

Spectral data showed ν_{\max} 3400, 3370, 1360, 1310, 1257, 1250, 1135, 1090, 1055, 1020, 817, 801, 735, 701 cm^{-1} ; ^1H nmr at 100 Mc in acetone- d_6 , 2.68 (s), 3.59 (m), 6.87, 7.02–7.50 (m), 7.80 ppm (q); ^{19}F nmr at 94.1 Mc in acetone- d_6 , 4486.6 (q), 5589.2 cps (q), $J_{\text{F-F}} = 166.6 \pm 2$ cps.

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Dihedral Angle and Bond Angle Dependence of Vicinal Proton–Fluorine Spin–Spin Coupling¹

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Abstract: From an analysis of the nmr spectra of compounds of fixed and known stereochemistry the vicinal proton–fluorine coupling constant has been found to be a function of dihedral angle; the dependence is like vicinal J_{HH} —a maximum at 0° (ca. 31 Hz), a minimum at 90° (ca. 0 Hz), and a maximum at 180° (ca. 44 Hz)—and *not* a linear dependence as has been reported. $J_{\text{HF-vic}}$ is extremely dependent on bond angle, being ca. 31 Hz for a bond angle near 109° and dropping to 0.9 Hz for a bond angle near 118° (dihedral angle fixed at 0°). Evidence is presented for a bond length dependence of $J_{\text{HF-vic}}$.

The dihedral angle dependence of vicinal proton–proton coupling constants has proved of immense value in structural studies of organic molecules. The purpose of the present work was to determine if a similar relationship exists for proton–fluorine coupling constants. It has been widely assumed that $J_{\text{HF-vic}}$ depends on the dihedral angle between the coupling nuclei in the same way that $J_{\text{HH'-vic}}$ does,³ *i.e.*, that $J_{\text{HF-vic}}$ should have a maximum value when the dihedral angle, ϕ , between H and F is 0 and 180° and a minimum value when the dihedral angle is 90° . However, White⁴ has reported that J_{HF} is a *linear* function of dihedral angle, being 5.8, 11.4, 14.6, and 17.8 Hz for 0 , 60 , 90 , and 120° , respectively.

Karplus,⁵ utilizing a nonionic six-electron, six-orbital fragment in a valence bond σ -electron calculation, predicted that the vicinal coupling constant in the fragment H-C-C'-H' should be a function of (1) the electronegativity of substituents on the system, (2) bond length, (3) bond angle, and (4) the dihedral angle between the coupling protons. In order to see if a similar relationship holds for H–F coupling, it is necessary to try to hold three of these variables constant while examining the fourth.

(1) Presented at the 2nd International Symposium on Nuclear Magnetic Resonance, Sao Paulo, Brazil, July 1968. See K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Am. Chem. Soc.*, **88**, 5678 (1966), for a preliminary report on a portion of this work.

(2) (a) From the M.A. thesis of Y.-F. Li Hsu. (b) National Science Foundation Undergraduate Research Participant.

(3) (a) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 39 (1961); (b) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.* **36**, 3353 (1962); (c) J. B. Stothers, J. D. Talman, and R. R. Fraser, *Can. J. Chem.*, **42**, 1530 (1964); (d) F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964); (e) M. Takahashi, D. R. Davis, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2935 (1962); (f) J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3981 (1965).

(4) H. F. White, *Anal. Chem.*, **37**, 403 (1965).

(5) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963); M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

In the present work, in order to focus our attention on the *dihedral angle* dependence of J_{HF} , we have attempted to minimize substituent effects in the compounds we have synthesized. Similarly, to determine the effect of *bond angle* on the vicinal proton–fluorine coupling constant we have examined compounds with dihedral angles constrained to 0° in which the H–C–C and C–C–F bond angles change by virtue of changes in the sizes of the rings in which the H–C–C–F system appears, again attempting in so far as possible to minimize the effect of substituents.

Naturally a large number of vicinal H–F coupling constants have been reported in the past few years but it has proved difficult to ascertain the dihedral angle dependence from these data because the molecules are conformationally flexible. Many of the studies have been made on highly halogenated alkanes in which rotation about the carbon–carbon bond can occur or on fluorinated cyclohexanes and cyclobutanes in which inversion of the ring system can occur. At sufficiently low temperature, ring inversion and rotation can be stopped, but exact values of J_{HF} are often not obtained because of the tendency of fluorine to couple with all protons within four or five chemical bonds, giving poorly resolved spectra. Even when this problem is overcome, one obtains values for J_{HF} at only two dihedral angles, 60 and 180° .

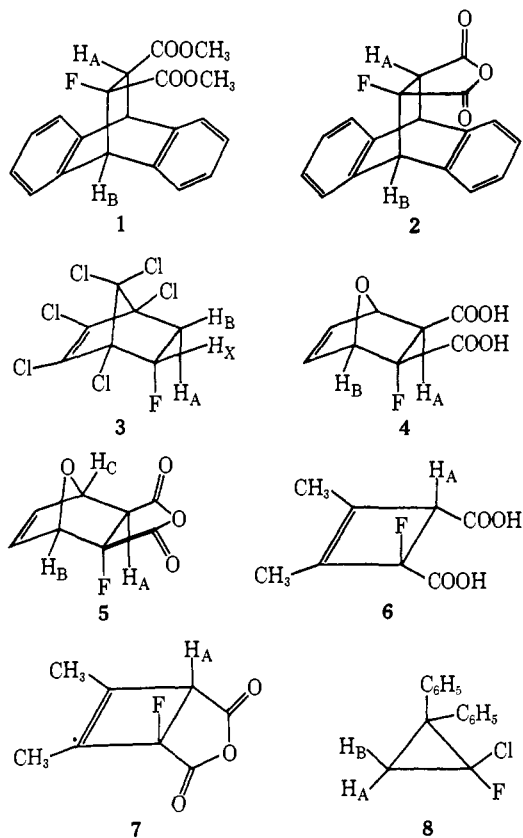
To obviate these difficulties, we have examined vicinal proton–fluorine coupling in bicyclic compounds where the dihedral angle is fixed and known. Since we can anticipate a large substituent effect on J_{HF} , as has been observed for J_{HH} ,⁶ we have, where possible, kept the substituents the same by preparing derivatives of fluoromaleic acid. In the compounds chosen for synthesis we have also attempted to keep the number of

(6) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

nearby protons small in order to obtain well-resolved, completely analyzable spectra. We have synthesized compounds having H-C-C-F dihedral angles of 0, 80, and 120°; values of J_{HF} at dihedral angles of 60 and 180° are available from various literature sources. Since the ring systems chosen to give certain dihedral angles also produce bond angle changes in the H-C-C-F system, we have studied the effect of bond angle change on vicinal J_{HF} when the dihedral angle is held at 0°.

Synthesis

We synthesized compounds 1-8 for this study (see Chart I). Compound 2 was prepared in 56% yield by Chart I



the Diels-Alder reaction of fluoromaleic anhydride⁷ with anthracene. It was assumed that fluoromaleic anhydride would add to the center ring of anthracene as has been found for maleic anhydride,⁸ chloro,⁹ bromo,¹⁰ and difluoromaleic⁷ anhydride, an assumption borne out by the physical properties of the product (see Experimental Section). Compound 1, mp 159-160°, was prepared in 36% yield by saturating a suspension of 2 in methanol with hydrogen chloride.

Compound 3, mp 70-71°, was prepared by the Diels-Alder reaction of vinyl fluoride with hexachlorocyclopentadiene. The fluorine atom is assumed to be in the *endo* configuration in accord with Alder's rules.¹¹ The three proton-proton coupling constants and the

(7) M. S. Raasch, R. E. Misgel, and J. E. Castle, *J. Am. Chem. Soc.*, **81**, 2678 (1959).

(8) (a) O. Diels and K. Alder, *Ann.*, **486**, 191 (1931); (b) E. Clar, *Ber.*, **64**, 2194 (1931).

(9) M. E. Synerholm, *J. Am. Chem. Soc.*, **67**, 1229 (1945).

(10) (a) W. E. Buchmann and L. B. Scott, *ibid.*, **70**, 1458 (1948); (b) W. R. Vaughan and K. S. Andersen, *J. Org. Chem.*, **21**, 673 (1956).

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

internal chemical shifts, $\delta_X - \delta_A$ and $\delta_X - \delta_B$, are in excellent agreement with those expected from our previous work on 5-*endo*-substituted hexachlorobicyclo[2.2.1]-heptanes⁶ (see Experimental Section).

Compound 5 was prepared in 92% yield by the thermodynamically controlled Diels-Alder reaction of furan with fluoromaleic anhydride. Woodward and Baer¹² showed that while the reaction of furan and maleic anhydride gives the *exo* adduct, the addition of maleic acid to furan gives the *endo* adduct. Compound 5 showed no coupling between H_A and H_C which have, from Dreiding models, a dihedral angle of 80°, thus indicating the *exo* configuration for the anhydride. This is in accord with the work of Anet¹³ who prepared both the *exo*- and *endo*-maleic anhydride adducts of furan and also examined the nmr spectra in detail. Hydrolysis of 5 gave 4, mp 141-142°.

Compound 7 was prepared by the photochemical condensation of fluoromaleic anhydride and 2-butyne in 41% yield using benzophenone as a photosensitizer. Similar reactions of maleic anhydride and maleimide with various acetylenes have been reported recently,¹⁴⁻¹⁸ all photosensitized by benzophenone. Compound 6 was prepared by hydrolysis of 7 in the nmr tube.

Compound 8 was prepared by the addition of fluoro-chlorocarbene to 1,1-diphenylethylene. Fluoro-chlorocarbene was generated by the action of potassium *t*-butoxide on *sym*-tetrachlorodifluoroacetone according to the procedure of Farah and Horensky.¹⁹ The physical and chemical properties are in accord with the cyclopropane structure and also with the recent report of Weyerstahl, *et al.*,²⁰ who prepared the compound by another method.

Results and Discussion

The coupling constants for compounds 1-8 are given in Table I. Two conclusions are immediately apparent

Table I. Vicinal Proton-Fluorine Coupling Constants^a

Compd	Approximate dihedral angles				
	0° (J_{AF})	60° (J_{BF})	80° (J_{BF})	120° (J_{BF})	132° (J_{BF})
1	30.8	3.8			
2	22.5	6.0			
3	24.7			12.2	
4	19.8		2.0		
5	10.55		2.3		
6	6.25				
7	0.9				
8	+17.7				+6.3

^a In hertz.

from these limited data: J_{HF-vic} is *not* a linear function of dihedral angle as previously reported⁴ and J_{HF-vic}

(12) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948).

(13) F. A. L. Anet, *Tetrahedron Letters*, 1219 (1962).

(14) R. Criegee, V. Zirngible, H. Furrer, D. Seebach, and G. Freund, *Ber.*, **97**, 2949 (1964).

(15) J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 597 (1963).

(16) G. O. Schenck, W. Hartmann, S. P. Mannesfeld, W. Mitzner, and C. H. Krauch, *Ber.*, **95**, 1642 (1962).

(17) H. D. Scharf and F. Korte, *ibid.*, **98**, 764 (1965); **98**, 3622 (1965).

(18) R. Steinmetz, W. Hartmann, and G. O. Schenck, *ibid.*, **98**, 3854 (1965).

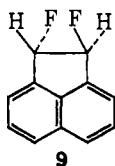
(19) B. Farah and S. Horensky, *J. Org. Chem.*, **28**, 2494 (1963).

(20) P. Weyerstahl, D. Klamann, C. Finger, F. Nerdel, and J. Budrus, *Ber.*, **100**, 1858 (1967).

depends on some factor in addition to dihedral angle for when the dihedral angle is held at 0° the coupling constant varies from 0.9 to 30.8 Hz.

Bond Angle Dependence. The geometry of the cyclic systems in compounds 1–8 constrains H_A and F to a dihedral angle of 0° in each compound. The vicinal coupling constant shows a monotonic decrease from 30.8 Hz in 1 to 0.9 Hz in 7 and then a jump to 17.7 Hz in 8. Compound 1 is the least strained of the eight molecules; the H–C–C–F system is part of a bicyclo-[2.2.2]octadiene system in which the H–C–C angle and the C–C–F angle are probably just a bit more than the normal tetrahedral angle. In compound 2 the incorporation of the H–C–C–F system into a cyclic five-membered ring anhydride has undoubtedly widened the H–C–C and C–C–F bond angles and caused an 8-Hz decrease in the vicinal coupling constant. The H_A –F coupling constants in 3 and 4 are comparable to 2, being 24.7 and 19.8 Hz. Again the H–C–C–F system is part of a five-membered ring. The 5-Hz difference between 3 and 4 may be due to a substituent effect, the electron-withdrawing carboxyls in 4 causing a smaller H–F coupling relative to 3. From a recent electron diffraction study on norbornanes²¹ it can be calculated that the $H_2C_2C_3$ bond angle is 112.3° in 1,4-dichloronorbornane. In compound 3, which has a norbornene skeleton, the H–C–C and C–C–F bond angles would be expected to be a bit larger than this value of 112° .

At this point we should note that 9, prepared and analyzed by Merritt and Johnson²² has $J_{HF-cis} = 19.4$ Hz. Since the substitution of two fluorine atoms for two hydrogens is not expected to have much effect on



the bond angles, it may be estimated that the H–C–C and C–C–F bond angles in 9 are approximately 113.5° as reported for acenaphthene.²³

Closing the carboxyls of 4 into the cyclic anhydride 5 must cause further widening of the H–C–C–F bond angles with a resultant decrease in J_{HF} to 10.55 Hz in 5. Compound 6 in which J_{HF} is 6.25 Hz may be roughly compared to methylcyclobutane²⁴ in which the CH_3 –C–C angle is 118° . In 6 which is a cyclobutene we would expect the H–C–C–F bond angles to be somewhat greater than 118° . Closing the carboxyls of 6 to the cyclic anhydride of 7 again causes a dramatic decrease in J_{HF} to 0.9 Hz.²⁵ To this point it would seem that the changes in J_{HF} in 1–7 can be rationalized almost entirely on the basis of bond angle changes. A logical extension of this concept would lead us to predict an even smaller value of J_{HF} for 8, a cyclopropane in which the H–C–C and C–C–F angles would be even larger. It is found that J_{HF} has values of 6.3 and 17.7 Hz in 6. If we assume that the larger value is J_{HF-cis} ²⁶ and that

J_{HF} is positive in sign as it undoubtedly is for 1–6,^{27,28} then we are left with what would seem to be an anomalously high value for J_{HF-cis} in 8. However it should be remembered that Karplus⁵ predicted that vicinal coupling should be a function of bond length as well as bond angle, therefore the large value of J_{HF} in 8 would seem to be due to the short C–C bond length of cyclopropanes²⁹ compared to the other compounds in Table I. Similarly the values of J_{HF} in the cyclobutenes 6 and 7 may be especially small because the C–C bond length of cyclobutenes is known to be a bit longer than the normal bond length of alkanes.²⁹

From the above comparisons of proton–fluorine coupling constants and bond angles in similar cyclic compounds it is obvious that J_{HF-vic} decreases as the H–C–C–F bond angle increases, just as was predicted by Karplus⁵ and observed experimentally for proton–proton coupling in cyclic ethylenic systems³⁰ and cyclopropanes.³¹

Dihedral Angle Dependence. To clearly demonstrate the dihedral angle dependence of J_{HF-vic} it would be necessary to examine compounds having similar bond angles, bond lengths, and substituents. From the work of Abraham and Cavalli³² it is known that J_{HF} depends linearly on the electronegativity of substituents on vicinal carbon atoms; the dependence is four times that of J_{HH-av} in ethanes. From the discussion above it is clear J_{HF} also depends markedly on bond angle and bond length.

Over the past few years a number of authors have assumed that $J_{HF-gauche} < J_{HF-trans}$ by analogy with J_{HH} . We shall present here selected values of J_{HF-vic} from our work and the literature for various dihedral angles which are, in so far as possible, capable of being compared to an ideal system of uniform substitution, bond length, and bond angle.

The best value for a 0° dihedral angle is compound 1. The 30.8-Hz coupling is lower than a theoretical value because of slight bond angle distortion and the presence of two electronegative carbomethoxy groups. J_{HF} at 60° in 1 is 3.8 Hz, a value which may be low for the same reasons. Low-temperature studies on cyclohexyl fluoride showed $J_{Feq-Hax}$ and $J_{Feq-Heq}$ (dihedral angles of 60°) “small, probably not exceeding $3 \approx 4$ cps.”³³ In a low-temperature study of 1,1-difluorocyclohexane,³⁴

(26) This assumption is justified on the basis of a complete, unequivocal analysis of the spectra of *cis*- and *trans*-1-chloro-1-fluoro-2-phenylcyclopropanes in which $J_{HF-trans}$ is found to be +1.8 to +7.5 Hz and J_{HF-cis} is +15 to +17 Hz (K. L. Williamson and D. E. Stedman, unpublished work).

(27) By relating the signs of J_{HH} to the signs of J_{HF} it has been shown for some fluorinated sugars that both vicinal and geminal H–F coupling constants have positive signs: L. D. Hall and J. F. Manville, *Chem. Ind. (London)*, 468 (1967).

(28) From line intensity calculations we know that J_{HF-cis} and $J_{HF-trans}$ in 8 have the same sign. Similarly we know that J_{HF-vic} in the 1-chloro-1-fluoro-2-phenylcyclopropanes all have positive signs.²⁶

(29) The C–C distance in 1,1-dichlorocyclopropane is 1.53 Å: W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, **36**, 200 (1962). The C–C distance in *trans*-1,3-cyclobutanedicarboxylic acid is 1.56 Å: T. N. M. argulis and M. S. Fischer, *J. Am. Chem. Soc.*, **89**, 223 (1967).

(30) O. L. Chapman, *ibid.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **84**, 2249 (1962).

(31) J. S. Waugh and S. Castellano, *J. Chem. Phys.*, **35**, 1900 (1961); J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

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

(33) F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964). See also E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.*, **90**, 682 (1968).

(34) J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965).

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

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

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

(24) H. P. Lemaire and R. L. Livingston, *J. Am. Chem. Soc.*, **74**, 5732 (1952).

(25) Cf. the 1–2 Hz J_{HF-vic} in 1-phenyl-3,3-difluoro-4,4-dichlorocyclobutene: C. M. Sharts and J. D. Roberts, *ibid.*, **79**, 1008 (1957).

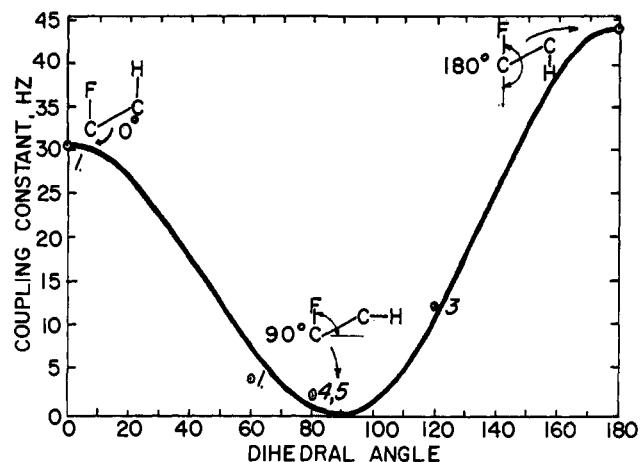
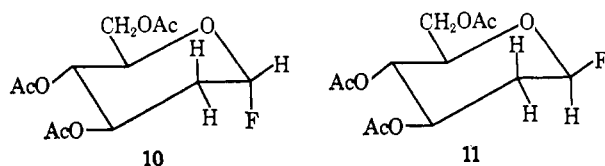


Figure 1. The dihedral angle dependence of $J_{\text{HF-vic}}$ for compounds with similar bond angles and substituents. Points are from coupling constants reported for **1**, **3**, **4**, **5**, and $J_{\text{HF-trans}}$ in cyclohexyl fluoride.³³

$J_{\text{Feq-Hax}}$ and $J_{\text{Feq-Heq}}$ were thought to differ somewhat in magnitude with the largest 5–8 cps. Both of these studies suffer from very poorly resolved spectra. Values for $J_{\text{HF-gauche}}$ have also been reported for some highly halogenated ethanes³⁵ but substituent effects and uncertainty as to the dihedral angle makes interpretation of these results difficult.

More precise values of $J_{\text{HF-gauche}}$ have been reported by Hall and his coworkers in an extensive investigation of fluorinated sugars. For compound **10**, $J_{\text{Fax-Heq}} = 5.3$ Hz, and for **11**, $J_{\text{Feq-H}} = 15.3$ and 10.7 Hz.³⁶ The differences in couplings noted here probably reflect an angular dependence of substituent effects.³⁷ Com-



pounds **4** and **5** with $J_{\text{F-HB}}$ of 2.0 and 2.3 Hz are the best representatives for dihedral angles near 80°. Seltzer³⁹ finds $J_{\text{HH}} = 0$ Hz for the coupling of the *endo* and bridgehead protons in the adduct of 2-methylfuran with maleic anhydride. He estimates (from Dreiding models) a dihedral angle of 80°.

$J_{\text{F-HB}}$ in **3** is 12.2 Hz; the dihedral angle is approximately 120°. As usual, substituent effects and bond angle strain tend to decrease this value relative to an unstrained compound. We shall neglect the 6.3-Hz coupling of **8** because of the very large and uncertain effects of bond angle and bond length on J_{HF} in this cyclopropane. At 180°, J_{HF} is reported to be 43.5 Hz for the axial fluorine conformer of cyclohexyl fluoride measured

(35) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

(36) (a) L. D. Hall and J. F. Manville, *Chem. Commun.*, **37** (1968); (b) L. D. Hall and J. F. Manville, *Can. J. Chem.*, **45**, 1299 (1967); (c) L. D. Hall and J. F. Manville, *Chem. Ind. (London)*, 991 (1965); (d) L. D. Hall and J. F. Manville, *Carbohydrate Res.*, **4**, 512 (1967).

(37) N. S. Bhacca and D. H. Williams, *J. Am. Chem. Soc.*, **86**, 2742 (1964).

(38) Merritt and Johnson²² report J_{HF} in the conformationally flexible *cis*- and *trans*-1,2-difluoro-2-methylindans are 9 and 15 Hz, respectively. They estimate, assuming a planar structure, dihedral angles of 90 and 0°, respectively, but in view of the present work we suspect this indan ring system may not be perfectly planar.

(39) S. Seltzer, *J. Am. Chem. Soc.*, **87**, 1534 (1965).

at low temperature.³³ This compound is unstrained and lacks electronegative substituents; therefore this value of J_{HF} should closely approximate the maximum value expected for $J_{\text{HF-vic}}$.

The diaxial (180° dihedral angle) H–F coupling in **10** is 38 Hz; Merritt and Stevens have reported a 32.6-Hz coupling between the 4 β -proton and the 5 α -fluorine atom in 4 α ,5 α -difluorocholestan-3-one.⁴⁰ The axial-axial coupling of H and F in the glycopyranosyl fluorides is 23.4–25.4 Hz.^{36c} These values are lower than cyclohexyl fluoride because of substituent effects.

In Figure 1 is the curve corresponding to the equation

$$J_{\text{HF}} = \begin{cases} 31 \cos^2 \phi & 0^\circ \leq \phi \leq 90^\circ \\ 44 \cos^2 \phi & 90^\circ \leq \phi \leq 180^\circ \end{cases}$$

where ϕ is the dihedral angle between vicinal H and F. This curve represents approximately the maximum values of J_{HF} to be expected at various dihedral angles, *i.e.*, J_{HF} for an unstrained hydrocarbon containing one fluorine atom. Increasing substituent electronegativity, bond angle, and bond length will each tend to lower $J_{\text{HF-vic}}$ at a given dihedral angle.

From the foregoing, it is clear that the dihedral angle dependence of J_{HF} is quite similar to the dependence of J_{HH} , confirming the assumptions that many previous spectroscopists have made.³ The linear dependence of J_{HF} on dihedral angle reported by White⁴ seems to be based on erroneous assumptions regarding the most favorable conformers for a series of terminal chlorinated 2,2-difluoropropanes. Simple inspection of models is not adequate for determining the most stable conformations in molecules of this type, *e.g.*, 1,1,2,2-tetrachloroethane has the hydrogens *gauche* and not *trans* as might be expected.³⁵

Experimental Section

Nmr spectra were recorded on Varian A-60, DP-60, DA-60, and HA-100 nmr spectrometers located at the University of Massachusetts, Cornell University, Dartmouth College, and Mount Holyoke College; samples were 15–20% solutions in the indicated solvents; proton shifts are recorded in parts per million (ppm) downfield from internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrometer. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken on a Thomas-Hoover capillary melting point apparatus.

11-Fluoro-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Anhydride (2). To a hot solution of 0.77 g (4.3 mmol) of anthracene dissolved in 10 ml of *p*-xylene was added 0.70 g (6 mmol) of fluoromaleic anhydride.^{7,41} The solution was refluxed 40 min, cooled to room temperature at which time crystals appeared, and then cooled in an ice bath. Filtration gave 0.70 g (56%) of crude **2**, mp 165–192°. Recrystallization from benzene gave pure material, mp 198–199.5°. The nmr spectrum was determined as a 15% solution in deuterated dimethylformamide.

Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{FO}_3$: C, 73.46; H, 3.77. Found: C, 73.54; H, 3.77.

Dimethyl 11-Fluoro-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (1). A suspension of 0.70 g (2.4 mmol) of **2** in 50 ml of methanol was saturated with hydrogen chloride until all of the anhydride dissolved. After standing at room temperature overnight the methanol was removed *in vacuo* and the residue recrystallized twice from methanol to give 0.48 g (39%) of the ester, mp 147–152°. A sample for analysis and spectra had mp 159–160°. The nmr spectrum was determined as a 15% solution in

(40) R. F. Merritt and T. E. Stevens, *ibid.*, **88**, 1822 (1966).

(41) We wish to thank Dr. J. E. Castle for a small sample of fluoromaleic anhydride used at the beginning of this work.

CDCl₃. The infrared spectrum in chloroform showed peaks at 5.84, 6.90, 7.05, 7.78, and 8.6 μ .

Anal. Calcd for C₂₀H₁₇FO₄: C, 70.58; H, 5.04. Found: C, 70.53; H, 5.12.

For comparison purposes, the Diels-Alder adduct, **12**, of anthracene and maleic anhydride was prepared⁸ (mp 262–263°). The adduct of maleic anhydride and 9-bromoanthracene⁴² was converted to the dimethyl ester, **13**, mp 165.5–166.5°. The infrared spectrum of **13** in chloroform showed peaks at 5.84, 6.95, 7.05, 7.66, 9.78, and 10.79 μ . The chemical shifts and coupling constants for these four compounds are given in Tables II and III. Proton

Table II. Chemical Shifts of the Adducts of Anthracene and Maleic Anhydride and Their Derivatives^a

Compd	H ₉	H ₁₀	H ₁₁	H ₁₂	Aromatic protons	Methyl protons
1	4.66 dd	4.61 dd		3.10 dd	7.37 m	3.53 s
2	5.18 m	5.16 m		4.03 dd	7.16 m	
12		4.99 dd		3.86 dd	7.16 m	
13		4.53 d	3.15 dd	3.51 d	7.16 m	3.43 s

^a In parts per million. Abbreviations used are: dd = doublet of doublets, m = multiplet, s = singlet, d = doublet.

Table III. Coupling Constants^a of the Adducts of Anthracene and Maleic Anhydride and Their Derivatives

Compd	J _{9,11}	J _{9,12}	J _{10,11}	J _{10,12}	J _{11,12}
1	1.7	2.0	3.8	0.5	30.8
2	3.0	3.9	6.0	0.7	22.5
13			2.0		11.5

^a In hertz.

spectra were determined on Varian A-60 and DA-60 spectrometers and fluorine spectra on a DP-60 spectrometer. Assignments were confirmed by frequency sweep proton decoupling on the DA-60 spectrometer and calculation of theoretical spectra using the listed parameters and the computer program LAOCOON II.⁴³

5-endo-Fluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (3). To 50 ml (0.3 mol) of hexachlorocyclopentadiene was added 42 g (0.9 mol) of vinyl fluoride under pressure in a stainless steel bomb. The bomb was heated at 150° for 80 hr. The viscous brown residue was fractionally distilled under reduced pressure. The fraction, bp 150–154° (5 mm), was redistilled on a spinning-band distillation column to give material, bp 54–55° (0.09 mm) (unreacted hexachlorocyclopentadiene); the residue solidified in the distillation apparatus and was purified by sublimation. The product, yellow waxy crystals, 1.96 g (0.61%), had mp 66–70°. Recrystallization from ligroin gave white waxy prisms, mp 70–71°. The infrared spectrum in carbon disulfide showed peaks at 6.28, 7.84, 8.57, 11.02, 12.04, 12.87, and 14.21 μ . The nmr spectrum (in CS₂) showed three protons at 5.35 (5-*exo*), 2.91 (6-*exo*), and 2.17 (6-*endo*) ppm with coupling constants of –55.1 (J_{HF-gem}), 12.2 (J_{HF-trans}), 24.7 (J_{HF-cis}), 7.1 (J_{HH-cis}), 1.8 (J_{HH-trans}), and –13.3 (J_{HH-gem}) Hz, in good agreement with expected values.⁶

Anal. Calcd for C₇H₃Cl₆F: C, 26.37; H, 0.95. Found: C, 25.78; H, 0.93.

exo-cis-1,4-Endoxo- Δ^2 -fluorotrihydrophthalic Anhydride (5). To 0.98 g (8.4 mmol) of fluoromaleic anhydride was added 1.12 g (16.4 mmol) of freshly distilled furan. After refluxing the mixture for 1.5 hr yellow crystals of product appeared. The crude crystals were collected and washed with chloroform to give 0.97 g (92%), mp 102.0–103.5°. Recrystallization from chloroform-acetone

gave pure product, mp 104.0–105.0°. The infrared spectrum (Nujol mull) showed peaks at 5.32, 5.56, 9.83, 10.24, 11.08, 11.27, and 13.55 μ . The nmr spectrum was run on an HA-100 spectrometer as a 15% solution in deuterated acetonitrile; the assignments of coupling constants and chemical shifts were confirmed by frequency sweep double resonance experiments. The proton spectrum consisted of a doublet at 2.85 (H₈), a sextet at 4.87 (H₁), a poorly resolved sextet at 4.92 (H₄), an octet at 6.07 (H₂), and an octet at 6.29 ppm (H₃). Coupling constants are 1.9 (J_{1,2}), 0.8 (J_{1,4}), 2.0 (J_{1,5}), 6.1 (J_{2,3}), 1.3 (J_{2,5}), 1.9 (J_{3,4}), 0.6 (J_{3,5}), 2.3 (J_{4,5}), and 10.5 (J_{5,6}) Hz. J_{1,6} is 0 Hz, confirming the *exo* stereochemistry for the anhydride. These values can be compared with those of other furan adducts.^{39,44,45}

Anal. Calcd for C₈H₅FO₄: C, 52.18; H, 2.74. Found: C, 51.70; H, 2.83.

exo-cis-1,4-Endoxo- Δ^2 -fluorotrihydrophthalic Acid (4). This compound was prepared by adding one drop of D₂O to the nmr tube containing **5**. In 7 min the hydrolysis of the anhydride was complete. The nmr spectrum of **4** was very similar to **5** except that the doublet at 2.85 ppm (H₈) was much broader, reflecting J_{5,6} = 19.8 Hz. J_{1,6} remained 0 Hz and J_{4,5} was found to be 2.0 Hz.

1-Fluoro-3,4-dimethyl-3-cyclobutene-1,2-dicarboxylic Acid Anhydride (7). In a 50-ml, round-bottomed Pyrex flask was placed 2.6 g (0.022 mol) of fluoromaleic anhydride, 12.9 g (0.24 mol) of 2-butyne (Columbia Organic Chemicals), and 0.55 g of benzophenone. The flask was suspended 125 cm from the center of a 450-W Hanovia ultraviolet lamp and surrounded by a 0.75 m diameter aluminum reflector. After 65 hr of irradiation infrared analysis indicated the reaction was complete. On cooling to room temperature the brown reaction mixture crystallized to give 4.1 g of crude product. Recrystallization from ligroin gave 1.55 g (41%) of large prisms, mp 104.5–105°. The infrared spectrum in chloroform showed peaks at 5.40, 5.60, 8.63, 10.46, 10.85, and 11.32 μ . The 100-MHz nmr spectrum showed three complex sets of peaks at 1.86 (the methyl at C-3), 1.98 (the methyl at C-4), and 4.01 (the proton at C-2) ppm. Careful analysis and decoupling experiments indicated coupling constants of 0.90 (J_{1,2}), 1.53 (J_{1,3}), 4.97 (J_{1,4}), 2.15 (J_{2,3}), 1.20 (J_{2,4}), and 1.40 (J_{3,4}) Hz. The two methyl groups, the C-2 proton, and the fluorine atom all couple with each other; the C-2 proton appears as a well-resolved, 11-line multiplet having a total width of 12 Hz.

Anal. Calcd for C₈H₇O₃F: C, 56.48; H, 4.15. Found: C, 56.47; H, 4.25.

1-Fluoro-3,4-dimethyl-3-cyclobutene-1,2-dicarboxylic Acid (6). To a solution of 0.3 g of **5** in 2 ml of deuterated acetone in an nmr tube was added one drop of deuterium oxide. The hydrolysis reaction was followed by nmr; the resulting spectrum of the diacid was quite similar to that of **5**. The nmr spectrum consisted of multiplets at 1.64 (the methyl at C-3), 1.88 (the methyl at C-4), and 3.66 (the proton at C-2) ppm. Coupling constants were found to be 6.25 (J_{1,2}), 2.22 (J_{1,3}), 5.23 (J_{1,4}), 2.50 (J_{2,3}), 1.26 (J_{2,4}), and 1.25 (J_{3,4}) Hz. It will be noted that except for J_{1,2} the coupling constants remain much the same as in the anhydride. The C-2 proton in this diacid appears as a well-resolved, 15-line multiplet having a total width of 19 Hz. Attempts to crystallize this compound were unsuccessful.

1,1-Diphenyl-2-chloro-2-fluorocyclopropane (8). Fluorochlorocarbene was prepared according to the procedure of Farah and Horensky.¹⁹

To 22.8 g (0.126 mol) of 1,1-diphenylethylene and 35.9 g (0.321 mol) of potassium *t*-butoxide in 200 ml of heptane was added 30.6 g (0.132 mol) of *sym*-difluorotetrachloroacetone (Allied) dropwise with stirring at –10° over a 3-hr period. After the completion of the reaction the organic layer was washed with water, dried over anhydrous magnesium sulfate, and distilled. The material boiling at 91–98° (0.025 mm) solidified in the condenser. It was recrystallized from ethanol-water to give 4 g (13% yield) of white plates, mp 76–77° (lit.²⁰ mp 74°). The infrared spectrum in carbon disulfide showed peaks at 6.20, 7.52, 8.35, 8.83, 9.86, 10.52, 11.60, 12.80, and 14.35 μ . The 60-MHz proton nmr spectrum run as a 20% solution in carbon disulfide consists of just four lines because of the small difference in chemical shifts between the two protons (1.92 ppm for the proton *trans* to the F and 2.02 ppm for the proton *cis* to the F). From the asymmetry of the proton and F¹⁹ spectra, assuming that J_{HH-gem} has a negative sign, coupling constants of

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-7.6 ($J_{\text{HF-gem}}$), $+17.7$ ($J_{\text{HF-cts}}$), and $+5.4$ ($J_{\text{HF-trans}}$) Hz were calculated. An equally good fit of the spectra was found if all signs were negative, but not for $-$, $+$, $-$ or $-$, $-$, $+$. As indicated above²⁸ we favor the $-$, $+$, $+$ combination of signs.⁴⁶

Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{ClF}$: C, 73.03; H, 4.90. Found: C, 72.89; H, 5.10.

(46) S. Terabe and W. Funasaka have independently arrived at the same conclusion regarding this compound (private communication from S. Terabe).

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Pseudorotation in Trigonal-Bipyramidal Molecules

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Abstract: A systematic geometrical analysis of isomerizations of trigonal-bipyramidal molecules by pseudorotation is presented. The consequences of introducing several types of constraints upon the processes are discussed.

Isomerization about 5-coordinated atoms has been discussed by a number of workers.^{1-5a} In particular, Berry⁵ and Muetterties¹ have called attention to the existence of an intramolecular bond-bending process which can result in positional exchange of the groups attached to a 5-coordinated atom such as phosphorus. This process has been called "pseudorotation"⁵ or "polyhedral rearrangement."¹ The recent literature contains several examples of isomerizations in the halophosphoranes,^{1,2} the arylphosphoranes,⁶ and the oxyphosphoranes.⁷⁻⁹

We present here a systematic geometrical analysis of isomerizations by pseudorotation in trigonal bipyramidal molecules which provides a useful classification and permits straightforward analyses of the consequences of various constraints upon the process. We identify some specific cases in which stereomutations and racemizations of certain phosphoranes by pseudorotation may be inhibited or altogether prevented.

Notation and Derivation of Isomers

A phosphorane derivative with five different but symmetrical substituents may be labeled as shown in formula a of Figure 1.

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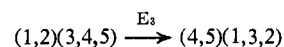
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The bonds terminated by substituents 1 and 2 will be called *apical*; those by substituents 3, 4, 5, *equatorial*. Our notation will describe this isomer as (1,2)(3,4,5). The first parentheses contain the apical substituents in numerical order. The second parentheses contain the equatorial substituents in a clockwise order, starting with the smallest number, as viewed from the side of the bipyramid that has the lower numbered apical substituent. A process geometrically equivalent to pseudorotation^{1,5} is carried out as follows (the actual process is, of course, a *concerted* one).

The bipyramid a is grasped by the "pivot" group 3, and the apical groups 1 and 2 are pushed back to close the angle $\angle 1P2$ from 180° to 120° ; this gives a *tetragonal pyramid* with substituents 1, 2, 4, and 5 in the same square plane. The groups 4 and 5 are now pulled forward to open the angle $\angle 4P5$ from 120° to 180° ; this gives a new trigonal bipyramid which will be denoted as (4,5)(1,3,2) and identified by the symbol \bar{j} , as defined below. This type of pseudorotation will be called an "E process" (to distinguish it from other less probable ones) and symbolized by



or $a(3)\bar{j}$. The subscript in E_s , or the parentheses in the shorter notation, refers to the substituent formally undisturbed during the isomerization, *i.e.*, to the "pivot." The pseudorotation moves *two* equatorial groups into apical positions.

There are ten different trigonal bipyramids corresponding to formula $P(1.2.3.4.5)$; these will be designated by the letters a, b, ...j. Each of these structures has an enantiomer \bar{a} , \bar{b} , ... \bar{j} . The notations for these 20 stereoisomers are given in Table I.

Since the trigonal bipyramid has three equatorial substituents, there will be three possible "E isomerizations." These processes, applied to isomer a, are shown in Figure 2. The corresponding notations