**Table II.** Temperature Dependences of the Pmr Parameters for **1**

| Temp,[a] °C | $N^b$ | $L^b$ | $\nu_H{}^c$ |
|---|---|---|---|
| 63 | 14.764 (0.033)[d] [19][e] | 2.264 (0.033)[d] [24][e] | 73.874 (0.039)[d] [12][e] |
| 46 | 14.814 (0.073) [18] | 2.419 (0.047) [19] | 73.729 (0.048) [17] |
| 30 | 14.939 (0.059) [17] | 2.718 (0.045) [14] | 73.606 (0.037) [14] |
| 24 | 14.833 (0.037) [15] | 2.781 (0.041) [16] | 73.525 (0.044) [10] |
| 10 | 14.936 (0.033) [17] | 2.954 (0.023) [15] | 73.423 (0.026) [9] |
| -10 | 15.126 (0.043) [15] | 3.266 (0.042) [21] | 73.249 (0.026) [14] |
| -30 | 15.244 (0.071) [23] | 3.608 (0.061) [24] | 72.998 (0.052) [12] |
| -53 | 15.389 (0.054) [21] | 3.974 (0.086) [20] | 72.728 (0.044) [18] |
| -62 | 15.490 (0.074) [14] | 4.232 (0.018) [11] | 72.603 (0.068) [13] |
| -70 | 15.592 (0.066) [24] | 4.385 (0.043) [21] | 72.459 (0.033) [12] |
| -80 | 15.716 (0.062) [21] | 4.620 (0.059) [25] | 72.285 (0.020) [9] |
| -91 | 15.765 (0.044) [22] | 4.970 (0.027) [21] | 72.112 (0.031) [15] |

[a] Accurate to ±1°. [b] In hertz. [c] Downfield from HMDS in hertz. [d] Parenthetical values are standard deviations. [e] Bracketed values indicate the number of traces used.

each temperature and afforded standard deviations of less than 0.06 Hz with the majority in the range of 0.02–0.04 Hz.

For $^{13}C$ satellite spectra, the region in which the satellites were observed was calibrated before and after the experiment using side bands from HMDS. The average calibrations both before and after were calculated as previously described and in all cases were within the probable error of each other at a given temperature. The average of these two values provided a scale factor which was applied to the frequency separations of the transitions of interest. An average of 26 traces (13 upfield and 13 downfield) was recorded and manipulated as previously described. As a result, about 20 spectra were used for each temperature, the transition frequency separations of which exhibit standard deviations of less than 0.08 Hz with the majority between 0.02 and 0.05 Hz.

For all experiments, satellite and methylene proton absorptions exhibit widths at half-heights comparable to those of HMDS (*i.e.*, between 0.3 and 0.6 Hz). The spectral data for **1** are compiled in Table II.

# Nmr Parameters of the Individual Fluorines of the Trifluoromethyl Group

**F. J. Weigert\* and W. Mahler**

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**Abstract:** The rotation barriers (5.2–8.5 kcal/mol) of the trifluoromethyl group and the chemical shifts of the individual fluorines have been measured by analysis of the variable temperature fluorine nmr spectra of 2,2-dichlorohexafluoropropane (**1**), 2,2-dibromohexafluoropropane (**2**), 2-iodo-2-(trifluoromethyl)hexafluoropropane (**4**), 1,1,1-trifluoro-2,2-dichloro-2-iodoethane (**5**), pentafluoroiodoethane (**6**), and 1,1,1-trifluoropentachloropropane (**7**). In addition, individual long-range coupling constants were observed for 2,2-diiodohexafluoropropane (**3**). The four-bond coupling constants between the fluorine nuclei of **3** are +34 and +16 Hz for eclipsed and gauche–gauche, +15 Hz for trans–trans, and −3.5 Hz for trans–gauche configurations. Chemical shift assignments have been made for each of the three distinct fluorine nuclei of 2-bromo-2-iodohexafluoropropane (**11**).

Fluorine nmr is an invaluable technique in structure determination,[1] but detailed configurational analysis is hampered by a lack of lore on specific geometric interactions. Progress has been made by investigating fluorines affixed to rigid rings,[2] but available synthetic methods limit the configurations attainable and unknown strain effects may be introduced by the small rings used.

Specific interactions can be observed in nmr spectra at those temperatures where conformational averaging is slow on the nmr time scale.[3] We have elaborated the individual fluorine chemical shifts in trifluoromethyl groups, the stereospecific coupling constants between the individual fluorines in *gem*-trifluoromethyl groups, and the rotation barriers of these groups.

**Results**

Chemical shifts and two-bond, fluorine–fluorine couplings were obtained for the compounds in Table I

(1) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1965, pp 871–968.

(2) (a) K. L. Williams, Y. F. Li, F. H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, **88**, 5678 (1966); (b) R. K. Harris and V. J. Robinson, *J. Magn. Resonance*, **1**, 362 (1969); (c) L. Cavalli, *Org. Magn. Resonance*, **2**, 233 (1970); (d) R. A. Felton, R. D. Lapper, and L. F. Thomas, *Chem. Commun.*, 1049 (1969); (e) G. L. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, **90**, 212 (1968); (f) J. B. Dence and J. D. Roberts, *ibid.*, **91**, 1542 (1969).
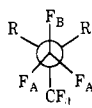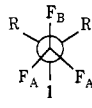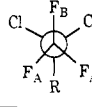
(3) (a) F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *ibid.*, **92**, 7359 (1970); (b) F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964); (c) F. R. Jensen and C. H. Bushweller, *J. Amer. Chem. Soc.*, **91**, 5774 (1969); (d) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965).

**Table I**

| Compound | δ, $F_A$[a] | δ, $F_B$[a] | $J_{AB}$, Hz | ΔG‡, kcal/mol (T, °C) | ΔH‡, kcal/mol | ΔS‡, eu |
|---|---|---|---|---|---|---|
| R = Cl, 1 | −76.8 | −74.5 | 108[b] | 6.1 (−140) | 5.1 | −7.4 |
| R = Br, 2 | −74.4 | −67.1 | 112[b] | 6.7 (−120) | 7.1 | +2.4 |
| R = I, 3 | −73.9 | −57.5 | 117[b] | 7.2 (−107) | 6.8 | −2.2 |
| R = CF₃, 4 | −60.6 | −72.5 | 107[b] | 5.5 (−150) | 6.0 | +4.1 |
| R = F, 6 | −81.6 | −94.6 | 97 | 5.2 (−150) | 4.9 | −2.3 |
| R = I, 5 | −76.0 | −89.1 | 101 | 8.5 (−72) | 8.2 | −1.6 |
| R = CCl₃, 7 | −71.3 | −60.7 | 106 | 5.6 (−139) | 5.7 | +1.0 |

[a] Chemical shifts were measured relative to internal dichlorodifluoromethane and converted to the δ scale ($CFCl_3$) by adding −7.0 ppm, the shift of $CF_2Cl_2$ vs. $CFCl_3$ measured in a 16 mol % solution at 38°. Negative shifts are to higher field. [b] Actually $J_{AB} + J_{trans-gauche}$.
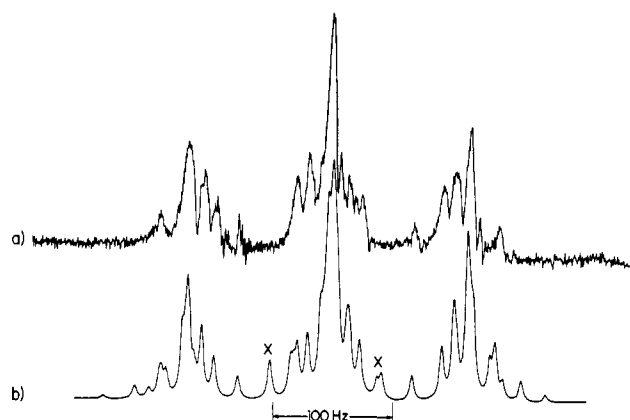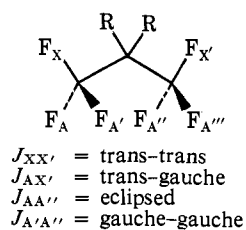


Figure 1. Nmr spectrum of the wing fluorines of diiodide **3**: (a) experimental at −150° in $CF_2Cl_2$; (b) calculated.



Figure 2. Variable-temperature fluorine nmr spectra of diiodide **3**: left, experimental; right, calculated by dnmr as a three-spin approximation.

from their low-temperature limit spectra at 94.1 MHz. The X portion of the $[[A]_2X]_2$ spectrum of diiodide **3** at −150° in dichlorodifluoromethane is shown in Figure 1a.

After many trial and error calculations using long-range couplings similar to those in perfluoromethyl-cyclohexane,[4] two groups of solutions were found which gave reasonable agreement with the observed spectrum of **3**, differing primarily in the sign of the trans–trans coupling. The iterative portion of LAOCOON II[5] converged to a solution with the positive trans–trans coupling, but diverged when the negative coupling was used as a starting point. The spectrum in Figure 1b was calculated using the parameters $Δδ_F = 1550$ Hz, $J_{AA'}$, $J_{AX} = 119.6$ (±0.7), $J_{XX'} = 15.5$ (±1.2), $J_{AX'} =$



$J_{XX'}$ = trans–trans
$J_{AX'}$ = trans–gauche
$J_{AA''}$ = eclipsed
$J_{A'A''}$ = gauche–gauche

(4) K. W. Jolly, L. H. Sutcliffe, and S. L. Walker, *Trans. Faraday Soc.*, **64**, 259 (1968).
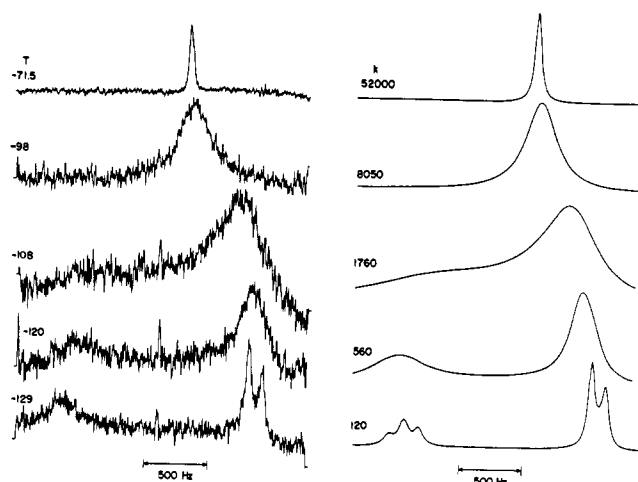(5) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

−3.6 (±0.8), and $J_{AA''}$, $J_{A'A''}$ = 34.1 (±1.2), 16.5 (±1.2). The values in parentheses are the standard deviation of the computed values. The lines marked X in the calculated spectrum were not observed because they may have already coalesced at the lowest temperature studied. Precedent exists for the early disappearance of weak transitions in AA′XX′ type spectra.[6] Distinguishing eclipsed from gauche–gauche coupling in **3** is not possible.

The low-temperature spectrum of dibromide **2** differs from that of the diiodide **3** because the chemical shift difference is smaller and thus the intensities of the triplet and doublet are distorted. Long-range coupling causes identical fine structure in the X regions of both **2** and **3**. Fine structure was either not resolved or absent in the other molecules studied.

All spectra broaden, coalesce, and sharpen to singlets as the temperature is raised. A typical set of experimental spectra is shown in Figure 2 with the set of theoretical spectra calculated by the DNMR computer program.[7] No attempt has been made to determine the rate constants more accurately than ±10% because

(6) M. Witanowski and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 737 (1966).
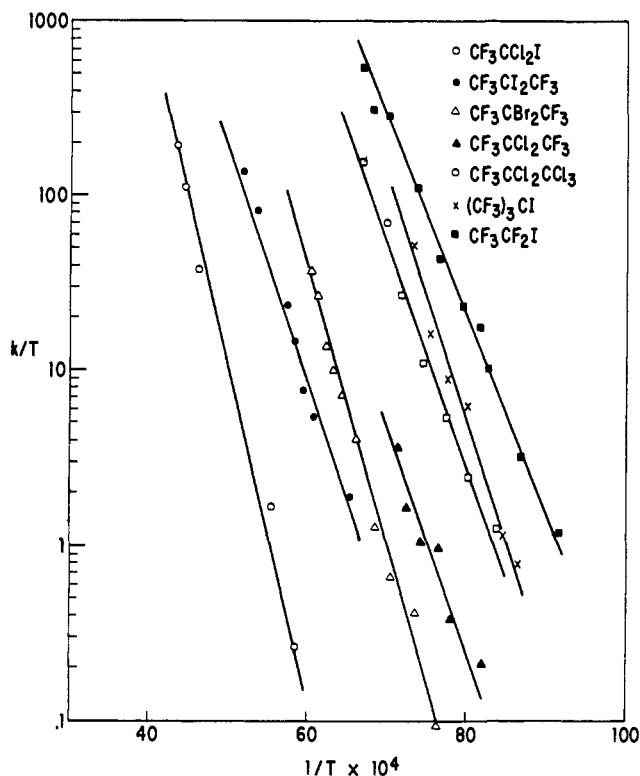(7) G. Binsch, *ibid.*, **91**, 1304 (1969).

Figure 3. Eyring plots for the rotation processes of trifluoromethyl compounds.

at this level errors in temperature and rate constant measurements affect the kinetics similarly. Table I gives the thermodynamic parameters for the rotation processes. Figure 3 shows the Eyring plots of the kinetic data. Rate constants for the rotations in bis(trifluoromethyl) compounds 1, 2, and 3 have been reduced by a factor of 2 and those of tris(trifluoromethyl) compound 4 by a factor of 3 for symmetry reasons.

Some further compounds investigated showed temperature-independent spectra down to $-150°$. Because the magnitudes of the barriers and chemical shifts can be predicted from compounds 1–7, the invariance is attributed to a preference for a single, symmetrical conformation. In particular, 1,2-diiodo-1,1,2,2-tetrafluoroethane (8) appears to be the trans rotamer and
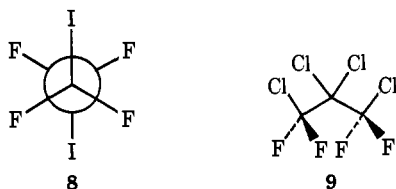
1,2,2,3-tetrachlorotetrafluoropropane (9) has the chlorines on the wing positions.

2-Iodoheptafluoropropane (10) shows a temperature-dependent spectrum, but the low-temperature limit could not be reached. Approximate chemical shifts for the three fluorines are $-73$, $-74$, and $-84$ ppm. The low-temperature spectrum of 2-bromo-2-iodohexafluoropropane (11) showed nonequivalent fluorines at $-62.5$, $-70.8$, and $-78.4$ ppm, but long-range couplings could not be resolved.

At $-150°$ the trifluoromethyl groups of 1-iodoheptafluoropropane (12) and 2-chloro-2-(trichloromethyl)-hexafluoropropane (13) were still singlets. Whether lower rotation barriers or changes in the relative chemical shifts cause this invariance is unknown.

**Fluorine–Fluorine Coupling.** Most observations of long-range fluorine–fluorine coupling have involved molecules with $\pi$ electron systems through which spin information may be transmitted.[8] Very few examples of stereospecific, long-range couplings are known in molecules without $\pi$ bonds. The five-bond, 72-Hz coupling in bis(trifluoromethyl)tetrachloroethane is stereospecific, but assignment to a particular pair of fluorines is less certain.[9] The five-bond, 19-Hz coupling in 1,4-difluorobicyclo[2.2.2]octane cannot be a through-space interaction in the commonly accepted sense.[10] Both the bicyclooctane coupling and the hexafluoropropane trans–trans coupling have in common the possible transmission of spin information via back lobes of carbon orbitals involved in carbon–fluorine bonds. This mechanism has been invoked to explain the W rule of four-bond proton–proton coupling.[11] Two-bond fluorine–fluorine coupling decreases as the electronegativity of the substituents on the $\alpha$ and the $\beta$ carbon increases, thus accounting for the unusually small geminal coupling of heavily halogenated ethanes.[12]

Jolly, Sutcliffe, and Walker[4] determined the magnitudes of four-bond, trans–trans, trans–gauche, and eclipsed couplings in perfluoromethylcyclohexane. Choosing 8 Hz for the average coupling of gem-trifluoromethyl groups, Abraham[13] calculated a gauche–gauche coupling and on that basis assigned a negative sign to the trans–trans coupling. However, if 10 Hz were selected for the average four-bond coupling, a positive trans–trans coupling would be derived. In fact, 10.5 Hz is the average value for the time averaged four-bond fluorine–fluorine coupling extracted from the room temperature $^{13}C$ satellite spectra of the hexafluoropropanes 1, 2, and 3 (Table II). The analysis of the

Table II. Coupling Constants of 1,1,1,3,3,3-Hexafluoropropanes

| Compound | $^1J_{CF}$ | Isotope shift, ppm[a] | $^4J_{FF}$ (av) | $^2J_{CF}$ |
|---|---|---|---|---|
| 1, R = Cl | 287 | 0.15 | $10.3 \pm 0.1$ | 38.2 |
| 2, R = Br | 281 | 0.16 | $10.5 \pm 0.5$ | |
| 3, R = I | 281 | 0.16 | $11 \pm 1$ | 35.5 |

[a] $^{13}C$ bonded fluorines are at high field.

low-temperature spectrum of the diiodide 3 is sensitive to the relative signs of the coupling constants, and a good fit could only be obtained with a positive value. More directly, for the diiodide 3, $^4J_{FF} = \frac{1}{9}[15.5 + 4(-3.6) + 2(34.1) + 2(16.5)] = 11.4$, which is in excellent agreement with experiment.

The practicing fluorine chemist has been eager to accept simplistic correlations of coupling constants with structural parameters which the spectroscopists have

(8) R. E. Graves and R. A. Newmark, J.Chem. Phys., 47, 368 (1967).
(9) F. J. Weigert and J. D. Roberts, J. Amer. Chem. Soc., 90, 3577 (1968).
(10) J. C. Kauer, Amer. Chem. Soc., Div. Petrol. Chem. Prepr., B 14, (1970).
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(12) J. Dyer, Proc. Chem. Soc., London, 275 (1963).
(13) R. J. Abraham, J. Chem. Soc. B, 1022 (1969).

been equally eager to provide. Few serious errors have become apparent, because the odds are quite sporting, and the experimentalist seldom allows his intuition to be contradicted by "theory." Each new set of correlations, however, reveals serious flaws in previous ones; the results of this work bring into question the correlation of magnitude of coupling constant with internuclear distance[14] which has been gaining acceptance and obviously has merit. However, specific F–C· · ·C–F configurations influence the coupling constants apart from the internuclear distance. Other subtleties are also undoubtedly important, and we urge great restraint in correlating structure with "through-space" coupling constants.

**Chemical Shifts.** The concept "chemical shift of a trifluoromethyl group" hides the reality that each fluorine may be in a unique environment and that substituent effects must be considered individually. Fluorine trans to iodine appears upfield of fluorine gauche to iodine. For example, replacing fluorine by iodine in hexafluoroethane shifts the trans fluorine upfield and the gauche fluorine downfield (cf. $C_2F_6$, $\delta = -91$, with **6**). Replacing bromine by iodine along the series dibromide **2**, bromoiodide **11**, and diiodide **3** shifts a gauche fluorine downfield by 4.5 ± 1 ppm and shifts a trans fluorine upfield by 3 ppm. Interestingly, the chemical shift differences in iodides **3**, **4**, **5**, and **6** are all close to 12 ppm although the average shift of the trifluoromethyl group varies considerably. This information permits the assignment of a specific chemical shift to each fluorine nucleus of the bromoiodide **11** as shown.
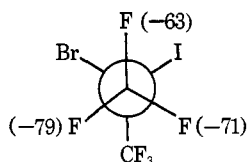


**Internal Rotation.** A 7.0 kcal/mol barrier in pentafluoroiodoethane has been derived from infrared studies,[15] but the 5 kcal/mol obtained in this nmr study is more reasonable on the basis of other known substituent effects. Substituting fluorine in **6** by trifluoromethyl **4** or trifluoromethyl in **1** by trichloromethyl **7** does not significantly raise the barrier. Trifluoromethyl and trichloromethyl are both small groups with respect to their effect on the barriers to rotation in substituted ethanes. Second-row or heavier elements do raise the barrier and in the series of hexafluoropropanes the heavier the halogen, the greater the increase.[16]

### Experimental Section

Room temperature fmr spectra were recorded on a Varian A-56/60. Low-temperature spectra were obtained with a Varian HA-100 locked to internal $CF_2Cl_2$ solvent by means of an external oscillator. The frequency sweep was also provided by an external oscillator which was used to drive the ramp of a Varian C-1024 time-averaging computer. Because of the wide sweeps needed to record these spectra, severe problems were encountered with baseline stability and phase variations. To minimize these problems high modulation frequencies and low modulation amplitudes were

used, thus requiring extensive time averaging, particularly in the extremely weak coalescence spectra. The weakness of these spectra may be best appreciated by considering that spectral intensity normally confined to less than 1 Hz is spread over a region of greater than 1 KHz. Solubility problems at low temperatures further limit the concentrations which could be used.

Temperatures were measured by inserting a chromel–alumel thermocouple into a dummy sample tube at the height of the receiver coil, holding the gas flow constant. Spectra for kinetic measurements were determined from nonspinning samples. The homogeneity-controlled line width of 40 Hz was taken as $T_2^{eff}$. The decrease in resolution makes the $A_2B$ approximation of the more complicated spin systems more valid though over a slightly narrower temperature range. Line widths of 4 Hz were observed at $-150°$ for dibromide **2** and diiodide **3** using spinning samples. Below coalescence no relative chemical shifts of the individual fluorines were seen. This was assumed for higher temperatures.

Pentafluoroiodoethane was obtained from Peninsular Chem-Research Corp. 1,1,1,3,3,3-Hexafluoro-2-iodo-2-(trifluoromethyl)-propane[17] was provided by D. C. England. 2,2-Dichlorohexafluoropropane and 1,2,2,3-tetrachlorotetrafluoropropane were prepared by the reaction of phosphorus pentachloride with the corresponding ketones.[18] 1,1,1-Trifluoro-2,2-dichloroiodoethane was prepared by the addition of "IF" to dichlorodifluoroethane.[19] 1,1,1,3,3,3-Hexafluoro-2-chloro-2-(trichloromethyl)propane was provided by Middleton.[20]

**2,2-Diiodo-1,1,1,3,3,3-hexafluoropropane.** Bis(trifluoromethyl)-diazirine[21] (8 mmol) and 5 mmol of $I_2$ were heated in a sealed tube at 175° for 7 hr. The products were fractionated in the vacuum line. The volatile yellow crystals that were retained in a $-30°$ trap had mp 127°. The mass spectrum showed 405 and 404 as the highest $m/e$ peaks, with the 405 peak 3.3% of the 404 peak as would be expected for the isotope distribution (calcd for $C_3F_6I_2$, 404). The observed vapor pressure of 4 mm at 25° and 1 mm at 0° allows a very rough estimate of a boiling point of 168°. The ultraviolet absorption spectrum in n-hexane shows maxima at 2120, 2760, and 2940 Å. The gas-phase infrared absorption is very strong at 1258, 1237, and 1219 cm$^{-1}$, and strong at 925, 881, 796, 730, 718, and 692 cm$^{-1}$. Reaction with oxygen, described below, served as an additional structure proof.

**Oxidation of 2,2-Diiodo-1,1,1,3,3,3-hexafluoropropane.** 2,2-Diiodo-1,1,1,3,3,3-hexafluoropropane (2.32 mmol) and 5 mmol of $O_2$ were heated in an 80-cc sealed tube for 15 min at 130°. The volatile products were fractionated in the vacuum line to give 2.0 mmol of hexafluoroacetone, identified by ir, and a recovery of 0.25 mmol of starting material. The nonvolatile yellow powder was $I_2O_5$.

**2,2-Dibromo-1,1,1,3,3,3-hexafluoropropane.** Bis(trifluoromethyl)-diazirine (4.5 mmol) and 3.75 mmol of bromine were heated together in an 80-cc sealed tube at 175° for 4 hr. The products were fractionated in the vacuum line. Material stopping in a $-35°$ trap and that passing a $-78°$ trap was rejected. The remainder, which showed the presence of some hexafluoroacetone azine by infrared, was brought into a vacuum separatory funnel and the liquid impurity drained from the solid. The solid was flash evaporated by exposing it briefly to the vacuum system with a trap cooled to $-196°$. This left 0.54 g of a product with mp 52°, a gas density corresponding to a molecular weight of 311 (calcd for $C_3Br_2F_6$, 310). The mass spectrum showed strong peaks at $m/e$ of 308, 310, and 312 with relative intensities in agreement with the expected isotope distribution. The vapor pressure was 115 mm at 25° and 37 mm at 0°, according to which the boiling point may be roughly estimated as 72°. Infrared absorption in the gas phase is very strong at 1263, 1243, and 1230 cm$^{-1}$, and strong at 933, 905, 850, 738, 716, and 698 cm$^{-1}$.

**2-Bromo-2-iodo-1,1,1,3,3,3-hexafluoropropane.** 2,2-Diiodohexafluoropropane (0.52 g) and 0.10 g of bromine were combined in a 5-mm i.d. nmr tube with 2 g of $CF_2Cl_2$. After 2 weeks at 25°, a new resonance amounting to 70% of the total was observed at 70.4 ppm upfield from reference $CFCl_3$ while unchanged diiodide amounted to 23% and 2,2-dibromohexafluoropropane accounted

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(15) O. Risgin and R. C. Tayler, *Spectrochim. Acta*, **15**, 1036 (1959).
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(17) R. P. Mochalina, L. Dyatkin, I. V. Galakhov, and I. L. Knunyants, *Proc. Acad. Sci. USSR*, **169**, 816 (1966).
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(21) D. M. Gale, W. J. Middleton, and C. G. Krespan, *ibid.*, **88**, 3617 (1966).

for 7% of the signal. At this time the tube was opened and fractionated in the vacuum line. The white crystals that passed through −35° and stopped at −60° had an mp of 80° and a vapor pressure of 25 mm at 25° and 8 mm at 0° (estimated bp 120°). The mass spectrum showed strong peaks at $m/e$ 356 and 358 corresponding

to the expected isotopes of $(CF_3)_2CBrI^+$, $m/e$ 229 and 231 corresponding to $(CF_3)_2CBr^+$, and weaker peaks at 337 and 339 corresponding to $C_3F_5BrI^+$. Infrared absorption in the gas phase is very strong at 1258 and 1222 cm$^{-1}$ and strong at 926, 892, 822, 735, and 695 cm$^{-1}$.

# Carbon-13 Magnetic Resonance. XXI.[1] Steric Interactions in the Methylcyclohexanes

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Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received November 20, 1971

**Abstract:** Carbon-13 magnetic resonance (cmr) data have been obtained for the four trimethylcyclohexanes having cis-1,2-substituted methyl groups. Assignments of resonance lines are made using previously developed parameters and empirical arguments. A factor analysis was undertaken to determine accurate parameters describing the $^{13}$C chemical shift effects associated with geometric features not found in previous data. A successful factor analysis was also executed on methyl chemical shifts, producing an accurate set of parameters for predicting them. The wide variation of chemical shifts associated with $\gamma$ gauche interactions is discussed. The cmr data for 1,1,4-trimethylcyclohexane are included to complete the data set for the trimethylcyclohexanes.

## Introduction

In a previous paper in this series[2] the conformational dependence of the carbon-13 chemical shifts in the methylcyclohexanes was presented, and a method for estimating the energy differences between conformers was proposed. It has been noted that the boat form of the cyclohexane ring is 5.3 kcal/mol[3,4] less stable than the chair forms, so that at room temperature methylcyclohexanes are conformationally inverting at rates which are rapid relative to the chemical-shift difference experienced by any particular carbon in its two environments. Thus, only average $^{13}$C chemical shifts are obtained at room temperature. Of course, the chemical shifts to be averaged are weighted by the relative populations of the respective conformers, so that only compounds having conformational isomers of equal or comparable energies will exhibit cmr spectra which differ significantly from those which would be produced by the lower energy conformer alone.

The addition of a methyl group into the cyclohexane ring also introduces steric interactions of the type found in n-butane. An equatorial (e) methyl group exhibits conformations which are like those of *trans*-butane, which has minimal steric strain energy, while an axial (a) methyl creates two significant steric interactions of the type found in *gauche*-butane. An additional gauche interaction occurs if methyls are substituted cis-1,2 (ea) or trans-1,2 (ee) to each other. The increment of energy gained due to a gauche interaction is estimated to be from 0.7 to 1.2 kcal/mol;[5-10]

the value used in this study to estimate the magnitude of such steric interactions is 0.9 kcal/mol. An additional 3.7 kcal/mol[11] of strain energy is attributed to the 1,3-diaxial or skew pentane conformation of cis-1,3 methyl groups. In ref 2 proton-decoupled, carbon-13 magnetic resonance data were presented for cyclohexane, methylcyclohexane, all seven configurational isomers of dimethylcyclohexane, and seven of the twelve possible trimethylcyclohexane isomers. Using approximate parameters derived from those chemical shifts which were unequivocably assignable, all carbon-13 resonance lines were associated with specific carbons in these compounds. A factor analysis executed on the chemical-shift data of the ring carbons was used to determine a more accurate set of additive parameters which described the detailed positional and configurational features found in this class of compounds.

Aside from the fact that there is no way to select a unique set of parameters, a further difficulty was encountered in determining the parameters describing the effects of two methyl groups in a vicinal ea configuration, since this interaction appeared in only two compounds studied in ref 2, 1,1,2-trimethylcyclohexane, which was somewhat anomalous, and cis-1,2-dimethylcyclohexane. Since the latter is rapidly interconverting between conformations of equal energy, only an average parameter could be elucidated to describe the effects of vicinal ea methyl groups on $^{13}$C chemical shifts. Proton-decoupled, carbon-13 chemical-shift data have now been obtained for four unreported trimethylcyclohexanes, depicted in Table I, each of which has vicinal ea methyls. The number of *gauche*-butane (G) and skew-pentane (AA) interactions is listed beneath each conformer, as well as an approximate en-

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