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NMR Studies of Conformational Equilibria in Substituted Ethanes

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NMR STUDIES OF CONFORMATIONAL EQUILIBRIA IN SUBSTITUTED ETHANES*

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Proton and fluorine magnetic resonance spectra have been observed in twelve liquid polysubstituted ethanes over temperature ranges of 250° to 450°K. In each of these compounds, reorientations about the C-C bond are fast enough to yield high resolution nmr spectra which are averages of the three rotational isomers. The change in the proportions of the isomers with temperature is large enough for $CHCl_2CHCl_2$, $CHCl_2CHF_2$, $CF_2ClCFCl_2$, $CHCl_2CHFCl$, and $CF_2BrCFBrCl$, and also $CFCl_2CHCl_2$ for which $\langle J_{HF} \rangle$ has been reported, to permit a least-squares type analysis of the averaged shifts $\langle \nu \rangle$ and coupling constants $\langle J \rangle$ with a high-speed digital computer. The latter evaluates the physical parameters, three or five depending upon molecular symmetry, which govern the temperature dependence of $\langle \nu \rangle$ and $\langle J \rangle$. These parameters, in our approximation, are the values of the spectral quantity in question for each of the "rotamers", and the relative energies ΔE of the latter. This procedure could not be applied to $CH\phi_2CH_2(C\phi)$, $CHBr_2CH_2Br$, $CH_2\phi CH_2Cl$ and $CH_2\phi CH_2Br$ for which ΔE is sufficiently small that $\langle J_{vic}^{HH} \rangle$ is virtually temperature independent. However, an approximation was developed for obtaining such small ΔE's (35 to 90 cal) by assuming $(J_t^{HH} - J_g^{HH})$ to be an average of values found in other compounds. A similar approximation was used for solutions of three CHXYCHYZ compounds in which ΔE is large, ~1000 cal, but thermal decomposition prevented measurements of $\langle J_{vic}^{HH} \rangle$ over a large enough temperature range. In addition, ΔE's were determined for $CHCl_2CHF_2$ and $CHCl_2CHFCl$ by analyzing the dependence upon solvent of infrared absorption bands assigned to <u>trans</u> and <u>gauche</u> rotamers.

There is fair to excellent agreement between values for a given ΔE obtained from different nmr observables and also from vibrational spectra. The results from chemical shift data appear to be least reliable, because of molecular association effects. Also, experimental errors are compounded when second order perturbations prevent measuring $\langle \nu \rangle$ or $\langle J \rangle$ directly as a splitting in the spectrum. The ΔE's in new cases appear compatible with previous results in their dependence upon steric factors and electric dipole interactions.

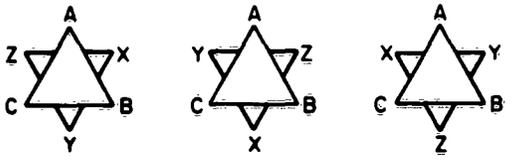
The vicinal coupling constants obtained for the individual rotamers are alike for H-H, H-F, and F-F in that they are smaller in magnitude when the nuclei are gauche to one another, i.e. $|J_g| < |J_t|$, and there are instances in which J_g and J_t are of opposite as well as of like sign. J_{gem}^{HF} and J_t^{HF} are of the same sign. $\langle J_{gem}^{HF} \rangle$ and $\langle J_{gem}^{FF} \rangle$ have temperature independent values of 49.1 ± 0.2 and 166.8 ± 0.5 cps in $CHCl_2CHFCl$ and $CF_2BrCFBrCl$, respectively. Other numerical values found are, for H-H: $J_g \pm 2.0$ to $\mp 2.6(4)$, J_t 10.2 to 16.5(3); for H-F: $J_g \pm 13.2$ to $\mp 2.8(3)$, J_t 37.3 to 18.2(2); and for F-F: $J_g \pm 5.3$ to $\mp 21.2(5)$, J_t 38.7 to 41.6(3). All are in cps with the number of results given in parentheses.

The nmr methods developed appear to be very versatile in principle. With improved instrumentation, higher quality data, and a better understanding of the factors which can affect the results, nmr may well be the best approach to ΔE for liquid or even gaseous molecules containing hydrogen or fluorine. Certainly, such studies are useful in establishing the dependence of nmr parameters upon rotational configuration.

I. Introduction

Early studies of configurational isomerism utilized dielectric constant measurements and vibrational spectra. The results of most such work have been summarized by Mizushima.[1] Problems studied include the energy differences and potential barriers between the various forms and the dependence of these quantities upon substituents, the nature of a solvent, the state of the sample, and similar factors. The basic question, which remains in large part, is the nature of the forces restricting intramolecular motions. Other means of making such studies have been provided[2,3] by the advent of high resolution nuclear magnetic resonance. The present work is concerned primarily with the extension of these techniques to the rotational isomerism of some substituted ethanes.[2-7]

The energetically favored forms, or rotamers, are the staggered configurations[1] shown below for the general case. The factors governing the appearance of the nmr



(1) (2) (3)

spectra include the relative energies of the rotational isomers, the potential barriers to internal rotation about the C-C bond, and the chemical shifts and coupling constants characteristic of each isomer.[2,3] These quantities can be obtained most completely and directly for a compound if the potential barriers are high enough that the nmr spectrum at lower temperatures is a superposition of spectra for the several rotamers. However, in most substituted ethanes, rotational averaging occurs, which simplifies the spectrum[2,3] and reduces its information content. This is the case for the ethanes we have investigated, and one of our major concerns was to see how much information could nonetheless be obtained.

In these compounds, the experimentally observed average resonance frequency or chemical shift for the $i^{\underline{th}}$ nucleus is given as

$$\langle \nu_i \rangle = x_1 \nu_1^i + x_2 \nu_2^i + x_3 \nu_3^i \qquad (1)$$

and the coupling constant between nuclei i and j, as

$$\langle J_{ij} \rangle = x_1 J_1^{ij} + x_2 J_2^{ij} + x_3 J_3^{ij} \ . \qquad (2)$$

The numerical indices refer to the rotamers, 1-3, and the x's designate the mole fractions. The x's, of course, may be expressed in terms of molecular properties. In particular, the potential energy of the molecule is a function of the dihedral angle ϕ between say the C-A and the C'-X bonds, as shown schematically in Fig. 1 where the numerical labeling of the three minima corresponds to the structural formulae given for the rotamers. The relative energies of the rotamers are defined by setting $\Delta E_1 = E_1 - E_3$ and $\Delta E_2 = E_2 - E_3$. Then, the ratio of the x's is given as

$$x_1 : x_2 : x_3 = Q_1' \exp(-\Delta E_1/RT) : Q_2' \exp(-\Delta E_2/RT) : Q_3' \ , \qquad (3)$$

where Q_n' is the partition function for a particular rotamer n, excluding the internal rotation coordinate ϕ. Q' will differ somewhat for the three rotamers, but to a good approximation we can set $Q_1' = Q_2' = Q_3'$ and eliminate them from Eq. (3). This permits the conversion of Eq. (1) for the averaged chemical shift to the form

$$\langle \nu_i \rangle = Q_\phi^{-1} \left(\nu_1^i \exp(-\Delta E_1/RT) + \nu_2^i \exp(-\Delta E_2/RT) + \nu_3^i \right) \ , \qquad (4)$$

where Q_ϕ is the internal rotation partition function for the three rotamers in thermal equilibrium,

$$Q_\phi = \exp(-\Delta E_1/RT) + \exp(-\Delta E_2/RT) + 1 \ . \qquad (5)$$

Similarly, Eq. (2) for the averaged coupling constant becomes

$$\langle J_{ij} \rangle = Q_\phi^{-1} \left(J_1^{ij} \exp(-\Delta E_1/RT) + J_2^{ij} \exp(-\Delta E_2/RT) + J_3^{ij} \right) \ . \qquad (6)$$

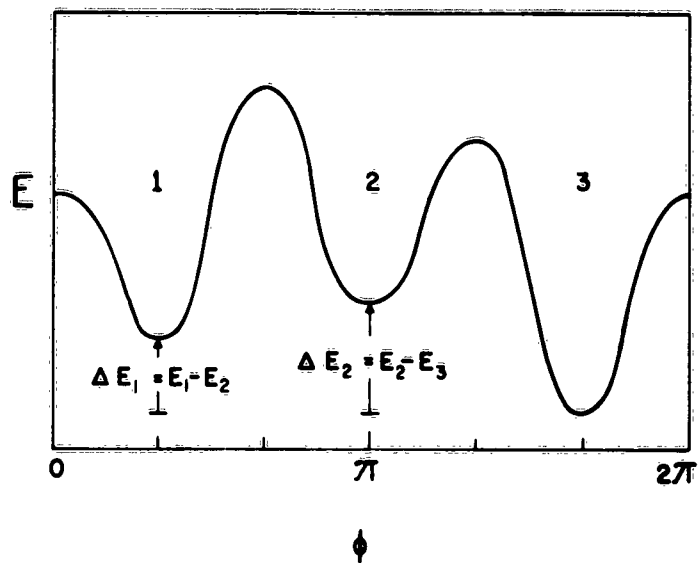


Fig. 1. The energy of a substituted ethane as a function of the dihedral angle ϕ between C-A and C'-X bands in A-C-C'-X group, with definitions of symbols used.

Inspection of Eqs. (5) and (6) shows that if the temperature dependence of $\langle \nu_i \rangle$ and $\langle J_{ij} \rangle$ results only from changes in the equilibrium proportions of the rotamers, then in principle it should be possible to determine experimentally the relative energies of the rotamers and also the chemical shifts and coupling constants characteristic of the individual rotamers.[8] The general case involves two energy terms and three chemical shifts or coupling constants (and sometimes more), and the functional form is relatively complicated. However, the equations become simple for the limiting values of $\langle \nu_i \rangle$ and $\langle J_{ij} \rangle$ which are approached asymptotically at low and at high temperatures. The low temperature limit is, of course, ν_n^i and J_n^{ij} for the stablest form, while the high temperature limit is the average obtained by weighting each form equally. Unfortunately, the changes in $\langle \nu_i \rangle$ and $\langle J_{ij} \rangle$ observed and predicted for the experimentally useful temperature ranges are modest, particularly for protons, and good limiting values have not been obtainable by simple inspection of the experimental curves. Nonetheless, we have found that it is possible to extract values for all of the unknowns, at least in favorable cases. The internal consistency and reliability of the results leave much to be desired. But, the general approach seems hopeful in view of instrumental improvements which can provide experimental data of higher quality.

As yet, relatively little is known concerning the dependence of chemical shifts and coupling constants upon molecular conformation. For the substituted ethanes, much attention has been given to the types of nmr spectra to be expected under various circumstances,[2-6,9-13] in part because of several errors[9-11] in early reports on the subject. But as to specific cases, only the H-H' coupling in the H-C-C'-H' group has been studied to any great extent. With the assumption of tetrahedral H-C-C' angles, the dependence of $J_{HH'}$ upon the dihedral angle ϕ has been calculated by valence bond methods[14] to be of the form $J_{HH'} \approx 9\cos^2\phi - 0.3$, in cps. The qualitative correctness of this result is shown by several experimental studies,[7,14-16] the most pertinent of which[16] involved altering the fractions of different rotamers present in several haloethanes at room temperature. This was accomplished by employing various solvents of different polarity. Values for the appropriate x's and ΔE's were obtained from

infrared spectra and were used in conjunction with experimental values for $\langle J_{HH'} \rangle$ to give two or more linear equations such as Eq. (2), with the J_n^{ij} as unknowns. In this manner, approximate values ranging from 10 to 18 cps were found for J_t^{HH}, the coupling constant in the rotamer where the protons are trans (J_{AX} in rotamer 2), and 1 to 3.5 cps for J_g^{HH}, the gauche rotamer (J_{AX} in rotamers 1 and 3).

In the work reported here, we have been able to obtain more accurate values for J_t^{HH} and J_g^{HH} and also some values for the proton shifts in the individual rotamers. Several fluoroethanes were studied in order to learn something about the ϕ-dependence of the H-F and F-F' coupling constants, and of the fluorine chemical shifts, in H-C-C-F and F-C-C'-F' groups. And, finally, the methods developed for analyzing the nmr data give ΔE values with relatively small statistical errors in favorable instances. In two cases we obtained ΔE values from infrared spectra, because of initial difficulties in calculating ΔE as well as the J_n^{ij} from the nmr data alone.

II. Experimental

The nmr spectra were observed with a Varian Associates Model V-4300-2 high resolution spectrometer equipped with the commercial Dewar inserts for 40 Mc and 60 Mc operation. The temperature of the sample was established by means of a copper-constantan thermocouple placed close to the sample tube; this reading was corrected by means of a calibration curve constructed by measuring simultaneously the temperature at this position and that directly in a non-spinning sample. The temperatures are considered to be accurate to within $\pm 1^{\circ}$.

Audiofrequency modulation of the magnetic field was used to produce sidebands for calibration. The F^{19} chemical shifts between the compounds studied and the $CFCl_3$ reference are relatively large, and it was found convenient to use a double audiomodulation procedure for their measurement. A fairly high frequency, about 2500 cps, was used to place a sideband of the compound resonance close to that of the reference; in addition, a low audiofrequency was used in the normal manner, that is to calibrate the sweep rate.

All of the results reported for protons were obtained using a resonance frequency of 60 Mc; and those for F^{19}, 40 Mc. The experimental values of chemical shifts and of coupling constants given in the tables and plotted in the figures are averages of about ten determinations and the errors shown are the standard deviations, with no allowance for any possible systematic errors.

The infrared studies were carried out by means of a Perkin-Elmer Model 21 spectrometer on samples at room temperature.

Most of the haloethane samples were obtained from various commercial sources and were used without further purification. The $CHCl_2CHCl_2$, $CH_2\phi CH_2Br$, and $CH_2\phi CH_2Cl$ were from Eastman Kodak Co.; the $CHCl_2CHFCl$, $CHCl_2CHF_2$, $CF_2BrCFBrCl$, and $CHBr_2CH_2Br$ were from K and K Laboratories, Jamaica, N. Y.; and the $CF_2ClCFCl_2$ (Freon 113) was from the Matheson Co. The remaining samples, of phenyl-haloethanes, came from the local stock of chemicals synthesized in connection with organic research; some of these samples required repurification.

III. Mathematical Analysis of the Data

NMR Experiments

The fitting of Eqs. (4) and (6) to the observed temperature dependence of $\langle \nu_i \rangle$ and $\langle J_{ij} \rangle$ presents some computational difficulty because of the exponentials in the unknown ΔE's. Initially, efforts were made at "hand solutions", using a desk calculator and also graphical methods. However, the work is tedious even when the two gauche forms, 1 and 3, are identical and the unknown parameters are reduced from five to three, $\Delta E = E_2 - E_3 = E_t - E_g$, and J_t and J_g or ν_t and ν_g. For this case, Eq. (6) takes the form

$$\langle J \rangle = \frac{2J_g + J_t \exp(-\Delta E/RT)}{2 + \exp(-\Delta E/RT)} , \qquad (7)$$

in which it is implicit that $E_t > E_g$. If one assumes a value for ΔE, or if a reliable result is available from another set of experiments such as infrared spectroscopy, then

the coefficients of J_g and J_t in Eq. (7) can be calculated for each temperature, T_1, ... T_k, at which there is an experimental value of $\langle J \rangle$. This leads to a set of k equations of the form

$$\langle J_k \rangle = a_k J_g + b_k J_t \ , \tag{8}$$

which is linear in the unknowns, J_g and J_t. The reduction to linear form permits the application of standard least squares methods to the evaluation of best trial values for J_g and J_t. With these and ΔE, it is possible to calculate $\langle J \rangle$ as a function of temperature with Eq. (7) and to obtain thereby the sum of the squares of the deviations of the experimental points from the theoretical curve. The sum is minimized by repeating the process with systematic variation of ΔE.

The time consuming nature of the calculations led to the writing of a program to do them on automatic digital computers.[17] The program for the case of three unknown parameters, e.g. Eq. (7), was written for the IBM 650. Calculations with this program were sufficiently time consuming that it seemed advisable to write the general, five-parameter program for the Illiac, a faster machine than the IBM 650. Even so, such general solutions were time consuming (~10 hrs) in cases where the observed temperature dependence was relatively small and the errors in the data relatively large.

In a general sense, the mathematical problem is the following. Given a set of experimental values F_k versus T_k, and an analytical function $F = F(\alpha,\beta,\gamma\ldots,T)$ involving the unknown parameters $\alpha,\beta,\gamma,\ldots$ we wish to determine values of $\alpha,\beta,\gamma,\ldots$ such that F is a "best fit" to the experimental data in the least squares sense. In other words, values of $\alpha,\beta,\gamma,\ldots$ are desired such that the auxilliary function,

$$\varphi = \sum_k [F_k - F(\alpha,\beta,\gamma,\ldots T_k)]^2 \ , \tag{9}$$

is a minimum. The programs written start with an initial set of trial parameters $\alpha,\beta,\gamma\ldots$; they calculate $F(\alpha,\beta,\gamma\ldots T_k)$, for instance Eq. (7); and then, φ according to Eq. (9). The programs locate a minimum in φ by stepping each of the parameters in

turn, in the direction of decreasing φ, until a complete cycle produces no further decrease. This procedure gives equal weights to the experimental points even though in some sets of data the standard deviations of various points differ appreciably.

An initial version of the five-parameter program attempted minimization by a gradient, or "steepest descent", method. A characteristic of this method, however, is that it tends to give erroneous results when the function minimized is a very slowly varying function of one of the variables. Unfortunately, this occurs in the cases treated below, the bad variable being one of the ΔE's.

After the minimizing values $\alpha_o, \beta_o, \gamma_o \ldots$ of $\alpha, \beta, \gamma \ldots$ were determined from a given set of experimental data, the probable errors in the parameters were estimated as follows. The function φ is expanded as a Taylor series in the neighborhood of the minimum. This gives

$$\varphi = (\alpha_o, \beta_o, \gamma_o, \ldots) + \left(\frac{\partial \varphi}{\partial \alpha}\right)_{\alpha_o} (\Delta\alpha) + \left(\frac{\partial \varphi}{\partial \beta}\right)_{\beta_o} (\Delta\beta) + \left(\frac{\partial \varphi}{\partial \gamma}\right)_{\gamma_o} (\Delta\gamma) + \ldots + \frac{1}{2}\left(\frac{\partial^2 \varphi}{\partial \alpha^2}\right)_{\alpha_o} (\Delta\alpha)^2 + \frac{1}{2}\left(\frac{\partial^2 \varphi}{\partial \beta^2}\right)_{\beta_o} (\Delta\beta)^2 + \frac{1}{2}\left(\frac{\partial^2 \varphi}{\partial \gamma^2}\right)_{\gamma_o} (\Delta\gamma)^2 + \ldots \tag{10}$$

Now, at the minimum in φ the first derivatives all vanish. Therefore, if in Eq. (10) we hold all parameters constant but one, we obtain equations of the form

$$\varphi - \varphi(\alpha_o, \beta_o, \gamma_o, \ldots) \approx \frac{1}{2}\left(\frac{\partial^2 \varphi}{\partial \alpha^2}\right)_{\alpha_o} (\Delta\alpha)^2 . \tag{11}$$

Furthermore, the accuracy of the experiments establishes an upper limit on allowed values of φ. This limit is defined by

$$\varphi_{exp} = \sum_k (\delta F_k)^2 , \tag{12}$$

where δF_k is the uncertainty in the measurement of F_k. Accordingly, a good estimate of the uncertainty $\Delta\alpha_o$ in α_o is obtained by solving for $\Delta\alpha_o$ in the equation

$$\Delta\varphi = \varphi_{exp} - \varphi(\alpha_o, \beta_o, \gamma_o, \ldots) \approx \frac{1}{2}\left(\frac{\partial^2 \varphi}{\partial \alpha^2}\right)_{\alpha_o} (\Delta\alpha_o)^2 . \tag{13}$$

This yields the result

$$\Delta\alpha_o \approx [2(\Delta\phi)\ (\partial^2\phi/\partial\alpha^2)_{\alpha_o}]^{1/2} , \qquad (14)$$

with similar equations for the other parameters.

The second derivatives at the minimum were estimated numerically from tabulated ϕ values, assuming that ϕ is a parabolic function of each of the parameters in the neighborhood of the minimum. The results reported herein are then given as $\alpha = \alpha_o \pm (\Delta\alpha_o)$, etc. The assumption that ϕ is a parabolic function appears to be good in the three-variable cases. In the five variable results, however, the surface near the minimum appeared more like a long, narrow trench, so that the maximum possible error in the most uncertain ΔE is much larger than the computed probable error.

Throughout the calculations it is assumed that the experimental errors of about $\pm 1^o$ in the temperatures T_k are negligible. This is justified by the relatively small changes and large errors in $\langle J \rangle$ and $\langle \nu \rangle$ over the large temperature ranges investigated.

Infrared Experiments

In the determination of the ΔE's between rotational isomers from vibrational spectra, the optical density A is measured for an absorption band of each isomer. The definition of A follows from the Beer-Lambert law,

$$A = \ln(I_o/I) = \kappa C d , \qquad (15)$$

where I_o and I are the intensities of the incident and transmitted radiation, κ is the molar extinction coefficient, C is the concentration of absorber in moles/cm^3, and d is the cell thickness in cm. For compounds having two equivalent gauche forms and a trans, the ratio of optical densities may be written as

$$\frac{A_g}{A_t} = \frac{\kappa_g C_g}{\kappa_t C_t} = \frac{\kappa_g x_g}{\kappa_t x_t} \approx \frac{2\kappa_g}{\kappa_t} \exp(+\Delta E/RT) . \qquad (16)$$

The A's are obtained directly from experiment. However, before ΔE may be determined, it is necessary to know κ_g/κ_t, the ratio of the extinction coefficients. This is accomplished usually[1] by observing A_g/A_t at two or more temperatures.

An alternate method, which we used, is to change the relative concentrations of the rotamers by changing the solvent, at a fixed (room) temperature. This method is applicable only when there is a difference in the dipole moments of trans and gauche forms so that a more polar solvent increases the concentration of the more polar rotamer, and vice versa. Partial differentiation of the numerator and denominator in Eq. (16), and rearrangement, leads to the equation

$$\frac{\kappa_g}{\kappa_t} = \frac{(\partial A_g/\partial x_g)}{(\partial A_t/\partial x_t)} \approx \frac{\Delta A_g}{\Delta A_t}\frac{\Delta x_t}{\Delta x_g} . \tag{17}$$

But $x_t + x_g = 1$ and $\Delta x_t = -\Delta x_g$. This enables us to rewrite Eq. (17) as

$$\kappa_g/\kappa_t \approx -\Delta A_g/\Delta A_t , \tag{18}$$

and to combine it with Eq. (16) to give

$$\exp(-\Delta E/RT) = -(A_g/A_t)(\Delta A_t/\Delta A_g) , \tag{19}$$

in which all parameters but ΔE are measurable. This derivation assumes that the extinction coefficients and ΔE are independent of solvent, and at least the last assumption is none too good.

IV. Experimental Results

A. $CHCl_2CHCl_2$

$\langle J_{HH} \rangle$.- The coupling constant in pure liquid s-tetrachloroethane was obtained from the satellites produced in the proton spectrum by the C^{13}-H coupling in the C^{13}-C^{12} isotopic species.[18] A doublet which is half of an ax type spectrum[2,3] is visible on each side of the single line from the C^{12}-C^{12} molecules, and the doublet splitting is $\langle J_{HH} \rangle$. The values measured over a range of temperatures are listed in Table I and they are plotted in Fig. 2.

Table I. The temperature dependence of $\langle J_{HH} \rangle$ and $\langle \nu_H \rangle$ observed in liquid $CHCl_2CHCl_2$.

Temperature	$\langle J_{HH} \rangle$	Temperature	$\langle \nu_H \rangle$[a]
238°K	2.67 ± 0.07 cps	266°K	77.10 ± 0.20 cps
263	2.84 ± 0.08	296	77.80 ± 0.12
264	2.90 ± 0.07	333	78.37 ± 0.18
295	3.10 ± 0.07	375	79.07 ± 0.18
300	3.06 ± 0.12	396	79.28 ± 0.29
327	3.24 ± 0.07	424	79.71 ± 0.07
361	3.40 ± 0.03	459	79.96 ± 0.16
395	3.55 ± 0.05		
414	3.67 ± 0.08		

[a]The chemical shifts were measured at 60 Mc with respect to an internal reference, $CHCl_3$; the larger shift at higher temperatures is an upfield displacement.

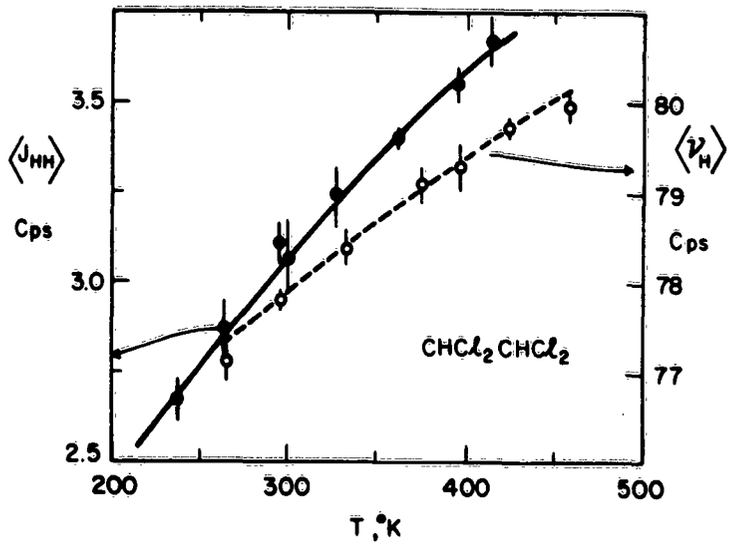


Fig. 2. The temperature dependence of $\langle J_{HH} \rangle$ and $\langle \nu_H \rangle$ in liquid $CHCl_2CHCl_2$. The chemical shift $\langle \nu_H \rangle$ is upfield with respect to the internal reference, $CHCl_3$, and was observed at 60 Mc. The best-fit lines drawn through the experimental points were calculated with Eq. (7). The values derived from the calculations are $J_g^{HH} = (+)2.01 \pm 0.08$ cps, $J_t^{HH} = (+)16.35 \pm 0.80$ cps, $\Delta E = E_t - E_g = +1085 \pm 30$ cal, and $\nu_g^H = 75.0 \pm 0.2$ cps, $\nu_t^H = 114.0 \pm 1.6$ cps, $\Delta E = +1100 \pm 35$ cal, from $\langle J_{HH} \rangle$ and $\langle \nu_H \rangle$ respectively.

In this compound, the two rotamers with the hydrogens gauche to one another are equivalent. Therefore, Eq. (7) was used to fit the temperature dependence of $\langle J_{HH} \rangle$, with the results given in Fig. 2. It is important to note that the denominator of Eq. (7) is not "symmetrical". Therefore, the data cannot be fitted equally well by interchanging the values for J_g^{HH} and J_t^{HH} with a change in the sign of ΔE. The analysis establishes unambiguous values for the three parameters, except for the usual uncertainty in the absolute sign of the J's.

$\langle \nu_H \rangle$.- The temperature dependence of $\langle \nu_H \rangle$ was obtained by measuring the position of the single line from the C^{12}-C^{12} molecules with respect to that from ~5% of an internal reference, $CHCl_3$. The proton resonance in $CHCl_2CHCl_2$ is about 80 cps upfield, at 60 Mc, from that in $CHCl_3$, and this difference increases by a few cps at higher temperatures, as shown by the experimental data listed in Table I. $CHCl_3$ was chosen as the reference because of the probability that hydrogen bonding, as well as the equilibrium between gauche and trans forms, contributes to $\langle \nu_H \rangle$ and its temperature dependence. The importance of hydrogen bonding was established by measuring $\langle \nu_H \rangle$ with respect to both $(CH_3)_4Si$ and $CHCl_3$ at two quite different temperatures in a solution containing 2 to 5% of each reference. The change in $\langle \nu_H \rangle$ with respect to $(CH_3)_4Si$ was found to be +5.8 cps while that with respect to $CHCl_3$ was only +1.8 cps.

The effects of the equilibrium between rotamers could be separated from those of hydrogen bonding, or other interactions, by observing $\langle \nu_H \rangle$ in a dilute solution with an appropriate solvent. But this would affect ΔE as well,[1] which is another type of problem. However, one would expect $CHCl_3$ and $CHCl_2CHCl_2$ to be similar in their hydrogen bonding properties, so that the temperature dependence of $\langle \nu_H \rangle$ with respect to $CHCl_3$ may depend primarily upon the equilibrium between rotamers. Therefore, the data were fitted by the $\langle \nu_H \rangle$ equivalent of Eq. (7), with the results shown in Fig. 2. It is seen that ν_t^H is upfield from ν_g^H. The agreement within experimental error of the ΔE value (1100 cal) from $\langle \nu_H \rangle$ with that (1085 cal) from $\langle J_{HH} \rangle$ could be fortuitous; nonetheless, it looks good.

B. $CHCl_2CHF_2$

$\langle J_{HH} \rangle$.- This compound is similar to $CHCl_2CHCl_2$ in having two equivalent rotamers in which the protons are gauche. The two protons and two fluorine nuclei constitute an an abx_2 system[2,3,19] such that the rotational averaging makes the two fluorines (x_2) magnetically as well as structurally equivalent. General expressions have been reported for the transitions and intensities in an abx_2 spectrum.[19] In our example, the proton spectrum consists of two overlapping "triplets". That at lower field has a large splitting and thus arises from the CHF_2 group. Upfield by about 10 cps, at 60 Mc, from the center of the first "triplet" is the second proton "triplet" with a smaller splitting and hence from the $CH\text{-}CF_2$ group. In addition, each component of both "triplets" is a close doublet because of splitting by $\langle J_{HH} \rangle$. The central part of the spectrum is distorted greatly by mixing of the spin states. A detailed fit of the room temperature spectrum gave the following values: $\langle \Delta\nu_H \rangle = 10$ cps, $\langle J^{HF}_{gem} \rangle = (+)55.0$ cps (in CHF_2 group), $\langle J_{HF} \rangle = (+)7.75$ cps (in $CH\text{-}CF_2$ group), and $\langle J_{HH} \rangle = |3.50|$ cps. The two outermost components of the CHF_2 triplet, which correspond to $M_F = \pm 1$, are virtually pure doublets whose splitting gives $\langle J_{HH} \rangle$ directly. The complexity of the rest of the spectrum limited our present measurements to $\langle J_{HH} \rangle$, the results for which are given in Table II. The fitting of these data by Eq. (7) is shown in Fig. 3.

$\langle J^{HF}_{gem} \rangle$ and $\langle J^{HF}_{vic} \rangle$.- The F^{19} resonance of $CHCl_2CHF_2$ is virtually identical with that discussed at length in Section IV.E. on $CHCl_2CHFCl$, consisting of three pairs of lines with a common center. (The x_2 spectrum of an abx_2 system is given by the same parameters as for an abx system.)[12,19] The outermost pair is the strongest, with unit intensity, and their splitting is assigned unambiguously as $\left| \langle J^{HF}_{gem} \rangle + \langle J^{HF}_{vic} \rangle \right|$. This proves that both H-F coupling constants are of like sign, as listed in the previous paragraph. It should be rather easy to analyze the temperature dependence of the fluorine spectrum, as described for $CHCl_2CHFCl$, but this was not done.

Table II. The temperature dependence of $\langle J_{HH} \rangle$ observed in liquid $CHCl_2CHF_2$.

Temperature	$\langle J_{HH} \rangle$	Temperature	$\langle J_{HH} \rangle$
210°K	3.09 ± 0.03 cps	328°K	3.59 ± 0.06 cps
239	3.24 ± 0.06	363	3.68 ± 0.09
267	3.38 ± 0.08	393	3.72 ± 0.06
296	3.47 ± 0.06	424	3.79 ± 0.11
298	3.46 ± 0.06	458	3.84 ± 0.09

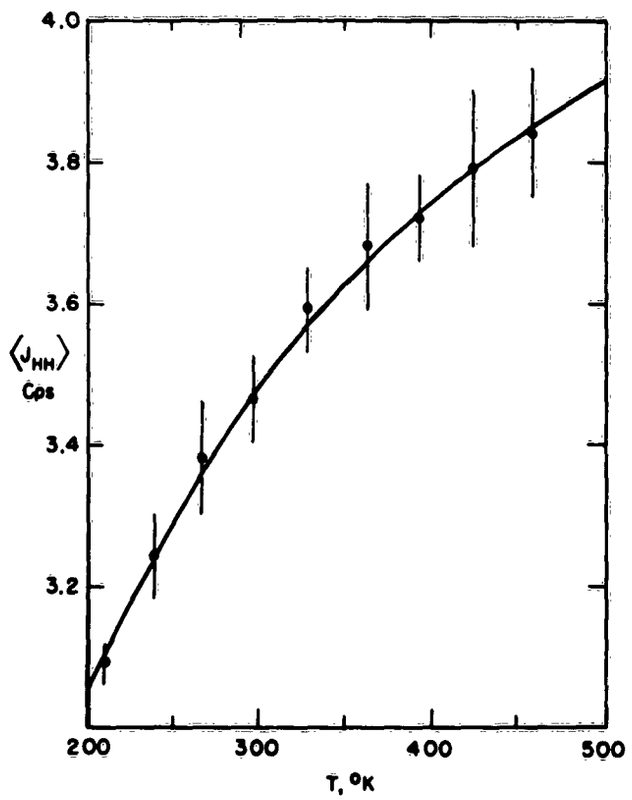
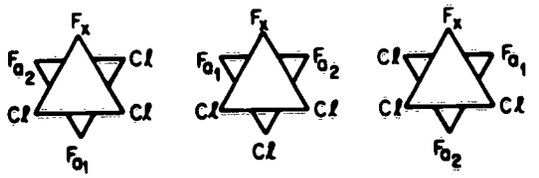


Fig. 3. The temperature dependence of $\langle J_{HH} \rangle$ in pure liquid $CHCl_2CHF_2$. The solid line through the experimental points was calculated with Eq. (7) using the best fit parameters $\Delta E = E_t - E_g = +495 \pm 40$ cal, $J_g^{HH} = (+)2.01 \pm 0.09$ cps, and $J_t^{HH} = (+)10.25 \pm 0.40$ cps.

Infrared.- These results are summarized in Table III. Analysis of the room temperature infrared spectrum of the liquid led to the assignment of a C-F stretching band at 1155 cm^{-1} to the gauche rotamer and one at 1095 cm^{-1} to the trans. The ratio of the extinction coefficients was obtained by measuring the optical densities of these bands in two pairs of solutions, 2% and 4% by volume of $CHCl_2CHF_2$ in $CHCl_3$ and in CS_2. The optical densities of these bands in the pure liquid then led to a value for $\Delta E = E_t - E_g$ of +350 ± 50 cal.

C. $CF_2ClCFCl_2$

General Aspects.- This compound is similar to the two preceding in that of the three forms shown below, two (1 and 3) are equivalent gauche forms. The trans rotamer, 2, is defined as that in which the Cl of the CF_2Cl group is trans to the F of $CFCl_2$.



(1) (2) (3)

Equation (7) applies to $\langle \nu_x^F \rangle$, the averaged shift of the fluorine in the $CFCl_2$ group. However, a somewhat different equation must be used for $\langle \nu_a^F \rangle$, the shift of the two fluorines in the CF_2Cl group, and for $\langle J_{vic}^{FF} \rangle$, the coupling between the $CFCl_2$ fluorine and each of the two CF_2Cl fluorines. The need for a new equation results from the non-equivalence within a given gauche molecule of the two fluorines in the CF_2Cl group; however, the equivalence of the two gauche forms and the rotational averaging make these two fluorines identical. Because of this we have

Table III. Infrared results used in determining $\Delta\bar{E}$ for pure liquid $CHCl_2CHF_2$.

Solvent pair[a]	$\frac{\kappa_g}{\kappa_t}$	Optical densities for pure liquid[b] A_g at 1155 cm^{-1}	A_t at 1095 cm^{-1}
$CHCl_3$-CS_2	0.205	0.308	0.457
$CHCl_3$-CS_2	0.183	0.398	0.586

[a]The ratio of extinction coefficients was obtained via Eq. (18) from measurements of A_g and A_t in two solutions of $CHCl_2CHF_2$, one in $CHCl_3$ and the other in CS_2. The first ratio is from 4% solutions; the second, 2%.

[b]The two sets of data are from samples of different thickness.

$$\langle J_{vic}^{FF} \rangle = \langle J_{a_1x}^{FF} \rangle = \langle J_{a_2x}^{FF} \rangle = (x_g/2)J_g^{FF} + x_t J_{g'}^{FF} + (x_g/2)J_{t'}^{FF} = \frac{J_g^{FF} + J_{g'}^{FF}\exp(-\Delta E/RT) + J_{t'}^{FF}}{2 + \exp(-\Delta E/RT)}, \quad (20)$$

where $\Delta E = E_t - E_g$. The subscripts on x and E denote the rotamer; and those on J, the structural relation between F_x and F_a (1 or 2).

In general, one would not expect J_g^{FF} and $J_{g'}^{FF}$ to be identical even though F_a and F_x are gauche to one another in both cases. This is because J_g^{FF} (unprimed) is a gauche parameter in a gauche rotamer, 1 or 3, while $J_{g'}^{FF}$ (primed) is a gauche parameter in the trans rotamer, 2. Undoubtedly, there are some differences in bond angles and other aspects of the electronic structure of the two rotamers, which in principle would cause at least small differences in the coupling constants. Therefore, Eq. (20) and its analogue for $\langle \nu_a^F \rangle$ involves four unknown physical parameters. Nonetheless, the functional form is identical with Eq. (7) and only three parameters may be obtained directly by analyzing the temperature dependence of $\langle J_{vic}^{FF} \rangle$; these are ΔE, $J_{g'}^{FF}$, and $(J_g^{FF} + J_{t'}^{FF})/2$. Similar considerations apply to $\langle \nu_a^F \rangle$.

$\langle J_{vic}^{FF} \rangle$.- The fluorine spectrum of this compound is virtually of the a_2x type;[2,3] and consists of a doublet ($\approx$1:1) for the CF_2Cl group and an upfield triplet ($\approx$1:2:1) for the $CFCl_2$ group. The chemical shift between the two sets of fluorine, $\langle \Delta\nu_F \rangle = \langle \nu_a^F - \nu_x^F \rangle \approx 150$ cps at 40 Mc, is over fifteen times as large as the intergroup coupling, $\langle J_{vic} \rangle \approx 9$ cps. Therefore, even though there are small deviations from the first order intensities, the splittings of the doublet and of the triplet are an accurate measure of $\langle J_{vic}^{FF} \rangle$. Values for it are listed in Table IV for temperatures between 236° and 471°K. These results have been fitted using Eq. (20), as shown in Fig. 4, and the best values obtained for the parameters are $\Delta E = E_t - E_g = 2760 \pm 120$ cal, $J_{g'}^{FF} = (-)21.17 \pm 0.13$ cps, and $(J_g^{FF} + J_{t'}^{FF}) = (+)18.86 \pm 0.13$ cps. The latter leads to a value of $(+)40.03 \pm 0.13$ cps for $J_{t'}$, if one assumes that $J_g^{FF} = J_{g'}^{FF}$.

$\langle \nu_a^F \rangle$ and $\langle \nu_x^F \rangle$.- The equivalence of the two fluorines in the CF_2Cl group makes unobservable their coupling, $\langle J_{gem}^{FF} \rangle$. Or the other hand, the chemical shifts $\langle \nu_x^F \rangle$ and $\langle \nu_a^F \rangle$ of the two sets of fluorine are given with sufficient accuracy by the

Table IV. The temperature dependence of $\langle J_{vic}^{FF} \rangle$ and of $\langle \nu_a^F \rangle$ and $\langle \nu_x^F \rangle$ observed in liquid $CF_2ClCFCl_2$.[a]

Temp. °K	$\langle J_{vic}^{FF} \rangle$ cps	Temp. °K	$\langle \nu_x^F \rangle$ cps	$\langle \nu_a^F \rangle$ cps
239	9.41 ± 0.04	232	2892.1	2724.9
270	9.37 ± 0.06	267	2886.5	2722.6
295	9.30 ± 0.05	295	2881.1	2721.1
330	9.17 ± 0.05	328	2874.3	2718.2
366	9.06 ± 0.08	362	2868.0	2715.3
397	8.92 ± 0.07	396	2858.4	2710.1
431	8.84 ± 0.05	433	2850.3	2705.4
470	8.59 ± 0.07	470	2839.9	2698.3

[a]The chemical shifts were measured at 40 Mc with respect to an internal reference, $CFCl_3$; the standard deviations of the shifts are all about ±0.06 cps. The larger shifts at lower temperatures are upfield displacements; moreover, $\langle \nu_x^F \rangle$ for $CFCl_2$ is upfield from $\langle \nu_a^F \rangle$ for CF_2Cl.

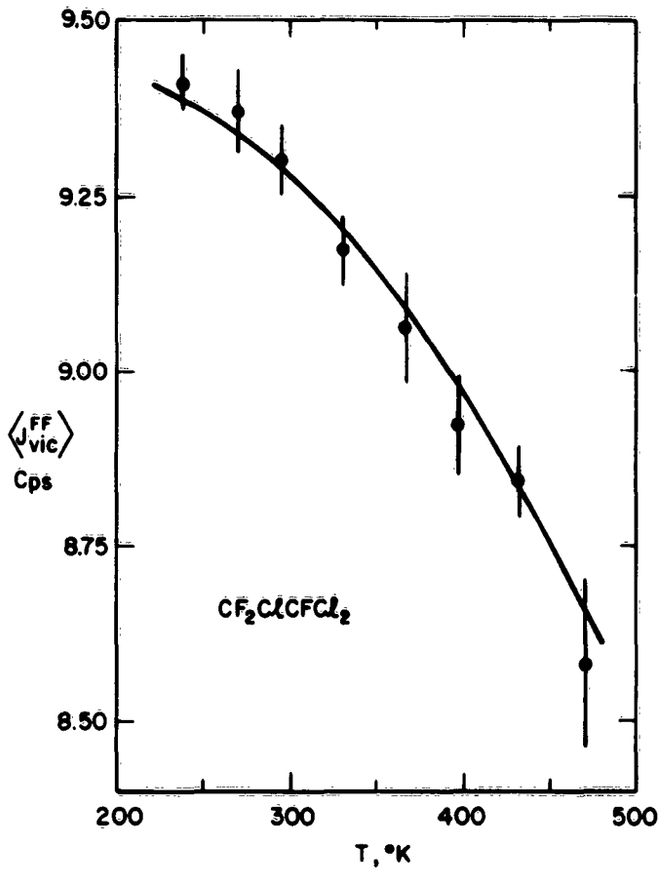


Fig. 4. The temperature dependence of $\langle J^{FF}_{vic} \rangle$ in pure liquid $CF_2ClCFCl_2$. The line through the experimental points was calculated with Eq. (20), using the best fit values $\Delta E = E_t - E_g = +2760 \pm 120$ cal, $J^{FF}_{g'} = (-)21.17 \pm 0.13$ cps, and $(J^{FF}_{g} + J^{FF}_{t'}) = (+)18.86 \pm 0.13$ cps.

center line of the triplet and by the midpoint of the doublet, respectively. They were observed as a function of temperature with respect to $CFCl_3$ as an internal reference;[20] the results are summarized in Table IV. It has been pointed out that the resonance position of $CFCl_3$ is concentration dependent.[20] This suggested that there might be temperature dependent shifts resulting from changes in the concentration of $CFCl_3$ because of its high volatility (bp = 24.1°C), even though the sample tubes were sealed. However, the total change found, at 22°C, in $\langle \nu_a^F \rangle$ and $\langle \nu_x^F \rangle$ for solutions ranging from 1 to 10% in $CFCl_3$ was only about 0.3 cps, which indicates that such effects were negligible.

The data for $\langle \nu_x^F \rangle$ and $\langle \nu_a^F \rangle$ have been fitted by the chemical shift versions of Eq. (7) and Eq. (20), respectively, and the results are shown in Fig. 5. No errors are given for the parameters calculated from $\langle \nu_x^F \rangle$ because the best fit of the data gives a least squares sum larger than that of the data, i.e. $\varphi_{min} = 3.2 > \varphi_{exp} = 2.0$ in Eq. (13). Thus, systematic error is present in the data or in the analysis. Furthermore, there is a rather large discrepancy among the three ΔE values: 2760 ± 120, 2000 ± 10, and 2675 cals, from $\langle J_{vic}^{FF} \rangle$, $\langle \nu_x^F \rangle$, and $\langle \nu_a^F \rangle$ respectively. A likely cause of these anomalies in the chemical shift results is molecular association. Therefore, an analysis was made of the internal shift $\langle \nu_x^F \rangle - \langle \nu_a^F \rangle$, with the hope of cancelling some of the deviations. This gave an intermediate value, 2300 ± 10 cal, for ΔE but the large value of 18.9 for φ_{min} shows that the fit of the data is even considerably worse than for $\langle \nu_x^F \rangle$, leading us to conclude that systematic errors occur in both sets of data, but in opposite directions. This was borne out by an analysis of the shift <u>sum</u>, $\langle \nu_x^F \rangle + \langle \nu_a^F \rangle$ which gave a value of 2220 cal for ΔE and a fit of the data almost within the experimental error, i.e. $\varphi_{min} = 5.2 \gtrsim \varphi_{exp}$.

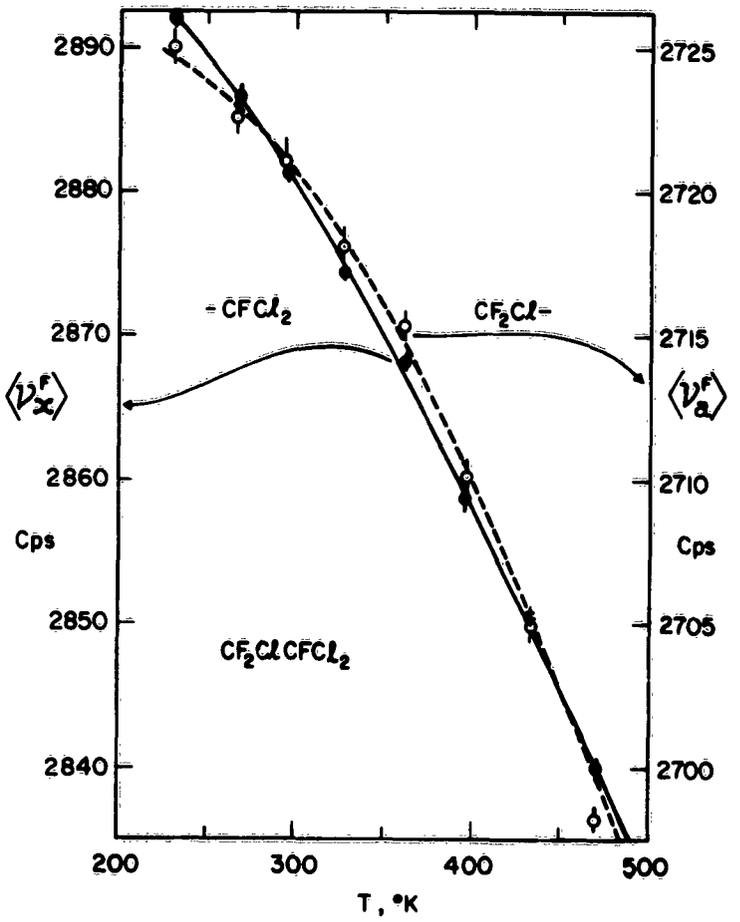


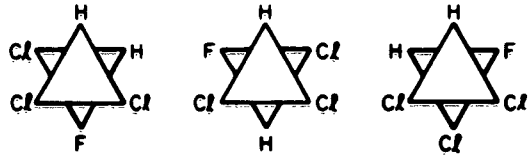
Fig. 5. The temperature dependence of the F^{19} chemical shifts in liquid $CF_2ClCFCl_2$. The shifts, observed at 40 Mc, are upfield with respect to the internal reference, $CFCl_3$. The lines through the experimental points were calculated with the equivalents of Eqs. (7) and (20) for $\langle \nu_x^F \rangle$ and $\langle \nu_a^F \rangle$, respectively, using the best-fit values $\Delta E = E_t - E_g = +2000 \pm 10$ cal, $\nu_g(F_x) = 2899.0 \pm 0.3$ cps, $\nu_t(F_x) = 1840 \pm 10$ cps, and $\Delta E = 2675$ cal, $\nu_{g'}(F_a) = 1777$ cps, $[\nu_g(F_a) + \nu_{t'}(F_a)] = 5452$ cps.

D. $CFCl_2CHCl_2$

$\langle J_{HF} \rangle$.- In the course of our work, Abraham and Bernstein[21] reported measurements of $\langle J_{HF} \rangle$ in the 60 Mc proton spectrum of $CFCl_2CHCl_2$, as a function of temperature. They used graphical methods to fit their data with the equivalent of Eq. (7) and obtained values of $\Delta E = E_t - E_g = +400$ cal, $J_g^{HF} = 1.03$ cps, and $J_t^{HF} = 18.08$ cps. Here, the designations of the rotamers correspond to the spatial relations of the H and F atoms. However, the values for $\langle J_{HF} \rangle$ calculated with these parameters show[21] small, but systematic, deviations from experiment, and probable errors were not given for the parameters. For these reasons, as well as the similarity of the compound to those reported here, we analyzed their data which is of particularly high quality because the spectrum lends itself to use of the wiggle-beat method to measure $\langle J_{HF} \rangle$. Our results are the following: $\Delta E = +400 \pm 4$ cal, $J_g^{HF} = (+)1.00 \pm 0.02$ cps, and $J_t^{HF} = (+)18.20 \pm 0.08$ cps.

E. $CHCl_2CHFCl$

General aspects.- This compound differs from those treated above in that the CHFCl carbon is asymmetric and, therefore, all three rotamers are non-equivalent as shown below for one of the two optically active molecules. Accordingly, the nmr ob-



servables should be described by the general five-parameter expression, Eq. (6). However, as a first approximation one might expect forms 1 and 3, in which the protons are

gauche, to have more nearly the same energy than the trans form, 2. Similarly, one would expect the gauche H-H coupling constants in 1 and 3 to be nearly the same, as well as the gauche H-F coupling constants in 2 and 3. These approximations were made initially in analyzing the observed values of $\langle J_{HH} \rangle$ and $\langle J^{HF}_{vic} \rangle$ with the three-parameter program. Five parameter analyses were made later.

$\langle J_{HH} \rangle$.- The nmr spectrum of the compound is of the abx type.[2,12] The proton resonance consists of two partially overlapping ab-type quartets, readily assignable by means of the symmetry required for each quartet. The proton resonance from the $CHFCl$ group is about 25 cps downfield, at 60 Mc, from that of the $CHCl_2$ group; the overlapping of the quartets discouraged us from determining the small temperature dependence of the proton shift. The shift assignment is based[12] on the fact that $\langle J^{HF}_{gem} \rangle$ is several-fold larger than $\langle J^{HF}_{vic} \rangle$. Within each proton quartet, $\langle J_{HH} \rangle$ is the splitting between an outer and the nearest inner line, and this quantity was measured directly on the recorded spectra. The temperature dependence observed for $\langle J_{HH} \rangle$ is given in Table V and plotted in Fig. 6, which includes the best-fit curves calculated with both the five- and the three-parameter functions, Eqs. (6) and (7). The results obtained are summarized in Table VI.

$\langle J^{HF}_{gem} \rangle$ and $\langle J^{HF}_{vic} \rangle$.- The F^{19} resonance, at 40 Mc, is of particular interest in that it exhibits all three pairs of allowed transitions.[12] Furthermore, the strongest pair of lines, with unit intensity, is the outermost. Their splitting is $\left| \langle J^{HF}_{gem} \rangle + \langle J^{HF}_{vic} \rangle \right|$, which demonstrates unequivocally that the two H-F coupling constants are of like sign. The other two splittings involve the difference between the two H-F coupling constants, $\langle J_{HH} \rangle$, and the chemical shift between the two protons. The latter can be eliminated from the expressions for these splittings by introducing[2] the value of $\langle J_{HH} \rangle$ obtained from the proton resonance. Thus, measurement of all three splittings in the F^{19} spectrum leads to values for the sum and difference of the two H-F coupling constants, and thereby to values for each. In addition, the analysis gives the chemical shift between the two protons, but the temperature dependence obtained for it in this way proved too small and uncertain to be useful.

Table V. The temperature dependence of $\langle J_{HH} \rangle$ and $\langle J^{HF}_{vic} \rangle$ observed in liquid $CHCl_2CHFCl$.[a]

Temperature	$\langle J_{HH} \rangle$	Temperature	$\langle J^{HF}_{vic} \rangle$
206°K	3.01 ± 0.07 cps	212°K	9.86 ± 0.11 cps
218	3.02 ± 0.02	246	9.54 ± 0.22
239	3.23 ± 0.06	271	9.25 ± 0.14
267	3.51 ± 0.02	295	9.07 ± 0.13
275	3.55 ± 0.06	323	8.98 ± 0.17
296	3.64 ± 0.07	327	8.94 ± 0.19
298	3.69 ± 0.04	360	8.67 ± 0.09
327	3.85 ± 0.08	397	8.54 ± 0.10
343	3.86 ± 0.06	423	8.42 ± 0.16
345	3.86 ± 0.06	424	8.59 ± 0.12
362	3.93 ± 0.08	457	8.35 ± 0.11
393	3.93 ± 0.07	470	8.37 ± 0.10
396	4.03 ± 0.11		
403	3.91 ± 0.08		
432	4.02 ± 0.06		
435	4.06 ± 0.09		
451	4.03 ± 0.09		
469	4.11 ± 0.07		

[a]The values for the H-C-C-F coupling, $\langle J^{HF}_{vic} \rangle$, were obtained from the F^{19} spectra and for $\langle J_{HH} \rangle$ from the H^1 spectra.

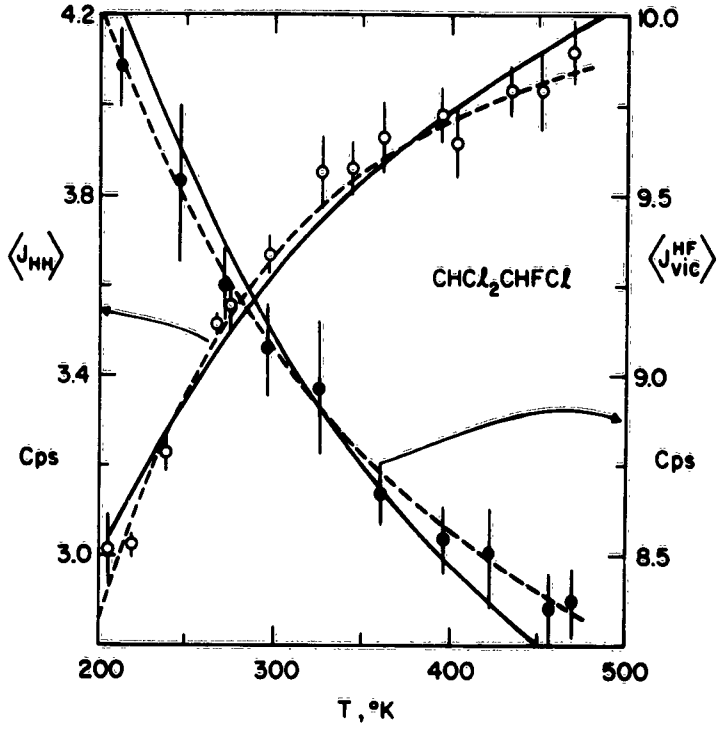


Fig. 6. The temperature dependence of $\langle J_{HH} \rangle$ and of $\langle J^{HF}_{vic} \rangle$ in pure liquid $CHCl_2CHFCl$. The solid lines through the experimental points are the best-fit, three-parameter functions, Eq. (7) and Eq. (20), assuming that the two gauche coupling constants are equal and that the two rotamers with the protons gauche are of equal energy. The dashed lines are the best-fit, five-parameter function, Eq. (6). The values of the parameters are summarized in Table VI.

Table VI. Results obtained from the three- and five-parameter analyses of the temperature dependence observed for $\langle J_{vic}^{HH} \rangle$ and $\langle J_{vic}^{HF} \rangle$ in pure liquid $CHCl_2CHFCl$.

	3-param. cps[a]	5-param. cps[a]		3-param.[b] cal	5-param. cal
$J_1^{HH}(g)$	+0.33 ± 0.09	+1.63 ± 0.15	E_1	0	0
$J_2^{HH}(t)$	+15.0 ± 0.3	+16.5 ± 0.3	E_2	325 ± 20	400 ± 15
$J_3^{HH}(g)$	$J_1^{HH}(g)$	-2.62 ± 0.65	E_3	E_1	970 ± 75
$J_1^{HF}(t)$	+38.0 ± 0.2	+37.3 ± 0.3	E_1	0	0
$J_2^{HF}(g)$	-9.58 ± 0.12	+13.2 ± 0.4	E_2	360 ± 15	110 ± 10
$J_3^{HF}(g)$	$J_2^{HF}(g)$	-2.8 ± 0.4	E_3	E_1	115 ± 72

[a]The signs given for the coupling constants are relative, and then only for the H-H and H-F constants separately, with the largest arbitrarily taken as positive. With the same convention, the temperature independent value of $\langle J_{gem}^{HF} \rangle$ is +49.1 ± 0.2 cps with respect to the J_{vic}^{HF} values.

[b]These results are to be compared with a value of $E_t - E_g = +375 \pm 160$ cal obtained from our analysis of infrared data, which assumes that both "gauche" forms have the same energy or else that one is much less stable than either of the other two forms.

Moreover, this indirect procedure, as well as the relatively large splittings involved, gives less reliable values for the coupling constants than direct measurements. In any case, $\langle J_{gem}^{HF} \rangle$ was found to have a constant value of (+)49.1 cps within an experimental error of $\pm$0.2 cps at twelve temperatures ranging from 212 to 470°K. The corresponding values for $\langle J_{vic}^{HF} \rangle$ are included in Table V and plotted in Fig. 6. In fitting the latter with three parameters, Eq. (20) must be used instead of Eq. (7) because the H-C-C-F dihedral angle is rotated 120° from that defining the gauche and trans rotamers. The results, as well as those from the five-parameter analysis, are summarized in Table VI.

In the latter, the assignment of the E's and the corresponding J's to the particular forms can not be made from the analysis alone, because the five-parameter equation is invariant to the assignment. However, from the preceding examples of more symmetrical compounds in which the asymmetry of the three-parameter function provides assignments, it appears that $|J_t| > |J_g|$ for both the H-H and H-F vicinal coupling constants. Therefore, rotamers 1 and 2 were assigned as those in which the magnitudes of J_{vic}^{HH} and J_{vic}^{HF} are the largest, respectively, and rotamer 3, as that remaining. The ΔE's obtained from the two sets of data agree rather poorly, and the assignments of $J_2^{HF}(g)$ and $J_3^{HF}(g)$ may be reversed. On the other hand, it is clear from the results for $\langle J_{HH} \rangle$, the most reliable in Table VI, that the assumption of $E_1 = E_3$ in the three-parameter analysis is invalid, even though the values calculated for the J's are reasonable. This may be seen also in Fig. 6, in which the best-fit, three-parameter curves deviate systematically from the experimental points. At best, it seems risky to simplify the analysis of molecules with three non-equivalent forms by assuming two to have the same energy.

Infrared.- These results are summarized in Table VII. Analysis of the room temperature infrared spectrum of the liquid led to the assignment of a C-Cl stretching band at 794 cm^{-1} to the trans rotamer and one at 820 cm^{-1} to the gauche. The ratio of the extinction coefficients was obtained by measuring the optical densities of these bands in four pairs of solutions. The optical densities of these bands in the pure

Table VII. Infrared results used in determining ΔE for pure liquid $CHCl_2CHFCl$.

Solvent pair[a]	$\frac{\kappa_g}{\kappa_t}$	Optical densities for pure liquid[b] A_g at 820 cm^{-1}	A_t at 790 cm^{-1}
C_6H_{12}-dioxane	0.362	0.446	0.406
CS_2-dioxane	0.412	0.169	0.159
CS_2-C_6H_{12}	0.216	0.165	0.154
CS_2-dioxane	0.233	0.185	0.163
		0.182	0.167

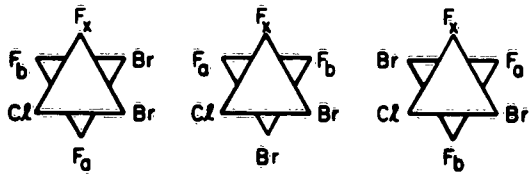
[a]The ratio of extinction coefficients was obtained via Eq. (18) from measurements of A_g and A_t in solutions of $CHCl_2CHFCl$, at the same volume concentration, in each of the two solvents listed. The first three ratios are from solutions containing 5% $CHCl_2CHFCl$; the last, 20%.

[b]The five sets of data are from samples of different thickness.

liquid then led to a value for $\Delta E = E_t - E_g$ of +375 ± 160 cal. This result, incidentally, is independent of whether only one or both gauche forms contribute to the 820 cm^{-1} absorption band.

F. $CF_2BrCFBrCl$

General aspects.- This compound is similar to $CHCl_2CHFCl$ in having three nonequivalent rotamers and an nmr spectrum which is of the abx type.[2,12] The rotamers are identified as shown below. The nmr spectrum is from the CF_2CF group which, however,



has lower symmetry than that discussed for $CF_2ClCFCl_2$ in Section IV.C, and, therefore, we will find the results in the latter to be helpful.

$\langle J_{gem}^{FF} \rangle$.- The F^{19} spectrum of the CF_2Br group in $CF_2BrCFBrCl$ is the ab part of the abx system. The "doublets" within each of the two "pseudo-quartets" are readily assigned on symmetry grounds, the splitting of each doublet being $\langle J_{gem}^{FF} \rangle$.[3,12] This quantity was found to have a temperature independent value of 166.8 cps, within an experimental error of ±0.5 cps in the temperature range -49°C to 133°C.

$\langle J_{ax}^{FF} \rangle$, $\langle J_{bx}^{FF} \rangle$, and $|\langle \nu_a^F - \nu_b^F \rangle|$.- At temperatures of +50°C and above, with the eight lines of the ab portion of the spectrum numbered consecutively from low to high field, the doublets are 1-3, 2-5, 4-7, and 6-8. One assignment into quartets is 1347 and 2568; the other 1368 and 2547. However, the 2547 assignment overlaps the doublets within the quartet, which is impossible; so the first assignment is correct. The separation of the quartet centers, about 14 cps, is $\frac{1}{2}\left|\langle J_{ax}^{FF} \rangle + \langle J_{bx}^{FF} \rangle\right|$.

The $CFBrCl$ part of the spectrum, throughout the range of temperature investigated, is about 370 cps upfield (at 40 Mc) from CF_2Br and consists of a 1:2:1 "triplet" with the center line an unresolved doublet. The 14 cps splitting of the outer lines is $\frac{1}{2}\left|\langle J_{ax}^{FF}\rangle \pm \langle J_{bx}^{FF}\rangle\right|$, and since it agrees with the separation of centers of the ab quartets, it must be the sum. This shows that $\langle J_{ax}^{FF}\rangle$ and $\langle J_{bx}^{FF}\rangle$ have the same sign throughout the temperature range in question, and enables the ab quartets to be assigned correctly at temperatures below 22°C where their centers overlap.

The central splittings of the ab quartets and of the outer pair of x lines were measured as a function of temperature. The results, along with the value of $\langle J_{gem}^{FF}\rangle$, were analyzed as for $CHCl_2CHFCl$ to obtain values for $\langle J_{ax}^{FF}\rangle$, $\langle J_{bx}^{FF}\rangle$, and $\left|\langle \nu_a^F - \nu_b^F\rangle\right|$, which are listed in Table VIII and plotted in Fig. 7. These data were fitted with the five-parameter function, Eq. (6), giving the results listed in Table IX and the curves drawn in Fig. 7. Again, there are systematic discrepancies in the chemical shift because for it the best fit gives $\varphi_{min} = 2.5 > \varphi_{exp} = 0.8$.

Assignment of the parameters to specific rotamers can be accomplished with certainty only in part. Matching of the E's from the three sets of data is unambiguous except for the two values of E = 0 from $\left|\langle \Delta\nu_F\rangle\right|$; the matching given in Table IX not only follows the relative values of E but it is required in order that $\left|J_t^{FF}\right| > \left|J_g^{FF}\right|$ as we found to be the case in $CF_2ClCFCl_2$. The greatest difficulty is that neither the spectrum itself nor the parameters derived from its temperature dependence differentiate directly between F_a and F_b; i.e. rotamers 1 and 3 are indistinguishable. Some information is contained in the fact that the central splitting of the downfield ab quartet is found to be larger than that of the upfield ab quartet. This asymmetry depends upon the chemical shift of the fluorine (F_a or F_b) which is coupled most strongly to F_x. In combination with the finding that $\langle J_{ax}^{FF}\rangle$ and $\langle J_{bx}^{FF}\rangle$ have the same sign, this leads[12] to the conclusion that the fluorine (F_a or F_b) with the smallest value of $\langle J_{vic}^{FF}\rangle$ is shifted upfield from that with the largest value. But further information is required to tell which is which. As at best a guess, it seems likely that in rotamer 2, the resonance of F_a will be downfield from F_b, and the entries in Table IX are labelled accordingly.

Table VIII. The temperature dependence of $\langle J_{ax}^{FF} \rangle$, $\langle J_{bx}^{FF} \rangle$, and of $|\langle \nu_a^F - \nu_b^F \rangle|$ observed in liquid $CF_2BrCFBrCl$.[a]

Temperature	$\langle J_{ax}^{FF} \rangle$	$\langle J_{bx}^{FF} \rangle$	$\langle \nu_a^F - \nu_b^F \rangle$[b]
224°K	13.32 ± 0.10 cps	14.90 ± 0.15 cps	84.75 cps
238	13.32 ± 0.15	14.70 ± 0.15	81.25
265	13.36 ± 0.25	14.58 ± 0.25	74.85
295	13.28 ± 0.20	14.54 ± 0.20	69.85
325	13.10 ± 0.15	14.55 ± 0.10	63.15
362	13.20 ± 0.15	14.40 ± 0.20	58.30
401	12.98 ± 0.10	14.28 ± 0.20	53.95
433	12.86 ± 0.15	14.18 ± 0.10	50.75
466	12.80 ± 0.15	13.92 ± 0.15	46.45

[a]The spectrum itself does not give the sign of the chemical shift nor does it differentiate between $\langle J_{ax}^{FF} \rangle$ and $\langle J_{bx}^{FF} \rangle$. The spectrum does show that the latter have the same sign; moreover, it requires that $|\langle J_{ax}^{FF} \rangle| - |\langle J_{bx}^{FF} \rangle|$ have a sign opposite to $\langle \nu_a^F - \nu_b^F \rangle$, as listed. In this regard, it is important to remember that a larger positive number is an upfield (down-frequency) shift.

[b]The standard deviations of the chemical shifts are all about ±0.3 cps.

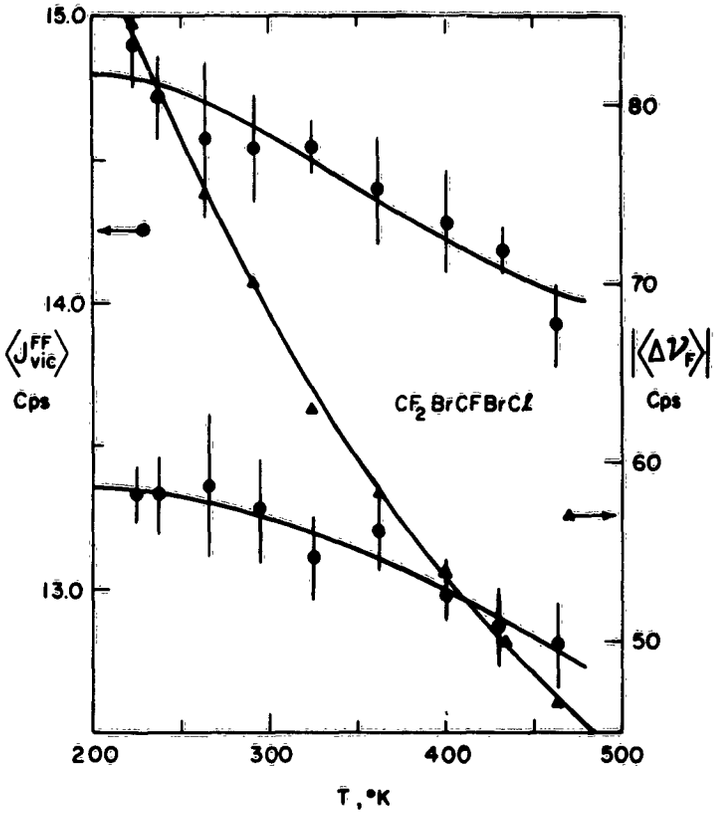


Fig. 7. The temperature dependence of $\langle J^{FF}_{ax} \rangle$, $\langle J^{FF}_{bx} \rangle$, and of $|\langle \Delta\nu_F \rangle| = |\langle \nu^F_a - \nu^F_b \rangle|$ in pure liquid $CF_aF_bBrCF_xBrCl$. The lines through the experimental points are the best-fit, five-parameter functions, Eq. (6). Values of the parameters are summarized in Table IX. The standard deviations of the observed chemical shifts are within the size of the points plotted.

Table IX. Results obtained from the five-parameter analyses of the temperature dependence observed for $\langle J_{ax}^{FF} \rangle$, $\langle J_{bx}^{FF} \rangle$, and $|\langle \nu_a^F - \nu_b^F \rangle|$ in pure liquid $CF_aF_bBrCF_xBrCl$.[a]

Rotamer[b]	E cal	$\langle J_{ax}^{FF} \rangle$ cps	E cal	$\langle J_{bx}^{FF} \rangle$ cps	E cal	$(\nu_a^F - \nu_b^F)$ [c] cps
1	0	+38.7 ± 0.3	0	+5.3 ± 0.2	0	+178
2	2695 ± 425[d]	-12.0 ± 0.3	605 ± 20	-10.5 ± 1.0	645	-273
3	0 ± 6	-8.9 ± 11.2	230 ± 10	+41.6 ± 0.4	0	+75

[a]The signs given for all of the coupling constants are relative, the largest arbitrarily listed as positive.

[b]The assignments are based in part on the assumption that $(\nu_a^F - \nu_b^F)$ is negative for rotamer 2. See text for details.

[c]A larger positive number corresponds to an upfield shift. The shift assignments for rotamers 1 and 3 are uncertain; they may be interchanged without affecting any of the other assignments. No errors are given because $\varphi_{min} > \varphi_{exp}$.

[d]This value is particularly unreliable because $\langle J_{ax}^{FF} \rangle$ changes by only about 0.5 cps over a 250°C temperature range, and this small change has to be obtained by indirect methods from the spectra.

G. CHX_2CH_2Y and CH_2XCH_2Y

Proton spectra were observed for several compounds with bulky groups in the hope that cases would be found in which the energetic preference for one rotamer would be great enough to make the observed H-H coupling constant a good approximation for J_{vic}^{HH} in that form. However, in four of these compounds, the values found for J_{vic}^{HH} were virtually temperature independent and of a magnitude supporting the interpretation that all three rotamers are of nearly the same energy. Nonetheless, the results which are summarized in Table X are of some interest as shown below.

$\langle J_{vic}^{HH} \rangle$ in $CH\phi_2CH_2(CO\phi)$ and $CHBr_2CH_2Br$.- The proton spectra of the $CHCH_2$ group protons in these compounds are of the a_2x type,[2] consisting of a 1:2:1 triplet with the a_2 1:1 doublet about 100 cps upfield at 60 Mc. The splittings within these multiplets are $\langle J_{vic}^{HH} \rangle$, and these are the quantities measured and listed in Table X. The over-all symmetry of the compounds is the same as that of $CF_2ClCFCl_2$, Section IV.C, and the same definitions are used for the rotamers. Furthermore, Eq. (20) applies to $\langle J_{vic}^{HH} \rangle$, except that the temperature dependence is too small to use the curve fitting procedures adopted thus far for evaluating the three parameters involved.

In $CH\phi_2CH_2(CO\phi)$ there is a small, 0.05 cps, but apparently real, decrease in $\langle J_{vic}^{HH} \rangle$ upon increasing the temperature from 295° to 402°K. Combining this with Eq. (20) and the fact that the magnitude of $J_t^{HH} >> J_g^{HH}$, we conclude that the energy of the trans rotamer, 1, must be greater than that of the two equivalent gauche rotamers, 2 and 3; i.e. $E_1 = E_t > E_2 = E_3 = E_g$. The trans rotamer is that in which the $CH\phi_2$ proton is trans to $(CO\phi)$ in $CH_2(CO\phi)$. Moreover, a good numerical approximation to $\Delta E = E_t - E_g$ can be obtained by noting that $\langle J_{vic}^{HH} \rangle$ is very close to the values found in cases where the rotational potential function has three-fold symmetry.[16,22,23] Therefore, it is reasonable to assume $\Delta E \ll RT$. With the further reasonable assumption that $J_g^{HH} = J_{g'}^{HH}$, Eq. (20) can be written in the form

$$\langle J \rangle \approx \frac{|J_t - J_g|}{9} \frac{\Delta E}{RT} + I \,, \qquad (21)$$

Table X. The small temperature dependence of $\langle J^{HH}_{vic} \rangle \cong (1/3)(J^{HH}_{t} + 2J^{HH}_{g})$ observed in some compounds of the CHX_2CH_2Y and CH_2XCH_2Y types, and the resultant approximate values of ΔE.[a]

Compound	Temperature	$\langle J^{HH}_{vic} \rangle$	ΔE[b]
$CH\phi_2CH_2(CO\phi)$	295°K	7.21 ± 0.05 cps	+80 cal
	402	7.16 ± 0.11	
$CHBr_2CH_2Br$	240	6.60 ± 0.06	+35
	295	6.62 ± 0.05	
	398	6.59 ± 0.05	
$CH_2\phi CH_2Cl$	295	7.48 ± 0.08	-60
	397	7.44 ± 0.09	
$CH_2\phi CH_2Br$	295	7.56 ± 0.04	-90
	398	7.50 ± 0.09	

[a] All of the measurements were made on the pure liquids except $\phi_2CHCH_2(CO\phi)$ which was in $CHCl_3$ solution.

[b] ΔE is defined as $E_t - E_g$, where *trans* refers to the rotamer of unique form and *gauche* to that having two equivalent forms; values approximated with Eqs. (21) and (24).

by first taking the derivative of $\langle J \rangle$ with respect to temperature, dropping all but the constant term in the series expansion of $\exp(-\Delta E/RT)$, and integrating.

The form of Eq. (21) does not lend itself to obtaining both $|J_t - J_g|$ and ΔE from the experimental data. However, our previous results give average values of 14 and 1.5 cps for J_t and J_g, the use of which in Eq. (21) should produce little error. The constant I is eliminated by fitting Eq. (21) to data at two temperatures. In this manner, we find for $CH\phi_2CH_2(CO\phi)$ that $E_t - E_g \approx +80$ cal.

The data for $CHBr_2CH_2Br$ show at most a possible slight decrease in $\langle J_{vic}^{HH} \rangle$ with increasing temperature. Averaging of the data in Table X, for 240° and 295°K, and application of Eq. (21) to it and to the data for 398°K gives a value for $E_t - E_g \approx +35$ cal. It is seen that the assumption $\Delta E \ll RT$ is satisfied very well in both of these compounds.

$\langle J_{vic}^{HH} \rangle$ in $CH_2\phi CH_2Cl$ and $CH_2\phi CH_2Br$.- The spectra of the aliphatic protons in these compounds are of the $a_2'b_2'$ type. In both compounds, the $CH_2\phi$ resonance is upfield from that of the CH_2X group, the shift being 35 cps in the chloride and 23 cps in the bromide, at 60 Mc; this assignment is based upon the broadening of the $CH_2\phi$ half of the otherwise symmetrical spectrum by the coupling with the aromatic protons.

The protons in each CH_2 group are structurally equivalent but magnetically nonequivalent,[3,12] i.e. $\langle J_{ab}^{HH} \rangle \neq \langle J_{ab'}^{HH} \rangle$, except in the high-temperature limit when all three rotamers are equally populated and then only if, as we will assume, the three structurally different gauche coupling constants are equal, and the two trans. The expressions for the temperature dependence of the two vicinal H-H coupling constants have the same form as Eqs. (7) and (20), respectively, where $\Delta E = E_t - E_g$ and the trans rotamer is that in which ϕ and X are trans.

Because $|\Delta E|$ is small, the two vicinal constants differ only slightly numerically, and the proton spectra are very nearly of the a_2b_2 type, shown in Fig. 6-13, p. 145 of reference 2. Lines 1 and 3, as labelled there, are readily identified; their separation is $\langle J_{ab}^{HH} \rangle + \langle J_{ab'}^{HH} \rangle$, the measured quantity, half of which is defined as $\langle J_{vic}^{HH} \rangle$ and is given in Table IX. Addition of the Eqs. (7) and (20) and application of the same

assumptions and procedure leading to Eq. (21), gives the general form

$$\langle J \rangle + \langle J' \rangle = \frac{-|J_t - J_g|}{9} \frac{\Delta E}{RT} + I \ . \qquad (22)$$

Application of this equation to the two sets of data, for $CH_2\emptyset CH_2Cl$ and for $CH_2\emptyset CH_2Br$, yields values for ΔE of -60 and -90 cals, respectively.

H. CHXYCHYZ

In three compounds of this type, the relatively large values of $\langle J_{vic}^{HH} \rangle$, about 11 cps, as well as their decrease at higher temperatures, demonstrate that the rotamer with trans hydrogens is the stablest form. The modest changes of the coupling constant over the accessible temperature range are too small for evaluating all of the parameters but, as in the previous section, some reasonable assumptions permit ΔE to be estimated. If we assume that the energies and the J_g^{HH} coupling constants are the same in the two non-equivalent forms with the protons gauche, $\langle J \rangle$ is given by the form of Eq. (7) which has E_t as the zero of energy. Solution of this equation and rearrangement so that ΔE is defined as before, namely $E_t - E_g$, gives

$$\Delta E = RT[\ln(J_t - \langle J \rangle) - \ln 2(\langle J \rangle - J_g)] \ . \qquad (23)$$

If we take the previously used values of 14 cps and 1.5 cps for J_t and J_g, then Eq. (23) will give ΔE from the value observed for $\langle J \rangle$ at one temperature. This result for ΔE should lie between the values for the two gauche forms, if they are different.

The compounds in question are solids which decompose at higher temperatures so their proton spectra were observed for dilute solutions over a limited temperature range. In fact, useable spectra of $(p\text{-Br}\emptyset)CHClCH\emptyset(CO\emptyset)$ were obtained only at room temperature. The spectra of the HCCH group protons are "quartets" of the ab type, and $\langle J_{vic}^{HH} \rangle$ is the splitting of the outer pairs of lines, which was measured. In $(CH_3)BrCHCHBr(CO\emptyset)$, half of the "quartet" was further split by coupling with the CH_3 protons so measurements were made only on the other half. The experimental data as

well as the corresponding values of ΔE calculated via Eq. (23) are summarized in Table XI. There are two sets of data for two of the compounds so that in principle a second parameter such as $2J_g/J_t$ could be evaluated as well as ΔE. But this was discouraged by the smallness of $d\langle J\rangle/dT$ in comparison to the experimental errors. Moreover, the apparent change in ΔE with temperature could result not only from error in the assumed values for J_g and J_t but also from changes in the dielectric constant of the polar, dimethylformamide, solvent, or in the solute-solvent hydrogen bonding.

V. Discussion and Conclusions

In spite of its length, this paper is primarily a survey of what may be accomplished by measurements and analyses of the types outlined. Certainly, we have not sought to be comprehensive in studying the dependence upon rotational configuration of either the internal energy, the electron coupling of the nuclear spins or the chemical shifts in the substituted ethanes. Therefore, our discussion of the results is limited to the more general aspects and implications.

A. The ΔE Values

The determination of ΔE's from the temperature dependence of the nmr coupling constants and chemical shifts requires assumptions which may or may not be reasonable in all cases. Therefore, it is encouraging to find fair to excellent agreement not only between ΔE's obtained from different nmr observables but also between the values from nmr and those from vibrational spectra, as shown by the results summarized in Table XII. The best case in this regard is $CHCl_2CHCl_2$, where the value of 1100 ± 35 cal from $\langle \nu_H \rangle$ agrees very well with the 1050 ± 30 and 1080 ± 40 cal from $\langle J_{HH} \rangle$ and the vibrational spectra, respectively, in spite of the hydrogen bonding which we know affects $\langle \nu_H \rangle$. Probably the worst case is $CF_2ClCFCl_2$, in which molecular association and/or the large experimental errors makes uncertain the ΔE values from the chemical shifts. But even worse than the large size and the 2000 to 2760 cal range of the ΔE's from the nmr data is their difference from the 350 ± 150 cal value, of

Table XI. The values of $\langle J^{HH}_{vic} \rangle \cong J^{HH}_{t}$ observed in some compounds of the CHXYCHYZ type, and the resultant approximate results for ΔE.

Compound	Temperature	$\langle J^{HH}_{vic} \rangle$	ΔE[a]
(p-Brϕ)CHClCHϕ(COϕ) in CS_2 + ϕOH	295°K	10.82 ± 0.10 cps	-1,040 cal
(CH_3)CHBrCHBr(COϕ) in dimethyl formamide	295 363	10.48 ± 0.06 10.06 ± 0.16	-960 -1,060
CHBrϕCHBr(COϕ) in dimethyl formamide	35 363	11.31 ± 0.10 11.04 ± 0.05	-1,170 -1,350

[a] ΔE is defined as $E_t - E_g$, where the trans form is that in which the two protons are trans; values approximated with Eq. (25). Each of the compounds has two asymmetric carbons and can exist, therefore, as two different dl pairs having different ΔE's. The actual isomeric composition of the samples studied is not known to us.

Table XII. Summary of ΔE's obtained in several ways for some liquid haloethanes which have two equivalent gauche forms.

Compound	ΔE[a]	Source	Compound	ΔE[a]	Source
$CHCl_2CHCl_2$	1050 ± 30 cal	$\langle J_{HH} \rangle$	$CFCl_2CHCl_2$	400 ± 4 cal	$\langle J_{HH} \rangle$[b]
	1100 ± 35	$\langle \nu_H \rangle$		420 ± 130	IR [c]
	1080 ± 40	IR, Ram.[d]	$CF_2ClCFCl_2$	2760 ± 120	$\langle J^{FF}_{vic} \rangle$
$CHCl_2CHF_2$	495 ± 40	$\langle J_{HH} \rangle$		2300 ± 300	$\langle \nu_F \rangle$
	350 ± 50	IR		(±)350 ± 150(gas)	IR, Ram [e]

[a] ΔE is defined as $E_t - E_g$ where gauche designates the two equivalent forms.

[b] From reference 21 and our reanalysis of their data.

[c] R. E. Kagarise, J. Chem. Phys. 29, 680 (1958).

[d] A. Langseth and H. J. Bernstein, J. Chem. Phys. 8, 410 (1940); and also R. E. Kagarise and D. H. Rank, Trans. Far. Soc. 48, 394 (1952).

[e] P. Klaboc and J. Rud Nielsen, J. Molec. Spectroscopy 6, 379 (1961).

uncertain sign, from the vibrational spectra. However, the vibrational analysis is difficult, the observations are further complicated by thermal decomposition of the sample, and finally the ΔE is for the gas phase and large changes in it often occur with a change in state.[1] Further study of the compound is needed. The internal consistency of the results calculated for $CHCl_2CHFCl$ and for $CF_2BrCFBrCl$ leaves considerable room for improvement. Many of the differences found in Tables VI and IX reflect inaccuracies compounded by the indirect manner required to obtain all but one of the five sets of data from the spectra.

A detailed scrutiny of all of the ΔE 's obtained in this study reveals that the usual two factors[1] govern the relative stability of the rotational forms. For the group of similar compounds, $CHCl_2CHCl_2$, $CHCl_2CHF_2$, and $CFCl_2CHCl_2$, in Table XII, the rotamer in which the two protons and, in the latter, the fluorine and the proton, are gauche, is that of lowest energy. This is counter to predictions based on steric considerations alone. However, in these cases, the gauche forms have the largest electric dipole moment and the net stabilization of the form is attributed to the resulting dipole interactions in the liquid.[1] $CHCl_2CHFCl$, Table VI, follows the same rule in that rotamer 1, with the two H's gauche and the H and F trans, not only has the largest dipole moment but also is the stablest form. However, the stabilities of the other two forms are the reverse of their dipole moments but they do follow the steric interactions.

At first glance, one might expect $CF_2ClCFCl_2$, Table XII, to be in the same class as the four haloethanes just discussed. However, its molecular symmetry differs in that the trans, rather than the gauche, form has all of the smaller substituents adjacent. Therefore, steric as well as dipole interactions tend to stabilize the gauche form. This addition rather than partial cancellation of the two effects may explain the large ΔE found; however, the difference in dipole moments and its contribution to ΔE is small. In $CF_2BrCFBrCl$, one would expect the two effects to be in opposition because the trans form, with the three fluorines adjacent, has the largest dipole moment. This is supported by the smaller value of about 700 cal, Table IX, found for ΔE compared with the 2500 cal for $CF_2ClCFCl_2$.

The remaining seven compounds, listed in Tables X and XI, all have ΔE's corresponding to the stablest form being determined by steric factors. The rotamers of highest energy are those in which all hydrogens are adjacent. The dominance of steric factors is supported by the fact that the four compounds in Table X, with three or four ethanic hydrogens, have the smallest ΔE's, 50 to 100 cal, while those in Table XI, with only two hydrogens, have $\Delta E \approx 1100$ cal.

In general, nmr data offer not only versatile means for evaluating the ΔE's but also they give reasonable results. Significant systematic error can occur in the use of chemical shifts; for the coupling constants, molecular association seems to be unimportant and the other likely source of error, averaging by torsional oscillations, is not major.[7] Moreover, with improved instrumentation[25] and a better understanding of the factors which can affect the results, nmr may well be the best method for ΔE studies in liquids and even in the gas phase. What is possible is suggested by the results for $CFCl_2CHCl_2$, for which Abraham and Bernstein[21] were able to measure $\langle J_{HF} \rangle$ over a 150° temperature range to an accuracy of ± 0.02 cps. Our analysis of their data gives a value for ΔE of 400 ± 4 cal compared to the 420 ± 120 cal obtained from infrared studies.

In addition, it appears feasible to determine with some assurance quite small values of ΔE and also the relative energies in cases where all three forms are nonequivalent. The former, *via* procedures such as those used in Section IV.G, requires a reliable estimate for $|J_t - J_g|$. At present, the accuracy of this is about 20 percent for J_{HH}, which can no doubt be improved because the linear relation found[22] between $\langle J_{vic}^{HH} \rangle$ and the electronegativity of X and Y in CH_3CH_2X and CH_3CHXY implies that similar relations should apply for J_t^{HH} and J_g^{HH}. Thus far, less is known of J_{HF} and J_{FF}, but they seem to vary more than J_{HH} so it is fortunate that the studies of them involve large ΔE's and generally large changes in $\langle J \rangle$ with temperature.

The determination of the relative energy for all three forms of ethanes with an asymmetric carbon is a tour de force difficult by other methods. Probably as much can be learned by studying simpler compounds; however, results such as those for

$CF_2BrCFBrCl$ when obtained more accurately may be of value in separating the various contributions to ΔE. In concluding this section, it should not be forgotten that there are assumptions common to the nmr and vibrational analyses. The most important of these are probably the neglect, in connection with Eq. (3), of differences in the partition functions Q_n', excluding the internal rotation coordinate, for the three rotamers, and the assumption that ΔE is itself temperature independent.[1]

B. The Coupling Constants

Our results for the rotational dependence of the coupling constants are summarized in Table XIII. One feature common to all three types of constants, J_{HH}, J_{HF} and J_{FF}, is that $|J_t| > |J_g|$, which corresponds to the fact that in ethylenic compounds $|J_t| > |J_{cis}|$.[14] Furthermore, there are instances in which they are of opposite sign as well as of the same sign.

Approximate values of J_{HH} have been reported for four substituted ethanes by Sheppard and Turner.[16] In the one molecule, $CHCl_2CHCl_2$ which we have studied also, our values of $J_g^{HH} = (+)2.01 \pm 0.07$ cps and $J_t^{HH} = (+)16.07 \pm 0.8$ cps for the pure liquid are to be compared with theirs, 2.5 ± 1 and 14 ± 7 cps respectively, for the compound in solution. Valence bond calculations for the ethanic fragment HCCH, with tetrahedral HCC angles, have given the dependence of J_{HH} upon the dihedral angle ϕ to be[14]

$$J_{HH} \approx A \cos^2 \phi + B = 9 \cos^2 \phi - 0.3 , \qquad (24)$$

which agrees qualitatively with our results. However, there is the quantitative discrepancy noted at the time of the calculations in that the values predicted are significantly less than those observed. A weighted average of our results for J_g^{HH} and J_t^{HH} leads to $A = 17$ cps and $B = -3$ cps instead of the 9 and -0.3 cps given in Eq. (24). And, of course, it is not known whether the signs agree for the experimental and theoretical coupling constants.[26]

Table XIII. Summary of coupling constants.[a]

Compound	J_g cps	J_t cps	J_{gem} [b] cps
	H-H Coupling		
$CHCl_2CHCl_2$	+2.01 ± 0.08	+16.08 ± 0.8	
$CHCl_2CHF_2$	+2.01 ± 0.09	+10.25 ± 0.4	
$CHCl_2CHFCl$	+1.63 ± 0.15 -2.62 ± 0.65	+16.5 ± 0.3	
	H-F Coupling		
$CFCl_2CHCl_2$	+1.00 ± 0.02	+18.2 ± 0.08	
$CHCl_2CHFCl$	+13.2 ± 0.4 -2.8 ± 0.4	+37.3 ± 0.3	+49.1 ± 0.2
$CHCl_2CHF_2$ (25°)	$\langle J_{vic} \rangle$ = +7.75	$\langle J_{gem} \rangle$ = +55.0	
	F-F Coupling		
$CF_2ClCFCl_2$ [c]	-21.17 ± 0.13	+40.03 ± 0.13	
$CF_2BrCFBrCl$	+5.3±0.2; -8.9±11.2 -12.0±0.3; -10.5±1.0	+38.7 ± 0.3 +41.6 ± 0.4	|166.8 ± 0.5|

[a] The relative signs given for the coupling constants apply only to each pair of nuclear species within each molecule; the largest value for the coupling between each pair is listed arbitrarily as +.

[b] The values given are independent of temperature within experimental error.

[c] It is assumed that $J_g^{FF} = J_{g'}^{FF}$.

In monosubstituted ethanes, where symmetry requires that $\langle J_{HH} \rangle = (1/3)(J_t+2J_g)$, it has been found that[22]

$$\langle J_{HH} \rangle = 8.4 - 0.4\ \bar{E}\ , \qquad (25)$$

where $\bar{E}$ is the Huggins electronegativity of the substituent. The limiting, "completely averaged" values for J_{HH} in the three tetrasubstituted methanes of Table XIII, $CHCl_2CHCl_2$, $CHCl_2CHFCl$, and $CHCl_2CHF_2$, are 6.70, 5.17, and 4.76 cps, respectively. While these values do not follow a linear relationship such as Eq. (25), their qualitative similarity is shown by the monotonic decrease with $\sum_i E_i$, the sum of the substituents' electronegativities. No doubt bond angle changes as well as other substituent effects are involved.

On the basis of our limited data, the H-F and F-F coupling constants appear to undergo larger fractional changes with substituents than does J_{HH}. In connection with the theory of the coupling, it is of interest to note that not only are J_{gem}^{HF} and J_t^{HF} both large, but they are undoubtedly of the same sign. Unfortunately, none of our results provide any sign inter-relations among the H-H, H-F, and F-F sets. The values found for J_g^{FF} and J_t^{FF} support the "cancellation" hypothesis advanced some time ago[3,27] for the observation that in compounds such as $CF_3^{\gamma}CF_2^{\beta}CF_2^{\alpha}X$, $\langle J_{vic}^{FF} \rangle$ often is close to zero although $\langle J_{\alpha}^{FF} \rangle \approx 10$ cps. A present finding which is somewhat of a surprise is the apparent temperature independence of $\langle J_{gem}^{HF} \rangle$ and $\langle J_{gem}^{FF} \rangle$. The different rotamers of a molecule should have at least small differences in the HCF and FCF bond angles and, by analogy to the known sensitivity of J_{gem}^{HH} to the HCH angle,[28] the expected result is a small but detectable temperature dependence of $\langle J_{gem}^{HF} \rangle$ and $\langle J_{gem}^{FF} \rangle$. Further analysis of the matter is needed.

Related somewhat to this question is the matter of the factors governing differences in J_g and in J_t, in non-equivalent rotamers of a given molecule. For example, in $CHCl_2CHFCl$ there are two values of J_g^{HH} and of J_g^{HF}. Angular distortions from tetrahedral should, on the average, be proportional to the relative energies of the rotamers. So, it may not be coincidental that for both J_g^{HH} and J_g^{HF} the sign of the coupling changes upon going from a rotamer of lower energy to one of higher, as shown in Table VI.

C. The Chemical Shifts

Our limited results for chemical shifts are disappointing in their confirmation of the anticipated, adverse effects of molecular association. Such effects not only decrease the reliability of the $\Delta E'$s but also of the shifts determined for the individual rotamers from the temperature dependence of $\langle \nu \rangle$. This is unfortunate because the latter is much larger than that of the coupling constants and is correspondingly easier to measure accurately. Nonetheless, the results summarized in Table XIV do exhibit an interesting regularity. For $CHCl_2CHCl_2$, the form with the proton resonance farthest downfield is that with both protons adjacent. Similarly, for $CF_2ClCFCl_2$, the resonances of both sets of fluorine are farthest downfield in the rotamer, defined as <u>trans</u>, in which all three fluorines are adjacent. In both compounds, the rotamer with the downfield shift(s) is apparently that in which the <u>vicinal</u> substituents would produce the largest net electrostatic interaction effect[3,29] upon the resonances of the nuclei in question. If supported by further studies, such correlations should prove useful in establishing unknown molecular configurations.

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Table XIV. Summary of chemical shifts.[a]

Compound	Nucleus	ν_g	ν_t
$CHCl_2CHCl_2$	H	75.0 ± 0.2 cps	114.0 ± 1.6 cps
$CF_2{}^aClCF^xCl_2$	F_x	2899.0 ± 0.3	1840. ± 10
	F_a	1777 [b]	3675 [b]

[a] Larger positive numbers are upfield shifts. In addition, internal chemical shifts are given in Table IX for $CF_2BrCFBrCl$.

[b] The symbols ν_g and ν_t refer here to the relative positions of F_a and F_x in the molecule; also, it is assumed that ν_g has the same value in the gauche and trans rotamers.

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