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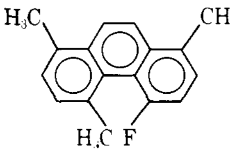
Proximity and Bond Orientation Effects on Long-Range Proton–Fluorine Nuclear Spin–Spin Coupling Constants

R. E. Wasylishen[1a] **and M. Barfield***[1b]

Contribution from the Departments of Chemistry, University of Winnipeg,
Winnipeg, Manitoba, Canada, and the University of Arizona,
Tucson, Arizona 85721. *Received December 18, 1974*

Abstract: A theoretical study is presented of the effects of H . . . F proximity and bond orientation on the long-range hydrogen–fluorine nuclear spin–spin coupling constants (LRHFC) in a variety of saturated and unsaturated fluoroorganic compounds. Calculated results for Fermi contact contributions are based on the finite perturbation theory (FPT) formulation for coupling constants in the semiempirical molecular orbital approximation of intermediate neglect of differential overlap (INDO). Calculated results are also given for intermolecular H–F coupling in several dimers since this makes it possible to vary the distances and orientations over ranges of distances and conformations which are not generally accessible for intramolecular coupling in individual molecules. In this way it is possible to demonstrate the complexity of the long-range coupling phenomenon, which is usually called "through-space", and which has been presumed to be dependent on only the internuclear separation. Indeed, large (usually negative) values of LRHFC are predicted when the nuclei are spatially close, but significant values can occur for other orientations. It is important to note that substantial *positive* values of LRHFC are obtained when the bond containing the hydrogen is directed *away* from the fluorine atom. This mechanism is shown to involve the orbitals on the fluorine and the carbon atom to which the hydrogen is bonded. In cases where one of the coupled nuclei can assume several orientations, the averaging of large values of opposite sign leads to small observed values. The calculated results are compared with the available experimental data and found to be in reasonable agreement for this level of approximate molecular orbital theory.

The importance of the effects of proximity of the atoms on long-range proton–fluorine coupling is clearly demonstrated[2a] by the 11.9-Hz value observed in the phenanthrene derivative **1**. Long-range H–F coupling (LRHFC) between the CH_3 and the F, which are separated by six bonds in **1**, would be much smaller in magnitude if the dominant mechanisms were σ–π exchange and delocalization in



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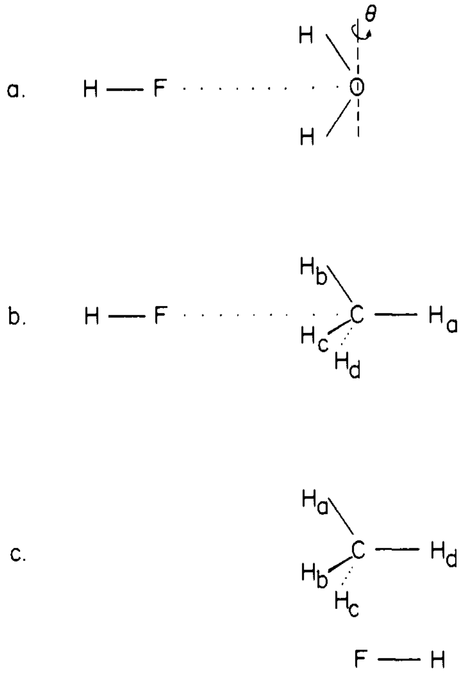
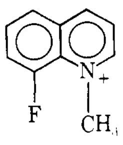


Figure 1. Molecular dimer arrangements used in the calculation of intermolecular H-F coupling. (a) In the H-F . . . H_2O dimer, the hydrogen atoms were rotated out of the plane by the angle θ. (b and c) H-F . . . CH_4 dimers in which the C . . . F distance was varied over a wide range in Tables II and III.

the π-electronic system of the ring. For example, the five-bond LRHFC of 8.3 Hz, which was observed in *N*-methyl-8-fluoroquinolinium iodide (**2**), does not occur over this many bonds in the 3-fluoro derivative **3**.[3] A LRHFC of magnitude 2.5 Hz has been observed[4] between the spatially proximate methyl protons and the fluorine in the transannular compound **4**. The number of bonds separating the coupled nuclei is nine, which appears to be the largest number for LRHFC.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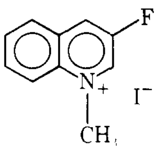
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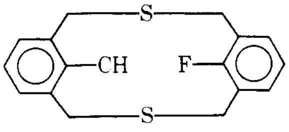
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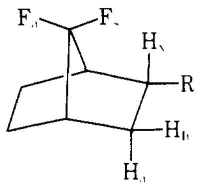
The observation of LRHFC over four or more bonds is not unusual, but the factors which determine the signs and magnitudes of such coupling constants have been poorly understood. The most frequently cited factor is the internuclear separation between the coupled nuclei, and it has been suggested[5,6] that LRHFC will become important when H and F are less than 2.5 Å apart.

An orientation dependence of LRHFC was inferred from studies[7] of a large number of fluorosteroids, and a "converging vector" rule was proposed as a criterion for coupling between an angular methyl group and a fluorine atom. Additional LRHFC not involving angular methyls, but which are also indicative of bond orientation effects, occur for the two series of multicyclic compounds **5**[8] and **6**[9]. LRHFC in **6** had magnitudes of 3.6 and 3.0 Hz to the syn and anti protons, respectively. As a consequence, it seems likely that proximity effects are not the sole criterion for LRHFC, and that orientation and proximity effects must be considered simultaneously.

Table I. Calculated INDO-FPT Results for the Intermolecular H-F Coupling in the Dimer System H-F . . . H_2O as a Function of the Rotational Angle θ for F . . . O Separations of 2.5 and 2.6 Å

Dihedral angle θ,[a] deg	*J*(H . . . F), Hz *r*(F . . . O) = 2.6 Å	2.5 Å
0	−21.07	−30.63
30	−14.30	−20.78
60	−5.05	−7.32
90	−1.12	−1.63
120	0.15	0.32
150	0.83	1.48
180	1.11	1.96

[a] The dihedral angle θ is measured about the line perpendicular to the H-F . . . O axis as depicted in Figure 1a.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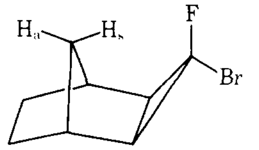
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Results and Discussion

In this study, the various factors determining LRHFC are examined by means of the coupling constant formulation of finite perturbation theory (FPT) in the approximation of intermediate neglect of differential overlap (INDO).[10] Except where noted otherwise, molecular geometries were based on the standard geometrical model.[11] Computations were performed on a CDC-6400 and in double precision on an IBM 370/165 digital computer. In each of the subsequent sections, individual molecular systems are discussed in terms of the relevant mechanisms, and calculated results are compared with available experimental data.

1. Intermolecular H-F . . . H_2O and H-F . . . CH_4 Coupling. A simple approach to the problems of orientation and proximity effects on LRHFC is to use two different molecules in which the distances between the nuclei and the directions of the bonds can be varied continuously. For this purpose, the three geometrical situations depicted in Figure 1 were selected. For these simple molecular dimers, many calculations were performed at minimal computational expense.

In the case of the H-F . . . H_2O dimer system depicted in Figure 1a, the F . . . O separations were set at 2.5 and 2.6 Å. To investigate the effects of directionality, the water angle was twisted at 30° intervals of the dihedral angle θ in Figure 1a. The calculated results are entered in Table I. The LRHFC value of greatest magnitude (30.6 Hz) is of negative sign and occurs for θ = 0°. As the H_2O molecule is twisted around, corresponding to quite different orientations of the O-H bonds, the coupling rapidly decreases in magnitude and changes sign!

Now consider the situation represented by intermolecular H-F coupling in the H-F . . . CH_4 dimer depicted in Figure 1b. For this pair, the F . . . C distances were varied from 5.0 to 2.0 Å. The calculated LRHFC results in Table II exhibit quite different trends from those in Table I. In this case, all of the results (with the exception of small negative values at 3.0 and 2.9 Å) are positive and become very large (202 Hz)

Table II. Calculated INDO–FPT Results for Intermolecular H–F Coupling in the H–F . . . CH_4 Dimer System as a Function of the F . . . C Distances for the Arrangement Depicted in Figure 1b

r(C . . . F), A	J(F,H_a), Hz	J(F,H_b) = J(F,H_c) = J(F,H_d), Hz
5.00	0.00	0.00
4.00	0.25	0.00
3.00	2.78	−0.12
2.90	4.30	−0.06
2.80	6.76	0.79
2.70	10.49	0.47
2.60	16.26	1.13
2.50	25.07	2.49
2.40	38.42	4.83
2.30	58.58	8.83
2.20	88.85	15.49
2.10	132.83	26.65
2.00	202.21	45.00

Table III. Calculated INDO–FPT Results for the Intermolecular H . . . F Coupling in the H–F . . . CH_4 Dimer System as a Function of F . . . C Separations for the Arrangement Depicted in Figure 1c

r(C . . . F), A	J(F,H_d), Hz	J(F,H_a), Hz	J(F,H_b) = J(F,H_c), Hz
3.0	−0.11	1.70	−0.41
2.8	−0.32	3.74	−0.76
2.6	−0.70	8.23	−1.13
2.5	−0.58	12.73	−0.73
2.4	−0.50	18.93	−0.37
2.3	−0.47	28.18	0.57
2.2	−0.36	42.01	2.54

as the electrons of the fluorine atom are pushed close to those of the methane molecule. *However, the largest magnitudes occur between the fluorine and the hydrogen atom directed away from it.* This is clearly indicative of a "rear lobe"[12,13] type of mechanism involving the carbon hybrid orbitals and the orbitals of the fluorine atom. To investigate the mechanisms, all of the resonance integrals (these are proportional to overlap integrals in these semiempirical schemes) between atomic orbitals on the fluorine atom and the atomic orbitals on the carbon atom of the methane were set equal to zero and the INDO–FPT calculation repeated for the case of a C . . . F internuclear separation of 2.5 Å. In this case, the LRHFC decreased from 25.06 to 1.33 Hz, indicating that the dominant interactions are with the orbitals of the carbon atom and not with hydrogen atoms of methane. This theoretical result is in accord with previous suggestions[2] that the most important interactions for LRHFC are associated with the orbitals of the florine and carbon atoms. This observation was based on the proportionality of the LRHFC in compounds of the type **1** to the corresponding long-range carbon–fluorine coupling constants to the same methyl group.

To investigate the effects of orientation on LRHFC, we also considered the situation depicted in Figure 1c in which the H–F molecule is parallel to one of the C–H bonds of the methane molecule. For C . . . F separations decreasing from very large values down to a value of 2.2 Å, the coupling constants entered in Table III only assume large (positive) values for the case in which the "rear lobe" of the H_a–C bond intersects the H–F axis.

From these results for intermolecular LRHFC in which there is no possibility for mechanisms involving the intervening electronic structure, there are at least two effects leading to substantial direct[14] (electron mediated) mechanisms. One of these gives coupling constants of negative sign when the proton and fluorine are proximate, and the other gives large positive values when the hydrogen points away from the fluorine. These mechanisms will be discussed in more detail in the next sections.

Table IV. Calculated Values of $^4J_{HF}$ in 1-Fluoropropane at 60° Intervals of the Dihedral Angles ϕ and ϕ'

Dihedral angles[a]			Dihedral angles[a]		
ϕ, deg	ϕ', deg	$^4J_{HF}$, Hz	ϕ, deg	ϕ', deg	$^4J_{HF}$, Hz
0	0	−25.91	180	0	−0.75
	60	−1.77		60	−1.78
	120	3.73		120	1.40
	180	10.20		180	4.80
	240	3.73		240	1.40
	300	−1.77		300	−1.78
60	0	−2.18	240	0	−0.67
	60	−2.63		60	−2.44
	120	−0.86		120	0.55
	180	−0.04		180	1.47
	240	−1.43		240	−2.04
	300	−0.86		300	−0.92
120	0	−0.67	300	0	−2.18
	60	−0.92		60	−0.86
	120	−2.04		120	−1.43
	180	1.47		180	0.04
	240	0.55		240	−0.86
	300	−2.44		300	−2.63

[a] The dihedral angles ϕ and ϕ' are measured in the same sense from the C_1–C_2–C_3 plane as depicted in Figure 2.

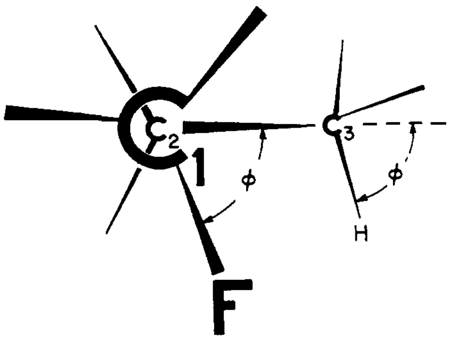
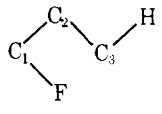


Figure 2. Specification of the dihedral angles ϕ and ϕ' in 1-fluoropropane. These are measured in the same sense from the C_1–C_2–C_3 plane.

2. The Conformational Dependence of LRHFC over Four Bonds in 1-Fluoropropane. Calculated values of $^4J_{HF}$ in 1-fluoropropane are given in Table IV at 60° intervals of the dihedral angles ϕ and ϕ'. These angles are measured from the C_1–C_2–C_3 plane as depicted in Figure 2. Although the magnitudes are nonvanishing for all conformations, the LRHFC becomes substantial for the planar conformations. It should be noted that the largest positive value (10.20 Hz) occurs for the "dipper" conformation **7**, corresponding to ϕ = 0° and ϕ' = 180° whereas, for the other possible "dipper" conformation **8** (ϕ = 180°, ϕ' = 0°), $^4J_{HF}$ = 0.75 Hz.



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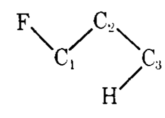

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The INDO–FPT result for H–H coupling over four bonds in the "dipper" orientation of propane is −0.13 Hz.[13,15] Therefore, the direct mechanism associated with the fluorine atom and the "rear lobe" of the C–H bond invokes different effects than the interaction of a proton with the "rear lobes" of either a C–H or a C–F bond. Inspection of the MO's for this arrangement indicates that the dominant contributions to LRHFC in a sum over virtual orbitals description would arise from the occupied and unoccupied MO's depicted schematically in Figure 3. In such formulations, coupling constants are based on the expression[16] given in eq 1, where π(1s,2s) is the mutual atom-atom polarizability

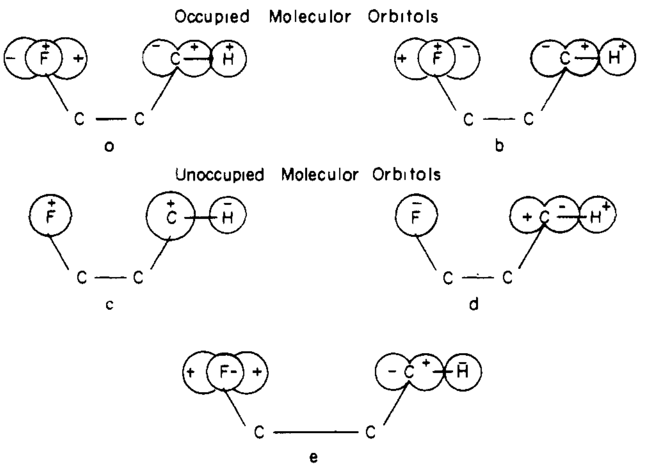


Figure 3. Nodal properties of the important occupied (a and b) and unoccupied (c, d, and e) molecular orbitals in the "dipper" arrangement **7** of 1-fluoropropane.

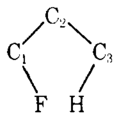
$$J_{HF} = -(4h)^{-1}(16\beta\pi\hbar/3)^2\gamma_H\gamma_F\phi_{1s}^2(H)\phi_{2s}^2(F)\pi(1s,2s) \quad (1)$$

associated with the 1s orbital on the H and the 2s orbital on the F; see eq 2, where c_{i1s} and c_{j1s} denote the coefficients of

$$\pi(1s,2s) = 4\Sigma_{i,j}[\epsilon_i - \epsilon_j]^{-1}c_{i1s}c_{i2s}c_{j1s}c_{j2s} \quad (2)$$

the 1s atomic orbital in the ith occupied and jth unoccupied MO's with energies ϵ_i and ϵ_j, respectively. The occupied and unoccupied MO's, which give the most important contribution to LRHFC in **7**, are depicted in Figure 3. From eq 1 and 2 and the signs of the 1s and 2s orbitals on the hydrogen and fluorine, it can be seen that only the high-energy excitation **a** → **e** will give a contribution to $^4J_{HF}$ which is of negative sign. Clearly, LRHFC in the "dipper" conformation **7** conforms to a direct mechanism of the type discussed in ref 14. In this case, the 2p atomic orbitals on both the fluorine and the C3 carbon atom are of importance in mediating the coupling.

A most interesting result is the calculated value of −25.9 Hz for LRHFC in the proximate orientation **9** for which $\phi = \phi' = 0°$. The very small H-F internuclear separation of 1.87 Å is clearly indicative of a through-space, direct mechanism[14] but would not be readily obtainable in actual molecules. This value may be compared with an essentially "normal" value of +4.8 Hz for the "W" orientation **10** for



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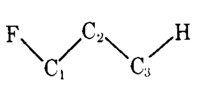

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which $\phi = \phi' = 180°$. Hirao et al.[17] have proposed a "fragment" coupling mechanism based on use of only the 2s and 2p atomic orbitals of fluorine and the 1s atomic orbital of the hydrogen. This leads to three MO's. Excitation from the second to the third, which gives a negative contribution to the H-F coupling constant, was presumed to be dominant for the arrangement **9**. However, consideration of MO's for the arrangement **9** of 1-fluoropropane in conjunction with eq 1 and 2 does not allow one to select any particular excitations as being primarily responsible for the LRHFC. This is not surprising since we have already concluded that the dominant interactions are associated with the carbon and fluorine atoms and not the hydrogen.[2] As a consequence, the introduction of the term "fragment" coupling would not appear to provide any useful basis for interpreting this physical situation. Another semiempirical theory has been proposed[18] in which the long-range fluorine-fluorine coupling constants are assumed to be proportional to the atomic valence s-electron density and the square of the overlap at these atomic s orbitals. The results presented here clearly indicate that such a simple interpretation is inadequate.

Table V. Calculated Values of $^4J_{HF}$ in 1-Fluoropropane for the Cases in Which the Methyl Group and the Fluoromethyl Group Can Assume All Trans Arrangements at 60° Intervals of the Dihedral Angles

ϕ,[a] deg	$^4J_{HF}$,[c] Hz	ϕ',[b] deg	$^4J_{HF}$,[c] Hz
0	2.22	0	−1.70
60	−1.15	60	−1.76
120	−0.63	120	−0.30
180	0.41	180	1.63

[a] The dihedral angle ϕ is measured about the C_1–C_2 bond as depicted in Figure 2. [b] The dihedral angle ϕ' is measured about the C_2–C_3 bond as depicted in Figure 2. [c] These coupling constants have a periodicity of 180° and were obtained from Table IV with the assumptions described in the text.

There is very little experimental data for LRHFC over four bonds in molecules of well-defined structure. In the series of fluorinated carbohydrate derivatives,[19] coupling constants between the equatorial fluorine and equatorial hydrogen were found to be between +4.0 and +5.2 Hz. Ignoring substituent effects and averaging of coupling constants due to ring interconversions, the corresponding calculated result in Table IV for $\phi = \phi' = 180°$ is +4.8 Hz. In addition, experimental values of coupling between the equatorial F and axial H were in the range 0 to −1.5 Hz.[19] The value for $\phi = 180°$, $\phi' = 60°$ in Table IV, by way of comparison, is −1.8 Hz. Experimental values of $^4J_{HF}$ between axial hydrogens and axial fluorines have been observed[20] to range from "small" to +2.5 Hz. Because of structural ambiguities in these compounds, failure to achieve agreement with experimental results may not be serious.

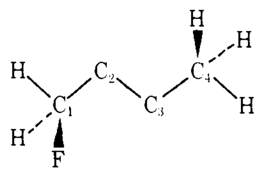
For those cases in which the hydrogens of the methyl group and/or the fluorines of the fluoromethyl group can assume all of the orientations available to such groups, it is necessary to average the calculated results in Table IV over the barriers to internal rotation. For simplicity, we shall use the usual procedure of considering three-fold barriers with equal weights at 60, 180, and 300° (a simple average over the staggered arrangement). Calculated values of LRHFC corresponding to rotation about C_2-C_3 and C_1-C_2 bonds in Figure 2 are entered in Table V. Because the averaging gives rise to cancellation of terms of opposite sign, and because those coupling constants of greatest magnitude do not enter the average, the calculated LRHFC values in Table V are relatively small. This is consistent with experimental observations[21] of $^4J_{HF}$ between equatorial fluoromethyl and axial hydrogens with magnitudes in the range 0.6 to 1.25 Hz.

3. The Conformational Dependence of LRHFC in 1-Fluorobutane. INDO-FPT results for the five-bond LRHFC in 1-fluorobutane are entered in Table VI for the several orientations **11–16** of this molecule. Since there are three dihedral angles, ϕ, ϕ', and ϕ'', measured about the C_1-C_2, C_2-C_3, and C_3-C_4 bonds, respectively, it would be prohibitively expensive to perform calculations in which all three angles were varied. Furthermore, the results in Table VI for these conformations are sufficient to exhibit the salient features of this type of coupling. For the staggered arrangements of the carbon atoms in **11** and **12,** the calculated coupling constants in Table VI are small and positive. An average over the nine possible (trans) arrangements of the methyl and fluoromethyl groups gives a calculated value of +0.53 Hz to be compared with the experimental value of +0.56 to ±0.77 Hz (solvent dependent) in a pentafluorobutane.[22] The authors[22] estimated values of 0.16 and 0.97 Hz for the trans

Table VI. Calculated Values of LRHFC over Five Bonds in Various Conformations of 1-Fluorobutane 11–16

Conformation	ϕ, deg	ϕ'', deg	$^5J_{HF}$, Hz	r(C–F), Å	r(H–F), Å
11[a]	60	60	0.21	4.27	4.42
	60	180	0.16	4.27	4.90
	60	300	0.30	4.27	4.85
12[a]	180	60	0.13	4.88	5.02
	180	180	3.13	4.88	5.80
	180	300	0.13	4.88	5.02
13[b]	0	60	87.16	1.73	1.49
	0	180	287.54	1.73	2.74
	0	300	87.16	1.73	1.49
14[b]	60	60	−39.57	2.47	1.77
	60	180	8.30	2.47	3.45
	60	300	−2.53	2.47	2.66
15[b]	120	60	−0.03	3.51	2.98
	120	180	0.27	3.51	4.55
	120	300	1.33	3.51	3.58
16[b]	180	60	0.77	3.93	3.71
	180	180	0.65	3.93	5.02
	180	300	0.77	3.93	3.71

[a] The dihedral angle ϕ', measured about the C_2–C_3 bond, is 180°. [b] The dihedral angle ϕ' is 0°.



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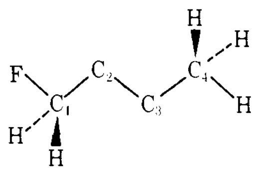

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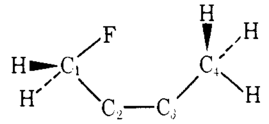

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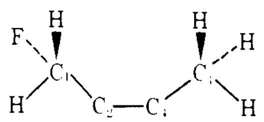

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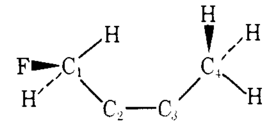

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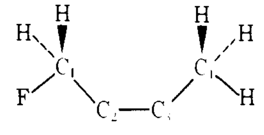

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and gauche coupling constants, respectively. The larger value for the gauche than the trans coupling was attributed to a "through-space" mechanism.

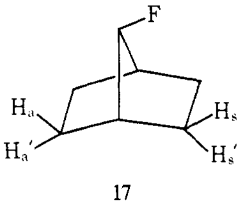
The most interesting calculated data occur for the cis arrangements of the carbon atoms in **13** and **14**, because we see once more the possibility of very large positive coupling (287 Hz for ϕ = 0°, ϕ'' = 180°) and negative coupling (−39 Hz for $\phi = \phi''$ = 60°). Relative sign measurements for the observed 3.6 and 3.0 Hz LRHFC to the syn and anti protons in **6** would be exceedingly useful since these could well be opposite in sign.

4. Axial and Equatorial LRHFC in Fluorocyclohexane. The calculated values of LRHFC over four bonds and five bonds with the fluorine in the axial and equatorial positions of fluorocyclohexane, respectively, are given in Table VII. The geometry was based on the microwave data of Pierce and Nelson.[23] Experimental measurements of LRHFC over four bonds in a series of fluorinated carbohydrate derivatives[24] gave values of $^4J(H_e,F_e)$ = +3.6, 4, and + 4.2 Hz. In cases where resolvable coupling between axial hydrogen and equatorial fluorine occurred, it was negative and in the range −0.8 to −0.7 Hz. Considering the number and nature of the substituents in these compounds, agreement with the data in Table VII is satisfactory. In addition, Foster et al.[24] observed a 1.5-Hz coupling between an equatorial fluorine and one of the protons separated by five bonds.

Table VII. Calculated LRHFC for F Axial and F Equatorial in Fluorocyclohexane

F axial	F equatorial
$^4J(H_a,F_a) = -0.69$	$^4J(H_a,F_e) = -1.92$
$^4J(H_e,F_a) = -2.12$	$^4J(H_e,F_e) = 3.05$
$^5J(H_a,F_a) = 0.28$	$^5J(H_a,F_e) = 0.84$
$^5J(H_e,F_a) = 0.36$	$^5J(H_e,F_e) = 6.68$

5. LRHFC in 7-Fluorobicyclo[2.2.1]heptane. A further example of the very strong orientation dependence of LRHFC is provided by the calculated results for 7-fluorobiclo[2.2.1]heptane (**17**). The calculated results are as follows:



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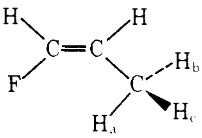
$^4J(F-H_a')$ = 3.61, $^4J(F-H_s')$ = −0.51, $^4J(F-H_s)$ = −0.81, $^4J(F-H_a)$ = −0.96 Hz. Most of these values are smaller than the magnitudes reported for a series of substituted 7,7-difluorobicyclo[2.2.1]heptanes.[8] Negative signs were deduced for these LRHFC's. However, the signs were deduced from the fairly large effects of the substituents instead of relative sign determination via spectral analyses or nuclear magnetic double resonance. A reexamination of the experimental data would be quite useful.

6. LRHFC in 1-Fluoro- and 3-Fluoropropene. Calculated INDO-FPT results for LRHFC over four bonds were obtained for 1-fluoropropene for the cases in which the fluorine is cis (**18**) and trans (**19**). LRHFC associated with the proximate in-plane hydrogen in **18** is $^4J(F-H_a)$ = −5.55 Hz and, for the out of plane hydrogens, the value is $^4J(F-H_b)$ = $^4J(F-H_c)$ = +4.19 Hz. The average of the three values is 0.94 Hz. The experimental value for this coupling is +2.6 Hz.[25] In the trans (**19**) arrangement, $^4J(F-H_a)$ = −3.00 and $^4J(F-H_b)$ = $^4J(F-H_c)$ = 5.35 Hz, which give an average of 2.57 Hz. The experimental value is +3.3 Hz.[25] The agreement of calculated and experimental results for **18** and **19** is reasonable and in accord with the observation that the smaller value for the cis LRHFC is due to a more negative contribution from the proximate fluorine and hydrogen atoms.



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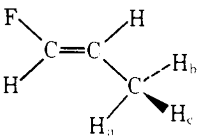

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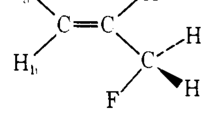
Calculated values of LRHFC in 3-fluoropropene were obtained with the fluorine cis (**20**) to the double bond and at an angle of 120° as in **21**. For the first of these, the INDO-FPT results are as follows: $^4J_{FH_a}(0°)$ = −5.32, $^4J_{FH_b}(0°)$ = 4.22 Hz. In the case of **21**, the results are $^4J_{FH_a}(120°)$ = −3.15 and $^4J_{FH_b}(120°)$ = −6.08 Hz. Experimental results[26] are quite sensitive to temperature because of variations in rotamer populations. At 36° the experimental values are $^4J(F-H_a)$ = −4.32 and $^4J(F-H_b)$ = −0.89 Hz. Assuming that the three rotamer populations are



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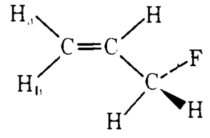

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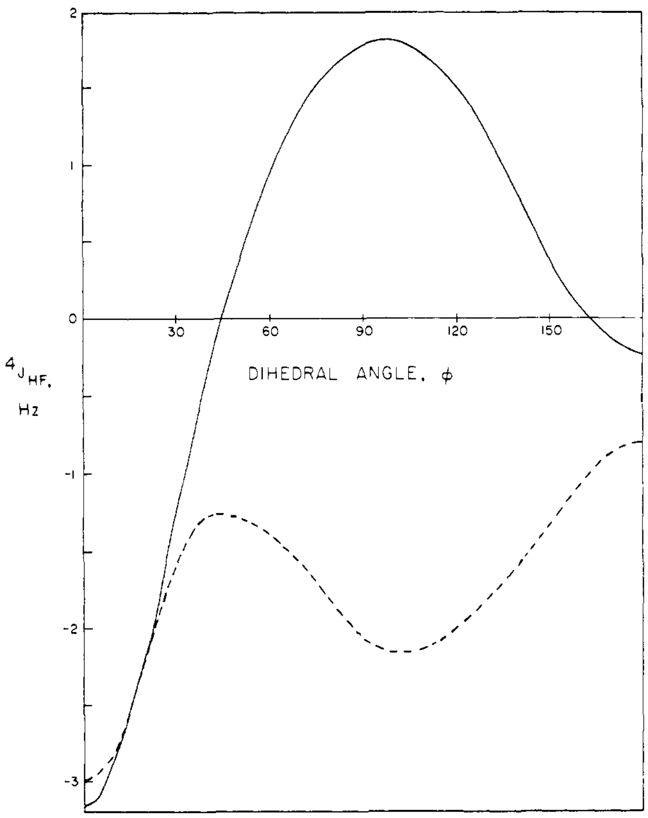


Figure 4. Plots of the calculated INDO-FPT results for ${}^4J$(H-F) in trifluoromethylbenzene (dashed line) and *o*-fluorotoluene (solid line) as functions of the dihedral angles ϕ, which are measured from the planes of the rings.

equal, calculated values are −3.87 and −2.64 Hz, respectively. With $p_a = 0.630$ (p_a denotes the relative population of the rotamer **20**) and the formula[26]

$${}^4J(\text{F-H}) = p_a{}^4J_{HF}(0°) + (1 - p_a){}^4J_{HF}(120°) \qquad (3)$$

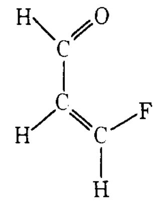
the respective values are −4.52 and 0.37 Hz. The disparity between the calculated and experimental results is certainly not worse than the uncertainty in the knowledge of the rotamer populations.

Both σ- and π-electron mechanisms are expected to be important for the LRHFC in **20** and **21**. However, if we compare the values for **20** with those for 1-fluoropropane ($\phi = 0$ and $\phi' = 0$ and 180°, respectively) for which the coupling constants from Table IV are −25.9 and +10.2 Hz, it may be reasonably assumed that the direct mechanism is dominant in both cases. The decrease in the magnitudes of coupling constants relative to 1-fluoropropane is due to the greater separation between the F and the C_1 carbon (2.64 Å in **20** vs. 2.51 Å in **9**) and between the H and the F (2.42 Å between H_a and F in **20** and 1.87 Å in **9**).

6. LRHFC in Fluoroacrolein and Fluoromethyl Vinyl Ketone. Calculated INDO-FPT results for LRFHC ${}^4J_{HF}$ were obtained in the *s-cis*-**22a** and *s-trans*-**22b** arrangements of fluoroacrolein and ${}^5J_{HF}$ in similar arrangements **23a** and **23b** of fluoromethyl vinyl ketone. The calculated values of the LRHFC over four bonds in **22a** and **22b** are −1.00 and +1.61 Hz, respectively. If the observed coupling were a simple average, it would be predicted to be only 0.3 Hz.

Table VIII. Calculated INDO-FPT Results for LRFHC in Trifluoromethylbenzene (24) as a Function of the Dihedral Angle ϕ Measured from the Plane of the Aromatic Ring

Dihedral angle ϕ, deg	${}^4J$(F,H$_o$), Hz	${}^5J$(F,H$_m$), Hz	${}^6J$(F,H$_p$), Hz
0	−2.98	−0.03	−0.01
15	−2.51	0.09	−0.19
30	−1.58	0.41	−0.62
45	−1.27	0.79	−1.21
60	−1.41	1.26	−1.81
75	−1.74	1.73	−2.25
90	−2.09	2.20	−2.40
105	−2.15	2.60	−2.25
120	−2.00	2.93	−1.81
135	−1.70	3.16	−1.21
150	−1.38	3.19	−0.62
165	−0.95	3.18	−0.19
180	−0.81	3.15	−0.01



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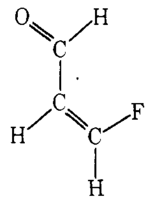

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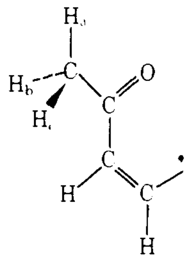

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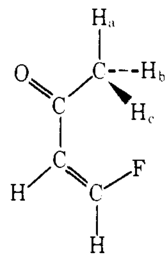
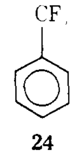


23b

Calculated LRHFC over five bonds in **23a** are as follows: ${}^5J$(F-H$_a$) = 0.30, ${}^5J$(F-H$_b$) = ${}^5J$(F-H$_c$) = −3.78 Hz, with a simple average of −2.42 Hz. In the case of **23b**, the corresponding calculated values are as follows: ${}^5J$(F-H$_a$) = 8.45, ${}^5J$(F-H$_b$) = ${}^5J$(F-H$_c$) = −5.08 Hz. The average of the last three values is −0.57 Hz and is another example of LRFHC in which cancellation between fairly large terms of opposite sign leads to small, possibly unresolved, coupling constants. Unfortunately, experimental data for LRHFC in these compounds are not available.

7. LRHFC in Trifluoromethylbenzene and *o*-Fluorotoluene. The calculated values for LRHFC in trifluoromethylbenzene (**24**) are listed in Table VIII at 15° intervals of the dihedral angle ϕ. The calculated values for LRHFC over four bonds are plotted in Figure 4 as a function of this angle, which is measured from the plane of the ring. Except for the small negative value of −0.03 Hz for ${}^5J$(F-H$_m$) at $\phi = 0°$, the LRHFC over four, five, and six bonds are negative, positive, and negative, respectively. This follows the usual sign reversal noted for long-range H-H coupling for cases in which a single mechanism is dominant.[27] Experimental values for these coupling constants are −0.74, +0.82, and −0.64 Hz, respectively.[28] Although the trend in the signs is reproduced by the calculated results, the magnitudes do not follow from any assumption regarding the orientation of the CF$_3$ relative to the aromatic ring. Inspection of space-filling models suggests that steric interactions between the fluorines and the ortho hydrogens would be minimized for the conformation in which one fluo-



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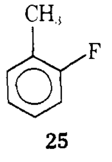

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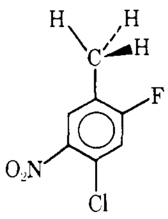
Table IX. Calculated INDO–FPT Results for LRHFC in *o*-Fluorotoluene (**25**) as a Function of the Dihedral Angle ϕ, Which is Measured from the Plane Formed by C_α–C_1–C_2 (the Plane of the Aromatic Ring)

Dihedral angle ϕ, deg	${}^4J(CH_3,F)$, Hz	Dihedral angle ϕ, deg	${}^4J(CH_3,F)$, Hz
0	−3.15	105	1.76
15	−2.56	120	1.48
30	−1.23	135	0.99
45	0.05	150	0.41
60	0.95	165	−0.06
75	1.51	180	−0.24
90	1.77		

rine is symmetrically disposed above or below the ring. With this assumption, the average of the values for $\phi = 90$, -30, and $-150°$ from Table VIII are −1.68, 1.94, and −1.21 Hz for the ortho, meta, and para hydrogen to trifluoromethyl LRHFC, respectively. If it is assumed, instead, that the conformation of lowest energy is one in which one of the fluorine atoms is in the plane, almost identical results are obtained.

Calculated values of LRHFC for *o*-fluorotoluene (**25**) are entered in Table IX at 15° intervals of the dihedral angle ϕ and are plotted (solid line) in Figure 4 as a function of this angle, which is measured about the C_1–CH_3 bond. In contrast to the four-bond LRHFC from the fluorine atoms of the trifluoromethyl group to the ortho hydrogen in **24**, ${}^4J(CH_3\text{–}F)$ assumes substantial positive values for the out-of-plane orientations. It is interesting to note that the two sets of results are similar for dihedral angles near the planar orientations (0 and 180°). It is reasonable to assume that the proximity and bond orientation effects of a direct mechanism are involved, but that these become less important as the C–F and C–H of the trifluoromethyl and methyl groups are moved out of the plane. Furthermore, as these are moved out of the plane, the σ–π configuration interaction mechanism becomes dominant. It is not possible to reconcile any type of average of the data in Table IX with the experimental value of +2.09 Hz in 2-fluoro-4-chloro-5-nitrotoluene.[29] In this case, the most stable conformation is expected to be **26** so that the average of the appropriate values from Table IX is +0.55 Hz.



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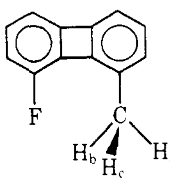
The sign reversal noted for the *o*- and *p*-fluorotoluene relative to the analogous couplings in trifluoromethylbenzene (**24**) for the out-of-plane orientations of the C_α–H or C_α–F can also be interpreted in terms of indirect mechanisms associated with σ–π exchange and transmission in the π-electron systems. It has been noted[29] that these results are consistent with a positive hyperfine interaction in the C–F bond. Since the C–H hyperfine is negative,[30] this follows from the proportionality of the coupling to the product of the hyperfine at the two nuclear sites.[31]

8. *N*-Methyl-8-fluoroquinolinium Iodide and 1-Fluoro-8-methylbiphenylene. There are a number of molecules for which experimental LRHFC data have been obtained, and which are amenable to calculations of the semiempirical INDO-FPT type. Two of these are the *N*-methyl-8-fluoroquinolinium iodide (**2**) and 1-fluoro-8-methylbiphenylene (**27**). In the absence of suitable structural data for these molecules, which would indicate the extent to which the proximity of the methyl and the fluorine would cause twisting of the rings and bending of the bonds, it was assumed that the ring systems were planar and that the fluorine and methyl would conform to the standard geometrical model.[11] Bond distances for quinoline and biphenylene were based on literature values.[32] An additional assumption is that the smallest steric repulsions would occur for the cases in which the fluorine was situated between two of the hydrogens of the methyl (H_b and H_c in **2** and **27**). The calculated values for **2** are as follows: $J(F\text{–}H_a) = 30.57$, $J(F\text{–}H_b) = J(F\text{–}H_c) = -17.30$ Hz. The average of these three values is only −1.34 Hz to be compared with the experimental value of ±8.3 Hz.[3] Because of the inadequacies in the knowledge of the geometry of the molecule and the cancellation between terms of comparable magnitude but opposite sign, disparities of this order of magnitude between calculated and experimental results would be expected. As we have noted, LRHFC is quite sensitive to small changes in internuclear separation and bond orientation. Because of the close proximity of the fluorine and the methyl group [$r(F\text{–}H_a) = 3.39$, $r(F\text{–}H_b) = r(F\text{–}H_c) = 2.05$ Å], changes of the order of a few hundredths of an angstrom in these distances could account for the difference. For example, consider the situation for intermolecular H–F coupling depicted in Figure 1c; at a C–F separation of 2.2 Å, the effect of an 0.1 Å increase in the C–F distance produces a decrease of only 2 Hz in the coupling to the proximate protons H_b and H_c but produces a decrease of about 14 Hz in coupling to the proton H_a in Table III. One possible distortion which could account for the disparity is the bending of the "cone" formed by the three hydrogens away from the C–C axis.



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The calculated values for the biphenylene derivative **27** are as follows: $J(F\text{–}H_a) = 0.17$, $J(F\text{–}H_b) = J(F\text{–}H_c) = 0.00$ Hz, with an average of 0.06 Hz. No LRHFC was observed in the NMR of this compound.[33] For the assumed geometry, the C–F distance in **27** is 3.82 Å, which is beyond the region in which proximity effects might be expected to be important for intermolecular H–F coupling (see Tables II and III).

Experimental data are available for a number of other bridged biphenyl derivatives,[33] but the absence of reasonable structural data would not justify the expense associated with INDO-FPT calculations of coupling constants in molecules of this size.

Conclusions

A very large number of calculations of intermolecular H–F and long-range intramolecular H–F coupling in saturated and unsaturated molecules indicates that the phenomenom usually described as "through-space" coupling is actually a very complicated combination of proximity and bond orientation effects. The effects of substituents are also expected to be of major importance but were not included within the scope of this investigation.

Computations performed at the INDO level of finite perturbation theory provide a generally adequate description of LRHFC. It seems likely that the greatest difficulties are due to the failure of the INDO method to include all types of spin polarization mechanisms and could be substantially improved by combining the spin polarization mechanisms associated with the one- and two-electron exchange integrals of valence-bond theory in addition to the electron-transfer mechanisms associated with an all-valence electron Hückel type of description. This was done in a recent very satisfactory description of long-range H–H coupling.[13] Therefore it should be clearly understood that there are sufficient inadequacies in both the molecular wave functions and our knowledge of the molecular structures to account for the disparities between calculated and experimental results in this investigation, and that it would be premature to invoke noncontact mechanisms for LRHFC.

A major factor to be considered in interpreting the experimental LRHFC is the possibility of large coupling of opposite sign depending on the relative orientations of the bonds containing the coupled nuclei. As a consequence, in circumstances in which molecular motion is possible, averaging effects may lead to relatively small observed coupling constants.

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