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An INDO MO Study of Conformational and Substituent Effects upon Vicinal ^{19}F–^{13}C Coupling Constants

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Abstract: Finite perturbation theory, at the INDO level of approximation, has been used to investigate conformational and substituent effects upon $^3J_{FC}$ and wherever possible the results are related to experimental situations. Methyl substituent effects upon the magnitude of the trans and gauche $^3J_{FC}$ values in various methyl-substituted fluorocyclohexanes are shown to be additive and demonstrate the importance of the degree of substitution of all the carbons on the coupling pathway. The conformational effects of electronegative substituents are investigated by calculations of the effects of fluorine substitution in the 1-fluoropropane system. Substitution on the coupled carbon causes an increase in $^3J_{FC}{}^{trans}$ while substitution on the other carbons causes a decrease. The decrease in the same coupling with a change to sp^2 hybridization of the central carbon on the coupling pathway accounts for several experimental anomalies. Couplings in the norbornane system are investigated and the effects of the variation of bond angles and bond lengths are considered. The cumulative importance of all these effects gives rise to important deviations from angular dependencies of the Karplus type for $^3J_{FC}$.

Considerable effort has been devoted to the study of the angular dependence of vicinal carbon–proton ($^3J_{CH}$) and carbon–carbon ($^3J_{CC}$) spin–spin coupling constants. The importance of substituent effects upon these has been recognized and thoroughly investigated theoretically.[1–4] Similarly it has been shown both theoretically[5] and practically[5,6] that vicinal fluorine–carbon spin–spin coupling constants ($^3J_{FC}$) have a Karplus-type dihedral angle dependence. Substituent effects are suggested to be analogous in nature to those upon $^3J_{CH}$ and $^3J_{CC}$[7] and consequently deviations from a strict Karplus dependence are expected. Thus it is important to establish the extent of these if $^3J_{FC}$ information is to be used in structural elucidation. In the present paper substituent effects upon $^3J_{FC}$ are thoroughly investigated by the use of semiempirical INDO MO theory and these results are related to the magnitudes of $^3J_{FC}$ found in various experimental situations.

Method

Finite perturbation theory at the INDO level of approximation[8] has been used, as described previously,[9] to calculate the Fermi-contact, orbital, and spin-doplar contributions to $^3J_{FC}$. As with $^3J_{CC}$ the Fermi-contact contribution was the predominant term in all cases[10] with contributions of less than 0.2 and 0.8 Hz for the latter two terms, respectively; hence only the values of the Fermi-contact term are reported here. Standard geometries,[11] with tetrahedral angles of 109.471°, have been assumed except where indicated. Values of the nuclear valence shell s electron densities[9] for carbon and fluorine of 4.0318 and 21.3126 au, respectively, have been used in the present work although these may not be the optimum values.[12] However, the complexity of the calculated substituent effects and the limited amount of experimental data do not warrant any attempt at optimization of these values. Calculations in the fluoropropane derivatives were performed at 30° intervals of the dihedral angle.

All computations were carried out in single precision on a PDP-10 computer.

Results and Discussion

1. Survey of Available Experimental Data for $^3J_{FC}$.

Inspection of the available literature data for $^3J_{FC}$ immediately indicates the limitations of applying a generalized Karplus-type equation and shows the extent of substituent effects. Although an angular dependence of $^3J_{FC}$ has been proposed previously,[6] the availability of more data and the use of crystallographic torsion angles for the norbornane system[13] allow a more satisfactory representation of this. All the data available from the literature are shown in Figure 1. Although an angular dependence is apparent, the actual magnitude of the coupling depends to a great extent upon the environment of the coupled atoms. In general $^3J_{FC}{}^{trans}$ is larger than $^3J_{FC}{}^{gauche}$ for any one system, but a decision as to the disposition of coupled nuclei cannot be safely made in cases where

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Table I. Additivity Coefficients (Hz) for $^3J_{FC}$ (Fermi-Contact Contributions) Calculated by INDO MO Theory for All 64 Possible Combinations of 1-, 2-, and 3-Methyl-Substituted 1-Fluorocyclohexane and Four Combinations of 4-Methyl-1-fluorocyclohexane[24]

	inter-cept	correl coeff corresponding to disposition of methyl group, Hz^a (std error of coefficient, Hz)												
		1e	1a	2e	2a	3e	3a	4e	4a	5e	5a	6e	6a	(1a-3a)^b
$^3J_{FC}{}^{trans}$	17.35		−3.04 (0.04)	−1.89 (0.04)	−1.94 (0.04)	−0.24 (0.04)	−1.14 (0.06)	−0.41 (0.13)	0.24 (0.13)	−0.06 (0.04)	0.02 (0.04)	0.11 (0.04)	0.02 (0.04)	2.15 (0.07)
		multiple correlation coefficient, 0.9983 std error of estimate, 0.13 Hz range of coupling, 10.53–17.50 Hz												
$^3J_{FC}{}^{gauche}$	6.24	−0.66 (0.05)		−0.39 (0.07)	−0.47 (0.07)	0.06 (0.07)	−5.35 (0.07)	0.18 (0.21)	−0.02 (0.21)	0.13 (0.07)	−1.66 (0.07)	0.09 (0.07)	0.04 (0.07)	
		multiple correlation coefficient, 0.9970 std error of estimate, 0.20 Hz range of coupling, −0.49–6.55 Hz												

^{a} e = equatorial and a = axial. ^{b} This additional coefficient is required when both 1-axial and 3-axial methyl groups are present.

only one coupling has been measured, unless further information about similar systems is known, as the magnitude of these couplings overlap.

The importance of substituents is clearly seen for the increase in $^3J_{FC}{}^{trans}$ for 1-fluoroadamantane of 10.6 to 17.2 Hz in 1,3,5,7-tetrafluoroadamantane,[14] while the change in hybridization of the central carbon of the coupling pathway has a pronounced effect upon the same coupling in 6α-fluoroandrost-4-ene-3,17-dione[15] where $^3J_{FC}{}^{trans}$ values range from 2.7 Hz ($^3J_{F6C10}{}^{trans}$) to 11.0 Hz ($^3J_{F6C8}{}^{trans}$).

The usefulness of INDO MO theory for untangling the intricacies of substituent effects upon $^3J_{CH}$ and $^3J_{CC}$ has been amply demonstrated by Barfield et al.[2-4] Indeed the similarity of the substituent effects upon the calculated couplines is shown rather well by the linearity of the equation $^3J_{CC}{}^{trans} = 0.487(^3J_{CH}{}^{trans}) - 0.012$, root mean square error 0.05 Hz and correlation coefficient 0.995 for the 14 calculations reported[3] ($^3J_{CC}{}^{trans}$ values are excluded when both β and γ substituents are present as the parent $^3J_{CH}{}^{trans}$ values are not available since for $^3J_{CC}{}^{trans}$ a γ substituent with respect to one coupled carbon is also a β substituent with respect to the other coupled carbon). Although similar patterns are found from the comparison of the calculated $^3J_{FC}{}^{trans}$ with $^3J_{CH}{}^{trans}$ values a strict linear correlation is not found.[24] It is quite noticeable that certain compounds possessing α and β substituents to the coupled carbon deviate from the correlation line. Clearly the nonbonded interactions in the two cases are not exactly analogous. Hence detailed series of calculations have been performed with the aim of elucidating, as comprehensively as possible, the nature of substituent effects upon $^3J_{FC}$. Detailed breakdown of the results into the nonbonded contributions associated with the couplings[2] is not warranted in the present context.

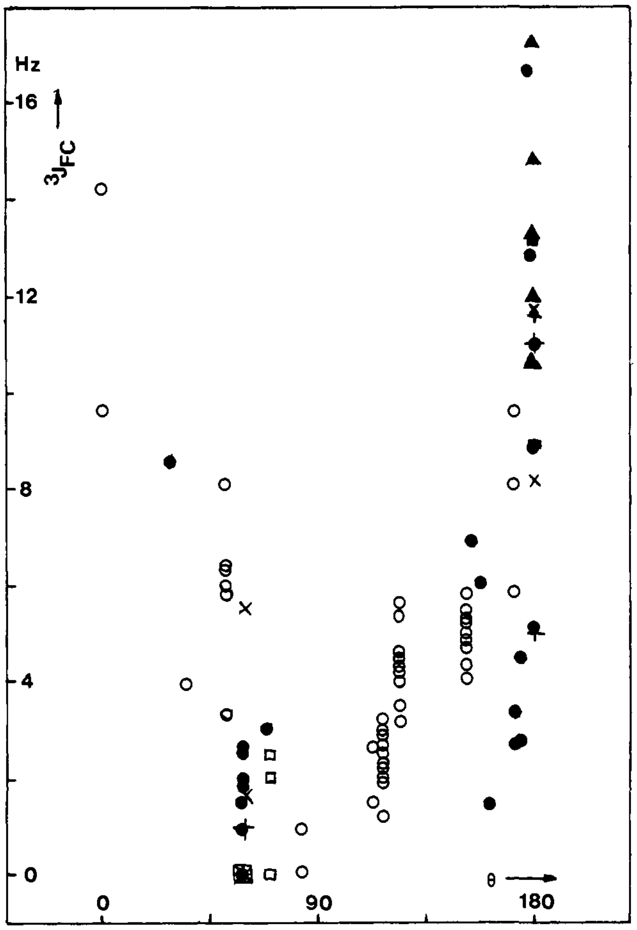

Figure 1. Correlation of $^3J_{FC}$ and the dihedral angle (θ) for all the data reported in the literature. The dihedral angles were taken from Dreiding models except where indicated. The compounds are: ▲, fluoroadamantanes,[14] ■, 1-fluorobicyclo[3.3.1]nonane,[16] ×, fluorocarboydrates,[5] +, fluorocyclohexanes,[6,17] ●, fluorosteroids,[6,15,18-20] □, 1α- and 3α-fluoro-*trans*-decalan-2-ones and their hydrates[21] (θ from ref 22), and, ○, methylfluoronorbornanes[23] (θ from ref 13).

2. α,β, and γ Methyl-Substituent Effects upon $^3J_{FC}$ in Fluorocyclohexane. The influence of the orientation and number of methyl groups attached to carbons on the coupling pathway upon the calculated gauche and trans $^3J_{FC}$ has been calculated for all 64 possible combinations of 1-, 2-, and 3-methyl-substituted 1-fluorocyclohexane and four combinations of 4-methyl-1-fluorocyclohexane.[24] Multiple regression analysis of these values, Table I, indicates an additivity of substituent effects. The range of the various couplings is particularly instructive. $^3J_{FC}{}^{trans}$ values de-

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(24) Details are found in the supplementary material.

(25) For certain orientations in the mono- and disubstituted compounds the change in $^3J_{FC}{}^{gauche}$ is minimal.[24]

(26) Although a linear correlation is found for the $^3J_{FC}$ and $^3J_{CH}$ trans and gauche values of Table V a similar correlation over the entire dihedral angle range of values is not found.

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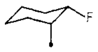
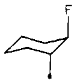
(28) Taking into account the dual pathway, a dihedral angle of 130°, the cyclohexane value of 11.9 Hz as the normal $^3J_{FC}{}^{180}$, and a normal dihedral angular dependence, the maximum $^3J_{FC}$ without strain is calculated to be $(2 \times 11.9 \times 11.2)/23.71 \sim 11$ Hz.

(29) Reference 27, p S15.

Table II. Additivity Coefficients $^3J_{FC}$ (Fermi-Contact Contributions) Calculated by INDO MO Theory for the Exocyclic Couplings to the 2-Methyl Groups in All the Relevant 1-, 2-, and 3-Methyl-Substituted 1-Fluorocyclohexanes[24]

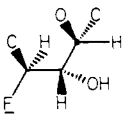
system (coupling range, Hz)	intercept	correl coeff (std error in coeff, Hz)				multiple correl coeff	std error of estimate, Hz
		1a	2a	3e	3a		
 (5.55 to 7.56)	7.53	−0.79 (0.01)	−0.64 (0.01)	−0.39 (0.01)	−0.17 (0.01)	0.9993	0.02
		1a	2e	3e	3a		
 (4.93 to 6.27)	6.34	−0.52 (0.03)	−0.51 (0.03)	−0.31 (0.03)	−0.01 (0.03)	0.9904	0.07
		1e	2a	3e	3a		
 (5.16 to 6.15)	6.16	−0.60 (0.04)	0.02 (0.04)	0.03 (0.04)	−0.40 (0.04)	0.9825	0.08
		1e	2e	3e	3a		
 (11.44 to 16.96)	16.80	−3.53 (0.05)	−1.76 (0.05)	−0.18 (0.05)	0.05 (0.05)	0.9990	0.10

crease by up to 40% of the value in equatorial fluorocyclohexane upon multiple methyl substitution, while $^3J_{FC}{}^{gauche}$ in axial fluorocyclohexane decreases from one-third the trans value to zero for the same substituents. Similar effects for $^3J_{FC}{}^{trans}$ but somewhat smaller for $^3J_{FC}{}^{gauche}$ are noted for the exocyclic couplings to the 2-methyl group, Table II. Thus for a particular orientation of the coupled nuclei the magnitude of the coupling depends to a substantial extent upon the degree of substitution of all the carbon atoms along the coupling pathway, with a decrease being observed for increased methyl substitution.

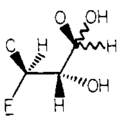
This particular phenomenon will account for a considerable amount of the spread in the experimental values observed in Figure 1. However, in many of the experimental compounds the presence of groups other than methyl (or methylene) complicates the situation. In order to clarify this, calculations of the influence of various substituents upon the angular dependence of $^3J_{FC}$ in molecules related to 1-fluoropropane have been performed and the results are reported in the following sections.

3. α, β, and γ Effects of Electronegative Groups upon $^3J_{FC}$ in 1-Fluoropropane. The results of the influence upon $^3J_{FC}$ in 1-fluoropropane of the introduction of fluorine substituents at the various carbon atoms along the coupling pathway are shown graphically in Figure 2. Detailed calculations for the partially substituted polyfluoropropanes[24] showed the same characteristics as those given here for $^3J_{FC}{}^{trans}$ ($\theta = 180°$) and $^3J_{FC}{}^{gauche}$ ($\theta = 60°$), although for $^3J_{FC}{}^{cis}$ ($\theta = 0°$) considerable variation occurs depending on the number and orientation of the fluorines with respect to the coupling pathway. The latter is not discussed further as this is not a common experimental situation.

Introduction of fluorine on the coupled carbon causes a decrease[25] in $^3J_{FC}{}^{gauche}$ and a substantial *increase* in $^3J_{FC}{}^{trans}$. Detailed experimental evidence for the operation of such an effect is found in the data for the substituted 1-fluoroadamantanes given in Table III. Here the calculated values for the system are in good agreement with the experimental values with the increase in the coupling with increased fluorine substitution being reproduced well. Additional evidence is found in the data for the fluorocarbohydrates[5] where the average $^3J_{FC}{}^{trans}$ for fragment **1** is 8.1 Hz and that for **2** is 11.7 Hz.



1



2

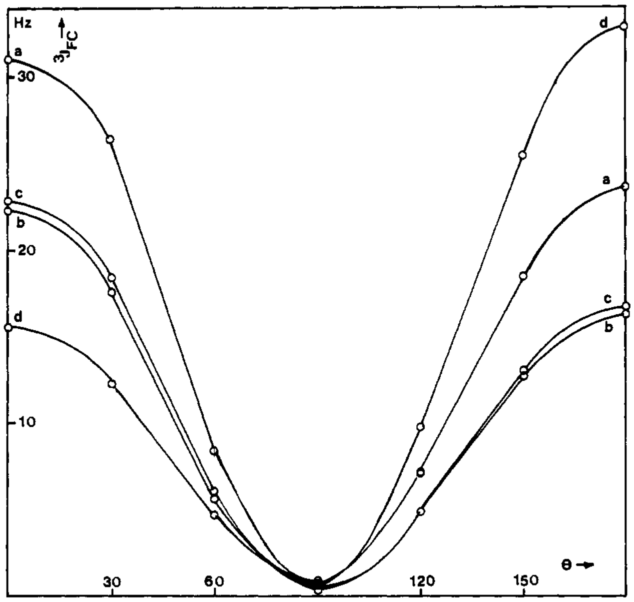


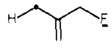
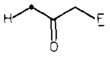
Figure 2. Dihedral angle dependence of $^3J_{F1C3}$, Fermi-contact term, as calculated by INDO MO theory in (a) 1-fluoropropane, (b) 1,1,1-trifluoropropane, (c) 1,2,2-trifluoropropane, and (d) 1,3,3,3-tetrafluoropropane.

Table III. INDO MO Calculations and Experimental $^3J_{FC}{}^{trans}$ Values to the 1-Fluorine Nucleus in Various Substituted 1-Fluoroadamantanes (Hz)

substituent	calculated			experimental[14]		
	$^3J_{FC_3}$	$^3J_{FC_7}$	$^3J_{FC_5}$	$^3J_{FC_3}$	$^3J_{FC_7}$	$^3J_{FC_5}$
1-fluoro	13.09	13.09	13.09	10.6	10.6	10.6
1,3-difluoro	14.87	13.66	13.66	13.3	10.3	10.3
1,3,5-trifluoro	15.74	14.37	15.74	14.8	12.0	14.8
1,3,5,7-tetrafluoro	16.85	16.85	16.85	17.2	17.2	17.2

Fluorine substitution on the carbon carrying the coupled fluorine causes an experimentally significant decrease for $^3J_{FC}{}^{trans}$. The only unambiguous piece of experimental data supporting these calculations is the coupling to C6 in the norbornane system which decreases from 9.8 Hz in 2-*exo*-fluoronorbornane to 5.8 Hz in 2,2-difluoronorbornane.[23]

Table IV. Dihedral Angle Dependence of $^3J_{FC}$, Fermi-Contact Term, as Calculated by INDO MO Theory for 3-Fluoro-2-methylpropene and Fluoroacetone

dihedral angle, θ, deg	molecule[a] $^3J_{FC}$, Hz 	
0	15.57	11.28
30	12.86	10.03
60	7.13	8.13
90	5.20	9.07
120	8.32	11.64
150	11.69	13.55
180	12.31	14.15

[a] In all cases the conformation with θ = 180° is shown.

Similarly introduction of fluorine on the central carbon of the coupling pathway decreases $^3J_{FC}$ over all orientations, the most significant being for $^3J_{FC}{}^{trans}$. Introduction of only one substituent produces an assymmetry in the curve[24] and this has been investigated previously for a hydroxyl substituent where calculations qualitatively reproduced the experimental results observed for various fluoropyranoses.[5]

A comparison of the fluroine substituent effects upon the calculated $^3J_{FC}$ values and those calculated for $^3J_{CH}$ and $^3J_{CC}$, where known, indicates that all three types of coupling respond qualitatively in the same manner to substitution.[24] This is sufficient to suggest that the direction of change of those $^3J_{CH}$ and $^3J_{CC}$ values, not considered previously, will be the same as those for $^3J_{FC}$ found here.

4. Effects of the Change of Hybridization of the Central Carbon on the Coupling Pathway on $^3J_{FC}$. The effects upon the angular dependence of $^3J_{FC}$ of having a central sp^2-hybridized carbon atom are shown in Table IV for 3-fluoro-2-methylpropene and fluoroacetone. In both cases the angular variation in the magnitude of $^3J_{FC}$ is considerably reduced with 46 and 40% reductions, respectively, in $^3J_{FC}{}^{trans}$ compared to the sp^3-hybridized central carbon of 1-fluoropropane, while there is little effect upon $^3J_{FC}{}^{gauche}$.

Such effects are observed experimentally in the unusually low value of $^3J_{FC}{}^{trans}$ involving C10 in 6α-fluoro-11β,17α,21-trihydroxy-16α-methylpregna-1,4-diene-3,20-dione 21-acetate[19] (1.5 Hz) and 6α-fluoroandrost-4-ene-3,17-dione[15] (2.7 Hz) which undoubtedly arise from the sp^2-hybridized carbon at C5 as similar couplings to C8 are of the expected magnitude (11.0 and 16.7 Hz, respectively). On the other hand $^3J_{FC}{}^{gauche}$ to C10 in 6β-fluoroandrost-4-ene-3,17-dione[15] (2.0 Hz) is similar to that for the saturated systems 6β-fluoro-5α-hydroxyandrostane-3,17-dione[15] (1.8 Hz), 6β-fluoro-3β,5α-dihydroxyandrost-17-one[15] (1.8 Hz) and 6β-fluoro-3β,5α-dihydroxycholestane 3-acetate[20] (2 Hz) as predicted.

5. Vicinal Coupling via a Heteroatom. The effects of substitution of the CH_2 group in 1-fluoropropane for O and NH are predicted[24] to decrease $^3J_{FC}{}^{trans}$. Such a reduction has been noted previously[5] for the ether system and is in agreement with the experimental results for the comparison of the coupling to C3 and C5 in 1-deoxy-1β-fluoro-D-glucose of 11.7 and 4.7 Hz, respectively.[5]

6. $^3J_{FC}$ in the Norbornane System. The Effects of Bond Angle Strain and Bond Length Changes. The difficulties in calculating $^3J_{FC}$ values in the norbornane system, for which there is extensive experimental data,[23] arise from the nonstandard geometries involved. For the calculations shown in Table V the norbornane skeleton and bond directions were taken from the crystal structure of 1,4-bibenzoyldecafluoronorbornane[13] with carbon–fluorine bond lengths of 1.36 Å and carbon–hydrogen bond lengths of 1.09 Å. The variations in the magnitudes of the couplings for 2-*exo*-fluoronorbornane are reproduced while those for 2,2-difluoronorbornane and its methyl derivatives appear to be more complex. Clearly only one coupling to C7 is observed as predicted, while the differences in magnitude of the couplinds to C4 can be rationalized by assuming the assignments in the table. The observation of only one coupling to the exocyclic carbon in the 1-methyl compound (4.0 Hz) is as expected for the dihedral angles of ~324° to F_{exo} and ~80° to F_{endo}, while the larger of the two couplings to the 3-methyl compounds arise from couplings to F_{exo} in the 3-*exo*-methyl (14.1 Hz) and with the F_{endo} in the 3-*endo*-methyl compound (9.7 Hz).

Table V. INDO MO Calculations and Experimental $^3J_{FC}$ Values in 2-*exo*-Fluoronorbornane and Methyl-Substituted 2,2-Difluoronorbornanes

compound	calcd[d]	$^3J_{FC}$, Hz	exptl[a] $^3J_{FC}$, Hz	
2-*exo*-fluoronorbornane	2-*exo*-C4	2.05	2.3	
	C6	18.73	9.8	
	C7	0.70	<1	
			A	B
2,2-difluoronorbornane	2-*exo*-C4	3.99	2.8[b]	1.2–3.2
	C6	14.52	5.8	3.4–8.1
	C7	−0.52	0[c]	0
	2-*endo*-C4	8.21	5.4[b]	3.2–5.6
	C6	7.94	5.8	3.4–6.8
	C7	19.48	4.9[c]	4.0–5.8

[a] A are the experimental values for 2,2-difluoronorbornane and B are the ranges of values for the nine methyl-substituted 2,2-difluoronorbornanes.[23] [b,c] Values interchangeable. [d] The norbornane skeleton was taken from crystallographic data[13] as described in the text.

Table VI. Bond-Angle and Bond-Length Dependence of the INDO MO Calculated Values of $^3J_{FC}{}^{trans}$, Fermi-Contact Term, in 1-Fluoropropane (Hz)

Bond-Angle Dependence

bond angle F1-C1-C2	$^3J_{F_1C_3}$	bond angle C1-C2-C3	$^3J_{F_1C_3}$
90	54.97	90	36.84
95	41.76	95	32.84
100	33.03	100	29.24
105	27.20	105	26.09
109.471	23.71	109.471	23.71
115	20.94	115	21.28
120	19.50	120	19.51

Bond-Length Dependence

bond length F1-C1, Å	$^3J_{F_1C_3}$	bond length C1-C2, Å	$^3J_{F_1C_3}$	bond length C2-C3, Å	$^3J_{F_1C_3}$
1.28	27.56	1.46	32.60	1.46	21.90
1.32	25.71	1.50	27.79	1.50	22.74
1.36	23.71	1.54	23.71	1.54	23.71
1.40	21.59	1.58	20.24	1.58	24.86
1.44	19.26	1.62	17.29	1.62	26.23

The predicted differences between the couplings to C6 are not apparent in the experimental data nor are the variations in the magnitude of the couplings particularly well predicted. At least part of the problem lies in the susceptibility of the calculations to bond angle strain as is seen in the results for the bond angle dependence of $^3J_{FC}{}^{trans}$ in 1-fluoropropane (Table VI). Such variations would explain the differences in the calculated value for $^3J_{FC6}$ in 2-*exo*-fluoronorbornane reported here and that calculated previously.[7] The unusually large value of $^3J_{FC}$ found for fluorocyclobutane of 19 Hz (dihedral angle 110–130°)[6] is consistent with this effect. The CCC and CCF bond angles[27] of ca. 89° and 106°, respectively, are predicted to substantially increase $^3J_{FC}$.[28]

A further possible source of error in the calculations lies in the use of standard bond lengths. Although the variations of $^3J_{FC}{}^{trans}$ in 1-fluoropropane are not large for the expected variation in bond lengths[29] of 0.05 Å (Table VI) they will lead to further scatter in the dihedral angle plot. The scarcity of experimental bond length data for the systems studied precludes any further investigation although these effects can be assumed to be smaller than those due to substituents.

Conclusion

INDO MO calculations have been useful in pinpointing the substantial variations in $^3J_{FC}$ caused by the number, type, and orientation of substituents which are sufficient to seriously hamper the use of this coupling in the derivation of conformational and configurational information. In particular small couplings require careful consideration before an interpretation in terms of the spatial relationship of the nuclei is attempted. In this context $^3J_{FC}$ displays the same intricacies of detail that are shown by other couplings involving carbon.

Supplementary Material Available: A figure of the correlation of the calculated $^3J_{CH}{}^{trans}$ (ref 3 and 7) with $^3J_{FC}{}^{trans}$ (ref 7 and this work) and a comparison of calculated $^3J_{FC}$ values for fluorine substitution in the 1-fluoropropane system with those of similar systems for $^3J_{CH}$ and $^3J_{CC}$ are given; a complete list of the INDO-FPT results for $^3J_{FC}$ in mono-, di-, tri-, tetra-, and pentamethyl-substituted 1-fluorocyclohexanes, 1-fluoropropane, 1,1-difluoropropane, 1,1,1-trifluoropropane, 1,2-difluoropropane, 1,2,2-trifluoropropane, 1,3-difluoropropane (two conformations), 1,3,3-trifluoropropane (two conformations), 1,3,3,3-tetrafluoropropane, fluoromethyl methyl ether and (fluoromethyl)methylamine (7 pages). Ordering information is given on any current masthead page.

Aspects of Artificial Photosynthesis. Photosensitized Electron Transfer across Bilayers, Charge Separation, and Hydrogen Production in Anionic Surfactant Vesicles

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Abstract: Photosensitized electron transfer from tris(2,2′-bipyridine)ruthenium cation, $Ru(bpy)_3{}^{2+}$, to methylviologen, MV^{2+}, has been investigated in the presence of negatively charged dihexadecyl phosphate, DHP, surfactant vesicles by steady state photolysis, fluorescence quenching, and nanosecond laser flash photolysis. Four different substrate–surfactant vesicle organizations have been used. In system I, $Ru(bpy)_3{}^{2+}$ was attached to the outer and MV^{2+} was placed onto the inner surfaces of DHP vesicles. In system II, MV^{2+} was attached to the outer and $Ru(bpy)_3{}^{2+}$ to the inner surfaces of DHP vesicles. In system III, both $Ru(bpy)_3{}^{2+}$ and MV^{2+} were localized on the outer surfaces of DHP vesicles. In system IV, both $Ru(bpy)_3{}^{2+}$ and MV^{2+} were localized on the inner surfaces of DHP vesicles. Extremely efficient electron transfers have been observed on the surfaces of surfactant vesicles in systems III and IV. Electron transfer from excited $Ru(bpy)_3{}^{2+}$ to MV^{2+} across the bilayers of vesicles in the presence of externally added EDTA in system I resulted in the formation of reduced methylviologen, $MV^{+}\cdot$, up to 75% conversion with a quantum efficiency of 2.40×10^{-2}. If additionally $\sim 10^{-5}$ M PtO_2 was entrapped in the interiors of DHP vesicles in system I, $MV^{+}\cdot$ promptly reformed with concomitant hydrogen evolution. Photolysis of this system leads to the net consumption of only EDTA at very low stoichiometric $Ru(bpy)_3{}^{2+}$, MV^{2+}, and PtO_2 concentrations. Dynamics of these processes have been determined and their relevance to photochemical solar energy conversions is discussed.

Photochemical energy conversion and storage are extremely active areas of current research.[1-8] Investigations are directed to catalytic sunlight initiated hydrogen production from water. One approach has involved mimicking photosynthesis in grossly simplified chemical systems.[7] Photosynthesis is brought about by the extremely efficient organization of appropriate molecules in the chloroplast.[9] Conceptually, photosynthesis involves four steps: energy deposition, charge separation, electron transfer, and utilization of suitable redox couples.

Completely synthetic surfactant vesicles have been found to be useful media for organizing sensitizers and electron donor-acceptor couples.[10] Sonic dispersal of long-chain dialkyldimethylammonium halides,[11-15] dialkyl phosphates,[16,17] sulfonates, and carboxylates[16] results in vesicle formation. Positively charged dioctadecyldimethylammonium chloride (DODAC) and anionic dihexadecylphosphate (DHP) vesicles have been characterized most extensively.[10] Well sonicated DODAC and DHP give fairly uniform single compartment prolate ellipsoid vesicles with (1–5) $\times$ 10^7 dalton molecular weights.[18] These surfactant vesicles have

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