

The Proton Magnetic Resonance Spectra of Olefins.

IV. 3-Fluoropropenes

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The high-resolution proton and fluorine magnetic resonance spectra of allyl fluoride, allylidene fluoride, and 3,3,3-trifluoropropene-1 have been obtained at 35 and -50° and have been analyzed in terms of chemical shifts and coupling constants, using a least-squares method. The temperature-sensitive coupling constants in allyl fluoride and allylidene fluoride indicate that the thermodynamically more stable rotamer is in each case the symmetrical one. The coupling constants in 3,3,3-trifluoropropene are at most only slightly temperature dependent. Information on the relative signs of the various coupling constants is given by the spectral analysis.

Introduction

Propene and substituted propenes have been investigated extensively by means of proton magnetic resonance spectroscopy.¹⁻⁸ Of particular interest in such studies is the effect of internal rotation about the carbon-carbon single bond on the energy of the molecule and on the magnitude of the spin-spin coupling constants. It appeared that a study of the fluorinated propenes might be rewarding because of the possibility of studying both the H-H and H-F nuclear spin coupling constants and relating these to each other as well as to rotamer population. Accordingly samples of allyl fluoride, allylidene fluoride, and 3,3,3-trifluoropropene were procured, and both proton and fluorine n.m.r. spectra were recorded at $+35^\circ$; proton n.m.r. spectra were also recorded at -50° . The spectra were analyzed in terms of chemical shifts and coupling constants using a least-squares technique. The analysis of the spectra and the interpretation of the results forms the body of this paper.

Experimental

Allylidene fluoride and allyl fluoride were obtained as gifts, the former from Dr. P. C. Lauterbur, the latter from Dr. E. Hirota. We greatly appreciate their generosity in supplying these materials.

3,3,3-Trifluoropropene was obtained from E. I. du Pont de Nemours and Co. All samples were used directly without further purification. The absence of

extraneous peaks in the n.m.r. spectra was taken as a sufficient criterion of purity.

Spectra. Neat samples were degassed and sealed into 5-mm. Pyrex cells together with 0.5-1.0% tetramethylsilane as an internal reference. Proton spectra were obtained on the Varian A-60 spectrometer, equipped with a variable-temperature probe, and modified so that full-scale spectra with a sweep width of 25 c.p.s. could be recorded. Calibration was by means of audio side bands. Peak positions were the average of at least six measurements, three made with increasing and three with decreasing field. Line positions are reported on a frequency scale with tetramethylsilane at $+600,000$ c.p.s. and with more positive numbers corresponding to increasing magnetic field. Fluorine spectra were obtained with a Varian DP-60 operating at 56.4 Mc. These spectra were also calibrated with audio frequency side bands.

Spectral Analysis

The computer programs, Exan II and Laocoon II, proved useful in the analyses of the spectra. Exan II is a Fortran program for the analysis of 3-spin spectra by the method of Castellano and Waugh⁹; it accepts as input either the experimental line positions or a deduced set of energy levels, and yields all sets of shifts and coupling constants not containing imaginary values and consistent with the input data. It also gives the calculated line intensities appropriate to each set. Laocoon II is a program which proceeds by single Newton iterations from a trial spectrum resembling the experimental spectrum to be fitted, to the best least-squares fit with the experimental spectrum.¹⁰ It will handle calculations on systems of up to seven coupled spin- $1/2$ nuclei. There is provision for the artificial introduction of infinite chemical shifts. The parameters may be varied in predetermined sets.

In the case of 3,3,3-trifluoropropene-1, the spectrum belongs to the ABCX₃ class. The proton spectrum may be considered as a superposition of four ABC spectra, corresponding to the values $+3/2$, $+1/2$, $-1/2$, and $-3/2$ for the total Z component of the fluorine nuclear angular momentum, I_{FZ} . The corresponding statistical weights of the fluorine states are 1, 3, 3, and 1, and the relative total intensities of the four ABC spectra are in this ratio. The effective chemical shifts in frequency units for the A nucleus, ν_A' , in the four spectra will be

$$\nu_A' = \nu_A + I_{FZ}J_{AF} \quad (1)$$

where ν_A is the unperturbed chemical shift. Similar expressions hold for nuclei B and C. Lines were assigned to the four expected ABC spectra using the repeated

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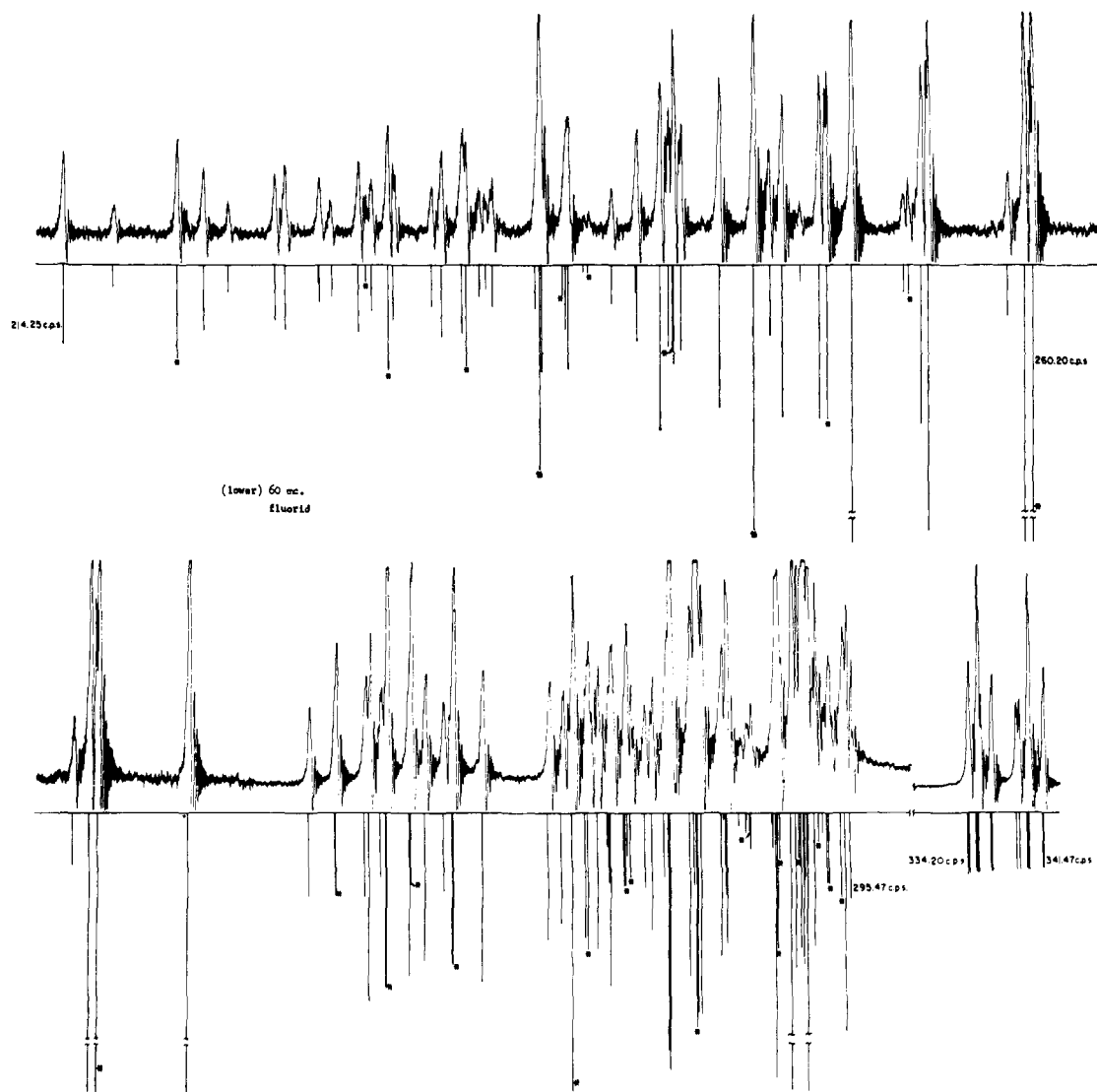


Figure 1. Observed and calculated spectra of allyl fluoride.

spacings rule, and subjected separately to analysis using Exan II. Three of the four assignments yielded sets of values for coupling constants which were identical to within a tenth cycle or so; the corresponding effective chemical shifts also marched in the expected arithmetic progression. The fourth ABC spectrum was clearly misassigned, but a calculation with the constants deduced from the other three ABC groupings yielded the correct assignment easily. The parameters were then refined using Laocoon II on the ABCX-type spectra obtained by combining the ABC spectra with $I_{FZ} = +1/2$ and $-1/2$ and also for that with $I_{FZ} = +3/2$ and $-3/2$. In the latter case the effective HF coupling constants were just three times that in the former. Both calculations gave constants agreeing within a few hundredths c.p.s., and the values quoted here are just the arithmetic mean from the two results. The fluorine spectrum being highly compressed and poorly resolved was not of much aid in the analysis.

Similar considerations aided in the analysis of the spectrum of allylidene fluoride, an ABCDX₂ case. Here I_{FZ} may assume the values -1 , 0 , and $+1$, with statistical weights 1 , 2 , and 1 . When $I_{FZ} = 0$, the partial spectrum produced is of the close-coupled

ABCD type. However, when $I_{FZ} = -1$ or $+1$, the large coupling of the D and X₂ nuclei results in an effective chemical shift for D, displacing it considerably from A, B, and C, and permitting the use of an ABCZ approximation. Thus again it is possible to choose four sets of lines corresponding to ABC spectra; analysis using Exan II yields sets of approximate values from which all parameters may be deduced; thus, for example, designating the four subspectra with superscript Roman numerals (eq. 2-4).

$$\nu_A = (\nu_A^I + \nu_A^{IV})/2 = (\nu_A^{II} + \nu_A^{III})/2 \quad (2)$$

$$J_{AD} = \nu_A^{II} - \nu_A^I = \nu_A^{IV} - \nu_A^{III} \quad (3)$$

$$J_{AX} = (\nu_A^{III} - \nu_A^I)/2 = (\nu_A^{IV} - \nu_A^{II})/2 \quad (4)$$

Final fitting *via* Laocoon II utilized lines from the partial spectrum with $I_{FZ} = 0$ as well as the fluorine resonance lines, and gave a mean error in fitting of 0.04 c.p.s. for the room-temperature spectrum and 0.06 c.p.s. for the spectrum at -50° .

In the allyl fluoride case, an ABCD₂X spectrum was obtained; two ABC subspectra may be chosen from this, corresponding to transitions between levels with

$J_{FZ} = +1/2$ or $-1/2$ and with the D_2 protons in a singlet antisymmetric state. From the results of Exan II analysis, values may be deduced for $\nu_A, \nu_B, \nu_C, J_{AB}, J_{AC}, J_{AX}, J_{BC}, J_{BX},$ and J_{CX} . Laocoon II was applied to yield the best values for the remaining constants. The final fit obtained for the room-temperature spectrum is illustrated in Figure 1. Asterisks mark the calculated lines arising from the two ABC subspectra. The mean error in fitting was 0.05 c.p.s.

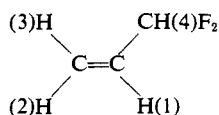
Results and Discussion

The values of the parameters obtained are presented in Table I.

Table I. Spectral Parameters for Fluorinated Propenes

Assign- ment ^{a, b}	$CH_2=CHCH_2F$		$CH_2=CHCHF_2$		$CH_2=CHCF_3$	
	36°	-50°	36°	-50°	36°	-50°
ν_1	246.87	246.76	245.17	244.05	245.82	245.35
ν_2	292.62	291.58	272.58	270.07	266.19	263.50
ν_3	285.62	284.45	265.88	264.29	248.67	247.04
ν_4	318.61	317.05	241.48	239.28
J_{12}	10.64	10.63	10.82	10.76	11.12	10.98
J_{13}	17.21	17.26	17.52	17.45	17.47	17.28
J_{14}	5.31	5.24	5.33	6.14
J_{23}	1.54	1.59	0.67	0.66	0.18	0.19
J_{24}	-1.27	-1.33	-0.79	-0.66
J_{34}	-1.63	-1.66	-0.82	-0.73
J_{1F}	14.53	15.20	8.63	7.82	6.28	6.32
J_{2F}	-0.89	-0.73	-0.14	(+)0.11	(+)0.03	(+)0.10
J_{3F}	-4.32	-4.35	-3.66	-3.86	-2.22	-2.26
J_{4F}	46.75	46.66	55.90	55.67

^a Chemical shifts in c.p.s.; tetramethylsilane at +600.00 c.p.s.; $\tau = \nu/60.00$. ^b Numbering scheme



Relative Signs of the Coupling Constants. The relative signs of all coupling constants are obtained unambiguously from the complete analysis of the spectra. In the case of the fluorine resonance, the signals are asymmetric. Reversing the signs of all the H-F coupling constants reverses the sense of the fluorine signal asymmetry. In all cases studied, both the $^2J_{HF}$ coupling constants ($J_{4,F}$) and the $^3J_{HF}$ constants ($J_{1,F}$) are positive, assuming the *cis* and *trans* olefinic proton-proton coupling constants to be positive. This is in accord with the findings of Barfield and Baldeschwieler¹¹ on ethyl fluoride, and of Evans, Manatt, and Elleman¹² on a variety of fluorine-containing compounds. The coupling of the allylic fluorine with the *cis* proton is negative, under the same assumption; the coupling with the *trans* proton is negative in allyl fluoride, but tends to become more positive with increasing fluorine substitution, and may be slightly positive in 3,3,3-trifluoropropene.

Effect of Temperature Changes. The signals of the protons are without exception displaced toward lower applied field by lowering the temperature. This is not a bulk susceptibility effect, since an internal stand-

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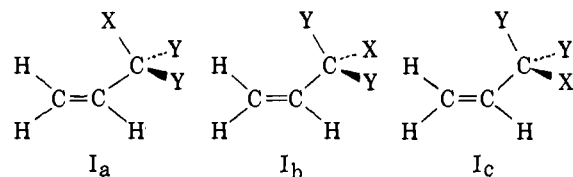


Figure 2. Stable rotamers in allyl fluoride (X = F and Y = H) and allylidene fluoride (X = H and Y = F).

ard is used. More probably, it may be explained on the basis that the protons in the sample substances are more sensitive to the van der Waals shifts than those in the reference. A second contribution but of less importance, is undoubtedly the variation in the distinguishable rotamer populations in the cases of allyl fluoride and allylidene fluoride.

Microwave studies¹³⁻¹⁵ have indicated that the minima in the potential curves for rotation about the C-C single bond in substituted propenes correspond to the forms $I_a, I_b,$ and I_c in Figure 2. The populations of these forms may be represented by p_a, p_b, p_c . In symmetrical media I_b and I_c are of equal energy and $p_b = p_c = (1 - p_a)/2$. If it is assumed that, for a single molecule, the coupling constants J_{HX} and J_{HY} may be represented by a suitably weighted average of characteristic *gauche* and *trans* coupling constants (i.e., that J_{HY} in form I_a is equal to one of the J_{HY} values in I_b), then

$$J_{HX} = p_a J_{HX}^t + (1 - p_a) J_{HX}^g \quad (5)$$

and

$$J_{HY} = \frac{1}{2} (1 - p_a) J_{HY}^t + \frac{1}{2} (1 + p_a) J_{HY}^g \quad (6)$$

If a change in temperature produces a change in the populations ($p_a \rightarrow p_a + \Delta p_a$), then changes in the coupling constants HX and HY will be observed, which are given by

$$\Delta J_{HX} = \Delta p_a (J_{HX}^t - J_{HX}^g) \quad (7)$$

and

$$\Delta J_{HY} = -\Delta p_a (J_{HY}^t - J_{HY}^g)/2 \quad (8)$$

Thus, the ratio of the changes $\Delta J_{HX}/\Delta J_{HY}$ may be expressed as

$$\frac{\Delta J_{HX}}{\Delta J_{HY}} = -2 \frac{J_{HX}^t - J_{HX}^g}{J_{HY}^t - J_{HY}^g} \quad (9)$$

In the case of allylidene fluoride (X = H and Y = F), the change in $J_{1,4}$ on going from +35 to -50° is +0.81 c.p.s., while the change in $J_{1,F}$ is -0.81 c.p.s. Substituting in eq. 9, one finds that $(J_{HF}^t - J_{HF}^g)$ is just twice $(J_{HH}^t - J_{HH}^g)$ in this compound. This seems very reasonable in the light of earlier findings¹⁶⁻¹⁸ on related systems. For instance, in the substituted

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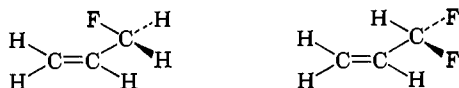


Figure 3. Most stable rotamers of allyl fluoride and allylidene fluoride.

ethane, $\text{CHCl}_2\text{—CH}_2\text{F}$, Gutowsky¹⁶ finds $J_{\text{HH}}^t - J_{\text{HH}}^g$ equal to ~ 15 or ~ 19 c.p.s. (two different values of J^g), while $J_{\text{HF}}^t - J_{\text{HF}}^g$ is 24 or 39 c.p.s. Similarly DeWolf and Baldeschwieler¹⁷ find for $\text{CH}_2=\text{CFCH}_3$ $J_{\text{HH}} = 6.4$ c.p.s. The ratio of ΔJ_{HH} to ΔJ_{HF} in allyl fluoride should be just 0.25, if the same ratio of $(J_{\text{HH}}^t - J_{\text{HH}}^g)$ to $(J_{\text{HF}}^t - J_{\text{HF}}^g)$ obtains; the observed value is in fact 0.10. However, the actual change observed for $J_{1,4}$ in this case was only 0.07 c.p.s., and considering the uncertainty in the measurement, the discrepancy may be less (or more).

Studies¹⁸ which have been made of internal rotation in systems containing the HCCF grouping suggest that the J_{HF} coupling constant depends on dihedral angle in the same way as J_{HH} in analogous systems,¹⁹ in that J^t is large and positive compared to J^g . In that case, it is a clear deduction from the temperature dependence of $J_{1,4}$ and $J_{1,F}$ that the more stable rotamers of allyl fluoride and allylidene fluoride are those shown in Figure 3. A calculation of the exact proportions would require a good estimate of J_t and J_g in each case, and is subject to uncertainty. One possible approximate analysis is as follows.

The quantities measured in the case of allylidene fluoride are J_{HH} and J_{HF} at two temperatures. The quantities required are ΔH , J_{HH}^g , J_{HH}^t , J_{HF}^g , and J_{HF}^t . In order to solve the problem, an extra relation between the unknowns must be found or assumed. We take $J_{\text{HH}}^t - J_{\text{HH}}^g = \Delta$ and examine the possible solutions for various values of Δ .

We have the relation (5), and can also derive

$$K_{\text{eq}} = 2p_a/(1 - p_a) \quad (10)$$

$$\Delta H = -RT \ln K_{\text{eq}} \quad (11a)$$

$$= -RT \ln 2(J_{\text{HX}} - J_{\text{HX}}^g)/(J_{\text{HX}}^t - J_{\text{HX}}) \quad (11b)$$

$$\Delta H = -RT \ln (J_{\text{HY}}^t + J_{\text{HY}}^g - 2J_{\text{HY}})/(J_{\text{HY}} - J_{\text{HY}}^g) \quad (12)$$

The last two equations are obtained from eq. 5, 6, and 11a assuming $\Delta S = 0$ for the equilibrium between rotamers¹⁹⁻²¹ and ΔH is constant over the temperature range investigated. The set of relations may not be

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solved directly, but may be solved numerically or graphically. For $\Delta = 8.0$ c.p.s., for example, two solutions are possible: in set 1, $J_{\text{HH}}^g = +0.3$, $J_{\text{HH}}^t = +8.3$, $J_{\text{HF}}^g = +5.7$, and $J_{\text{HF}}^t = +21.7$ c.p.s.; $p_a(-50^\circ) = 0.725$ and $p_a(+35^\circ) = 0.630$; and $\Delta H = -750$ cal. In set 2, $J_{\text{HH}}^g = -0.9$, $J_{\text{HH}}^t = +7.1$, $J_{\text{HF}}^g = +6.9$, and $J_{\text{HF}}^t = +22.9$ c.p.s.; $p_a(-50^\circ) = 0.88$ and $p_a(+35^\circ) = 0.78$; and $\Delta H = -1200$ cal. For $\Delta \leq 7.5$ c.p.s., there are no solutions. In the range $7.5 \text{ c.p.s.} < \Delta < 9.0 \text{ c.p.s.}$, the numerical values in set 1 do not change greatly, while those in set 2 move over a small range. For example J_{HH}^g varies from $+0.1$ to -2.0 c.p.s., while J_{HH}^t stays almost constant, and ΔH varies from ~ -1000 to -1400 kcal.

Since it seems unlikely that $J_{\text{HH}}^t - J_{\text{HH}}^g > 9.0$ c.p.s., we conclude that ΔH is in the range 0.5–1.4 kcal, and that J_{HH}^g lies in the range -2.2 to $+0.3$, J_{HH}^t in the range $+6.8$ to $+8.3$, J_{HF}^g $+4.8$ to $+7.1$, and J_{HF}^t $+21.8$ to $+25.1$ c.p.s. In the case of allyl fluoride, the analysis is confined to the HF coupling constants, since the variation in the HH coupling constants is so small. In this case, the range of values obtained for $\Delta = J_{\text{HH}}^t - J_{\text{HH}}^g = 14.0$ to 18.0 , $J_{\text{HF}}^g = +8.7$ to 9.6 , and $J_{\text{HF}}^t = +23.6$ to $+26.7$ c.p.s., and $\Delta H = \sim 0.100$ kcal., in satisfactory agreement with the findings of Hirota.¹⁵

In both cases, the ranges of values for J_{HF}^g , J_{HF}^t are reasonable and in agreement with measurements on rotationally averaged systems. Thus J_{HF} in 2-fluoropropene has the value¹⁷ $+16.0$, in 1,1-difluoroethane the value¹⁷ $+20.9$, and in fluoroethane the value²² 25.2 c.p.s.

It is interesting that the rotamer of lowest energy for allylidene fluoride is that one with the proton eclipsed with the olefinic methylene group, while in allyl fluoride, the rotamer of lowest energy is that one with the fluorine eclipsed. The finding in the case of allyl fluoride confirms the conclusions of Hirota on the rotameric forms of this compound, based on his microwave studies.¹⁵ We suppose that the reversal in the stabilities of the rotamers of the two compounds is traceable to the different characters of the C–F bonds in the CH_2F and CHF_2 groups. The van der Waals attraction between the F and H of the olefinic methylene group should be more favorable in the compound with the more polar C–F bond, allyl fluoride.

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