Communications to the Editor

Fluorine Magnetic Resonance Studies of Conformational Equilibria in Triphenylcarbonium Ions

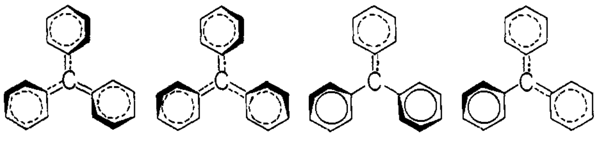
Sir:

We report herein the results of n.m.r. studies which establish the conformations of several fluorine-substituted triphenylcarbonium ions. The interconversion rates and corresponding activation energies are derived in the accompanying communication.[1]

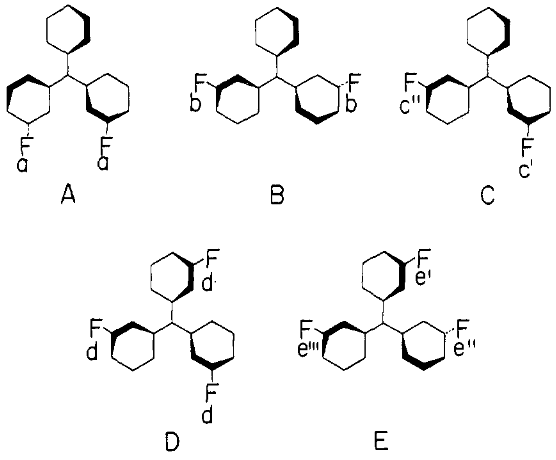
The 56.4-Mc.p.s. F^{19} n.m.r. spectra of 3-fluoro-, 3,3′-difluoro-, 3,3′,3′′-trifluoro-, 4-fluoro-, 4,4′-difluoro-, and 4,4′,4′′-trifluorotriphenylcarbonium ions (hereafter, mF_1, mF_2, mF_3, pF_1, pF_2, and pF_3, respectively) in liquid hydrogen fluoride all show complicated patterns. At room temperature (*ca.* 34°) the patterns of the mF_1, mF_2, and mF_3 ions are the same in form, differing only in the position of the mean frequency, as are the patterns of the pF_1, pF_2, and pF_3 species (Figures 1a and 1b). The effects of H^1–F^{19} spin coupling are washed out when a strong irradiating field at *ca.* 60 Mc.p.s. is simultaneously applied; the decoupled spectra for each of the six ions show a single line at room temperature.[2] The decoupled spectra of mF_1, pF_1, pF_2, and pF_3 each show a single line down to $-80°$. However, the decoupled spectra of mF_2 and mF_3 show a marked and complicated temperature variation which is discussed in greater detail in the accompanying communication.[1] At temperatures from -60 to $-80°$ the decoupled spectra of mF_3 show two lines of equal intensity with a spacing of 11.4 c.p.s. (Figure 2a). The mF_2 spectra show a pattern of four lines with a 1:1:1:1 intensity ratio (Figure 2b).

The low-temperature spectra of mF_2 and mF_3 indicate the presence of nonequivalent fluorines; these fluorines interchange more rapidly as the temperature is raised until at room temperature only one line, corresponding to the time average, is seen. The presence of only one line in the mF_1, pF_1, pF_2, and pF_3 low-temperature spectra indicates either (i) a much higher interconversion rate between nonequivalent fluorines than that for the mF_2 or mF_3 species or (ii) only one type of fluorine per species. Inasmuch as fluorine substituted in the *para* or *meta* position should not significantly affect the barrier to interconversion (*i.e.*, the barrier to rotation of a phenyl group about the bond to the central carbon), conclusion ii is the more plausible.

Propeller (I), skew-helix (II), and plane-propeller (III) conformations have been proposed for triphenylcarbonium ions.[3-5] (For each of these, coplanarity of the central carbon and the three carbon–phenyl bonds is assumed.) In light of the n.m.r. data we prefer I, the propeller conformation, in which each of the three phenyl rings has the same angle of twist. We shall amplify the reasons for this choice below, noting however that the propeller conformation requires that mF_1, pF_1, pF_2, and pF_3 each have only one kind of fluorine and that mF_2 and mF_3 each have four kinds. The four nonequivalent fluorines are shown below in the diagrammatic representations of the conformations A–E. Magnetically equivalent fluorines are labeled a, b, c′, and c′′ for mF_2 and d, e′, e′′, and e′′′ for mF_3.



I II III



For an equilibrium mixture of conformers, N_i/N_j, the relative number of conformers i to j is just the ratio of the corresponding molecular partition functions. Assuming the ground-state energies of conformers i and j to be equal and the vibrational frequencies and rotational constants to be correspondingly 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 function. It follows then that $n_a = n_b = n_{c'} = n_{c''}$ and that $n_d = n_{e'} = n_{e''} = n_{e'''}$, where n_i is the number of fluorines of kind i.

Thus an equilibrium mixture of noninterconverting conformers of either mF_2 or mF_3 should show four lines of equal intensity in the decoupled F^{19} n.m.r. spectra. The presence of only two lines in the low-temperature mF_3 spectrum may be explained as an accidental coincidence of lines from fluorines d and e′′′ and of lines from e′ and e′′ to yield two lines of equal intensity.[6]

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(1) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Am. Chem. Soc.*, 87, 2279 (1965).

(2) Spectra were measured with a Varian 4302 DP-60 spectrometer at 56.4 Mc.p.s. on 10% (w./v.) solutions in liquid hydrogen fluoride. Frequency measurements, precise to ±0.3 c.p.s., were made by the usual audio side-band interpolation technique, using trifluoroacetic acid as an internal reference. A Nuclear Magnetic Resonance Specialties, Inc. Model SD-60 spin decoupler was used to irradiate protons. The irradiating frequency (*ca.* 60 Mc.p.s.) was stable to 2 c.p.s./hr. Temperature measurements were made *via* an external thermocouple calibrated against a thermocouple in the sample position and are considered accurate to ±1°.

(3) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1774 (1942).

(4) M. S. Newman and N. C. Deno, *ibid.*, 73, 3644 (1951).

(5) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, 19, 155 (1954).

(6) The above explanation is not as *ad hoc* as it might first appear. There are two principal sources of the shielding which will also differ in their effect in the various conformations. The first of these is the shielding effect of one fluorine on another; this effect should fall off rapidly with increasing distance between the fluorines and, accordingly, the contribution of this effect to the shieldings of fluorines b, c′, and c′′

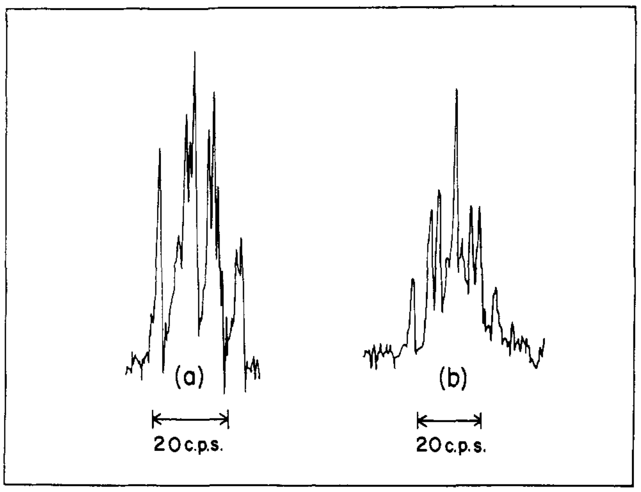

Figure 1. Room-temperature F^{19} spectra of mF_3 (a) and pF_3 (b).

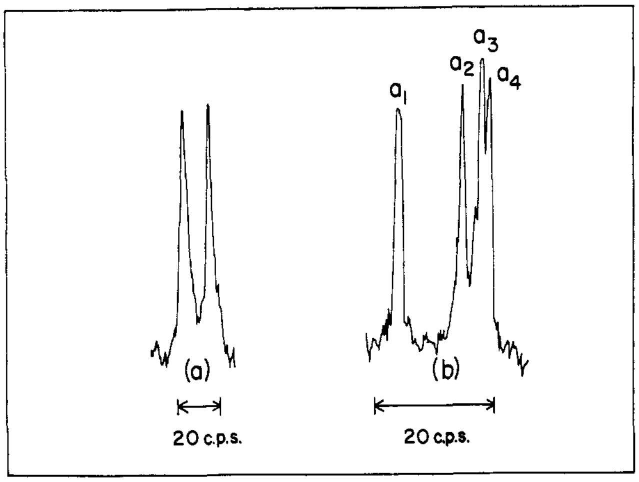

Figure 2. Low-temperature decoupled F^{19} spectra of mF_3 (a) and mF_2 (b).

We may then assign the low-field line of the mF_3 doublet to fluorines e′ and e′′ and the high-field line to fluorines d and e′′′. We may assign line a_1 of the four-line mF_2 spectrum to fluorine a, a_2 and a_3 to fluorines c′ and c′′, and a_4 to fluorine b.

For either conformation II or III above, the presence of more nonequivalent fluorines than appear to be present would be required; furthermore, the mF_1 and pF_3 species would be expected to show nonequivalent fluorines. In addition, the temperature variation of the decoupled mF_2 and mF_3 spectra may be quantitatively explained on the basis of the propeller conformation and the spectral assignments given above.[1]

The chemical shifts of the F^{19} lines at room temperature are given in Table I. An interpretation of these shifts and analyses of the proton n.m.r. spectra of these ions will be published.

Table I. Room Temperature F^{19} Chemical Shifts

Ion	Chemical shift, p.p.m.[a]	Ion	Chemical shift, p.p.m.[a]
pF_1	8.72	mF_1	34.7
pF_2	9.24	mF_2	34.0
pF_3	9.77	mF_3	33.3

[a] Relative to trifluoroacetic acid internal standard.

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and to fluorines d and e′′′ should be approximately the same, *viz.*, zero. This effect should be much larger (but nearly the same) for fluorines a, e′, and e′′, since the pairs of fluorines involved are near neighbors. The second effect is that produced by the ring current of the adjacent phenyl rings. The principal ring current effect will be that of the closer of the two rings to the fluorine in question (*e.g.*, for fluorine b the unsubstituted ring) and will depend slightly on whether the ring is substituted or not. Thus, this effect should give a different contribution to the shieldings of fluorines c′ and c′′ while it would give essentially the same contribution to fluorines d, e′, e′′, and e′′′.

Fluorine Magnetic Resonance Studies of Conformational Interconversion Rates in Triphenylcarbonium Ions

Sir:

The temperature variation of the decoupled F^{19} n.m.r. spectra of 3,3′-difluoro- and 3,3′,3′′-trifluorotriphenylcarbonium ions (mF_2 and mF_3, respectively) has been used to obtain interconversion rates between the conformers discussed in the preceding communication.[1]

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 c.p.s. as the temperature is lowered to −51°, remaining unchanged down to −80° (Figure 1). The mF_2 line broadens at about −38°, splitting into a doublet of 3:1 intensity ratio; the separation of these lines increases as the temperature is lowered, the larger of these lines (a in Figure 2a) splitting into two lines of intensity ratio 2:1 at −57° (Figure 2b). The stronger of these two lines (aa_1 in Figure 2b) splits into a barely resolved doublet at −59° (Figure 2c); this four-line pattern remains unchanged down to −80°.

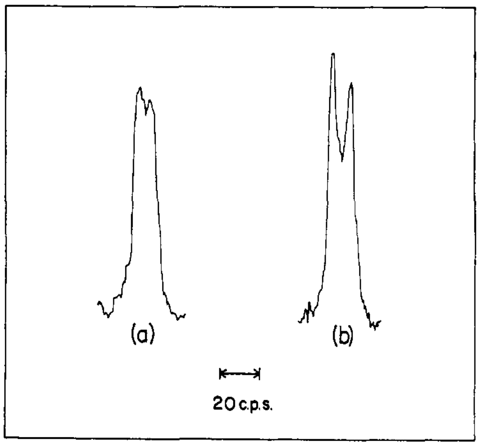

Figure 1. Decoupled F^{19} spectrum of mF_3 at (a) −31.0°, (b) −37.7°.

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(1) A. K. Colter, I. I. Schuster, and R. J. Kurland, *J. Am. Chem. Soc.*, **87**, 2278 (1965).