and the fragment third from the end has its π MO raised about 0.0068 au (see Table V). One can also view the buildup of the polymer as $\mathrm{FH} \rightarrow \mathrm{FH} \cdots \mathrm{FH} \cdots$; in this type of approach (hydrogen first), all the MO's on the previously formed polymer decrease and eventually converge (Figure 4). In this case the "primary donor" decrease is about 0.0472, the "secondary donor" decrease 0.0151, and the "tertiary donor" 0.0067 au. For both of these viewpoints, the σ MO's display the same general trends.

Water Pentamer. A single calculation was carried out on water in a tetrahedral water environment. Figure 5 shows the population changes. The stabilization energy for the pentamer is 8.3 kcal/H bond, very slightly less than that found in the dimer using CNDO determined monomer geometries. A more complete geometry search is now underway, in which we hope to map out the potential which a water molecule feels in hexagonal ice and liquid water. The many comparisons of CNDO with *ab initio* and experimental data given in the first section of this paper show quite conclusively that the *forte* of the CNDO is in distinguishing most stable geometries within a single system, so we may expect our multi-molecule water results to be physically meaningful.

In conclusion we emphasize that the CNDO/2 is the best of the three semiempirical schemes (CNDO, NDDO, and extended Hückel) for studying hydrogen bond interactions. One has most confidence in the CNDO for studying different possible geometries involving the same molecules. However, one must be cautious in making intersystem comparisons or in attaching too much significance to the quantitative energy of dimerization found. The failure of the NDDO method to give physically meaningful results is somewhat disturbing and shows the not uncommon phenomenon that an increase in sophistication of the method (CNDO → NDDO) causes worse agreement with reality.

The studies of the HF polymer indicate some interesting features: (1) the band-like MO-energy trend, (2) the nonlinear energy increments (the energy gain in trimerization is more than that of dimerization), and (3) the prediction that the cyclic hexamer is the most stable HF polymer.

A beginning was made on the structure of liquid water and hexagonal ice through a calculation on $(\mathrm{H_2O})_5$.

Acknowledgments. The authors are grateful to Dr. Reiner Sustmann for providing the NDDO program used in these calculations, and appreciate helpful discussions with him and Dr. R. B. Davidson. The services made available to us by the Princeton University Computer Center (supported in part by National Science Foundation Grants GJ34 and GU3157) are very much appreciated. One of us (P. A. K.) thanks the National Science Foundation for fellowship support.

Combined Substituent and Angular Effects upon Vicinal Hydrogen–Fluorine Coupling Constants[1]

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Abstract: The nmr spectra from a series of fluoro-substituted bicyclo compounds reveal that vicinal H–F coupling constants are extremely sensitive to substituent electronegativity with $^3J_{\mathrm{HF}}$ *trans* exhibiting a 40-fold change. The magnitude of the substituent effect varies with dihedral angle (ϕ) and is largest for $\phi = 0$ and 180°. Limited data indicate that $^3J_{\mathrm{HF}}$ may be estimated from Karplus-type expressions of the form $A \cos^2 \phi, 0° \leq \phi \leq 90°$; $B \cos^2 \phi, 90° \leq \phi \leq 180°$ where A and B are inversely proportional to the sum of the substituent electronegativities. Substituent effects on vicinal H–H coupling constants are also compared.

Recent empirical evidence confirms that the guidelines outlined in the Karplus equation[2–4] for estimating vicinal H–H coupling constants apply equally well for vicinal H–F coupling constants.[5–8] Parameters affecting ^3J are (1) dihedral angle, (2) bond length, (3) bond angle, and (4) electronegativity of neighboring groups. Recently Williamson, *et al.*, elucidated the angular dependence of $^3J_{\mathrm{HF}}$ in a series of rigid molecules having groups of similar electronegativity.[6,9] Their data demonstrated that a 12° increase in the C–C–H and C–C–F bond angles at a constant dihedral angle ($\phi = 0°$) causes $^3J_{\mathrm{HF}}$ to vary from 30.8 to 0.9 Hz. Furthermore at a constant bond angle θ, $^3J_{\mathrm{HF}}$ is related to the dihedral angle ϕ by the following expression.

$$^3J_{\mathrm{HF}} = \begin{array}{ll} 31 \cos^2 \phi & 0° \leq \phi \leq 90° \\ 44 \cos^2 \alpha & 90° \leq \phi \leq 180° \end{array} \qquad (1)$$

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[1] Presented in part at the 7th International Meeting of the Society for Applied Spectroscopy, Chicago, Ill., Sept 1967.

[2] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[3] M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

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[5] R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, **11**, 271 (1966).

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

[7] J. Lambert and J. D. Roberts, *ibid.*, **87**, 3891 (1965).

[8] F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964).

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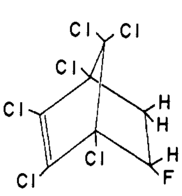
Investigating a series of polysubstituted alkanes, Abraham and Cavalli observed that both $^{3}J_{\mathrm{HH}}$ and $^{3}J_{\mathrm{HF}}$ vary linearly with substituent electronegativity.[10] Vicinal H–F coupling constants are approximately four times more sensitive to substituents effects than are vicinal H–H couplings. Both $^{3}J_{\mathrm{HH}}$ and $^{3}J_{\mathrm{HF}}$ decrease linearly with electronegativity in accordance with $^{3}J_{\mathrm{HH}} = 18.0 - 0.80\Sigma E$ and $^{3}J_{\mathrm{HF}} = 53.0 - 3.38\Sigma E$, where ΣE is the sum of the electronegativities of all substituents bonded to the carbons possessing the coupled nuclei.

Direct and indirect methods have provided values for *J gauche* (60°) and *J trans* (180°), but these procedures have inherent difficulties. Direct determination of *J gauche* and *J trans* at low temperatures is limited to those compounds whose rotational barriers are greater than 10 kcal mole^{-1}. Measuring *J trans* and *J gauche* indirectly, using different solvents,[10] or evaluating ΔJ at various temperatures,[11,12] may lead to considerable systematic errors due to changes in $^{3}J_{\mathrm{HF}}$ which are independent of the rotational distributions.[13] These problems make the use of rigid molecules the more desirable approach.

To determine the extent of the substituent effect, under conditions which minimize the angular dependence, a series of rigid Diels–Alder adducts of hexachlorocyclopentadiene and various fluorethylenes were synthesized. The meager temperature change for $^{3}J_{\mathrm{HF}}$ confirms that these bicyclo compounds are extremely rigid.[14] Electron diffraction studies on similar systems have shown that the C–C–H bond angles are a little more than 113°.[15] The dihedral angles should be 0 and 120° and remain fixed as the fluorine substitution is varied.



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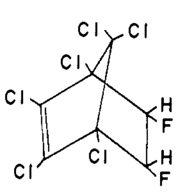

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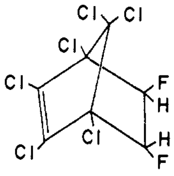

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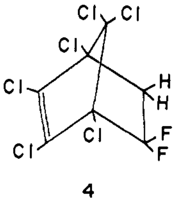

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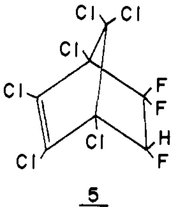

5

Compounds **1–5** are assumed to form the *endo* adducts in accordance with the rules of Alder and Stein.[16] With the exception of the trifluoroethylene adduct **5**, all proton spectra were analyzed using LAOC'N III with root mean square (rms) errors less than 0.05 Hz.[17] The proton chemical shifts and the six coupling constants of the vinyl fluoride adduct **1** are in excellent agreement with the values reported by Williamson, *et al.*[6,9] Analysis of the AA'XX' spectrum of the *cis*-1,2-difluoroethylene adduct **2** is straightforward, with the assumption that $J_{\mathrm{HH}} \leq J_{\mathrm{FF}}$, and J_{HF} *trans* ($\phi = 120°$) $\leq J_{\mathrm{HF}}$ *cis* ($\phi = 0°$).[18] The nmr spectra of the *trans*-1,2-difluoroethylene adduct **3** is completely first order since J_{HH} and J_{FF} are less than 0.5 Hz, while δ_{H} and δ_{F} are ~1.0 and ~7.0 ppm, respectively. The *endo* proton was assigned to the upfield resonance as predicted from the substantial investigations of the [2.2.1]-2-heptene systems.[19,20] The coupling pattern in the fluorine spectra permitted an unambiguous assignment of the upfield fluorine resonance to the *endo* fluorine. The adduct of 1,1-difluoroethylene **4** is a tightly coupled spectrum requiring a computer analysis of both the proton and fluorine spectra. Reasonable values for $^{2}J_{\mathrm{HH}}$, $^{3}J_{\mathrm{HF}}$, and $^{2}J_{\mathrm{FF}}$ were obtained. The only discrepancy is that the best computer fit (rms error = 0.05 Hz) assigns the upfield fluorine to the *exo* position. Both the proton and fluorine spectra of the trifluoroethylene adduct **5** were examined. The methine fluorine was ~105 ppm upfield from the methylene fluorines. The coupling pattern from the proton spectrum indicates that the *endo* fluorine is upfield from the *exo* fluorine. Although the spectrum of the methylene fluorines is slightly perturbed, the proton spectrum appeared to be first order and was analyzed as such.

Results and Discussion

The chemical shifts and H–H, H–F, and F–F coupling constants for compounds **1–5** are presented in Tables I and II. Examination of the data reveals a large substituent effect, for both $^{3}J_{\mathrm{HF}}$ *cis* and *trans*, as exemplified by the 40-fold reduction for $^{3}J_{\mathrm{HF}}$ *trans* from 12.01 Hz in the vinyl fluoride adduct to 0.31 Hz in the trifluoroethylene adduct. Similar substituent effects have been reported for a series of fluoro-substituted acenaphthalenes[21] whose C–C–H and C–C–F bond angles are similar to those of the Diels–Alder adducts.[22] The two vicinal H–F coupling constants decrease linearly with electronegativity, as illustrated in Figure 1 in a plot of $^{3}J_{\mathrm{HF}}$ *vs.* the sum of the substituent electronegativities. The substituent effect is dependent upon the dihedral angle ϕ as illustrated in the two equations $^{3}J_{\mathrm{HF}}$ *cis* $= 53.11 - 3.311\Sigma E$ (std dev, 2.44) and $^{3}J_{\mathrm{HF}}$ *trans* $= 34.5 - 2.65\Sigma E$ (std dev, 1.83) for the lines in Figure 1.[23] The first equation is very similar to that obtained by Abra-

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

(11) S. L. Manatt and D. D. Elleman, *J. Amer. Chem. Soc.*, **84**, 1305 (1962).

(12) R. A. Neward and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965).

(13) S. L. Smith and A. M. Ihrig, *ibid.*, **46**, 1181 (1967).

(14) Temperature changes for J_{HF} were less than 0.30 Hz/100° and paralleled the changes in the bulk dielectric constant. See R. C. Hopkins, *J. Mol. Spectrosc.*, **27**, 494 (1968), for an account of the temperature effects on J_{HF} in a series of cyclobutanes.

(15) J. H. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

(16) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

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(18) H. M. McConnell, A. D. McLean, and C. A. Reilly, *ibid.*, **23**, 1152 (1955).

(19) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1963).

(20) J. I. Musher, *Mol. Phys.*, **6**, 94 (1963).

(21) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).

(22) H. W. W. Ehrlich, *Acta Cryst.*, **10**, 699 (1957).

(23) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); B. P. Dailey and J. M. Shoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955).

Table I. H–H and H–F Coupling Constants for Diels–Alder Adducts of Hexachlorocyclopentadiene and Various Fluoroethylenes[a]

Addend	J_{HH} *gem*	J_{HH} *cis*	J_{HH} *trans*	J_{HF} *gem* *endo* H	J_{HF} *gem* *exo* H	J_{HF} *cis* *endo* H	J_{HF} *cis* *exo* H	J_{HF} *trans* *endo* H	J_{HF} *trans* *exo* H
Vinyl fluoride	13.41	7.22	1.85		54.31	25.10			12.01
cis-1,2-Difluoroethylene		6.01			52.10				1.87
trans-1,2-Difluoroethylene			1.03	52.06	51.73	17.71	13.85		
1,1-Difluoroethylene	13.54					15.86	13.07	4.46	7.36
Trifluoroethylene			0.35		51.72		9.13		0.31

[a] All values for solute in carbon tetrachloride.

Table II. Chemical Shifts and F–F Coupling Constants for Diels–Alder Adducts of Hexachlorocyclopentadiene and Various Fluoroethylenes[a]

	J_{FF} *gem*	J_{FF} *cis*	J_{FF} *trans*	δ *endo*	δ *exo*
Vinyl fluoride				$+181,^c -2.20^b$	$-5.37,^b -2.94^b$
cis-1,2-Difluoroethylene		16.1		$215,^c 215^c$	$-5.37,^b -5.37^b$
trans-1,2-Difluoroethylene			0.30	$-4.62,^b +202^c$	$-5.47,^b +95^c$
1,1-Difluoroethylene	221.6			$-2.64,^b +96^c$	$-3.00,^b +95^c$
Trifluoroethylene	230	4.57	0.30	$100,^c 214^c$	$-5.24,^b 114^c$

[a] All values for solute in carbon tetrachloride. [b] Parts per million downfield from TMS. [c] Parts per million upfield from $CFCl_3$.

ham and Cavalli.[10] Slopes for these expressions indicate $^3J_{HF}$ *cis* ($\phi = 0°$) to be more sensitive to changes in electronegativity than $^3J_{HF}$ *trans* ($\phi = 120°$). These results, in conjunction with those for the fluoro substituted alkanes,[5] demonstrate that the magnitude of the substituent effect differs for each dihedral angle. The substitution pattern undoubtedly can alter the substituent effect.[24,25] For example, the low value for $^3J_{HF}$ of the *cis*-1,2-difluoroethylene adduct compared to the 1,1-difluoroethylene adduct might be attributed to the fact that vicinal fluorine substitution has a larger influence on *J trans* than geminal substitution. A recent report on a series of fluoro-substituted polysaccharides points out the strong stereo dependence of H–F coupling constants, since $J_{F_aH_e}$ = 1.0–1.5 and $J_{F_eH_a}$ = 7.5–9.6 Hz.[25]

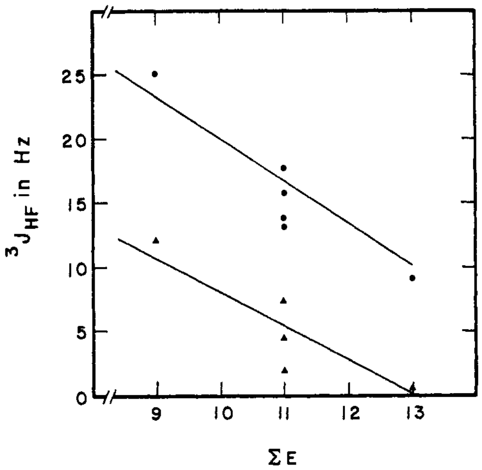

Figure 1. Plot of *cis* (●) and *trans* (▲) $^3J_{HF}$ *vs.* ΣE of the noncoupled substituents on the carbons possessing the coupled nuclei (H = 2.0, F = 4.0, $-C(C_2)Cl$ = 2.5).

A systematic investigation of the substituent and angular effects over a large range of θ, ϕ, and electronegativities (E) is greatly hampered by the limited number of molecules possessing the proper geometries. Even the small difference between the normal tetrahedral bond angle of 108° and the 113° for the C–C–H and C–C–F bond angles in the Diels–Alder adducts[15] is sufficient to permit only qualitative comparisons between the two systems. Having shown that the magnitude of the substituent effect depends upon the dihedral angle ϕ, an interesting possibility is to vary ϕ at a constant electronegativity. The vicinal coupling constants of 1-chloro-2-fluoroethane,[5] along with those of the vinyl fluoride adduct **1**, yield values for $^3J_{HF}$ at 0, 60, 120, and 180° when ΣE = 9.25 and 9.0, respectively. Average values for $^3J_{HF}$ calculated from the 1,1-difluoroethylene and *trans*-1,2-difluoroethylene adducts plus $^3J_{HF}$ *gauche* and *trans* of 1,1-difluorocyclohexane[26] form a second series of H–F coupling constants at various dihedral angles with ΣE = 11.0 and 10.9, respectively. Likewise, vicinal coupling constants from 1,1,2,2-tetrachlorofluoroethane[27] and the trifluoroethylene adduct **5** provide a third set of J's where ΣE = 13.0. These results are illustrated in Figure 2 for a plot of J *vs.* the dihedral angle (ϕ) for ΣE = 9, 11, and 13.0. Expressions for the lines drawn in Figure 2 can be written in a modified form of the Karplus expression as exemplified in eq 1.[28] With the

$$\Sigma E \sim 9 \quad {}^3J_{HF} = \begin{matrix} 24\cos^2\phi & 0 \le \phi \le 90° \\ 52\cos^2\phi & 90 \le \phi \le 180° \end{matrix} \qquad (2)$$

$$\Sigma E \sim 11 \quad {}^3J_{HF} = \begin{matrix} 15\cos^2\phi & 0 \le \phi \le 90° \\ 32\cos^2\phi & 90 \le \phi \le 180° \end{matrix} \qquad (3)$$

$$\Sigma E \sim 13 \quad {}^3J_{HF} = \begin{matrix} 8\cos^2\phi & 0 \le \phi \le 90° \\ 16\cos^2\phi & 90 \le \phi \le 180° \end{matrix} \qquad (4)$$

exception of the point for $^3J_{HF}$ *gauche* for 1,1-difluoro-

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(24) H. Booth, *Tetrahedron Lett.*, 7, 411 (1965).

(25) L. H. Hall, J. F. Manville, and N. S. Bhacca, *Can. J. Chem.*, 47, 1 (1969).

(26) H. S. Gutowsky, *J. Chem. Phys.*, 42, 3396 (1965).

(27) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *ibid.*, 36, 3353 (1962).

(28) The originally derived theoretical expression of the Karplus equation for $^3J_{HH}$ is $8.5\cos^2\phi - 0.28$, $0° < \phi < 90°$; $9.5\cos^2\phi - 0.28$, $90° < \phi < 180°$. Several modified forms are $J = 4.22 - 0.5\cos\phi + 4.5\cos 2\phi^4$ and $10\cos^2\phi$, $0° < \phi < 90°$; $16\cos^2\phi$, $90° < \phi < 180°$: K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, 83, 4623 (1961). The latter expression is the form that Williamson suggests for vicinal H–F coupling constants.[6]

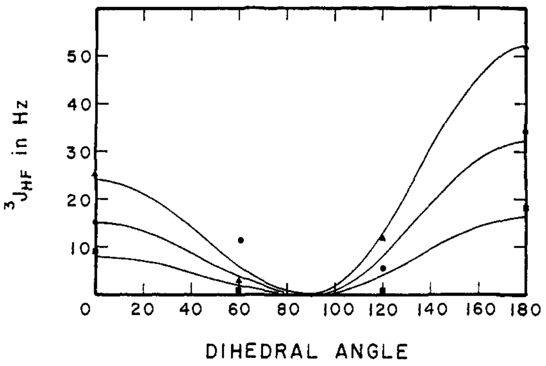

Figure 2. Plot of $^3J_{HF}$ *vs.* $\cos^2 \phi$ for values of ΣE = 9.0, 11.0, and 13.0.

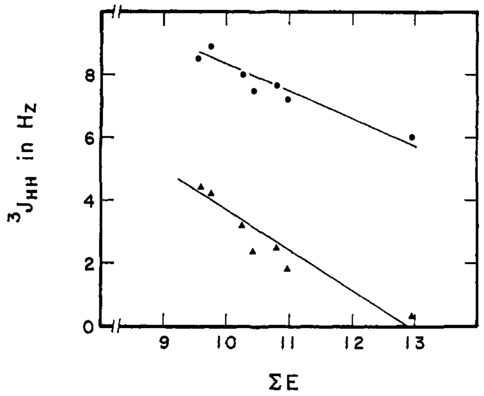

Figure 3. Plot of *cis* (●) and *trans* (▲) $^3J_{HH}$ *vs.* ΣE of the noncoupled substituents on the carbons possessing the coupled nuclei. $^3J_{HH}$ *cis* = $-0.88\Sigma E + 17.174$, $\sigma = 0.355$; $^3J_{HH}$ *trans* = $-1.25\Sigma E + 16.132$, $\sigma = 0.419$.

cyclohexane, the entire series of compounds follows roughly eq 2–4. The anomalous result for 1,1-difluorocyclohexane may well arise from a difference in the bond angle θ. Two factors are apparent. First, the dihedral angle dependence of $^3J_{HF}$ may be expressed by a family of curves of the form

$$^3J_{HF} = \begin{matrix} A \cos^2 \phi & 0° \leq \phi \leq 90° \\ B \cos^2 \phi & 90° \leq \phi \leq 180° \end{matrix}$$

where $B \approx 2A$. Second, the value of the coefficient varies inversely with the sum of the electronegativities of the substituents bonded to the carbons of the coupling path. The limited results considered here give the empirical relationship

$$A = \frac{2 \times 10^4}{(\Sigma E)^3}$$

In an investigation of the Diels–Alder adducts of hexachlorocyclopentadiene and various vinyl compounds, Williamson, *et al.*,[29] have shown that over a limited electronegativity range (ΣE = 9.49 to 10.80), $^3J_{HH}$ varied linearly with ΣE. Using the data for the *cis*- and *trans*-1,2-difluoroethylene adducts, it is possible to drastically extend the previous correlation to ΣE = 12.94. Despite the dramatic increase in ΣE, both $^3J_{HH}$ *cis* and *trans* remain linear with ΣE as illustrated in Figure 3 for a plot of $^3J_{HH}$ *vs.* ΣE. The slopes of the lines in Figures 1 and 3 confirm again that vicinal H–H coupling constants are $\sim^1/_3$ as sensitive to electronegative groups as their vicinal H–F counterparts.

Conclusions

For most systems $^3J_{HH}$ and $^3J_{HF}$ can be considered as functions of the bond angle θ, dihedral angle ϕ, and electronegativity E. This study has shown that at a constant θ and ϕ, $^3J_{HH}$ and $^3J_{HF}$ vary with ΣE. Furthermore, the magnitude of the substituent effect is largest when ϕ = 0 and 180°.[30] At a constant θ, plots of J *vs.* ϕ yield a family of curves with each curve corresponding to a different ΣE. A probable reason for the proliferation of expressions between ϕ and J[28] is the fact that the various empirical forms of the Karplus equation did not consider the electronegativity of neighboring groups. The stereo dependence of $^3J_{HF}$ as exemplified by the large differences between $J_{\mathrm{H_aF_e}}$ and $J_{\mathrm{H_eF_a}}$ in a series of fluoro-substituted polysaccharides[25] remains unexplained. The determination of a relation between J and θ may be difficult, since changes among the C–C–H and C–C–F bond angles may effect J_{HF} differently. Hopefully, further study will be successful in deriving a more quantitative expression for predicting vicinal HF coupling constants.

Experimental Section

Proton and fluorine spectra were obtained on a Varian HA-60-IL. In addition, the spectra of 5,5-difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (**4**) were run at 100 and 94.1 MHz. Samples were prepared as 5 mol % solutions in carbon tetrachloride containing 3% tetramethylsilane. For fluorine work, samples were prepared as 5% solutions with 5% trichlorofluoromethane or 1,1,-2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane serving as an internal reference. The proton spectra were calibrated in the frequency sweep mode with the final line positions representing the average of at least five independent scans.

The fluoroethylenes were purchased from the Pierce Chemical Company, Rockford, Ill. Nmr spectra indicated that all samples were free of impurities with the exception of 1,2-difluoroethylene which was a mixture of the *cis* and *trans* isomers. Sufficient quantities of *trans*-1,2-difluoroethylene were prepared by the iodine-catalyzed isomerization of Craig and Entemann.[31] A careful bulb distillation, aided by Dry Ice-acetone baths, afforded pure samples of *trans*-1,2-difluoroethylene. Infrared spectra were recorded on a Beckman IR-8. Melting points were determined on a Fisher–Jones melting point apparatus. Elemental analyses were performed by Daryl Sharp, University of Kentucky, Lexington, Ky.

Initially the preparation of all five Diels–Alder adducts was similar. A general procedure for preparing these compounds is to add 0.02 mol of liquified olefin to an evacuated Carrius tube containing 10 ml (0.06 mol) of hexachlorocyclopentadiene. The tube is sealed off under vacuum and allowed to react at 200 to 220°. Length of the reaction period depended upon the dienophile. Dienophiles that form adducts in the *exo* positions react much slower than those that give products with fluorine exclusively in the *endo* position. Reaction periods of 3 to 4 days were sufficient to form the adducts of *cis*-1,2-difluoroethylene and vinyl fluoride, while the adducts of 1,1-difluoroethylene, *trans*-1,2-difluoroethylene, and trifluoroethylene required 2 to 3 weeks.

Column chromatography using activated alumina and Skelly solvent A as the eluate readily separated the adduct from the excess cyclopentadiene. Several sublimations at reducted pressure removed the residual traces of organic solvents.

5-*endo*-Fluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (1). The vinyl fluoride–hexachlorocyclopentadiene adduct was formed in 57.8% yield (based on fluoroethylene) and melted at 117–118° (lit.[6] mp 70–71°). The fluorine nmr spectrum consisted of an octet centered ~181 ppm upfield from trichlorofluoromethane. Infrared

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[29] K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963).

[30] It should be noted that on a fractional basis both the HH and HF coupling constants discussed here show approximately the same dependence on ΣE, *i.e.*, $J = J_0(1 - c\Sigma)$, where c is approximately 0.077 for *trans* HH and HF couplings, 0.05 for *cis* HH couplings, and 0.06 for *cis* HF couplings.

[31] N. Craig and E. Entemann, *ibid.*, **83**, 3047 (1961).

absorption bands (KBr pellet): 3450 (w), 2980 (w), 1608 (m), 1140 (m), 1350 (m), 1282 (m), 1265 (m), 1210 (m), 1180 (s), 1100 (s), 1050 (s), 990 (s), 910 (s), 860 (w), 830 (m), 775 (m), 705 (m), 645 (m), and 620 (w) cm^{-1}.

Anal. Calcd for $C_7H_3Cl_6F$: C, 26.35; H, 0.94. Found: C, 26.63; H, 0.91.

5,6-*endo,endo*-Difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (2). The *cis*-1,2-difluoroethylene–hexachlorocyclopentadiene adduct was formed in 65.6% yield, mp 157–158°. The fluorine spectrum is a typical AA'XX' multiplet centered at ~210 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3400 (m), 2990 (w), 1605 (s), 1355 (m), 1292 (m), 1258 (w), 1185 (s), 1160 (s), 1050 (s), 1015 (s), 915 (s), 888 (m), 825 (s), 730 (s), 698 (m), and 670 (s) cm^{-1}.

Anal. Calcd for $C_7H_2Cl_6F_2$: C, 24.94; H, 0.59. Found: C, 24.99; H, 0.59.

***endo,exo*-5,6-Difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (3).** The *trans*-1,2-difluoroethylene–hexachlorocyclopentadiene adduct was formed in 10.8% yield, mp 95–96°. Extensive *cis–trans* isomerization of the olefin occurred during the reaction since the adduct of the *cis*-1,2-difluoroethylene isomer was isolated in 83% yield. Careful chromatography using alumina and Skelly solvent A separated the isomeric adducts. Then fluorine nmr spectrum consisted of two octets centered at ~195 and ~202 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3340 (w), 3000 (3), 1615 (s), 1380 (m), 1350 (w), 1275 (s), 1185 (s), 1165 (w), 1130 (s), 1115 (s), 1065 (s), 1015 (m), 930 (s), 865 (m), 800 (s), 760 (w), 720 (s), and 650 (m) cm^{-1}.

Anal. Calcd for $C_7H_2Cl_6F_2$: C, 24.94; H, 0.59. Found: C, 24.50; H, 0.57.

5,5-Difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (4). The 1,1-difluoroethylene–hexachlorocyclopentadiene adduct was formed in 33.7% yield, mp 104–105°. The fluorine nmr spectrum was an intense octet with a pair of very weak wing quartets separated by ~200 Hz. The fluorine chemical shifts are 13.1 and 14.2 ppm upfield from 1,1,2,2-tetrafluoro-3,3,4,4-tetrachlorocyclobutane or ~95 and 96 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3450 (m), 1610 (s), 1438 (m), 1300 (s), 1240 (s), 1195 (s), 1125 (m), 1092 (m), 1075 (s), 1045 (s), 950 (s), 930 (m), 920 (m), 870 (w), 830 (s), 722 (s), 700 (s), 660 (w), and 622 (w) cm^{-1}.

Anal. Calcd for $C_7H_2Cl_6F_2$: C, 24.94; H, 0.59. Found: C, 24.94; H, 0.56.

***endo*-5,6,6-Trifluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (5).** The trifluoroethylene–hexachlorocyclopentadiene adduct was formed in 25.1% yield, mp 145–146°. The fluorine nmr spectrum contains three octets occurring at ~102, 114, and 214 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3440 (s), 2990 (w), 1608 (s), 1360 (m), 1290 (s), 1230 (s), 1185 (s), 1160 (s), 1140 (m), 1070 (s), 920 (s), 827 (m), 765 (s), 712 (s), 695 (s), and 630 (w) cm^{-1}.

Anal. Calcd for $C_7HCl_6F_3$: C, 23.61; H, 0.28. Found: C, 23.31; H, 0.27.

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The Electrochemiluminescence of Anthracene and 9,10-Dimethylanthracene. The Role of Direct Excimer Formation[1a]

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Abstract: Electrochemiluminescence (ecl) spectra have been obtained for anthracene and 9,10-dimethylanthracene (DMA) using an image intensifier spectrograph and single pulse excitation. Rapid decomposition of the anthracene cation during ecl production leads to formation of products (9-anthranol and 9,10-dihydroxyanthracene) which emit at longer wavelengths than anthracene. The long wavelength component of anthracene ecl, previously assigned to an anthracene excimer, is shown to arise from energy transfer or from a mixed annihilation reaction involving cation decomposition products. The ecl of DMA contains less "excimer" component than previously reported. Substitution at the 9 and 10 positions of anthracene protects the cation radical and prevents decomposition product participation in the ecl process. The small amount of long wavelength component observed for DMA may result from directly formed excimers or those formed by triplet–triplet annihilation.

The nature of the excited states formed during the electrochemiluminescence (ecl) of aromatic hydrocarbons has received considerable attention in recent years. One of the more controversial proposals has been direct formation of an excimer by the ecl annihilation reaction.

$$R^+ + R^- \longrightarrow R_2^* \longrightarrow 2R + h\nu_{ex}$$

Excimer formation was proposed to explain ecl emission observed at longer wavelengths than normal hydrocarbon fluorescence.[2]

Chandross, *et al.*, concluded that excimer formation during ecl is more efficient than excimer formation *via* photoexcitation.[2] It was suggested that a "charge-transfer" type excimer, isomeric to the normal photoexcited excimer, could be formed during ecl. If the charge-transfer excimer were capable of more efficient fluorescent emission than the photoexcited one, the discrepancy in the ecl and hydrocarbon fluorescence could be understood.[2]

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