

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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(3) R. I. Walter, *ibid.*, **77**, 5999 (1955).

(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 hfsc in the spectra (recorded at various temperatures between -60° and room temperature) is 10.16 gauss.

(5) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965).

(6) The SO_2 - BF_3 mixture was first proposed as a convenient oxidation agent for aromatics by E. de Boer and J. P. Colpa, *Mol. Phys.*, **7**, 333 (1964).

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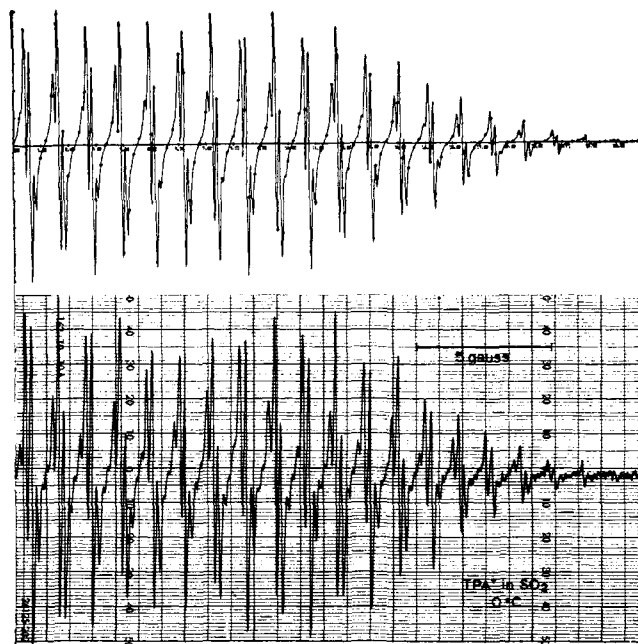


Figure 1. dX''/dH vs. H for triphenylamminium in SO_2 at 0° (half-spectrum). The top figure represents a computer-simulated spectrum in which the hfs parameters given in Table I have been employed in addition to a line width between points of extreme slope of 0.1 gauss. The similarity between calculated 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_1			-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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(10) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

(11) R. Wilson and D. Kivelson, *ibid.*, **44**, 154 (1966).

generacy of the hyperfine components in the spectrum of TAA⁺² prevents a quantitative interpretation of the line-width variations.¹⁰ Since the spin density at the nitrogen nucleus is high (Table I), one can predict, however, that relaxation contributions due to the ¹⁴N nucleus will be considerably larger than those due to the protons (*cf.* ref 12). The differences in line widths between the three groups of hyperfine components, therefore, can be attributed primarily to terms linear and quadratic in the ¹⁴N nuclear quantum number

$$T_2^{-1} = KM_N^2 + LM_N$$

where K and L are constants^{10,12} and T_2^{-1} is the contribution to the line width. The second right-hand term in this expression can be used, together with the observation that the high-field components are broader than the corresponding low-field components, to derive the sign of the ¹⁴N hfs constant.¹²⁻¹⁴ Following the arguments which have been presented previously,^{12,14} one can show that L , a constant containing the g -tensor components and the electron spin-¹⁴N nuclear spin dipolar interaction component along the trigonal axis of the radical, must be negative. The group with $M_N = -1$ will, therefore, be broader than the group for which $M_N = +1$, so that our experimental finding leads to the conclusion that the ¹⁴N hfs constant must be positive. This is in agreement with the sign derived with the help of the modified Karplus-Fraenkel formula¹⁵ relating the ¹⁴N hfsc to the spin densities on ¹⁴N and its neighboring carbon atoms.^{16,17}

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 (17) J. C. M. Henning, *ibid.*, **44**, 2139 (1966).

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Vibrational Bands of Alkali Metal Salts in Dimethyl Sulfoxide

Sir:

Recently Edgell and co-workers have reported¹ their observation on the vibrational spectra of Li⁺, Na⁺, and K⁺ salts of Co(CO)₄⁻ and Mn(CO)₅⁻ anions in tetrahydrofuran solutions. The three salts of the first anion show infrared bands at 407, 190, and 150 cm⁻¹, respectively, while the corresponding bands of the Mn(CO)₅⁻ salts are shifted to higher frequencies by 20-30 cm⁻¹.

We wish to report our observation of the spectra of ammonium and alkali metal salts in dimethyl sulfoxide solutions. The data are given in Table I. It is seen that in our case the absorption band is essentially independent of the nature and the mass of the anion and, therefore, should be due to the interaction of the cation with the solvent molecules.

We made an admittedly very crude assumption that

- (1) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 1815 (1966).

Table I. Absorption Band of Alkali Salts in Dimethyl Sulfoxide

Compound	Concn, M	ν_{\max} , cm^{-1}
LiCl ^a	0.4	429 ± 2
LiBr	0.4	429 ± 2
LiI	0.9	429 ± 2
LiNO ₃	0.4	429 ± 2
LiClO ₄	0.5	429 ± 2
NH ₄ Cl	Satd	214 ± 5
NH ₄ Br	0.4	214 ± 4
NH ₄ I	0.7	214 ± 4
NH ₄ NO ₃	0.4	214 ± 4
NH ₄ ClO ₄	0.5	214 ± 4
NH ₄ SCN	0.5	214 ± 4
NaCl	Satd	199 ± 5
NaBr	Satd	199 ± 3
NaI	1.0	198 ± 3
NaNO ₃	1.0	206 ± 3
NaSCN	1.0	200 ± 3
NaPh ₄ B	0.26	198 ± 3
NaNO ₃	0.60 (in 2:1 C ₆ H ₆ -DMSO mixt)	205 ± 3
KBr	0.5	153 ± 3
KI	1.0	153 ± 3
KNO ₃	1.0	154 ± 3
KSCN	1.0	153 ± 3
RbI	3.0	129 ± 4
RbNO ₃	0.5	123 ± 5
CsI	Satd	118 ± 6
	(~1.5 M)	

^a The Li⁺ bands have a shoulder at ~414 ± 2 cm⁻¹.

Table II. Calculated and Observed Band Frequencies

Cation	ν_{calcd} , cm^{-1}	ν_{obsd} , cm^{-1}
Li ⁺	335	429
NH ₄ ⁺	221	214
Na ⁺	...	200
K ⁺	165	153
Rb ⁺	132	125
Cs ⁺	120	118

the observed absorption bands are due to a cation-solvent molecule vibration and that the force constants did not change with the change in the cation. Taking the Na⁺ band as the standard, we calculated the frequencies of other bands. The results are shown in Table II.

It is, of course, quite evident that the force constants would vary with the nature of the cation and that the alkali metal ions are solvated by several molecules of DMSO. Nevertheless the trends are consistent and seem to indicate the ion-solvent interaction. The large disagreement in the case of lithium salts is to be expected in view of the known coordinating ability of the lithium ion. Further studies of the above and similar systems are now in progress.

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A Peroxide Fragmentation Reaction

Sir:

Tertiary dialkyl peroxides are normally insensitive to base.¹ We wish to report a unique decomposition of a tertiary peroxide in a basic medium.

When 2-*t*-butylperoxy-2-methylpropionic acid (I) was treated with triethylamine in chlorobenzene at

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