Magnetic Resonance Studies of Triphenylcarbonium Ions. I. Fluorine-19 Nuclear Magnetic Resonance Studies of Conformational Equilibria and Interconversion[1]

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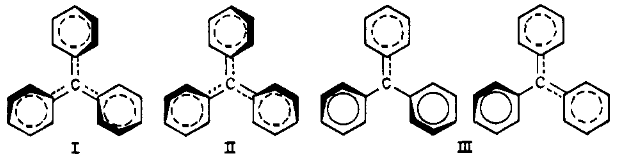
Abstract: Fluorine-19 nmr spectra of 3-fluoro-, 3,3′-difluoro-, 3,3′,3′′-trifluoro-, 4-fluoro-, 4,4′-difluoro-, and 4,4′,4′′-trifluorotriphenylmethyl cations (mF_1, mF_2, mF_3, pF_1, pF_2, and pF_3, respectively) have been measured in liquid hydrogen fluoride solvent. Both the ^{19}F chemical shifts and the pK_{R^+} values, which were also measured for these ions, suggest that the electron-supplying ability of the aryl rings studied decreases in the order: 4-fluorophenyl > phenyl > 3-fluorophenyl. The ^{19}F spectra of dihydroxy-3-fluorophenylmethyl and dihydroxy-4-fluorophenylmethyl cations were also measured. Low-temperature decoupled ^{19}F spectra establish the propeller conformation for the triphenylmethyl cations. An analysis of temperature-dependent changes in the decoupled ^{19}F nmr spectra of mF_2 and mF_3 indicates that the most favorable mechanism of interconversion of propeller conformers is one in which three phenyl rings pass through a plane perpendicular to the plane defined by the three central carbon to phenyl bonds (three-ring flip). The standard free energy of activation for the three-ring flip, which is identical within experimental uncertainty for mF_2 and mF_3, is much smaller than that predicted from Hückel molecular orbital theory. Possible reasons for this discrepancy are considered.

The triphenylmethyl cation, as the earliest known long-lived carbonium ion, has been studied experimentally by several physical methods.[2–5] Nevertheless, the fine details of structure have remained a topic of some interest and controversy to the present time.

Lewis and Calvin[6] were apparently the first to point out that the coplanar geometry required for maximum resonance stabilization is prevented by steric interference between *o*-hydrogens in neighboring rings. Several different models have been suggested as best compromises between the conflicting requirements for minimum steric repulsion and maximum resonance stabilization. These include propeller (I), skew-helix (II), and plane-propeller (III) conformations. Lewis, Magel, and Lipkin[7] noted that the visible spectrum of 4,4′,4′′-tris(dimethylamino)triphenylcarbonium ion (crystal violet) was temperature dependent with one band, appearing as a shoulder on the short-wavelength side of the long-wavelength maximum, decreasing in relative intensity with decreasing temperature. The results were interpreted in terms of an equilibrium between propeller and skew-helix conformations with the latter higher in energy by an estimated 580 cal mol^{-1}. Barker,[8] however, has argued that the skew-helix form should be further from coplanarity than the propeller form and that such deviation, like that resulting from *ortho* substitution,[8] should lead to a bathochromic shift in the long-wavelength maximum.



The similarity between the ultraviolet–visible absorption spectra of related di- and triarylcarbonium ions has been interpreted as evidence for a conformation (III) in which positive charge is delocalized into only one or two benzene rings.[9,10] However, more detailed analyses of the problem using molecular orbital theory[2,11] have led to the conclusion that the electronic spectra are consistent with the propeller form. The nearly constant difference between pK_{R^+} values for related di- and triarylcarbonium ions has been interpreted[12] as evidence for a plane-propeller conformation and a steric origin for the effect of the third ring. This interpretation has also been questioned;[13] nevertheless there is strong evidence that steric effects can have an important influence on pK_{R^+} values of triarylcarbonium ions.[14] The results of LCAO–MO calculations on *planar* triphenylmethyl and related cations[15,16] have been presented in support of the idea that the π-electron energy is the dominant factor contributing to triarylcarbonium ion stabilities.

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Several proton magnetic resonance studies[5a–e,g,h] have failed to provide evidence for nonequivalent phenyl rings in triphenylmethyl cation at room temperature. Significantly, Moodie, Connor, and Stewart[5a] observed that the 40-MHz spectra of 4,4′,4′′-trimethyl- and 4,4′,4′′-trimethoxytriphenylcarbonium ions in trifluoroacetic acid–trifluoroacetic anhydride showed only single methyl absorptions to −80°. Dehl, Vaughan, and Berry[5b] have reported that the 40-MHz spectrum of 2,2′,2′′-trimethyltriphenylcarbonium ion in liquid SO_2 showed a single methyl peak at room temperature.

Finally, infrared[3] and X-ray crystallographic[4] studies indicate that triphenylcarbonium ion is a propeller in the crystalline state.

Results and Discussion

Compounds Studied. The triarylcarbonium ions studied in the present work were 3-fluoro-, 3,3′-difluoro-, 3,3′,3′′-trifluoro-, 4-fluoro-, 4,4′-difluoro-, and 4,4′,4′′-trifluorotriphenylmethyl (hereafter denoted by mF_1, mF_2, mF_3, pF_1, pF_2, and pF_3, respectively). Syntheses of the corresponding fluorine-substituted carbinols were patterned after those of Marvel, *et al.*[17] Also studied were dihydroxy-3-fluorophenyl- and dihydroxy-4-fluorophenylmethyl cations, generated from 3- and 4-fluorobenzoic acids, respectively.

Basicity Measurements. pK_{R^+} values for the triarylcarbonium ions studied in this work were desired in order to have an independent measure of the relative abilities of the phenyl, 3-fluorophenyl, and 4-fluorophenyl rings to accommodate a positive charge. These measurements were carried out in sulfuric acid–water mixtures. The equilibrium is that represented by eq 1; pK_{R^+} is the negative logarithm of K_{R^+}, a thermodynamic equilibrium constant referred to a standard state of infinite dilution in water. pK_{R^+} values were calculated

$$R^+ + H_2O \xrightarrow{K_{R^+}} ROH + H^+ \qquad (1)$$

by means of eq 2, where C_{R^+} and C_{ROH} are molar concentrations of carbonium ion and carbinol, respectively.

$$pK_{R^+} = H_R + \log\,(C_{R^+}/C_{ROH}) \qquad (2)$$

Values of the acidity function H_R[18] were obtained by interpolation from values reported by Arnett and Bushick[19] for 15 and 30°. The values listed in Table I are averages of four to six separate determinations, each at a different per cent sulfuric acid, within the approximate range $\log\,(C_{R^+}/C_{ROH}) = -1$ to $+1$. The use of eq 2 to calculate pK_{R^+} values depends on the assumption that the activity coefficients of R^+ and ROH change in the same way throughout a given range of sulfuric acid concentration as the corresponding activity coefficients for the carbinols used to define the H_R scale.[19] As one test of the validity of this assumption, plots of $\log\,(C_{R^+}/C_{ROH})$ *vs.* per cent H_2SO_4 led to slopes ranging from 0.17 for pF_3 (41.2–50.5% H_2SO_4) to 0.26 for mF_3 (64.2–69.4% H_2SO_4), in close agreement with results of Deno[20] and Arnett[19] for sulfuric acid–water mixtures of similar composition.

Table I. pK_{R^+} Values of Some Fluorine-Substituted Triphenylmethyl Cations

Cation	pK_{R^+} Measd[a]	pK_{R^+} Calcd[b]
Triphenylmethyl	−6.44[c]	. . .
mF_1	−7.81 ± 0.03 (5)	−7.76
mF_2	−9.17 ± 0.10 (4)	−9.08
mF_3	−10.71 ± 0.13 (6)	−10.39
pF_1	−6.41 ± 0.08 (5)	−6.28
pF_2	−6.22 ± 0.05 (5)	−6.12
pF_3	−5.96 ± 0.08 (6)	−5.96

[a] Listed with average deviations and number of determinations (in parentheses). [b] Using eq 3. [c] Reference 19.

Also listed in Table I are pK_{R^+} values calculated by eq 3, a modification of the equation of Yukawa and Tsuna,[21] using $(pK_{R^+})_0 = -6.44$,[19] $\sigma(m\text{-F}) = \sigma^+(m\text{-F}) = 0.337$,[22] $\sigma(p\text{-F}) = 0.062$,[22] $\sigma^+(p\text{-F}) = 0.073$,[22] $r =$

$$pK_{R^+} = (pK_{R^+})_0 - \frac{n\rho}{3}[\sigma + r(\sigma^+ - \sigma)] \qquad (3)$$

0.764,[21] $\rho = 11.73$;[21] n is the number of fluorine substituents. Calculated and measured pK_{R^+} values are in excellent agreement, and both lead to the prediction that the ability of the aryl rings to accommodate positive charge falls in the order: 4-fluorophenyl slightly better than phenyl, which is substantially better than 3-fluorophenyl.

Room-Temperature Nmr Spectra. All spectra were measured in liquid HF solvent using as an internal standard the CF_3 resonance of trifluoroacetic acid. H_0 for anhydrous hydrogen fluoride is about −9.9.[23] pK_{BH^+} values of −7.6 and −7.3 for 3- and 4-fluorobenzoic acids[24] then lead to the prediction that these acids should be greater than 99% protonated in this medium. Although we are aware of no estimate of H_R for anhydrous hydrogen fluoride, if it is comparable to about 98% H_2SO_4 ($H_0 = -9.4$, $H_R = -20.4$), then all carbinols studied in this work should be essentially 100% ionized.

The ^{19}F spectra of pF_1, pF_2, and pF_3 are equivalent in each case consisting of a symmetrical 9-line pattern (Figure 1) differing only in the chemical shift of the entire spectrum. Progressive *p*-fluorine substitution is accompanied by a nearly constant upfield shift of about 0.5 ppm (Table II), discussed below. The ^{19}F spectra of mF_1, mF_2, and mF_3 are again equivalent, consisting roughly, under highest resolution, of an 11-line spectrum (Figure 2). Progressive *m*-fluorine substitution is accompanied by a nearly constant downfield shift (Table II).

The ^{19}F nmr spectra of the protonated 3- and 4-fluorobenzoic acids in HF resemble the spectra of mF_3 and pF_3, respectively, except for the chemical shift relative to the internal standard. The ^{19}F lines of dihydroxy-3-fluorophenylcarbonium ion are furthest upfield while those of dihydroxy-4-fluorophenylcarbonium ion lie between those of mF_3 and pF_3 (Table II).

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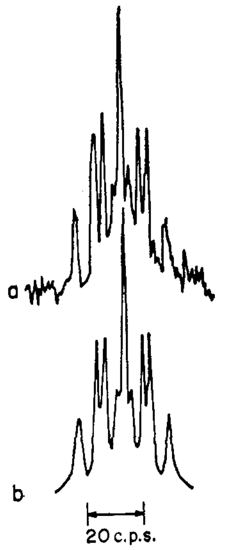

Figure 1. Fluorine-19 nmr spectrum (56.4 MHz) of pF_3 in liquid HF at 35°: (a) experimental spectrum, (b) theoretical spectrum calculated using a Lorentz line-shape function.

^{19}F Chemical Shifts. The ^{19}F chemical shifts for the carbonium ions studied in this work are listed in Table II.[25] The expected trends are observed; the ^{19}F resonance moves progressively downfield in each series as the electron-relaeasing ability of the substituents on the central carbon decreases,[5g,h,26] if it is assumed that the ability of the aryl rings to accommodate a positive charge decreases in the order: 4-fluorophenyl > phenyl > 3-fluorophenyl.

Table II. Room-Temperature ^{19}F Chemical Shifts[a]

Ion	Chemical shift, ppm[b]	Ion	Chemical shift, ppm[b]
$3\text{-}F\text{-}C_6H_4C^+(OH)_2$	35.3	$4\text{-}F\text{-}C_6H_4C^+(OH)_2$	19.3
mF_1	34.7	pF_3	9.77
mF_2	34.0	pF_2	9.24
mF_3	33.3	pF_1	8.72

[a] At ambient temperature, 35 ± 2°, and 56.4-MHz frequency.
[b] Upfield from trifluoroacetic acid internal standard; line positions were measured with an average precision of ±0.005 ppm.

Temperature-Dependent Changes in Spectra. The ^{19}F spectral patterns of pF_1, pF_2, and pF_3 remained unchanged with decreasing temperature other than for a line broadening attributable to increased sample viscosity. The nine-line carbonium ion spectrum showed a nonlinear upfield shift, relative to trifluoroacetic acid standard, with decreasing temperature. The shift varied from roughly 2–3 Hz per 10° for the approximate interval 34 to −30° to roughly 4–4.5 Hz per 10° for the approximate interval −30 to −70°.

Figure 2. Fluorine-19 nmr spectrum (56.4 MHz) of mF_3 in liquid HF at 35°.

The ^{19}F spectrum of mF_1 remained unchanged with decreasing temperature except for loss of resolution. The spectra of mF_2 and mF_3, however, were altered by the appearance of additional peaks. Thus, with mF_2 the pattern observed at room temperature (a quartet under low resolution) appeared as a quintet at −38.3°, a sextet at −66.0°, a heptet at −73.0°, until at −96.4° distinction of the peaks was no longer possible because of loss of resolution. The ^{19}F spectra of the three *meta* ions showed an upfield shift with decreasing temperature which was similar to that shown by the *para*-substituted ions but more difficult to estimate, especially for mF_2 and mF_3. The shift varied from about 1.5–2.5 Hz per 10° over the approximate range 34 to −40° to about 3–4.5 Hz per 10° over the approximate range −40 to −70°.

The ^{19}F spectra of the protonated 3- and 4-fluorobenzoic acids were unchanged with decreasing temperature except for a downfield shift of both ions, relative to trifluoroacetic acid. The shift amounted to approximately 6 and 20 Hz per 10° for the 3- and 4-fluoro ions, respectively, over the approximate range 34 to −40°.

The similarity between the temperature-dependent changes of the *average* ^{19}F chemical shift for the *meta*- and *para*-substituted triphenylcarbonium ions strongly suggests a common source, namely, a downfield shift of the internal standard with decreasing temperature. If these changes were a result of temperature-dependent changes in solvation of the triarylcarbonium ions we should expect much larger changes for the *para*-substituted ions than the *meta*-substituted ions,[27] as observed with the protonated fluorobenzoic acids. The same downfield shifts apparently occur to an even greater extent in the spectra of the protonated fluorobenzoic acids. The downfield shift is possibly a result of increasing localization of the oxygen lone pairs through stronger hydrogen bonding with hydrogen fluoride with decreasing temperature.

Decoupled ^{19}F Spectra. In order to simplify interpretation of the temperature variation of the ^{19}F spectra of mF_2 and mF_3 (above) the fine structure due to ^1H–^{19}F spin coupling was washed out by simultaneous irradiation at 60 MHz. The decoupled spectra of pF_1, pF_2, pF_3, and mF_1 showed a single line down to −80°. The decoupled spectra of mF_2 and mF_3, however, showed a complicated temperature variation which

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(25) These chemical shifts have been derived from the decoupled spectra and from an analysis of the proton and ^{19}F nmr spectra which is to be published elsewhere.

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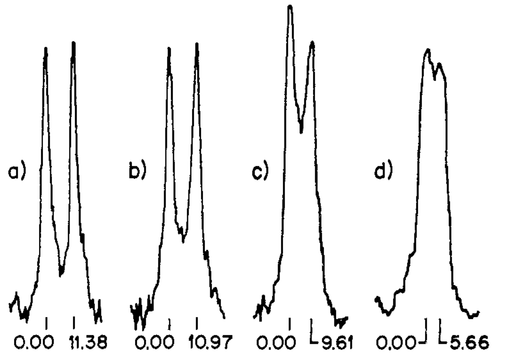


Figure 3. Temperature variation of decoupled ^{19}F nmr spectra of mF$_3$: (a) −80.2°, (b) −45.4°, (c) −37.7°, and (d) −31.0°.

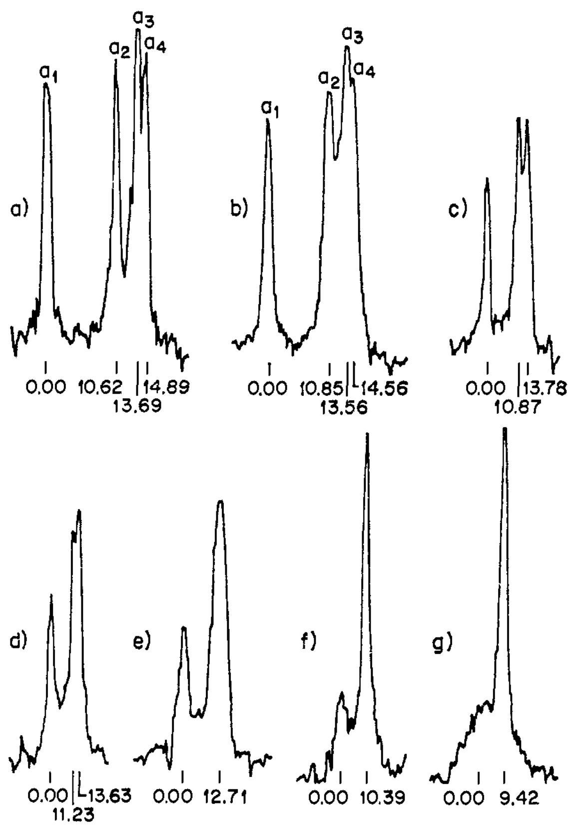
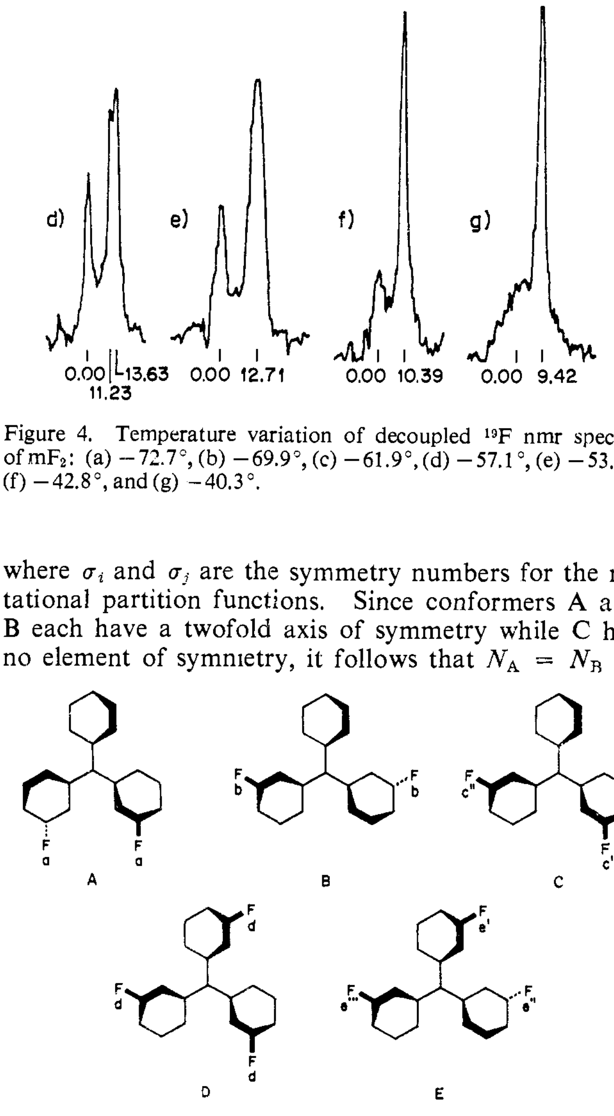


Figure 4. Temperature variation of decoupled ^{19}F nmr spectra of mF$_2$: (a) −72.7°, (b) −69.9°, (c) −61.9°, (d) −57.1°, (e) −53.7°, (f) −42.8°, and (g) −40.3°.

is summarized in Figures 3 and 4. At about −30° the single line of the decoupled mF$_3$ spectrum broadens, splitting into two lines of equal intensity as the temperature is lowered; this doublet separation increases to a limiting value of 11.4 Hz as the temperature is lowered to −51°, remaining unchanged down to −80° (Figure 3). The single line in the decoupled mF$_2$ spectrum broadens at about −38°, splitting into a doublet of 3:1 intensity ratio (Figure 4g); the separation of these lines increases as the temperature is lowered, the larger of the two lines splitting into two lines of intensity ratio 2:1 at −57° (Figure 4d). The stronger of these two lines splits into a barely resolved doublet at −69° (Figure 4b); this four-line pattern of intensity ratio 1:1:1:1 remains unchanged down to −80°.

The low-temperature decoupled spectra of mF$_2$ and mF$_3$ indicate the presence of nonequivalent fluorines. As the temperature is raised, the rates of exchange increase until only the time average is seen. The presence of a single peak in the low-temperature decoupled ^{19}F spectra of pF$_1$, pF$_2$, pF$_3$, and mF$_1$ indicates either (i) a much faster interconversion rate for these ions or (ii) only one type of fluorine per species. Since substitution of fluorine at the *meta* or *para* position should not significantly affect the barrier to interconversion (*i.e.*, the barrier to rotation of a phenyl ring around the bond to the central carbon), we are led to conclusion ii. It is therefore clear that the low-temperature spectra are compatible only with a propeller conformation in which similarly substituted phenyl rings have identical angles of twist.[28] Only a single such propeller conformation is possible for pF$_1$, pF$_2$, pF$_3$, and mF$_1$, leading in each case to only one type of fluorine. For mF$_2$, three propeller conformations (A, B, and C) are possible, leading to four nonequivalent fluorines (a, b, c′, and c″). For mF$_3$, two propeller conformations (D and E) are possible, leading again to four nonequivalent fluorines (d, e′, e″, and e‴). Each of the conformations A–E has a nonsuperimposable mirror image in which the phenyl rings are twisted in the opposite sense.

For an equilibrium mixture of conformers, N_i/N_j, the relative number of conformers i to j is equal to the ratio of the corresponding molecular partition functions. Assuming the ground-state energies to be equal and the vibrational frequencies and rotational constants to be approximately equal, the ratio N_i/N_j is equal to σ_j/σ_i, where σ_i and σ_j are the symmetry numbers for the rotational partition functions. Since conformers A and B each have a twofold axis of symmetry while C has no element of symmetry, it follows that $N_A = N_B = N_C/2$ and therefore that $n_a = n_b = n_{c'} = n_{c''}$, where n_i is the number of fluorines of kind i. Similarly, since conformer D has a threefold symmetry axis, $N_D = N_E/3$ and $n_d = n_{e'} = n_{e'} = n_{e'''}$.[29]



Thus an equilibrium mixture of noninterconverting propeller conformations of either mF$_2$ or mF$_3$ should

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(28) The results do not, of course, exclude a mixture of plane-propeller conformations with average lifetimes too short at −80° to detect by nmr spectroscopy.

(29) The same conclusions can be reached by other kinds of arguments. Thus, for example, in the absence of energy differences the probability of two fluorines being on the same side of the molecule (x_C) must exactly equal the probability of the two fluorines being on opposite sides ($x_A + x_B$). Similarly, with three fluorines, the probability of having fluorines on opposite sides of the molecule (x_E) is three times the probability of having all fluorines on the same side (x_D). Kinetic arguments (below) likewise lead to identical conclusions.

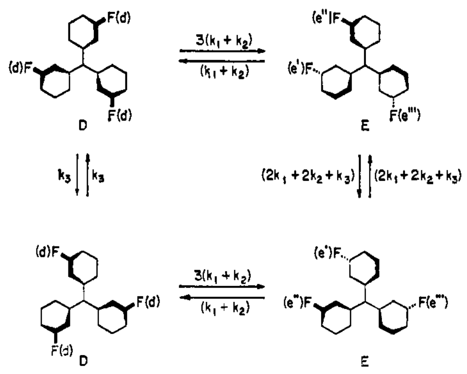

Figure 5. Conformational interconversion of mF_3.

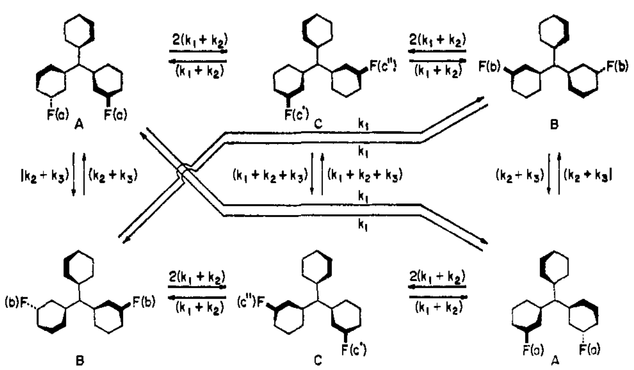

Figure 6. Conformational interconversions of mF_2.

show four lines of equal intensity in the low-temperature decoupled ^{19}F spectra. Spectral assignments for mF_2 are based on the following arguments. The shielding effects which will vary from one conformation to another are, first, the shielding of one fluorine by another; this effect should fall off rapidly with fluorine–fluorine separation and accordingly should be largest for fluorine a and almost equal for fluorines b, c′, and c″, and, second, the shielding produced by the ring currents of the two adjacent phenyl rings. The principal ring-current effect will be that due to the closer of the two rings to the fluorine in question and will depend somewhat on whether the ring is substituted or not. Thus, this effect should give equal contributions to fluorines a and c′ and different but equal contributions to fluorines b and c″. Thus, we tentatively assign the peak a_1, Figure 4a, to fluorine a, peaks a_2 and a_3 to fluorines c′ and c″, respectively, and peak a_4 to fluorine b. Further evidence for these assignments is provided by an analysis of the temperature variation of the decoupled ^{19}F spectrum of mF_2 (see below). The presence of only two lines in the low-temperature spectrum of mF_3 may be plausibly explained as an accidental superposition of lines from fluorines d and e‴ and of lines from fluorines e′ and e″ to yield two lines of equal intensity.[1b] The ring-current effect leading to different chemical shifts for fluorines c′ and c″ is absent in the symmetrically substituted ion mF_3. One might predict a separation between the peaks due to fluorines d and e‴ resulting from differences in fluorine–fluorine interactions of about the same magnitude as the separation between the c″ and b peaks (~1.2 Hz). That the actual separation is not experimentally observable is, however, not too surprising.[30]

Mechanism of Conformational Interconversion. There are only three reasonable mechanisms for interconversion of the conformers discussed above. The three processes, which we shall call one-ring, two-ring, and three-ring flips, correspond, respectively, to rotation of one, two, or three phenyl rings through a plane perpendicular to that defined by the three central carbon–phenyl bonds. In order to retain the required propeller conformation the rings which do not flip must necessarily reverse pitch by passing (more or less simultaneously) through the plane of the central carbon–phenyl bonds. A fourth process in which three rings pass through 0° can be excluded on theoretical grounds since the energy required to overcome the van der Waals repulsion in planar triphenylcarbonium ion exceeds that necessary to break the three central carbon–phenyl bonds.[31] In any case, this process is kinetically equivalent to the three-ring flip and consequently does not change the analysis which follows.

All possible interconversions resulting from the three processes are shown in Figures 5 and 6. The quantities k_1, k_2, and k_3 are the probabilities per unit time per molecule of *each* one-ring flip, *each* two-ring flip, and a three-ring flip. For each conformer there is a possibility of three one-ring flips, three two-ring flips, and one three-ring flip. Not all of these processes result in exchange of nonequivalent fluorines nor do different one- or two-ring flips necessarily result in equivalent exchanges. We assume in these schemes and in the analysis which follows that the rate constants for all processes of the same kind (*e.g.*, all one-ring flips) are the same for all conformers, and independent (for one- and two-ring flips) of the rings which flip. It can be seen from Figures 5 and 6 that exchange between all fluorines can be achieved by combinations of one- or two-ring flips but that the three-ring flip alone cannot lead to crossover between conformers A or B and C, or between D and E.

If the rate constant $k_{ij} = 1/\tau_{ij}$ is defined for exchange between fluorines of kinds i and j as $(1/n_i)(\mathrm{d}n_{i\rightarrow j}/\mathrm{d}t)$, the interconversions pictured in Figures 5 and 6 lead to the following relationships.

For mF_2

$$k_{ac'} = k_{c'a} = k_{ac''} = k_{c''a} = k_{bc'} = k_{c'b} = k_{bc''} = k_{c''b} = (k_1 + k_2) \qquad (4)$$

$$k_{ab} = k_{ba} = k_{c'c''} = k_{c''c'} = (k_2 + k_3) \qquad (5)$$

For mF_3

$$k_{de'} = k_{e'd} = k_{de''} = k_{e''d} = k_{de'''} = k_{e'''d} = k_{e'e''} = k_{e''e'} = k_{e''e'''} = k_{e'''e''} = (k_1 + k_2) \qquad (6)$$

$$k_{e'e'''} = k_{e'''e'} = (k_2 + k_3) \qquad (7)$$

If fluorine pairs d,e‴ and e′,e″ are treated as equivalent, the mean rate constant $k_{\bar{d}\bar{e}} = 1/\tau_{\bar{d}\bar{e}}$ is given by

$$k_{\bar{d}\bar{e}} = 0.5(3k_1 + 4k_2 + k_3) \qquad (8)$$

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(30) The above analysis is qualitative at best. The average angle by which the phenyl rings are twisted from coplanarity is not necessarily exactly the same for the substituted and unsubstituted rings in mF_2 or for the substituted rings in mF_2 and mF_3. Consequently neither of the deshielding effects discussed are necessarily the same in mF_2 and mF_3.

(31) I. I. Schuster, Thesis, Carnegie Institute of Technology, 1965.

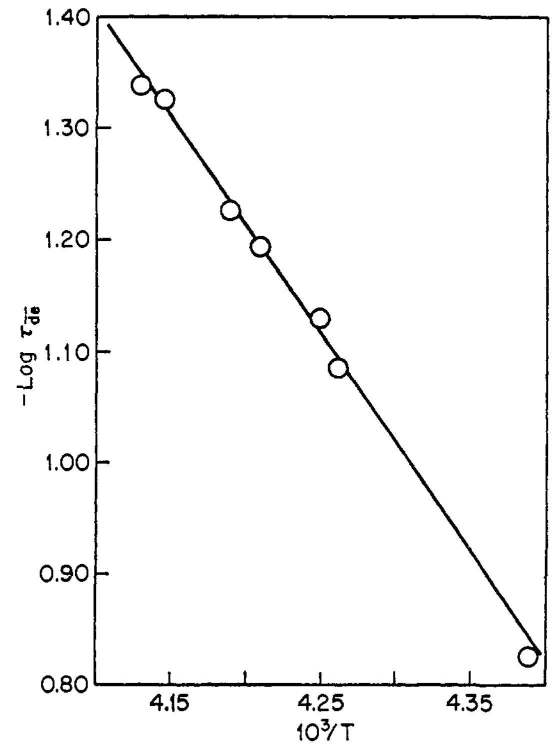

Figure 7. Plot of log $k_{\bar{d}\bar{e}}$ *vs.* $1/T$ for mF_3.

where d denotes the equivalent pair d,e‴ and e the equivalent pair e′,e″.

The line-shape behavior for exchange between several sites can be analyzed by means of modified Bloch equations.[32] For the mF_3 case, if fluorine pairs d,e‴ and e′,e″ are treated as equivalent one may derive an explicit formula for the over-all rate constant, $k_{\bar{d}\bar{e}}$, formally similar to that for exchange between two sites.[33] The separation of frequencies was taken as 11.4 Hz, the low-temperature limit. A plot of log $k_{\bar{d}\bar{e}}$ *vs.* $1/T$ (°K) is shown in Figure 7; the activation parameters thus derived are listed in Table III.

Table III. Activation Parameters for Conformational Interconversion, −43.3°

Cation	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
mF_2	9.1 ± 0.5	−17.3 ± 2.2
mF_3	8.6 ± 0.5	−16.2 ± 2.2

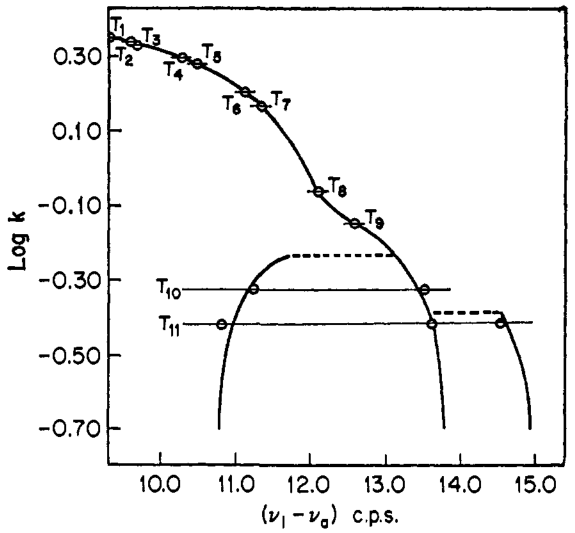

Figure 8. Plot of log k *vs.* calculated peak positions for trial function iv, $\beta = 10$.

For the more complicated mF_2 case, line-shape functions were calculated for the following trial functions (see Appendix I): (i) $k = k_1, k_2 = k_3 = 0$; (ii) $k = k_2, k_1 = k_3 = 0$; (iii) $k = k_1 = k_2, k_3 = 0$; (iv) $k = (k_1 + k_2) = (k_2 + k_3)/\beta$, where $\beta = 1, 2, 6, 10, 20, 50$, and 100 and where the parameter β is assumed to be approximately constant over the temperature range covered by the spectral analysis. The relative positions of the absorption peaks used in the derivations, taken from the experimental spectrum at −67.3°, were: $\nu_a = -9.97$ Hz, $\nu_b = 5.12$ Hz, $\nu_{c'} = 0.86$ Hz, and $\nu_{c''} = 3.99$ Hz. For each trial function the following general procedure was followed. Using a computer program, the theoretical line-shape function $v(\nu)$ was calculated as a function of k and values of ν for which $v(\nu)$ showed a relative maximum plotted *vs.* log k. Figure 8 shows such a plot for trial function iv, $\beta = 10$. Experimental spectra at various temperatures were then matched as closely as possible to the theoretical spectrum to obtain a best fit of log k for each experimental temperature (Figure 8). These data were then used to construct a plot of log k *vs.* $1/T$.

For trial functions i, ii, iii, and iv, $\beta = 1$ or 2, agreement between experimental and theoretical peak positions was poor where more than two peaks were involved. Further, these cases gave curved plots of log k *vs.* $1/T$. For trial functions iv, where $\beta = 6, 10, 20, 50$, and 100, plots of log k *vs.* $1/T$ were approximately linear, the best straight line being obtained for $\beta = 10$ (Figure 9). The activation parameters obtained from Figure 9 are listed in Table III. Values of β ranging from 6 to 100 gave enthalpies of activation between 8.8 and 9.1 kcal mol^{-1} (estimated uncertainty *ca.* ± 0.5 kcal mol^{-1}).

The effect of interchanging peak assignments for mF_2 was tested for the case of trial function iv, $\beta = 10$. Interchange of the peak assignments of fluorines a and b or of fluorines c′ and c″ has no effect on the line-shape function since these are kinetically equivalent fluorine pairs. All other permutations with line a_1 assigned to fluorine a (or fluorine b) resulted in plots of log k *vs.* $1/T$ with pronounced curvature or poor agreement between experimental and calculated peak positions.

While nothing in the preceding analysis *requires* that k_1, k_2, and k_3 be identical for mF_2 and mF_3, it would be very surprising if this were not approximately true. Combination of eq 8 with trial function iv leads to the following expression.

$$k_{\bar{d}\bar{e}}(mF_3)/k(mF_2) = {}^1/_2(3 + \beta) \qquad (9)$$

For $\beta = 10$ eq 9 predicts $k_{\bar{d}\bar{e}}(mF_3)/k(mF_2)$ to be 6.5 while the experimental value at −43.3° is 5, confirming our feeling that k_1, k_2, and k_3 are about the same for mF_2 and mF_3. The close agreement between formal

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(32) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 224.

(33) Reference 32, p 224, eq 10–31.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for mF_2 and mF_3 (Table III) lends further support for this proposal.

An interesting result of the analysis of the temperature dependence of the decoupled ^{19}F spectra is the finding that k_3, the rate constant for the three-ring flip, is much greater than k_1 or k_2. While the reasons for this preference are not immediately obvious from examination of molecular models, the three-ring flip appears to be the mechanism which can most completely avoid unfavorable nonbonded interactions. However, a synchronous rotation of three rings by way of a transition state in which the three phenyl rings are perpendicular to the plane defined by the three bonds to the central carbon would involve the greatest loss in delocalization energy, and therefore appears unlikely. We have attempted to gain some insight into the detailed mechanism for the three-ring flip by carrying out some simple calculations. As a basis for these calculations we have assumed the following bond lengths: central carbon to phenyl, 1.477 Å; C–C (benzene), 1.397 Å; C–H, 1.080 Å. All bond angles were taken as 120°. To obtain an estimate of the loss in delocalization energy accompanying conformational interconversion we have carried out Hückel molecular orbital calculations[34] for several geometries using a value of $0.87\beta \cos \theta$ for the resonance integral of the central carbon to phenyl bond, where β is the resonance integral for the C–C bond in benzene, θ is the angle of rotation of the particular phenyl ring from coplanarity, and the factor of 0.87 is a bond length correction.[35] A large number of functions have been used to estimate the magnitude of nonbonded interaction.[36] However, all of the commonly used functions lead to curves of potential energy *vs.* angle of twist which are so much steeper than the plot of delocalization energy *vs.* angle of twist that it was considered sufficient for the present purposes to approximate the van der Waals repulsion by a hard sphere model in which the distance of closest approach between two nonbonded hydrogen atoms is 2.4 Å, twice the van der Waals radius of hydrogen.[37] The assumed bond lengths and angles then lead to a minimum angle of twist of 31° for the symmetrical propeller. This estimate is close to the 35° obtained from X-ray analysis of crystalline triphenylmethyl perchlorate.[4]

Rotation of one phenyl ring in the ground-state propeller can proceed through 90° without van der Waals repulsion (in the hard sphere approximation) to yield a skew-helix conformation. Since the maximum loss of delocalization energy occurs at $\theta = 90°$, this conformation corresponds to a potential energy maximum. The first intermediate is, then, a skew-helix conformation. We have not attempted to calculate the most favorable skew-helix geometry since the energy of this intermediate is not directly related to the experimental rate constant. The smallest angle of twist for a skew helix in which all rings have the same angle of twist is 79°. Rotation of a second ring through 90° now leads to the same (in unsubstituted triphenylcarbonium ion) skew-helix intermediate. If there is a single transition state for this process, the principle of microscopic reversibility requires that the two rings have equal angles of twist. The most favorable geometry for the high-energy transition state thus has two rings twisted by 79° in the opposite sense with the third twisted by 90°. Using an inclined straight line to represent an end-on view of each phenyl ring, the over-all propeller conformational interconversion can be summarized by the following scheme.

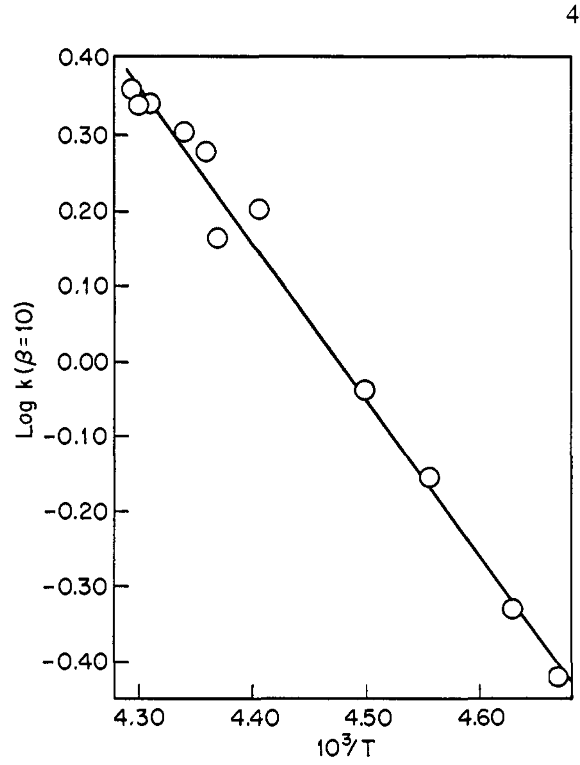
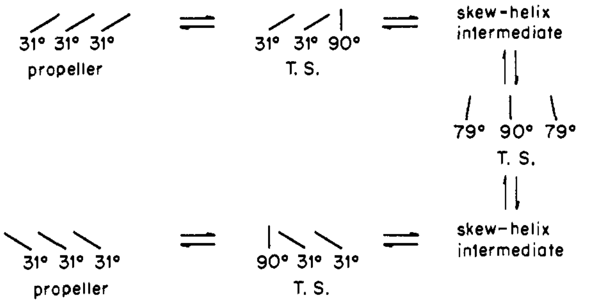


Figure 9. Plot of log k *vs.* $1/T$ for mF_2, trial function iv, $\beta = 10$.



This mechanism leads to a predicted barrier of 1.0742β.[38]

A comparison of calculated and experimental barriers now requires a value for β. To obtain an appropriate value we have calculated the delocalization energy of the benzhydryl cation for an angle of twist of 31°. If the difference of pK_{R^+} values for the benzhydryl and triphenylmethyl cations (~6.7 pK units at 25°, or 9.2 kcal mol^{-1} [39]) is to be attributed entirely to a difference in delocalization energy[15,16] (0.3282β), we require a value of 28.0 kcal for β. The estimated potential energy

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[34] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

[35] R. S. Mulliken, C. A. Riecke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[36] C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19**, 523 (1963).

[37] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

[38] For a reaction in solution it is probably more correct to compare this quantity with the standard free energy of activation than with the enthalpy of activation; see ref 34, pp 207–313.

[39] This value should be a good estimate for the fluorine-substituted ions also since the difference in pK_{R^+} values between related di- and triphenylmethyl cations is approximately constant.[12]

barrier for the three-ring flip is therefore 28.0 kcal $\beta^{-1} \times 1.0742\beta$, or about 30.1 kcal mol^{-1}. This estimate is very insensitive to the choice of angle of twist for the ground-state propeller or choice of β for the carbon to phenyl bonds since any change lowering the calculated barrier (in units of β) has a similar effect on the difference between the delocalization energies of the benzhydryl and triphenylmethyl cations. The predicted value is thus more than twice as large as the experimental standard free energy of activation (~14 kcal mol^{-1} at 25°).

There are at least three possible reasons for the large discrepancy between the energy barrier for conformational interconversion and the theoretical estimate based on the difference in standard free energies of ionization of benzhydryl and triphenylmethanol. First, as suggested by Deno,[12] part of the pK_{R^+} difference may be a result of greater relief of strain in ionization of the triphenylcarbinol. Secondly, the Hückel method may grossly underestimate the loss in delocalization energy and charge delocalization resulting from twisting of the phenyl rings. Finally, solvation effects, neglected in the theoretical estimate, may be important. There is presumably a greater concentration of positive charge on the central carbon in the transition state for the three-ring flip than in the ground-state propellor. We therefore expect the barrier to conformational interconversion to be sensitive to solvent effects. In liquid hydrogen fluoride it is possible that conformational interconversion may involve a fluoride ion and that the transition state is an ion pair. Theoretical and experimental work designed to shed more light on these questions is in progress. Whatever the reasons for the unexpectedly low barrier for the three-ring flip, the experimental result leads to the prediction that *ortho*-substituted triarylcarbonium ions should be unexpectedly stable, in striking agreement with the findings of Martin and Smith.[14] The results of this work also lead to the prediction that the barrier to conformational interconversion (*via* the three-ring flip) should be unchanged or decreased by *ortho* substituents.

Experimental Section[40]

Compounds. Syntheses of the fluorine-substituted triarylcarbonium ions were patterned after the procedures of Marvel, *et al.*[17] The crude products were crystallized from cyclohexane before use. 3-Fluorotriphenylcarbinol, prepared by reaction of phenylmagnesium bromide with methyl 3-fluorobenzoate, had mp 118–120.5° (lit.[17] 117°). 3,3′-Difluorotriphenylcarbinol, prepared by reaction of 3-fluorophenylmagnesium bromide and ethyl benzoate, had mp 116–117.5° (lit.[17] 114–114.5°). 3,3′,3″-Trifluorotriphenylcarbinol, prepared from 3-fluorophenylmagnesium bromide and ethyl carbonate or methyl 3-fluorobenzoate, had mp 119–121.5° (lit.[17] 118.5–119°). 4-Fluorotriphenylcarbinol, prepared from phenylmagnesium bromide and methyl 4-fluorobenzoate, had mp 124–126° (lit.[41] 121–122°). 4,4′-Difluorotriphenylcarbinol, prepared from 4-fluorophenylmagnesium bromide and ethyl benzoate, had mp 99–101° (lit.[17] 100°). 4,4′,4″-Trifluorotriphenylcarbinol, prepared from 4-fluorophenylmagnesium bromide and ethyl carbonate or methyl 4-fluorobenzoate, had mp 93.5–95° (lit.[17] 94°).

3-Fluorobenzoic and 4-fluorobenzoic acids (Pierce Chemical Co.) were used without further purification.

Sulfuric acid solutions were prepared from Baker Analyzed Reagent Grade sulfuric acid and water freshly distilled over potassium permanganate. Exact compositions of the mixtures were determined in the following way. About 5 ml of acid solution was accurately weighed into a 50-ml volumetric flask and diluted to the mark. Aliquots of the diluted solution were titrated with carbonate-free standard aqueous sodium hydroxide using phenolphthalein indicator. Volumetric flasks, pipets, and burets were calibrated; accurate temperature control was maintained. The entire procedure was repeated for each mixture until consistent agreement within one part per thousand was obtained.

Basicity Determinations. Optical densities were measured in 1-cm, matched quartz cells with a Gilford Model 200 spectrophotometer equipped with a thermostated cell compartment. The temperature of the sample was maintained at 25.0 ± 0.1°. Stock solutions containing about 1 mg/ml of purified triarylcarbinol in freshly distilled reagent grade acetic acid were prepared just prior to use. Samples were prepared by dilution of 0.05-ml aliquots of the stock solution with aqueous sulfuric acid in a 10-ml volumetric flask. The reference cell contained a solution identical with that in the sample cell except for the triarylcarbinol. Measurements were made at four or more acid concentrations covering approximately 10 to 90% ionization. The maximum optical density for greater than 99% ionization of the carbinol was determined in each case by using 96% sulfuric acid. The quantities (C_{R^+}/C_{ROH}) used in eq 2 were calculated by means of the equation

$$(C_{R^+}/C_{ROH}) = \frac{(OD)_{obsd}}{(OD)_{R^+} - (OD)_{obsd}}$$

where $(OD)_{obsd}$ and $(OD)_{R^+}$ are the observed optical densities in the aqueous sulfuric acid and in 96% sulfuric acid, respectively. Measurements were carried out at the absorption maximum of the carbonium ion. These were: mF_1, mF_2, and mF_3, 410 mμ; pF_1, 432 mμ; pF_2 and pF_3, 434 mμ.

Nmr Measurements. Spectra were measured with a Varian 4302 DP-60 spectrometer operating at 56.4 MHz, equipped with a variable-temperature probe, on 10% (w/v) solutions in liquid hydrogen fluoride. Frequency measurements, precise to ±0.3 Hz, were made by the usual audio side-band interpolation technique using trifluoroacetic acid as an internal reference. An NMR Specialties, Inc. Model SD-60 spin decoupler was used to irradiate the protons in the decoupling experiments. The irradiating frequency (*ca.* 60 MHz) was stable to 2 Hz hr^{-1}. Temperature measurements were made *via* an external thermocouple calibrated against a thermocouple in the sample position and are considered accurate to ±1°.

Sample tubes resistant to attack by hydrogen fluoride were prepared from KEL-F (the Fluorocarbon Co.) tubing (0.160 cm o.d., 0.020 cm wall) by fusing one end of an 8-in. tube in the nonreducing part of a gas flame. (Charring of the tube while fusing leads to eventual leakage.) About 100 mg of carbinol was weighed into the tube. To the outlet of a hydrogen fluoride tank was fused a narrow copper tube which was inserted into the sample tube well below the surface of a Dry Ice–carbon tetrachloride cooling bath. The rigidity of the cooling mixture served to support the sample tube as hydrogen fluoride was introduced to a level corresponding to about 0.7 ml of liquid. The internal standard (*ca.* 0.03 ml of trifluoroacetic acid or 0.1 ml of acetic acid) was added and the tube sealed with a flame. The KEL-F tubes were enclosed in glass nmr tubes to prevent wobbling during spinning of the sample.

Acknowledgment. We wish to thank the National Science Foundation for partial support of this project, Duane Smith for technical help, and Professor Brown L. Murr for stimulating discussions.

Appendix

Derivation of $v(\nu)$, Line-Shape Formula. Although the derivation of the line-shape function for the mF_2 interconversion is straightforward,[42] we give here the final expressions for the most general case (iv) inasmuch as a certain amount of manipulation is required to arrive at the final form given below.

$$v(\nu) = \{[2(\beta + 1)k\sum_i f_i - 2(\beta - 1)kR]Q - W[(\sum_i 2\pi(\nu - \nu_i)f_i) + 2(\beta - 1)kS]\}/(Q^2 + W^2)$$

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[40] Melting points are uncorrected.

[41] S. T. Bowden and T. F. Watkins, *J. Chem. Soc.*, 1249 (1940).

[42] Reference 32, p 225, eq 10–34 and 10–35.

where

$$Q \equiv 1 - 2\beta(\beta + 1)k^2\sum_i f_i + (\beta^2 - 1)k^2R$$

$$W = \beta k\sum_i 2\pi(\nu - \nu_i)f_i + (\beta^2 - 1)k^2S$$

$$R = 4(\beta + 1)^2k^2\sum_{i=\mathrm{a,b}} f_i\sum_{i=\mathrm{c',c''}} f_i - \sum_{i=\mathrm{a,b}} 2\pi(\nu-\nu_i)f_i\sum_{i=\mathrm{c',c''}} 2\pi(\nu - \nu_i)f_i$$

$$S = -2(\beta + 1)k\Big[\sum_{i=\mathrm{a,b}} f_i\sum_{i=\mathrm{c',c''}} 2\pi(\nu - \nu_i)f_i + \sum_{i=\mathrm{c',c''}} f_i\sum_{i=\mathrm{a,b}} 2\pi(\nu - \nu_i)f_i\Big]$$

$$f_i = [4(\beta + 1)^2k^2 + (2\pi)^2(\nu - \nu_i)^2]^{-1}$$

$$k = k_1 + k_2$$

$$\beta = (k_2 + k_3)/(k_1 + k_2)$$

and ν_i is the resonant frequency (hertz) for site i = a, b, c′, c″.

A Nuclear Magnetic Resonance Study of Hindered Rotation in Biphenyls. Podototarin Diacetate and Podototarin Dimethyl Ether[1]

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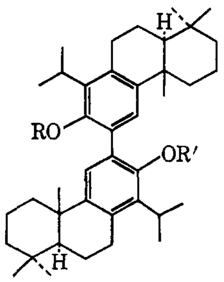
Abstract: Activation energies and other kinetic data have been obtained for rotation of the hindered biphenyl system in podototarin diacetate (I, R = R′ = Ac) and podototarin dimethyl ether (I, R = R′ = CH_3). Asymmetry inherent in these molecules results in the rotational conformers being diastereomeric. Rotational rate constants at various temperatures have been determined from line-shape analysis of the superimposed, nonidentical, nmr spectra of the conformers, using an iterative nonlinear least-squares computer program. The activation energies for biphenyl rotation determined from these rate constants are lower than can be measured by the racemization method.

Podototarin[3,4] (I, R = R′ = H) is a naturally occurring biphenyl obtained from the New Zealand species *Podocarpus totara* G. Benn. The identity of the stereochemistry of the two halves of the molecule has been established by synthesis.[4] Since the biphenyl system carries substituents in the *ortho* and *ortho′* positions, it is to be expected that the molecule will prefer conformations in which the dihedral angle between the two aromatic rings is large. That this is the case is shown by the ultraviolet and nmr spectra of podototarin.[3,4] It has been estimated earlier[3,4] from chemical shift data that the preferred dihedral angle of podototarin is about 70°.



I

Because each half of the molecule is intrinsically asymmetric, the two major conformers resulting from rotation about the central bond of the biphenyl system are not identical. Instead, they are diastereomers. In order to visualize the difference between these conformers it is convenient to use the approximation that the aromatic rings are at right angles to each other. A simplified representation of the two isomers in this conformation is shown in Newman projection in Figure 1. The substituents in which we are interested are represented by "X" and the asymmetric portions of the molecules by the triangles. Form A is converted to form B by rotating the front half of the molecule through 180°. The difference in the environments of the "X" groups in forms A and B is clear from these diagrams. Within each conformer the environments of the two "X" groups are indistinguishable. There are two possible transition states in which the biphenyl system is planar, but only the less energetic of these is likely to make a significant contribution to the interconversion process. This transition state can be approximately represented by I.

If these diasteriomeric conformers have long enough lifetimes on the nmr time scale, we may expect that the nmr spectrum will show the superimposed (nonidentical) spectra of the two species. Further, the spectrum should be temperature dependent, collapsing to a single time-averaged spectrum as the temperature is raised and the lifetimes of the conformers are reduced.

At normal temperatures (about 40°) the 60-MHz spectrum of podototarin itself shows no unusual fea-

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[1] This work was supported by Grant No. GM-12468 from the National Institutes of Health, U. S. Public Health Service.

[2] National Science Foundation Summer Research Participant, 1964.

[3] R. C. Cambie, W. R. J. Simpson, and L. D. Colebrook, *Chem. Ind.* (London), 1757 (1962).

[4] R. C. Cambie, W. R. J. Simpson, and L. D. Colebrook, *Tetrahedron*, **19**, 209 (1963).