

Figure 1. Nmr spectrum of *t*-hexyl cations in $\text{FSO}_3\text{H-SbF}_5$ solutions.

known to rearrange extremely rapidly to ion II). Alkanes with more than seven carbon atoms in $\text{FSO}_3\text{H-SbF}_5$ solution at room or more elevated temperature all convert to ion I. Investigated examples are: *n*-heptane, 2,2,3-trimethylbutane, 3-ethylpentane, 2,4-dimethylpentane, 2-methylhexane, 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, 2,2,3-trimethylpentane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, and hexadecane. Even paraffin wax and polyethylene gave ion I. Obviously complex isomerization and fragmentation processes in the strong acid solution lead ultimately to the very stable *t*-butyl cation (I).

Methane does not ionize under the reaction conditions. Ethane gives a mixture of 90% I and 10% V through some dimerization and trimerization pathway. Propane forms also I and V, the amount of the latter decreasing with increasing acid strength.

The fate of the hydride ion abstracted is not yet fully determined in the reactions. In all probability it forms molecular hydrogen by adding to a proton, part of which is observed to escape from the reaction mixture. The bulk of the nascent hydrogen, however, seems to reduce fluorosulfonic or fluoroantimonsulfonic acid.

In a typical experiment, the alkane and a tenfold (weight) excess of acid (1:1 $\text{FSO}_3\text{H-SbF}_5$) were vigorously stirred at room temperature until they formed a homogenous colorless mixture. The reaction is carried out with exclusion of moisture and is generally completed in 10–30 min. When using gaseous alkanes they are bubbled through the acid mixture in a slow stream.

The most surprising observation of our work is that salts of the alkyl cations I, II, and V (probably highly solvated) can be obtained and crystallized from SO_2 or SO_2ClF solutions at low temperatures (–60 to –100°). They are stable, at least to room temperature. Resolved in SO_2 they give the unchanged nmr spectra of the ions. Studies (with Professor M. Sundaralingam) on the X-ray crystallographic investigation of these alkyl-carbonium ion salts are in progress.

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The Relative Sign of $J_{\text{C}^{13}-\text{C}^{13}}$

Sir:

Proton stabilization of the magnetic field in an analog frequency sweep spectrometer (Varian AFS-60) allows one to use time-averaging techniques (Varian C-1024) in the observation of C^{13} signals of relatively low intensity. This enhanced sensitivity is utilized to observe the $\text{C}^{13}-\text{C}^{13}$ splittings in an acetic acid sample which has been enriched in the carboxyl position with C^{13} to 20 atom %. Under these conditions only 0.2% of the sample molecules contains the C^{13} label in both carbon positions of acetic acid, as the 1.1% natural abundance still obtains in the methyl carbon. Figure 1 exhibits the proton-decoupled C^{13} spectrum of the

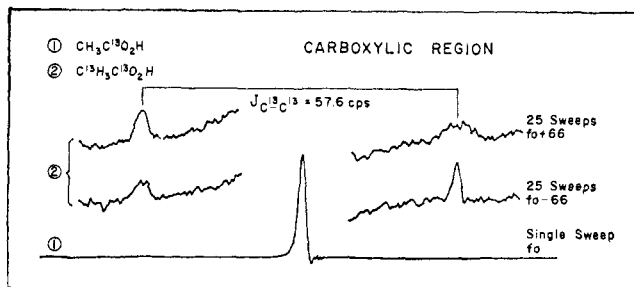


Figure 1. Carbon-13 magnetic resonance spectra of the carboxylic region of acetic acid with proton decoupling. The frequency, f_0 , is the methyl proton resonance frequency for acetic acid at the magnetic field strength used in this study.

carboxylic region of acetic acid. With the heteronuclear decoupler adjusted to the center of the methyl proton resonance frequency, f_0 , an intense carboxyl C^{13} singlet, lowest trace, is observed for the $\text{CH}_3-\text{C}^{13}\text{O}_2\text{H}$ molecules (about 20%) existing in the sample. The less intense carboxyl doublet, arising from the $\text{C}^{13}-\text{C}^{13}$ splitting in the doubly labeled species, is shown in the upper two traces for the proton decoupling frequencies $f_0 - 66$ and $+66$ cps, respectively. As the directly bonded $\text{C}^{13}-\text{H}$ coupling constant in this compound is 132 cps, these two decoupling frequencies correspond to the resonance positions of the methyl C^{13} satellites in the proton spectrum. With the magnetic field locked to the same external water sample in each instance, irradiation of the lower frequency proton line enhances the lower C^{13} line of the methyl-induced doublet. Conversely, irradiation with a frequency of $f_0 + 66$ resulted in the higher frequency carboxyl line being enhanced (note: frequency increases to the left in Figure 1 in order to have a consistent spectral appearance with field-sweep spectra). These data indicate that the directly bonded $J_{\text{C}^{13}-\text{C}^{13}}$ has the same relative sign as the directly bonded $J_{\text{C}^{13}-\text{H}}$. As the absolute sign of directly bonded $\text{C}^{13}-\text{H}$ couplings¹ has already been shown to be positive, it follows that the directly bonded $J_{\text{C}^{13}-\text{C}^{13}}$ should have a positive absolute sign. Furthermore, as the coupling magnitudes of Frei and Bernstein² are comparable with the 57.6-cps $\text{C}^{13}-\text{C}^{13}$ coupling observed here for acetic acid, it is reasonable to conclude that other directly bonded $\text{C}^{13}-\text{C}^{13}$ couplings will also be positive.

Early theoretical considerations³ of directly bonded

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coupling constants predicted that the coupling would be positive if the Fermi hyperfine contact term dominates the spin-spin coupling mechanism. The observation of a positive C^{13} - C^{13} coupling constant is, therefore, consistent with a coupling model based on the hyperfine contact mechanism, and it is not surprising that hybridizational and inductive effects on $J_{C^{13}-C^{13}}$ have been observed.² In this regard the C^{13} - C^{13} coupling is probably unlike the C^{13} - F^{19} coupling in CF_4 which is rather sizable and has a negative sign⁴ relative to the C^{13} - H coupling. It has already been suggested that the unusually small B^{11} - F^{19} coupling^{5,6} in BF_4^- may be due to cancellation between two terms of comparable magnitude but of opposite sign. Thus, the positive C^{13} - C^{13} coupling is somewhat unusual for spin-spin interactions between two atoms in the first long row of the periodic table.

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The Electron Spin Resonance Spectrum of the Triphenylamminium Radical

Sir:

A number of papers have been published recently on the molecular electronic structure and stability of substituted triphenylamminium radicals.^{1,2} These radicals were obtained either by chemical^{1,3} or electrolytic² oxidation of the parent amines. Unsubstituted triphenylamminium (TPA^+) itself reportedly is very unstable^{1,2} and has not been studied so far.⁴

We found that TPA^+ can be conveniently prepared by oxidation of TPA dissolved in SO_2 with BF_3 ⁶ and is relatively stable in this polar solvent. The recorded well-resolved esr spectrum of TPA^+ solutions in SO_2 could be analyzed with the help of computer calculations (Figure 1). The hyperfine splitting constants of the nitrogen atom and protons thus derived are listed in Table I. The spin densities on the carbon atoms derived from the proton hfsc with the McConnell relation⁷ ($Q = 27$ gauss) are also given in Table I. They agree reasonably well with the spin densities obtained with a McLachlan calculation,⁸ in which the ^{14}N Cou-

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(4) We are grateful to a referee who called to our attention a short communication of Norman, *et al.*⁵ These authors obtained a partly resolved spectrum of TPA^+ prepared in CH_2Cl_2 with lead tetraacetate and BF_3 . They reported a nitrogen splitting of 8.55 gauss. We have checked their results and found that TPA in CH_2Cl_2 treated with BF_3 gives a well-resolved spectrum identical with the spectrum in Figure 1; the nitrogen hfs in the spectra (recorded at various temperatures between -60° and room temperature) is 10.16 gauss.

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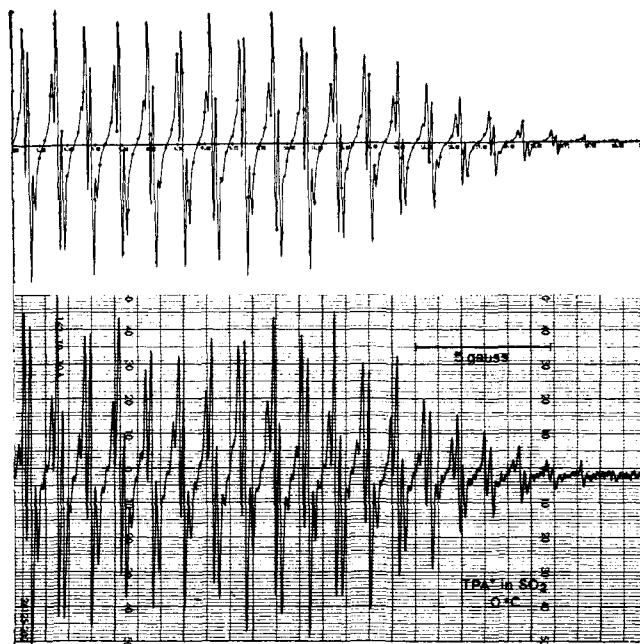


Figure 1. dX''/dH vs. H for triphenylamminium in SO_2 at 0° (half-spectrum). The top figure represents a computer-simulated spectrum in which the hfs parameters given in Table I have been employed in addition to a line width between points of extreme slope of 0.1 gauss. The similarity between calculated and recorded spectra is very satisfactory except for a small deviation in the fifth and sixth groups of lines from the left. This deviation might be due to the anomalous line-width variation.

lomb integral was taken to be $\alpha_N = \alpha_0 + \beta_0$ and the C-N resonance integral $\beta_{CN} = 0.8\beta_0$,⁹ considering the uncertainty in these parameters (Table I).

Table I. Hyperfine Splitting Constants and Spin Densities in TPA^+

Position	Hfsc, gauss	Exptl spin densities ⁷	Theor ⁸ spin densities
^{14}N	10.16		0.4481
C_i			-0.0160
ortho	2.28	0.0844	0.0843
meta	1.22	-0.0452	-0.0659
para	3.32	0.1230	0.0846

The ^{14}N hfs constants in tri-*p*-tolylamminium and tri-*p*-anisylamminium prepared likewise in SO_2 did not deviate significantly from the values obtained when other solvents were used. The fact that the magnitude of the ^{14}N hfsc in TPA^+ is larger than in any of the *para*-substituted triphenylamminium radicals studied thus can be attributed with reasonable certainty to the substituent effect. Walter's conclusion¹ that the spin density distribution over triarylaminium radicals must be affected in the same direction by both donor and acceptor substituents, therefore, is clearly supported by our results.

The esr spectra of the aminium salts all have high-field hyperfine components which are broadened with respect to the low-field components. This effect is most pronounced in the esr spectrum of tri-*p*-anisylaminium² (TAA^+). The line-width variation, which has also been mentioned by Walter,¹ can be attributed to modulation of the anisotropic g tensor and electron spin-nuclear spin dipolar interaction tensor by the Brownian motion of the radical.^{10,11} The large de-

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