as that of cyclopentadiene.[11]



all C–H = 1.09 Å
a = 1.46
b = 1.35
c = 1.53
$\angle ab = 110°$ $\angle HCH = 109°$

The structural parameters assumed for indole anion (**VII**) are



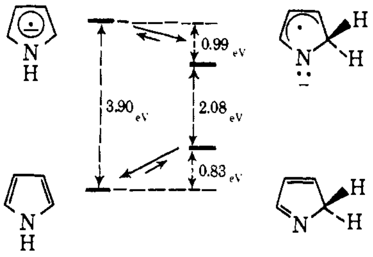
all C–H = 1.09 Å
$a = b$ = 1.40
c = 1.50

$\angle aa = 120°$, $\angle ab = 110°$
$\angle HCH = 109°$

In spite of the assumptions made for the structures of the radicals, the overall agreement between the observed and calculated coupling constant is quite reasonable, and can be accepted as a further substantiation to the proposed assignments.

As stated earlier, the tautomerism between pyrrole (IIA) and α-pyrrolenine (IIB) is almost nonexistent, the pyrrole form IIA totally dominating the equilibrium. The observed reversal of the tautomeric equilibrium in the anionic state must be a consequence of the fact that α-pyrrolenine is a much better electron acceptor than pyrrole. We have examined the energetic relations between pyrrole and α-pyrrolenine both in their neutral state and anionic form using INDO molecular orbital theory. The known structural parameters were used for pyrrole,[6] and the structure of cyclopentadiene was assumed for α-pyrrolenine. Comparison of the total energies of the respective species gave the result shown in Chart I. Because of the assumptions made for the structures of pyrrole anion, α-pyrrolenine and its anion, the exact energy differences given above should be accepted with some reservation. Nevertheless, the relative stabilities of the four species predicted by the theory are in complete agreement with the experimental results encountered in this study.

Chart I



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[11] (11) V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.*, **61**, 1796 (1939).

Theoretical Study of the Fluorine–Fluorine Nuclear Spin Coupling Constants. II. Stereochemical Dependences

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Contribution from the Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received April 3, 1972*

Abstract: Stereochemical dependences of F–F coupling constants are studied theoretically by using the INDO–MO's and the sum-over-states perturbation method. The F–F coupling is sensitive to the geometrical relationship of the two spin-coupled fluorines although far different from that of the H–H coupling. The origin of the angular dependence of geminal F–F coupling on the FCF angle is chiefly due to the FC term and both the SD and OB terms are insensitive to the angular changes. In vicinal F–F coupling, no clear tendency as a function of the dihedral angle is found. The long-range F–F coupling exhibits steric dependence strongly, which originates also from the FC term. The "fragment" coupling shows a dramatic dependence on the internuclear separation of the coupled fluorines. The origin of the fragment coupling is considered in more detail. From the striking angular dependences of the five-bond F–F couplings, nonplanarity of hexafluorobutadiene is supported.

As nuclear magnetic resonance (nmr) spectroscopy takes first place in importance for the organic chemist, the number of experimental values of coupling constants between fluorine nuclei is increasing rapidly. However, unlike H–H coupling constants, there is no satisfactory theoretical interpretation of these data until recently because of the lack of knowledge of the mechanisms of F–F coupling constants. In this series of papers our aim is to present a systematic theoretical study of the F–F coupling constants. In part I of this

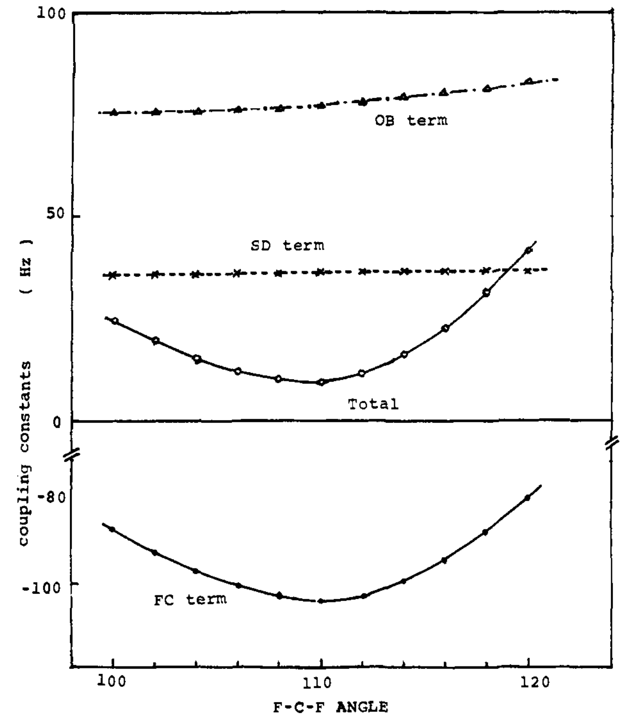

Figure 1. Plots of J_{FF}^{gem} *vs.* the FCF angle for H_2CF_2*.

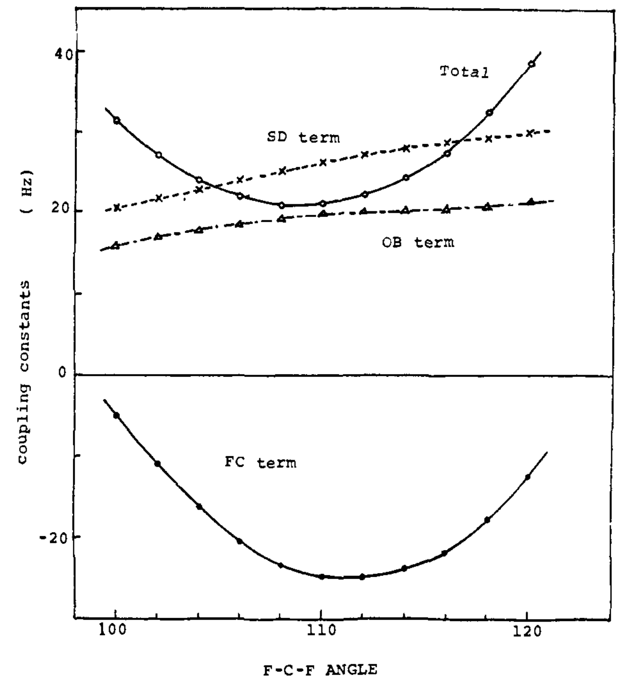

Figure 2. Plots of J_{FF}^{gem} *vs.* the FCF angle for $CH_2{=}CF_2$*.

series,[1] all the contributions to the F–F couplings in various fluorine-containing compounds were examined theoretically in order to elucidate the mechanisms responsible for F–F couplings. For F–F couplings, the orbital (OB) and spin dipolar (SD) terms are very important and sometimes make decisive contributions over the Fermi contact (FC) term.[1-3] One cannot discuss the geminal F–F couplings and trans F–F couplings in fluoro olefins without considering the OB and SD terms. This is in marked contrast to the results established for H–H couplings. The SD term makes an important contribution only to geminal couplings and it is worth noticing that both the SD and OB terms become small in magnitude for long-range F–F couplings apart by more than four bonds and the FC term becomes significant.[1]

The aim of this work is the theoretical investigation of the stereochemical dependence of F–F couplings in various chemical situations: the dependence of geminal F–F couplings on the FCF angle, the dependence of vicinal F–F couplings on the dihedral angle, and the conformational dependences of the long-range F–F couplings, etc.

Dependences of geminal and vicinal H–H couplings on the stereochemical relationship between the coupled hydrogens are now well established. The theoretical predictions made chiefly by Karplus,[4,5] based on the assumption that the FC term gives the dominant contribution to the coupling constants, were verified through experimental investigations and have been widely used in the structural study of molecules by nmr. Similar use of F–F coupling has been much more restricted. Geminal and vicinal F–F coupling constants are expected to show quite different stereochemical relationships from H–H couplings, since there exist some essential differences in the mechanisms of these couplings. Therefore, it is interesting to investigate theoretically the angular dependences of these F–F couplings in order to extract possible regularities. It may help us to understand part of the experimental complexities of the F–F couplings.

Additionally, the behavior of long-range F–F coupling constants has been the subject of considerable interest for several years. As examined in paper I, to the F–F couplings separated by more than four bonds, the FC term becomes significant. Especially for the s-cis conformation of fluorobutadienes, surprisingly large five-bond couplings originate from the FC term. These long-range couplings, known experimentally as "through-space" couplings,[6,7] were named by the present authors as "fragment" couplings from the quantum-chemical considerations. In view of the continuing discussion of the importance and significance of the "fragment" coupling, it is of interest to study the conformational dependence of long-range F–F couplings theoretically. In this work, we examined the conformational dependence of four- and five-bond F–F couplings and at the same time, make fuller considerations

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(1) K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Amer. Chem. Soc.*, **94**, 4078 (1972), hereafter called paper I.

(2) H. Nakatsuji, I. Morishima, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **44**, 2010 (1971).

(3) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).

(4) For the geminal H–H coupling constants see (a) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959); (b) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **83**, 4726 (1961); (c) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 4151 (1970).

(5) For the vicinal H–H coupling constants see (a) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); (b) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960); (c) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); (d) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 4497 (1970).

(6) A "through space" coupling is defined as one that is transmitted entirely through space; see (a) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); (b) S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

(7) (a) K. L. Servis and K. N. Fang, *J. Amer. Chem. Soc.*, **90**, 6712 (1968); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **90**, 3577 (1968); (c) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970); (d) S. L. Manatt and M. T. Bowers, *J. Amer. Chem. Soc.*, **91**, 4381 (1969); (e) R. A. Fletton, R. D. Lapper, and L. F. Thomas, *Chem. Commun.*, 1049 (1969).

on the origin of the "fragment" coupling. The summary of the origins of the F–F coupling constants examined in this series will be given in the last section.

Results and Discussions

The calculations of the F–F coupling constants were carried out by using the INDO-MO's[8] and the sum-over-states perturbation method. Computational details were described in paper I. The equilibrium molecular geometries were cited from Sutton's tables.[9] In the following paragraphs, we discuss the general trends in the order of geminal, vicinal, and long-range F–F coupling constants.

(i) Angular Dependence of Geminal F–F Couplings. Figures 1 and 2 show the dependences of the calculated geminal F–F couplings on the FCF angles in CH_2F_2 and $CH_2{=}CF_2$. The dependence of geminal F–F couplings on the FCF angle is quite different from that of geminal H–H couplings.[4] That is, although the geminal H–H couplings increase monotonically with increasing HCH angle,[4c] the geminal F–F couplings change markedly with the FCF angle and have a minimum near 110°. As shown in both figures, the FC term is sensitive to the FCF angle, having a minimum near 110°, while both the SD and OB terms are insensitive to the change of the FCF angle. As discussed in paper I, for geminal F–F couplings, the transitions from the lone-pair orbital to the C–F antibonding pσ orbitals determine the SD term and the primary features of the OB term. Since these two orbitals are localized approximately in the CF_2 region, the constancy of the SD and OB terms may be understood. On the other hand, the mechanism of the FC term is much more complicated. The sensitivity of the FC term to the FCF angle would reflect the change of hybridization with that of the FCF angle.

The FCF bond angles for CH_2F_2 and $CH_2{=}CF_2$ at their equilibrium states are 108.5 and 109.3°, respectively.[9] These FCF angles correspond nearly to the ones at which geminal F–F couplings take a minimum. Therefore, the FCF angular change from these optimum angles would produce the larger geminal F–F couplings. Large variations in the magnitude of geminal F–F couplings observed in the experiment[10] are due in part to changes in the bond angle between two C–F bonds.

To conclude, geminal F–F couplings depend on the FCF angle in a quite different way from geminal H–H couplings. The origin of the angular dependence is the FC term and both the SD and OB terms are insensitive to the angular change.

(ii) Angular Dependence of Vicinal H–F Couplings. Figure 3 displays the results of the vicinal H–F couplings calculated for CH_2F–CH_2F and CH_2F–CF_3 with a variety of HCCF dihedral angles. Each curve resembles the analogous results for vicinal H–H couplings reported previously.[5] That is, vicinal H–F couplings have maximum values when the dihedral angle is near 0 and 180° and minimum values when the dihedral angle is near 90 and 270° and the values at $\theta = 180°$ are higher than those corresponding to $\theta = 0°$. Although from an analysis of the nmr spectra of compounds of fixed and known stereochemistry, Williamson, *et al.*, found[11] that the vicinal H–F coupling constant is a function of dihedral angle like the vicinal H–H coupling constant, it is also verified from the present calculations.[12]

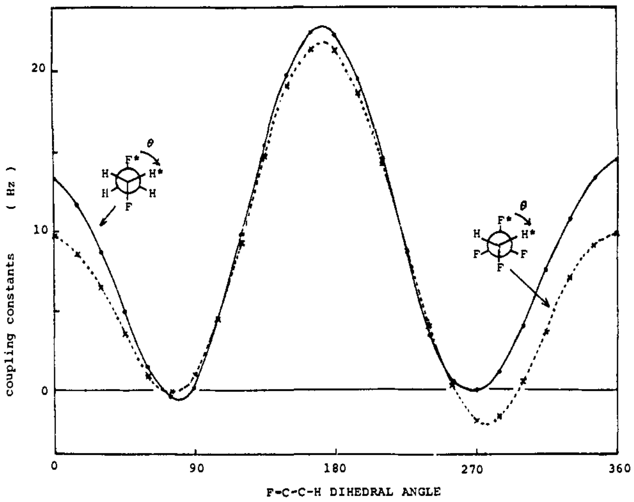

Figure 3. Plots of J_{HF}^{vic} *vs.* the FCCH dihedral angle, θ, for CH_2F^*–CH_2F^* and F_2CF^*–CH_2F^*.

(iii) Angular Dependence of Vicinal F–F Couplings. The dependence of vicinal H–H couplings upon the dihedral angle between the coupled hydrogens attached to carbons connected by single bonds has been considered, especially for substituted ethanes. The angular dependence of vicinal H–H couplings in ethane has been treated by Karplus[5] with the valence-bond method and the result has been used as a guideline in interpreting the experimental data for substituted ethanes. On the other hand, little has been known about the dependence of vicinal F–F couplings both experimentally[13] and theoretically. However, from the experimental studies on cyclobutane derivatives, the dihedral angle dependence of vicinal F–F couplings has been suggested[14] to be different from that of H–H couplings.

The calculated angular dependences of vicinal F–F couplings on the FCCF dihedral angle are given in Figures 4–7. The former two figures demonstrate the angular dependences for vicinal fluorine pairs in perfluoroethanes and the latter two figures show the same information in perfluoroacetaldehyde and propene.

From Figure 4 calculated for CH_2F–CH_2F, it is obvious that the dihedral angle dependence of the vicinal F–F coupling is far different from the corresponding

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[8] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).

[9] "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

[10] H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

[11] K. L. Williamson, Y. F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, **90**, 6717 (1968).

[12] In preparing this manuscript, similar conclusions were reported by Govil by using the extended Hückel theory; G. Govil, *Mol. Phys.*, 21, 953 (1971).

[13] Gutowsky, *et al.*, determined $J_{FF}^{gauche} = 21$ Hz and $J_{FF}^{trans} = 40$ Hz, following the temperature dependence of the average coupling constant in CF_2Cl–$CFCl_2$; H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3553 (1962). The opposite situation was found in CF_2Br–CF_2Br, where the trans coupling (1.5 Hz) is smaller than the gauche coupling (12 Hz); R. K. Harris and N. Sheppard, *Trans. Faraday Soc.*, **59**, 606 (1963). Manatt and Elleman determined from frozen rotational isomers of CF_2Br–$CFBr_2$ as $J_{FF}^{gauche} = 18.6$ Hz and $J_{FF}^{trans} = 16.2$ Hz; S. L. Manatt and D. D. Elleman, *J. Amer. Chem. Soc.*, **84**, 1305 (1962). Thus, no clear tendency as a function of dihedral angle was observed.

[14] R. R. Ernst, *Mol. Phys.*, **16**, 241 (1969).

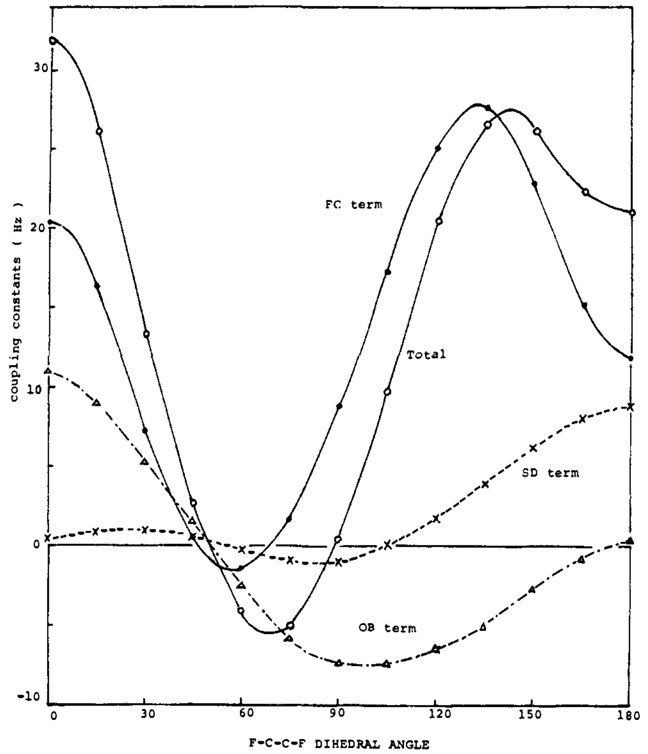

Figure 4. Plots of J_{FF}^{vic} *vs.* the FCCF dihedral angle, θ, for $CH_2F^*-CH_2F^*$.

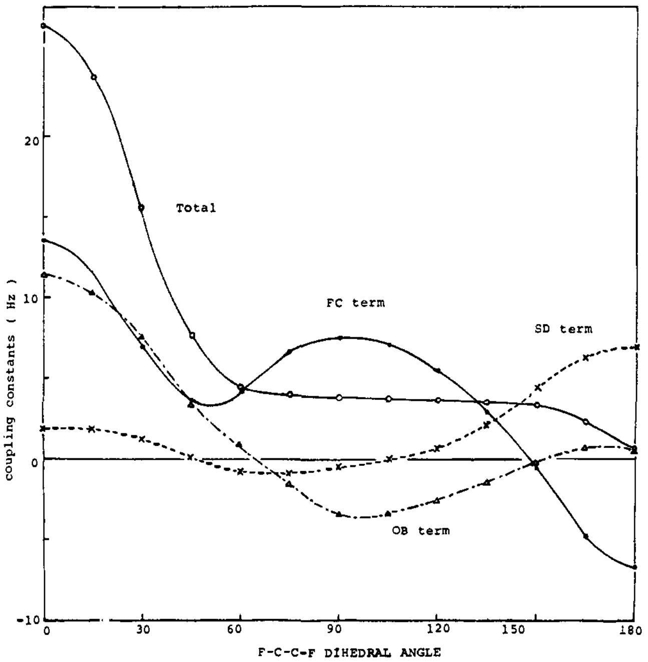

Figure 5. Plots of J_{FF}^{vic} *vs.* the FCCF dihedral angle, θ, for $F_2CF^*-CH_2F^*$.

one of H-H couplings. The FC contribution takes positive sign in most angular regions and has minima for the staggered form (θ = 60 and 180°) and maxima for the eclipsed form (θ = 0 and 120°). The SD contribution is nearly zero for small angles (θ = 0–90°) and becomes an appreciably large positive value near 180° (s-trans conformation). The OB contribution has maxima near 0 and 180° but becomes an appreciably large negative value for intermediate dihedral angles,

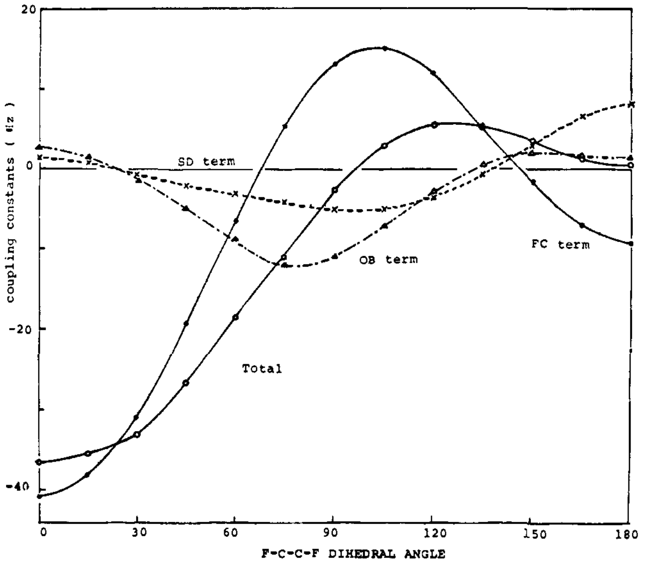

Figure 6. Plots of J_{FF}^{vic} *vs.* the FCCF dihedral angle, θ, for $F_2CF^*-COF^*$.

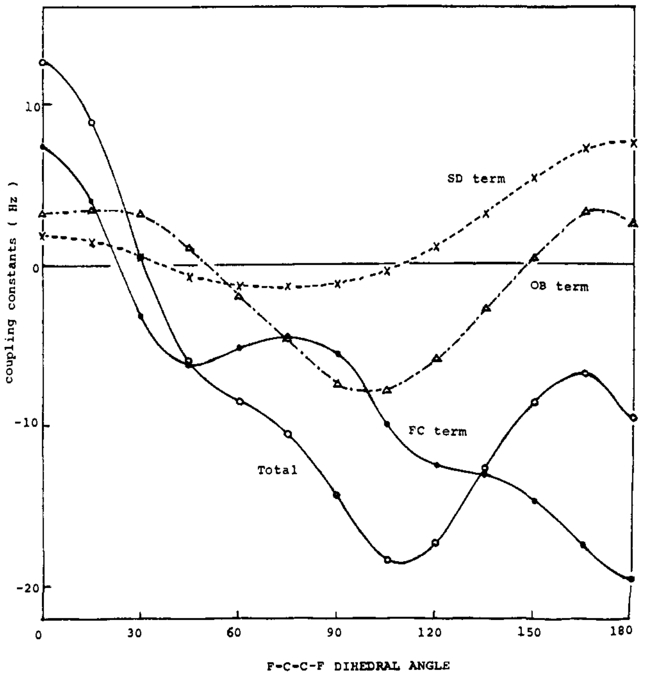

Figure 7. Plots of J_{FF}^{vic} *vs.* the FCCF dihedral angle, θ, for $F_2CF^*-F^*C{=}CF_2$.

having a minimum at 90°. In consequence, the total vicinal coupling constant is mainly affected by the FC term, changing its sign twice[15] between 0 and 180°. The complicated curve of the FC term is considered to be due to the change of the extent of sp hybridization in fluorine atoms through rotation.

In Figure 5 the dihedral angle dependence of CH_2F-CF_3 is given. Comparing two figures we found that the dependences of the SD and OB terms on the dihedral angle are almost similar. These features are

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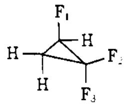
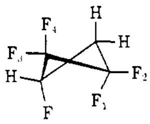
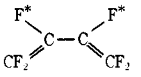
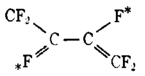
(15) The sign of the vicinal F–F couplings is not always negative, as discussed in paper I. Experimentally Harris, *et al.*, found the cis and trans vicinal F–F couplings to be opposite in sign for fluorinated cyclobutanes and cyclobutenes; R. K. Harris and V. J. Robinson, *J. Magn. Resonance*, 1, 362 (1969); R. A. Newmark, G. R. Apai, and R. O. Michael, *ibid.*, 1, 418 (1969).

expected to hold for all of the compounds containing a fragment –CF–CF–. For example, in Table I the SD and OB contributions in J_{cis} ($\theta = 0°$) coupling in perfluorocyclopropane are respectively near zero (0.1 Hz) and a relatively large positive value (8.3 Hz). Also in J_{trans} ($\theta = 140°$) the calculated couplings agree with those expected from the above dependence. For hexafluorobutadiene both the SD and OB terms in vicinal F–F couplings between the fluorines at the 2 and 3 positions agree with those expected from the dihedral angle dependences. As discussed in paper I, the trans F–F couplings for fluoro olefins have a large negative OB term through π-electron contributions. However, the calculated OB term of this coupling for the s-trans hexafluorobutadiene is only 0.8 Hz. This implies that the calculated F–F coupling at the 2 and 3 positions of the compound is considered as one across the C–C *single* bond rather than the partial double bond. Thus, both the SD and OB terms of vicinal F–F couplings show a dihedral dependence common to the –CF–CF– fragment; the SD term has a relatively large positive value in the s-trans conformation although little contribution in the s-cis one, while the OB term has a relatively large positive value in the s-cis conformation and little in the s-trans form. On the other hand, the FC term decreases in magnitude involving the sign in going from CH_2F–CH_2F to CH_2F–CF_3, although the angles of maxima and minima are almost invariant. This change may be attributed to the increase in electronegativity of the substituent group.[16]

Table I. Calculated Vicinal F–F Coupling Constants (Hz)

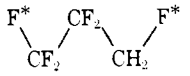
Compound	J	FC	SD	OB	Total
	J_{12}^{cis}	−55.5	0.1	8.3	−47.1
	J_{13}^{trans}	−6.5	3.0	−9.3	−12.8
	J_{14}^{diax}	−3.9	3.1	−4.9	−5.7
	J_{23}^{dieq}	−3.9	1.9	−4.3	−6.4
	$J_{13}^{\mathrm{ax\text{-}eq}}$	−10.5	0.8	4.6	−5.0
	$J_{24}^{\mathrm{ax\text{-}eq}}$	−11.1	0.9	7.1	−3.0
	$J^{\mathrm{s\text{-}cis}}$	−5.0	0.9	4.5	0.4
	$J^{\mathrm{s\text{-}trans}}$	12.6	8.3	0.8	21.7

In Figures 6 and 7, the calculated dihedral angular dependences of vicinal F–F couplings for CF_3—COF and CF_2=CF—CF_3 are given. Although the curves for the SD and OB terms are similar as above, that of the FC term is far different from those for CH_2F–CH_2F and CH_2F–CF_3 (Figures 4 and 5). In particular, the FC term for CF_3–COF[17] has a minimum at 0° and only *one* maximum at near 105°. This nonreguarlity means that not only the magnitude but also the angular dependence of the FC term in the vicinal F–F couplings are the function of substituents. Therefore, it is difficult to predict the vicinal F–F coupling constants for structurally rigid molecules only by the dihedral angle since the total coupling is mainly affected by the FC contribution.

The values obtained for vicinal F–F coupling constants in different dompounds have been the subject of considerable interest for several years. Reported values for vicinal F–F couplings in perfluoroethyl groups are usually less than 1 Hz (the near-zero coupling)[6a] whereas the corresponding couplings in more heavily substituted fluoroalkanes can be considerably large.[18] In terms of the angular dependence of vicinal F–F coupling constants, it is a little difficult to rationalize this confusing situation. We believe that this anomaly may be a consequence of the averaging effects due to the internal rotation about the C–C single bond and in part, attributed to the cancellation of the three (FC, SD, and OB) terms of nonuniform signs, as mentioned in paper I. Note in Figure 4, the trends in the angular dependence of the vicinal coupling accord approximately with that of the rotational potential curve of the compound. That is, the vicinal coupling takes a minima for the staggered form. This seems to be a reason for the near-zero coupling.

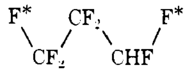
(iv) Stereochemical Dependences of Four-Bond F–F Couplings. In paper I, it has been found that the calculated F–F couplings over four and five bonds differ markedly in different chemical situations and the FC contribution is significant. In this paragraph, we examine the mechanisms of these long-range F–F couplings in more detail, paying attention to the stereochemical relationships.

Table II summarizes the calculated results of angular dependences of four-bond F–F couplings in hexafluoropropene on the terminal rotation angle θ of the CF_3 group. First, let us examine trans ($\theta = 0°$) F–CF_3 couplings which correspond to the zigzag ("W") couplings. Near zigzag conformation ($\theta < 30°$) there exists a fairly large positive FC contribution, while both the SD and OB terms are negligibly small although the OB contribution becomes appreciable for small angles. Moreover note that a slight distortion from the planar configuration makes the coupling constants decrease suddenly and it becomes nearly zero in magnitude for $\theta = 75°$. Similar behavior has also been demonstrated in allylic proton couplings.[19] In case of F–F couplings the tendency becomes extreme. This kind of large four-bond F–F couplings was also found in paper I for the following fluoroalkanes. Note that for these fluoroalkanes, the OB term is small in magnitude since π-electron contributions do not exist.



$\mathrm{F^*CF_2CF_2CH_2F^*}$

$^4J_{FF} = 30.5$ Hz
FC = 29.8, SD = 2.7, OB = − 2.0



$\mathrm{F^*CF_2CF_2CHF^*}$

$^4J_{FF} = 23.5$ Hz
FC = 23.0, SD = 1.8, OB = − 1.3

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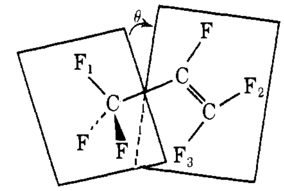
(16) R. J. Abraham and L. Cavalli, *Mol. Phys.*, **9**, 67 (1965).

(17) The calculated angular dependence of the vicinal F–F couplings in CF_3–COF on the dihedral angle (Figure 6) is most similar to that proposed by Ernst, see ref 14.

(18) R. R. Dean and J. Lee, *Trans. Faraday Soc.*, **64**, 1409 (1968).

(19) (a) D. J. Collins, J. J. Hobbs, and S. Sternhell, *Tetrahedron Lett.*, 197 (1963); (b) T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *J. Amer. Chem. Soc.*, **85**, 1699 (1963).

Table II. Calculated Trans and Cis F–CF$_3$ Couplings (Hz) in CF$_2$=CFCF$_3$

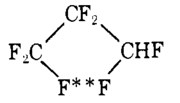


$J_{\text{trans F-CF}_3} = J_{F_1F_2}, J_{\text{cis F-CF}_3} = J_{F_1F_3}$

Dihedral angle, θ	Trans F–CF$_3$ coupling FC	SD	OB	Total	Cis F–CF$_3$ coupling FC	SD	OB	Total
0	69.7	2.3	6.8	78.8	−35.2	−1.0	−2.6	−38.8
15	72.3	1.7	6.6	80.6	−33.2	−1.1	−2.0	−36.3
30	70.8	0.2	5.7	76.7	−30.7	−0.9	−1.5	−33.1
45	51.8	−1.2	2.9	53.5	−29.7	−0.5	−1.4	−31.6
60	19.8	−1.2	−1.7	16.9	−25.2	0.4	−2.0	−26.8
75	0.7	−0.3	−2.0	−1.6	−17.3	0.9	−3.9	−20.3
90	−4.8	0.2	−1.4	−6.0	−11.6	0.4	−3.1	−8.9
105	−1.1	0.3	−0.8	−1.6	−9.3	0.6	−2.1	−10.8
120	6.8	−0.3	−2.1	4.4	−10.1	0.1	−1.2	−11.2
135	7.7	−0.6	−3.4	3.7	−13.7	−0.4	−0.9	−15.0
150	−1.7	−0.3	−2.7	−4.7	−19.0	−0.5	−0.6	−20.1
165	−8.2	0.0	−1.9	−10.1	−24.3	−0.3	−0.4	−25.0
180	−7.2	0.0	−1.3	−8.7	−27.4	−0.4	−0.8	−28.6
Exptl[a]	8.7				22.0			

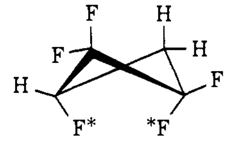
[a] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **34**, 2122 (1961).

To the cis F–CF$_3$ coupling, the FC term also makes a predominant contribution. Note that the sign is negative in this case. It takes a minima at $\theta = 0$ and 180° and a maximum at $\theta = 90°$. A similar large negative FC contribution to four-bond F–F couplings was also found for the following compounds in paper I.



$^4J_{FF} = -75.8$ Hz

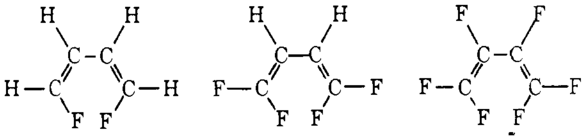
FC = −74.9, SD = −0.7, OB = −0.3



$^4J_{FF} = -21.2$ Hz

FC = −21.6, SD = −0.7, OB = 1.0

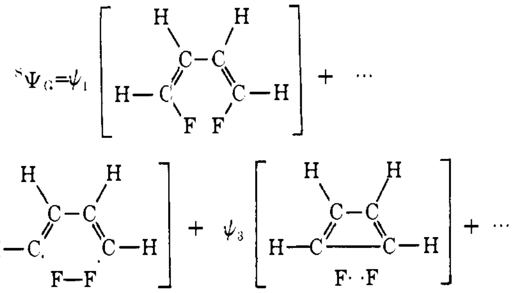
(v) Conformational Relationship of the "Fragment" Coupling. In paper I, it has been found that surprisingly large positive five-bond F–F coupling originates from the FC term for s-cis fluorobutadienes. These



$^5J_{FF} = 166.1$ Hz $^5J_{FF} = 217.0$ Hz $^5J_{FF} = 172.8$ Hz

long-range couplings are known experimentally as "through space" couplings. However, there appears to be some confusion in the use of this terminology "through space" because it is not clearly defined in any theoretical point of view. Barfield and Karplus[20] have provided a theoretical interpretation for the various coupling mechanisms through valence-bond bond-order formulation for the FC term. Terms in the coupling constant expression which are of first order in bond orders are called "direct" contributions, whereas terms which are of second or higher order are called "indirect" contributions. This classification is a useful description of the coupling mechanism. In paper I, the above F–F couplings are named by the present authors as "fragment" couplings from the quantum-chemical considerations. The fragment coupling is considered as a special case of a "direct" coupling mechanism of Barfield and Karplus and is named for the long-range coupling with extremely large magnitude between nuclei which are in close proximity. The reason for introducing this terminology will become clear later on. Experimentally the fragment couplings are found for (F,F),[6,7] (F,P),[21] (F,H),[22] and (F,Hg)[23] pairs, while not found for the (H,H) pair. As was briefly discussed in paper I, the fragment F–F coupling originates from the FC term through the transition from F–F antibonding pσ orbitals to corresponding bonding orbitals. In the following we will examine the origin of the fragment coupling in more detail with the similar treatment of Barfield and Karplus.

Scheme I



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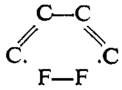
[20] M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).

[21] G. R. Miller, A. W. Yankowsky, and S. O. Grim, *J. Chem. Phys.*, **51**, 3185 (1969).

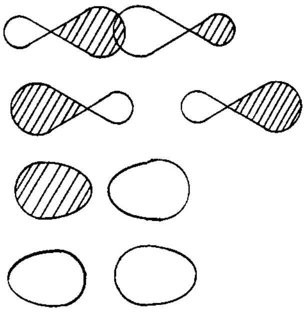
[22] (a) P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Amer. Chem. Soc.*, **88**, 2459 (1966); (b) G. W. Gribble and J. R. Douglas, Jr., *ibid.*, **92**, 5764 (1970); (c) K. L. Servis and F. R. Jerome, *ibid.*, **93**, 1535 (1971); (d) E. Abushanab, *ibid.*, **93**, 6532 (1971).

[23] W. McFarlane, *Chem. Commun.*, 609 (1971).

In the valence-bond treatment, the wave function for the s-cis fluorobutadiene is given by a linear combination of the canonical structures illustrated as shown in Scheme I, where ${}^{S}\Psi_G$ is the ground-state canonical structure and ${}^{T}\Psi_E$ the triplet excited state one. Then, this large FC term is expected to arise chiefly from the Fermi-induced interaction between ${}^{S}\Psi_G$ and ${}^{T}\Psi_E$. Therefore, it must be necessary for the fluorine pair to approach each other within the region where



may become stable (in the perturbation theory, the energy difference between ${}^{S}\Psi_G$ and ${}^{T}\Psi_E$ becomes small). To understand the situation more easily let us now examine the molecular orbitals for the fluorine molecule F_2, where the four σ-molecular orbitals are constructed from $2s_F$ and $2p_{\sigma F}$ AO's (π-type orbitals do not contribute to the FC term). Since the $2s_F$ energy is far below the $2p_F$ energy, the molecular orbitals and their levels are approximately as shown below where s, s′,



$\psi_4 = 1/\sqrt{2}[(p - p') + \mu(s - s')]$

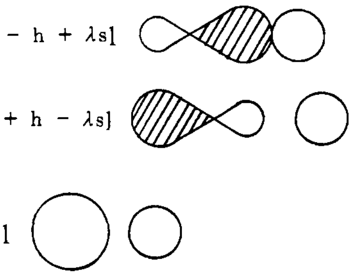
$\psi_3 = 1/\sqrt{2}[(p + p') - \lambda(s + s')]$

$\psi_2 = 1/\sqrt{2}[(s - s') - \mu(p - p')]$

$\psi_1 = 1/\sqrt{2}[(s + s') + \lambda(p + p')]$

p, and p′ designate $2s_F$ and $2p_{\sigma F}$ atomic orbitals on the two atoms and λ, μ are small quantities. Open contours mean positive lobes and shaded contours negative ones. ψ_1 and ψ_2 are bonding and antibonding MO's formed mainly from two $2s_F$ orbitals of fluorine, while ψ_3 and ψ_4 are bonding and antibonding formed mainly by two $2p_\sigma$ orbitals, respectively. Note that ψ_3 has antibonding character by the mixing of $2s_F$ orbitals and is originally in a high energy level. The FC term is determined by the three excitations $\psi_1 \rightarrow \psi_4$, $\psi_2 \rightarrow \psi_4$, and $\psi_3 \rightarrow \psi_4$. The lowest excitation $\psi_3 \rightarrow \psi_4$ gives a positive contribution to the coupling constant. However, at the equilibrium bond length (*ca.* 1.42 Å in F_2), this is not necessarily dominant for it is proportional to $\lambda^2\mu^2$, while the contributions of $\psi_1 \rightarrow \psi_4$ and $\psi_2 \rightarrow \psi_4$ are proportional to μ^2. That is, the combined effect of the transitions $\psi_1 \rightarrow \psi_4$ and $\psi_2 \rightarrow \psi_4$ dominates the contribution from $\psi_3 \rightarrow \psi_4$ and gives a negative coupling constant. However, with the increase in the F–F bond length, the transitions from $\psi_1 \rightarrow \psi_4$ and $\psi_2 \rightarrow \psi_4$ begin to cancel each other since the split between ψ_1 and ψ_2 becomes small. On the other hand, with the increase of the F–F length, the split between ψ_3 and ψ_4 becomes small and then the contribution from the lowest excitation $\psi_3 \rightarrow \psi_4$ increases rapidly, dominating the combined effect of $\psi_1 \rightarrow \psi_4$ and $\psi_2 \rightarrow \psi_4$. This is the origin of the "fragment" coupling and therefore the sign is positive. The transitions $\psi_1 \rightarrow \psi_4$, $\psi_2 \rightarrow \psi_4$, and $\psi_8 \rightarrow \psi_4$ in the F_2 molecule correspond to $\psi_1 \rightarrow \psi_3$, $\psi_2 \rightarrow \psi_3$, and $\psi_4 \rightarrow \psi_3$, respectively, if considered in a nonbonded F···F pair in the s-cis fluorobutadiene and the above argument holds good if ψ_4 is exchanged for ψ_3. In fact, from the careful examination of the transitions which contribute to the fragment coupling, it has been found that the excitation from the antibonding $p\sigma$ orbitals of a nonbonded F···F pair to the corresponding bonding ones determines the coupling constant. The fragment F–P coupling is expected to occur in the same mechanism.

A rather similar argument can be developed for the H–F pair. The energy diagram and approximate molecular orbitals for the H–F molecule are shown below,

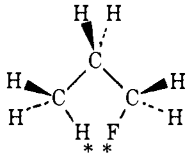


$\psi_3 = 1/\sqrt{2}[p - h + \lambda s]$

$\psi_2 = 1/\sqrt{2}[p + h - \lambda s]$

$\psi_1 = [s + \lambda h]$

where suffixes s, p, and h are used for $2s_F$, $2p_F$, and $1s_H$ orbitals, respectively. The FC term has contributions from the two excitations $\psi_1 \rightarrow \psi_3$ and $\psi_2 \rightarrow \psi_3$. Note that the $2s_F$ energy is sufficiently far down and that the bonding orbital ψ_2, formed mainly by $2p_{\sigma F}$ and $1s_H$ orbitals, has antibonding character from the mixing of the $2s_F$ orbital. If the internuclear distance increases, the contribution from $\psi_2 \rightarrow \psi_3$ becomes predominant because this excitation energy becomes small. That is, the transition $\psi_2 \rightarrow \psi_3$ is the origin of the fragment H–F coupling. Of course, in the actual case of the nonbonded H···F pair, this transition becomes $\psi_3 \rightarrow \psi_2$. Since the excitation $\psi_2 \rightarrow \psi_3$ in the H–F molecule produces a negative FC term, the present theory predicts a negative sign for fragment H–F couplings. We calculated the four-bond H–F coupling in C_3H_7F by deforming the C–C–C angle in order to shorten the H···F separation and the results were as shown below. The



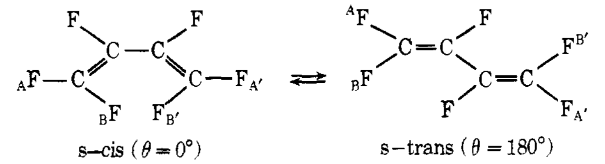
$r_{H-F} = 1.95$ Å, ${}^4J_{HF} = -8.5$ Hz
$r_{H-F} = 1.57$ Å, ${}^4J_{HF} = -47.2$ Hz

increase in the smaller internuclear distances from $J_{HF} = -8.5$ Hz at 1.95 Å to $J_{HF} = -47.2$ Hz at 1.57 Å is striking and the sign is negative as predicted above. By the examination of the transitions which produce this fragment coupling, the transitions from the H···F antibonding $p\sigma$ orbitals to corresponding bonding ones have been proved dominant. The Hg–F coupling is expected to occur in the same manner.

Thus, the fragment coupling originates through the transitions from the X···Y antibonding $p\sigma$ orbitals to the corresponding bonding ones. Therefore, it must be necessary for the fragment X–Y pair to form the $p\sigma$ orbitals with the antibonding character as well as the spatially proximity. Since in H···H there is no $p\sigma$ orbital, no fragment coupling should be observed.

Figure 8 shows the dependency of the fragment coupling on the internuclear distances between two

Table III. Calculated Five-Bond F–F Couplings (Hz) in Hexafluorobutadiene[a] with a Dihedral Angle, θ



θ	$J_{AA'}$ FC	$J_{AA'}$ SD	$J_{AA'}$ OB	$J_{AA'}$ Total	$J_{BB'}$ FC	$J_{BB'}$ SD	$J_{BB'}$ OB	$J_{BB'}$ Total
0	0.5	1.6	−0.8	1.3	176.9	0.9	−5.0	172.8
15	3.7	1.5	0.9	6.1	106.4	−0.1	−1.8	104.6
30	4.3	0.9	0.5	5.7	40.6	−0.1	1.0	41.5
60	5.2	−0.2	0.2	5.2	17.8	−0.6	3.4	20.6
90	6.5	−0.4	−0.9	5.2	12.8	−0.1	2.7	15.4
120	10.2	−0.3	2.9	12.8	8.9	0.8	2.0	11.7
150	9.5	3.0	7.2	19.7	−1.1	1.6	2.6	3.1
165	8.2	4.6	8.4	21.2	−0.5	2.2	2.4	4.1
180	3.4	4.2	5.6	13.3	−1.2	1.9	−1.1	−0.4
Exptl[b]		+4.80				+11.31		

[a] The geometry is C–F = 1.32 Å, ∠FCF = 114°, and the carbon skeleton is used for butadiene. [b] See ref 35.

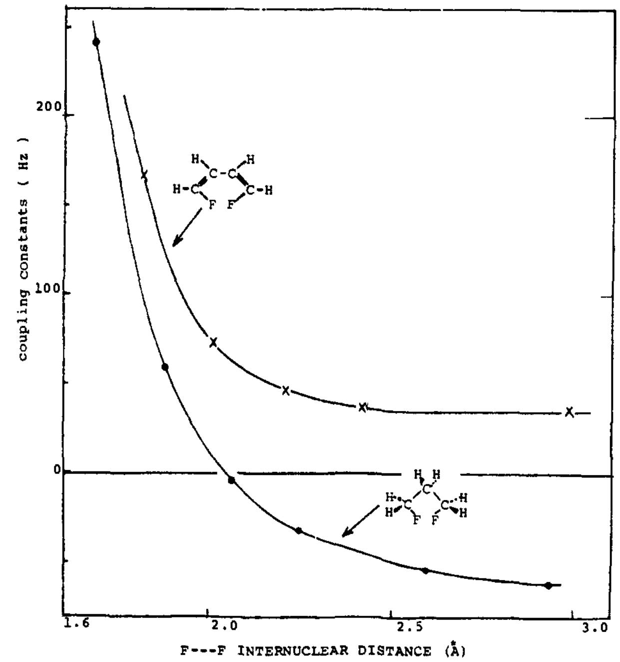


Figure 8. Plots of $^4J_{FF}$ and $^5J_{FF}$ *vs.* the F· · · F internuclear distance.

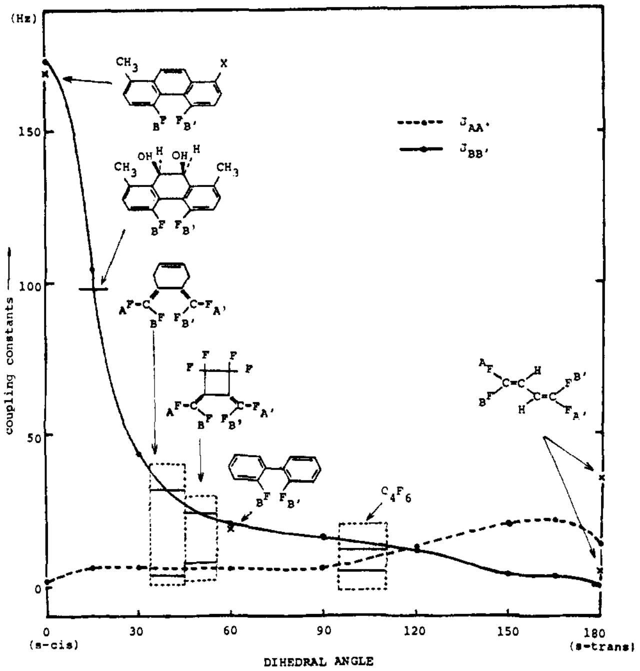
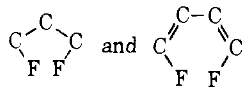


Figure 9. Plots of $^5J_{FF}$ *vs.* the dihedral angle, θ, for hexafluorobutadiene.

fluorines in

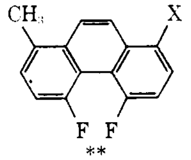


where only the bond angles of the carbon skeletons are deformed symmetrically on the molecular plane. As expected from the above discussion, the "fragment" couplings are extremely sensitive to the internuclear separation of the coupled fluorines, especially in the short F· · ·F length region. This trend is common for both four- and five-bond F–F couplings although the latter surpasses the former in magnitude at the same internuclear distance. Similar sensitivity to the internuclear separation has been found[22a] also in five-bond H–F couplings. Both four- and five-bond couplings are positive in sign at small internuclear distances. Experimentally Chambers, *et al.*, have found[24] the sign of these fragment couplings to be positive. The present calculations confirm the positive sign for this type of long-range F–F couplings. Note that the four-bond coupling changes the sign and becomes negative in the region where the internuclear distances become larger than 2.0 Å, while the five-bond coupling remains positive in sign. In paper I, the internuclear F–F distances for four-bond couplings were around 2.5 Å, so the calculated four-bond couplings had negative signs in general as mentioned previously. However, even for four-bond F–F couplings, the positive large values are expected if the interacting fluorines approach each other within 2.0 Å.

In Table III and Figure 9, the calculated five-bond F–F coupling constants of hexafluoro-1,3-butadiene

[24] R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, **66**, 1025 (1970).

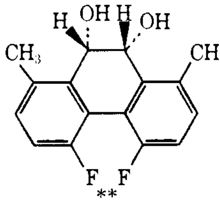
with various dihedral angles, θ, between trifluorovinyl groups are summarized. The calculated results of $J_{AB'}$ are omitted since they are insensitive to θ. Calculated $J_{BB'}$ has an extraordinarily large value in the s-cis conformation ($\theta = 0°$), in which $J_{BB'}$ corresponds to the "fragment" coupling. As shown in the figure, $J_{BB'}$ drops rapidly in magnitude with a slight distortion (θ = 0–30°) from the s-cis planar conformation and afterwards decreases monotonically with the increase of θ. Qualitatively similar angular dependence has been proposed experimentally by Gutowsky, *et al.*,[25] in the four-bond F–F coupling between a CF_3 group in the 1 position on an aromatic ring and a fluorine in the 2 position. Servis[7a] has reported the five-bond F–F couplings in 1-substituted 4,5-difluoro-8-methylphenanthrenes (assumed to be planar, $\theta = 0°$) as



$^5J_{FF}$ = 167–170 Hz

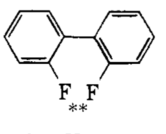
X = $-CH_2Br$, $-CH_2OH$, $-CO_2Et$, $-NH_2$

The calculated $J_{BB'}$ in the s-cis conformation is 172.8 Hz, which agrees quite well with the above experimental values, while the five-bond F–F coupling of *cis*-1,8-dimethyl-4,5-difluoro-9,10-dihydro-9,10-phenanthrenediol was also determined[22a] experimentally to be 98 Hz.



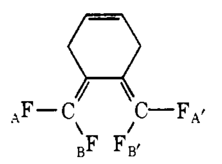
$^5J_{FF}$ = 98 Hz

Referring to Figure 9, this dramatic decrease from 170 to 98 Hz is considered to reflect the conformational difference between these compounds. From chemical argument, a nonplanar structure was suggested for the 1,3-cyclobutadiene ring in 9,10-dihydrophenanthrene.[26] The calculated $J_{BB'}$ agrees with the experimental value (98 Hz) if the dihedral angle between two phenyl groups is 16°, which agrees quite well with the dihedral angle in 1,3-cyclohexadiene, 17.5°, estimated from the microwave data.[27] Cooper, *et al.*, reported the five-bond F–F coupling in 2,2′-difluorobiphenyl as shown.[28]

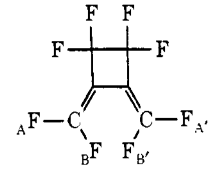


$^5J_{FF}$ = 18.2 Hz (16.5 Hz)[29]

It is known from the electron diffraction study that the phenyl rings of difluorobiphenyl are not planar and the angle between the two phenyl rings is estimated at about 60°.[30] The calculated $J_{BB'}$ at $\theta = 60°$ is 20.6 Hz, which also agrees fairly well with the experimental one. Other experimental support of the angular dependence of $J_{BB'}$ is the following. The analyses of the fluorine nmr spectra of bis-4,5-(difluoromethylene)cyclohexene and perfluoro-1,2-dimethylenecyclobutane were reported[31] as shown below. From Figure 9, we can assign these five-bond F–F couplings as $J_{BB'} = +31.4$ Hz, $J_{AA'} = +3.3$ Hz for the former and $J_{BB'} = +23.3$ Hz, $J_{AA'} = +7.6$ Hz for the latter. The twisting angles are estimated to be 40 and 50°, respectively. These angles are reasonable since in these twisting angles these molecules become strain free.

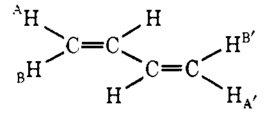


$J_{AA'}$ = +3.3 or +31.4 Hz
$J_{BB'}$ = +31.4 or +3.3 Hz



$J_{AA'}$ = +7.6 or +23.3 Hz
$J_{BB'}$ = +23.3 or +7.6 Hz

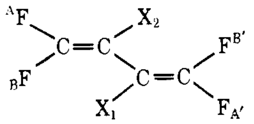
On the other hand, $J_{AA'}$, the zigzag (trans–trans) coupling in the s-trans planar form ($\theta = 180°$), has a relatively large value (13.3 Hz) for five-bond F–F couplings, much exceeding $J_{BB'}$ (−0.4 Hz). Similar tendency has been known in the five-bond H–H couplings in 1,3-butadiene.[32] That is, $J_{AA'}$ is much larger than $J_{BB'}$ as shown below. In the case of H–H couplings,



$J_{AA'}$ = +1.30 Hz
$J_{BB'}$ = +0.60 Hz

this tendency originates from the FC term. However, in F–F couplings, as listed in Table III, the large value of $J_{AA'}$ in the s-trans conformer (θ = 150–180°) originates from the fact that the three (FC, SD, and OB) terms are cooperative and the signs are all positive. The same tendency was also reproduced in the s-trans planar fluorobutadienes, as summarized in Table IV.

Table IV. Calculated Five-Bond F–F Couplings (Hz) in s-Trans Planar Fluorobutadienes



		$J_{AA'}$				$J_{BB'}$			
X_1	X_2	FC	SD	OB	Total	FC	SD	OB	Total
H	H	7.5	4.6	7.2	18.9	10.1	2.0	−0.4	11.7
H	F	14.2	3.9	6.1	24.2	2.7	1.0	−2.8	0.9
F	F	3.4	4.2	5.6	13.3	−1.2	1.9	−1.1	−0.4

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(25) J. Jonas, L. Borowski, and H. S. Gutowsky, *J. Chem. Phys.*, **47**, 2441 (1967).

(26) A. H. Beckett and B. A. Mulley, *Chem. Ind.* (*London*), 146 (1955).

(27) S. S. Butcher, *J. Chem. Phys.*, **42**, 1830 (1965).

(28) M. A. Cooper, H. E. Weber, and S. L. Manatt, *J. Amer. Chem. Soc.*, **93**, 2369 (1971).

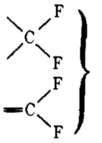
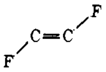
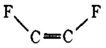
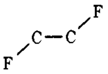
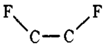
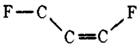
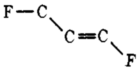
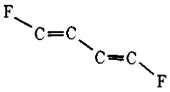
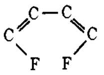
(29) A value of 16.5 Hz was given by Servis for this molecule from an approximate analysis of the ^{13}C satellites, see ref 7a.

(30) O. Bastiansen and L. Smedvik, *Acta Chem. Scand.*, **8**, 1593 (1954).

(31) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1339 (1965).

(32) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

Table V. Summary of the Origins of F–F Couplings[a]

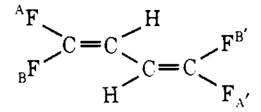
Compd	J	FC	SD	OB	Sign of total coupling	Principal term of angular dependence
	$^2J_{gem}$	×	×	×	+	FC
	$^3J_{trans}$	○	−	×	−	
	$^3J_{cis}$	○	−	○	±	
	$^3J_{s\text{-}trans}$	○	○	−	±	FC
	$^3J_{s\text{-}cis}$	○	−	○	±	FC
	$^4J_{F-CF_3}{}^{cis}$	×	−	−	−	FC
	$^4J_{F-CF_3}{}^{trans}$	×	−	−	+	FC
	$^5J_{zigzag}$	○	○	○	+	FC, SD, OB
	$^5J_{fragment}$	×	−	−	+	FC

[a] ×, very important origin; ○, important origin; −, negligibly small origin.

In all cases, $J_{AA'}$ exceeds $J_{BB'}$ in magnitude. Generally speaking, when one is dealing with systems with intervening π electrons, the contributions through π electrons cannot be discarded. This is also different from the four-bond zigzag F–F couplings, to which the FC term makes a predominant contribution.

(vi) Conformation of Hexafluorobutadiene. In this paragraph, we will discuss the conformation of hexafluorobutadiene, based on the calculated results of five-bond F–F coupling constants. Recently from the study of photoelectron and optical spectroscopy, it has been suggested[33] that hexafluorobutadiene is nonplanar and the dihedral angle is 42° from the s-cis planar conformation. In the previous paragraph, it was shown that the calculated angular dependence of $J_{BB'}$ given in Figure 9 reproduces fairly well the experimental data for compounds of fixed and known stereochemistry.

First let us examine $J_{AA'}$ and $J_{BB'}$ of tetrafluorobutadiene which has been shown[34] to exist in a trans-planar conformation. The experimental five-bond F–F couplings for this compound were reported as shown,[31] but the final assignments were not made. The calculated results of tetrafluorobutadiene in the stable s-trans planar form were $J_{AA'} = 18.9$ Hz and $J_{BB'} = 11.7$ Hz. Although the calculated couplings are not in good agrement with the experimental ones, we assign the experiment as $J_{AA'} = +35.7$ Hz and $J_{BB'} = +4.8$ Hz since $J_{AA'}$ is the trans–trans coupling, which is expected to have relatively large positive value exceeding $J_{BB'}$ as discussed in the previous paragraph. The same assignment has been proposed by Manatt and Bowers,[35] based on the experimental study of hexafluorobutadiene. The present calculations support their assignment. Keeping this in mind, let us now examine the five-bond F–F couplings in hexafluorobutadiene. The experimental couplings were determined[35] as $J_{AA'} = +4.80$ Hz and $J_{BB'} = +11.31$ Hz. Note first that the relative magnitudes of experimental $J_{AA'}$ and $J_{BB'}$ are opposite to the results established for tetrafluorobutadiene. This means that there exist significant differences between two fluorodienes. The calculations of five-bond couplings in fluorobutadienes reproduced the same relationship in the relative magnitudes of $J_{AA'}$ and $J_{BB'}$ in the s-trans planar conformation (Table IV). This implies that a substituent effect cannot explain the differences. However, the differences may be attributed to the importance of a nonplanar skewed geometry of hexafluorobutadiene. Note in Figure 9 that $J_{AA'}$ and $J_{BB'}$ reverse their relative magnitude near $\theta = 120°$. Therefore, the present calculations indicate that the experimental values of hexafluorobutadiene, averaged



$J_{AA'} = +35.7$ or $+4.8$ Hz
$J_{BB'} = +4.8$ or $+35.7$ Hz

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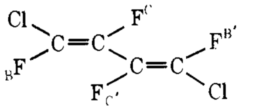
(33) C. R. Brundle and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 5550 (1970).

(34) (a) R. M. Conrad and D. A. Dows, *Spectrochim. Acta*, **21**, 1039 (1964); (b) R. A. Beaudet, *J. Amer. Chem. Soc.*, **87**, 1390 (1965).

(35) S. L. Manatt and M. T. Bowers, *ibid.*, **91**, 4381 (1969).

in the energetically favored conformations, correspond to those at the dihedral angle near $\theta = 100°$. This dihedral angle is far different from that estimated by the spectroscopy data (42° from the s-cis planar form). However, if hexafluorobutadiene exists in cisoid with the angle being 42°, a much larger $J_{BB'}$ (*ca.* 30 Hz) is expected from Figure 9. Although it may be difficult to estimate the dihedral angle precisely in the present approximations. At least nonplanarity of hexafluorobutadiene is supported from the above discussions.

Likewise, the experimental five-bond couplings for 1,4-dichlorotetrafluoro-1,3-butadiene are reported as follows[36]



$J_{CC'} = +22.7$ or $+34.4$ Hz
$J_{BB'} = +34.4$ or $+22.7$ Hz

Although it is difficult to give final assignment, this compound is also expected to be nonplanar whether $J_{BB'}$ is +22.7 Hz or +34.4 Hz and the twisting angle from the s-trans conformation may be larger than that of hexafluorobutadiene.

Concluding Remarks

In this paper, we have been concerned mainly with the stereochemical relationship of the F–F coupling constants. The F–F coupling constants are sensitive to the geometrical relationships of the two coupled fluorine nuclei although their trends are far different from and more complicated than those of H–H coupling constants. Angular dependence of *geminal* F–F couplings is a rather simple function of the FCF angle, having a minimum near 110°. The origin is chiefly due to the FC term and both the SD and OB terms are insensitive to the FCF angle. In *vicinal* F–F couplings, although the SD and OB terms are a rather simple function of the dihedral FCCF angle, the FC term is a function strongly depending on both the substituents and the dihedral angle. Therefore in total vicinal F–F couplings, to which the FC term makes an important contribution, it is difficult to find a clear relationship as a function of dihedral angle. The *long-range* F–F couplings exhibit steric dependence strongly, which is also due mainly to the FC term. The "fragment" coupling shows a truly dramatic increase in magnitude as the internuclear distance decreases. The five-bond F–F couplings in fluorobutadiene show remarkable dependences on the dihedral angle. From these angular dependences, nonplanarity of hexafluorobutadiene is supported.

In Table V, the summary of the origins of F–F coupling constants and the principal term in angular dependences studied in this series are presented. At a glance, it is obvious that both the OB and SD terms make important contributions to F–F coupling constants as well as the FC term. Note also that the principal term in angular dependences is the FC term in all cases with an exception. This table may help us to understand the experimental complexity of the F–F coupling constants.

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