Proton Hyperfine Coupling Constants from NMR Contact Shift Studies of Triarylaminium Cation Radicals

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Abstract: The hitherto little-used sideband spectrum deconvolution NMR method has been applied to the observation of the broad-line contact-shifted proton NMR spectra of a series of 4,4′,4″-trisubstituted triphenylaminium ion free radicals in trifluoroacetic acid-*d* solutions at concentrations in the range 0.8–1.5 M. Analysis of these spectra gives the signs and magnitudes of electron–proton hyperfine coupling constants for the compounds in which the three para substituents are fluorine, chlorine, bromine, methyl, ethoxy, or phenyl groups. The results for the fluorine and the methyl substituents are consistent with hyperfine coupling constants from the analysis of ESR spectra, but the data for the chlorine-substituted radical differ from published values. Data for the remaining cases are not available from ESR studies. The results afford an indication of the range of applicability of the sideband deconvolution NMR method to spectra which contain incompletely resolved lines, or lines with a wide range of widths.

Exchange of a proton between two structurally distinct sites is known to affect the NMR signal of that proton. As the exchange frequency increases, the two sharp lines which arise from the proton fixed at its two possible sites first broaden, then merge, and finally again narrow to a single line at the population-weighted average position of the two original lines. The parameter which determines the NMR pattern is the ratio of exchange frequency to the separation (in frequency units) of the original lines.[2]

In principle, the same sequence of spectra can arise from solutions of free radicals. Here, the two states of the proton are due to the two possible orientations of the unpaired electron spin in that same molecule. These states are averaged by paired transitions between electron spin states in neighboring molecules (Heisenberg exchange), with the proton permanently fixed at one site. The electron–proton hyperfine coupling (hereafter referred to simply as the hyperfine interaction) will produce NMR shifts at the *i*th proton given by:

$$\Delta H_i = a_i m_s \gamma_e / \gamma_i \qquad (1)$$

where a_i is the hyperfine coupling constant (including sign) in gauss, m_s is the net electron spin quantum number of the molecule ($\pm\frac{1}{2}$), and γ_e and γ_i are the electronic and nuclear gyromagnetic ratios. These shifts are measured relative to a hypothetical diamagnetic molecule whose electronic structure is identical with that of the radical, but with its unpaired electron magnetic moment "turned off". This situation has not, to our knowledge, been observed. Instead, the Heisenberg exchange rate is always at least sufficiently rapid in liquid solution to broaden the individual shifted lines beyond detectability and sometimes still more rapid to yield a single exchange-narrowed NMR line.[3] The Boltzmann distribution of electron spin causes a shift of the position of this NMR line relative to the NMR line of the diamagnetic molecule given by:[4]

$$\Delta H_i = -a_i(\gamma_e/\gamma_i)(g_e\beta_e H_0/4kT) \qquad (2)$$

Line widths in these free-radical NMR spectra can be used to estimate Heisenberg spin exchange rates. Under conditions where the contributions to line width by all intermolecular electron–nuclear interactions are the same for all lines in the spectrum, the Heisenberg exchange rate is given to good approximation for most of our free radicals by:

$$r_{\mathrm{HE}} \simeq \tfrac{1}{4}\gamma_e^2[\partial(a_i^2)]/[\partial(W_i/2)] \qquad (3)$$

Here, a_i is the coupling constant in gauss, and $(W_i/2)$ is the half-width of the line in radians/second. This relationship involves a number of important approximations which can be rationalized by evaluating the contributions to T_2 and which appear to be justified by our results. A discussion of these approximations and of the validity of eq 3 is given in the Appendix.

Small exchange-narrowed line widths are favored by fast Heisenberg spin exchange, which is in turn favored by low solvent viscosity, high solute concentration, or high temperature. Lines due to nuclei with small coupling constants a_i are more readily observed, since line width is a function of a_i^2. Under the conditions generally used, free-radical samples in liquid solution at concentrations up to 1 M can give observable NMR lines for protons with coupling constants having magnitudes up to about 0.5 G.[4–6] Kreilick has extended the observable range to about 2 G at this concentration by dissolving his samples in a liquid paramagnetic solvent.[6,7] de Boer and co-workers[8] have been able to resolve considerably broader lines, for example, that due to the α protons, which have a coupling constant of 4.9 G, in naphthalene anion radical samples. Their total radical concentration (including labeled species, which also contribute to the total electronic exchange rate) was ca. 2.25 M for their published derivative spectrum; this is more than twice the solubility of most of our samples.

Our interest in the properties of triarylaminium ion free radicals has led us to apply the NMR method to a series of these compounds, each with a set of three identical substituents in the ring para positions. The NMR method offers the advantages of simultaneous determination of both magnitudes and algebraic signs of the coupling constants and direct access to values which cannot be extracted unambiguously from incompletely resolved EPR spectra. However, we have been unable to use Kreilick's paramagnetic solvent technique with the aminium cations. They reacted with our samples of di-*tert*-butylnitroxide, with 2,2,5,5-tetramethyl-1-aza-3-oxacyclopentanooxy, and with 2,2,6,6-tetramethyl-4-oxopiperidinooxy, although we cannot say whether these reactions were with the nitroxy radicals or with small amounts of impurities in them. Some unsuccessful attempts also were made to use concentrated solutions of paramagnetic metal ions or chelates as spin relaxers in diamagnetic solvents. The following substances either reacted with our aminium ion samples or gave insufficient enhancement of the electron spin relaxation rate: acetylacetonates of Cr(III), Mn(III), Fe(III), Co(II), Co(III), Ni(II), Cu(II); tris(dipivaloylmethane) chelates of Gd(III) and Ho(III); and trifluoroacetates of Gd(III) and Ho(III).

All of our free radicals give at least one relatively broad (6 to 21 kHz) NMR line. In addition, there is always one line about 2 kHz wide (meta protons) and a narrow (ca. 0.1 kHz) line for the diagmetic reference. This combination of (partially overlapping) broad and narrow lines leads to severe problems in the choice of conditions for recording undistorted spectra at low modulation frequencies (conventional broad-line conditions); these problems have already been considered.[9a] It is not possible to overcome these difficulties by selecting conditions to give more effective exchange narrowing of the lines, because the minimum line widths attainable for a given sample are limited by the solubility of that sample. So far as we are aware, all determinations of very large coupling constants by the broad-line NMR technique have been carried out on more soluble substances at concentrations well above the solubility limit, about 1.0 M, of most of our samples. Furthermore, we cannot use sufficiently high-frequency modulation to avoid sideband overlap with these broad spectra, given the limitations imposed by the instrumentation available to us.[9]

Finally, pulse Fourier transform spectra cannot be obtained for these samples with our instrumentation. This is because the free induction decay (FID) rate constants lie in the range 15–49 μs for the broadest lines. These FID's are essentially complete before a useful number of data points (i.e., enough to define the broadest lines) can be accumulated after the receiver recovers from the rf transmitter pulse.

We estimate that the sideband spectrum deconvolution NMR method applied here gives spectra in which the signal to noise is improved by about one order of magnitude compared to conventional broad-line NMR spectra *of the same samples* (with concentration limited by solubility). There are a number of reasons for this improvement. The method used to analyze these spectra makes use of the contributions of all of the observable sidebands to signal intensity, and the spectra can be recorded at higher power levels without saturation. Furthermore, random noise is reduced in our instrument by operating with high-frequency modulation. Finally, RF and AF phase adjustments are straightforward and unambiguous, in contrast with the uncertainties in these with conventional broad-line NMR on our instrument. An additional convenience in use of this NMR method arises from the fact that the optimum modulation amplitude is independent of sample. Consequently, a series of samples can be run without resetting instrument parameters, once these have been determined.

Experimental Section

The syntheses of all but one of the symmetrically trisubstituted triphenylamines and aminium perchlorates used for this work have already been described.[10]

4,4′,4″-Triethoxytriphenylamine. Reaction of 1-ethoxy-4-iodobenzene with 4-ethoxyacetanilide by the Ullman method followed by alcholysis of the amide gave the known[11] secondary amine, mp 95 °C. Another Ullman reaction with the secondary amine and 1-ethoxy-4-iodobenzene gave the crude tertiary amine in 75% yield. Isolation of crystalline product was complicated by its tendency to oil out. Crude tertiary amine was purified by extraction into hexane, conversion to the aminium perchlorate, and reduction back to amine with zinc dust. Final recrystallization from ethanol gave needles, mp 43–45 °C. Anal. ($C_{24}H_{27}O_3N$) C, H, N.

4,4′,4″-Triethoxytriphenylaminium Perchlorate. The amine (18.5 g, 0.049 mol) in 25 mL of ether was dropped into a solution of 10.4 g (0.05 mol) of dried and powdered silver perchlorate dissolved in 200 mL of dry ether and cooled to 0 °C. The dark bluish mixture was stirred 1 h at room temperature, filtered, and washed with ether. The radical was dissolved in 150 mL of methylene chloride and separated from precipitated silver metal by filtration, and this solution added to 1500 mL of anhydrous ether. Cooling overnight gave 21.0 g or 90% of the radical; blue plates with mp 133–5 °C. Anal. ($C_{24}H_{27}ClO_7N$) C, H, N.

Preparation of Sample Solutions. Samples were made up in trifluoroacetic acid-*d* (DTFAA) by two methods. In some cases solid aminium perchlorate was dissolved in the solvent. In other cases the amine was oxidized with a small excess of thallium(III) trifluoroacetate; solutions of this oxidant were made up and used in a drybox. In all cases the sample was stirred with the solvent for several hours and filtered into the NMR tube. Most of these solutions are quite viscous and do not attain saturation even with prolonged stirring, as evidenced by the fact that they could be further concentrated by 10–20% on the vacuum line without precipitating the radical. Solution concentrations were calculated from the weight of radical dissolved and the measured total volume of the solution produced, since the solute contribution to solution volume is not negligible at these concentrations. We believe that those solutions which gave useful NMR spectra contained little free amine, since signals in the aromatic region due to protons in diamagnetic molecules generally were weak in the absence of added marker.

NMR spectra were collected on a Bruker HFX-90 spectrometer using a modulation frequency ν_m near 10.9 kHz; the exact frequency was measured for each run. Details of these measurements and our instrumentation have already been published.[9a]

Chemical Shifts in the Amines. Calculation of proton NMR contact shifts for these free radicals requires data on the chemical shifts of protons at corresponding sites in the triarylamines from which the aminium ions are obtained by oxidation. These parameters were determined from NMR spectra recorded on a Varian A-60 spectrometer using degassed solutions of the amines, usually in DTFAA solution. Two problems arose in this work. Some of these amines are too little soluble to obtain good spectra in this solvent, and solvent effects on the chemical shifts often are rather large. NMR parameters obtained from deuteriochloroform solutions of 4,4′,4″-trichlorotriphenylamine and the tribromo compound were corrected for the solvent shift in the midpoint of the A_2B_2 pattern in DTFAA. Only the four most intense lines can be identified in these very dilute saturated solutions in DTFAA. Tribiphenylylamine is almost totally insoluble in the usual NMR solvents; chemical shifts in this compound were estimated from parameters used to fit roughly the published spectrum[12] of 4-methylbiphenyl. This compound was selected because the aromatic proton A_2B_2 pattern for tri-*p*-tolylamine in deuteriochloroform is a single line;[13] this indicates that *in this solvent* the methyl and diphenylamino groups are equivalent in their effects on the NMR spectrum.

The second major problem arises with the amines substituted by fluoro, methyl, or alkoxyl groups in the three para positions: these amines are quickly oxidized in DTFAA solution, even if solvent and solute are carefully degassed before mixing. These samples were degassed and sealed together with a small quantity of zinc dust; they were then reduced by heating with the zinc and the excess metal separated to the upper end of the NMR tube in a centrifuge before recording the NMR spectra. The amine chemical shifts so determined are recorded in Table I.

Treatment of Data. An appropriate linear combination of three or more experimental spectra is generated to provide a phase-corrected spectrum with sloping "baselines" continuous through all of the sidebands of the sharp diamagnetic lines.[9b] These phase-corrected spectra contain up to seven overlapping sidebands and cannot be directly interpreted. Simplification can be effected by a direct numerical deconvolution scheme called DECON.[9a] This produces the pure absorption spectrum with no prior assumptions, and line separations can then be measured directly on the plotted spectrum. A second simplification method fits a calculated sideband spectrum to the experimental spectrum;[9b] we call this procedure CONFIT. It optimizes the calculated spectrum by adjusting line widths, positions, and intensities.

Chemical Shift Markers. The NMR line positions obtained by either method are measured relative to a diamagnetic line of known chemical shift determined in samples in DTFAA solvent with no free radical present. In all cases in which benzene or acetonitrile was added as an internal marker, the ever-present HTFAA impurity (in the DTFAA solvent) line was also found. The position of this line is quite sensitive to the presence of water absorbed by the solvent. However, the separation of the HTFAA and benzene lines, when the latter was added as a second marker, varied less than 0.1 ppm in our spectra. Thus we estimate the position and error for the HTFAA line as 11.4 ± 0.2 ppm. Since this error range is smaller than the uncertainty in the positions of the broad radical lines, this impurity was usually used as the only internal standard, and our measured line positions are reported relative to it in the DECON procedure. The diamagnetic markers added to some samples are listed in the first column of Table I.

Table I. Experimental Results and Analysis of Proton NMR Sideband Spectra

Para sub,[a] soln prep, soln concn	Proton position[b]	Data analysis method[c]	Calcd no. protons per ring[d]	Obsd freq of line center, kHz[e]	Calcd chem shift, ppm. vs TMS	Ref chem shift, ppm[f]
F, dissolve salt, 1.53 M, no marker	Ortho	CONFIT	2.19	9.043	−146.5 ± 8.5	7.24
	Ortho	DECON		14.31	−147.6 ± 7.9	7.24
	Meta	CONFIT	1.81	−11.60	82.8 ± 1.4	7.13
	Meta	DECON		−6.410	82.6 ± 1.4	7.13
Cl, dissolve salt, 1.13 M, benzene marker	Ortho	CONFIT	2.03	4.552	−150.7 ± 5.1	7.03
	Ortho	DECON		14.69	−151.8 ± 4.3	7.03
	Meta	CONFIT	1.97	−16.86	87.2 ± 1.3	7.20
	Meta	DECON		−6.850	87.5 ± 1.2	7.20
Br, oxid of Tl(III), 1.07 M, no marker	Ortho	CONFIT	2.08	14.52	−146.0 ± 9.4	6.97
	Ortho	DECON		14.27	−147.2 ± 8.9	6.97
	Meta	CONFIT	1.92	−6.579	88.4 ± 2.3	7.40
	Meta	DECON		−7.010	89.3 ± 2.2	7.40
CH_3, dissolve salt, 1.44 M, no marker (ref line at 7.81 ppm)	Ortho	CONFIT	2.28	21.52	−146.9 ± 6.1	7.25
	Ortho	DECON		13.96	−147.3 ± 5.5	7.25
	Meta	CONFIT	2.02	0.666	84.8 ± 1.3	7.40
	Meta	DECON		−6.990	85.4 ± 1.2	7.40
	p-CH_3	CONFIT	2.70	−18.18	294.2 ± 16.0	2.45
	p-CH_3	DECON		−24.82	283.6 ± 17.0	2.45
OC_2H_5, dissolve salt, 1.26 M, benzene marker	Ortho[j]	CONFIT	1.21	8.393	−183.3 ± 12.0	7.36
	Meta	CONFIT		−13.02	54.6 ± 3.3	7.17
	Meta	DECON	2.57	−3.760	53.2 ± 3.2	7.17
	p-CH_2	CONFIT		−13.02	54.6 ± 3.3	3.92
	p-CH_2	DECON	2.57	−3.760	53.2 ± 3.2	3.92
	p-CH_3	CONFIT		−8.059	−0.6 ± 0.13	1.33
	p-CH_3	DECON	3.86	1.043	−0.2 ± 0.15	1.33
C_6H_5, oxid of Tl(III), 1.02 M, no marker	Ortho	CONFIT	1.90	8.153	−132.6 ± 7.5	7.03
	Ortho	DECON		12.80	−130.8 ± 7.3	7.03
	Meta	CONFIT	2.05	−10.65	76.4 ± 1.8	7.41
	Meta	DECON		−5.890	76.8 ± 1.8	7.41
	Ortho′	CONFIT	1.81	−0.616	−35.2 ± 0.74	7.25
	Ortho′	DECON		4.270	−36.1 ± 1.00	7.25
	Meta′	CONFIT	2.01	−5.943	24.0 ± 0.19	7.31
	Meta′	DECON		−1.181	24.5 ± 0.23	7.31
	Para′	CONFIT[l]	1.24	−0.123	−40.6 ± 1.1	7.25
	Para′	DECON				

[a] Each compound has the same substituents at each of the three para positions. Samples were prepared either by dissolving crystalline triarylaminium perchlorate in the solvent or by oxidizing the amine with Tl(III). [b] Proton positions are specified relative to the site of attachment of the amine nitrogen to the aromatic ring. [c] These methods are described in the text. [d] Calculated from the observed integrated intensity of the line. [e] Frequencies are given relative to the diamagnetic center line of each sideband spectrum and relative to the HTFAA reference line

Results

Some of the spectra which have been analyzed successfully are reproduced in Figures 1-5. In each figure, the upper curve is the sideband spectrum, the lower curve is the deconvoluted spectrum obtained from it by DECON, and field increases from left to right. All spectra are positioned along the magnetic field axis with the diamagnetic peak of the deconvoluted spectrum lined up under the diamagnetic peak in the center band of the sideband spectrum. Analysis of the sideband spectra requires that they contain long featureless ends outside the sideband pattern in order to establish the spectrum baseline. These ends have been cropped in the figures to save space. The spikes which appear in some of the deconvoluted spectra at 10.9-kHz (the modulation frequency) intervals above and below the reference peak are artifacts introduced by the deconvolution procedure as a consequence of saturation and the resulting distortion of the diamagnetic sideband intensity pattern.[9a] The peaks assigned to ortho meta, para, or reference protons are identified by an o, m, p, or R on the deconvoluted spectra. Spectra for the tribromo-substituted compound have already been published[9a] and are not repeated here.

Quantitative results from the analysis of these spectra are summarized in Table I. The fraction of the total integrated NMR intensity which is due to one structurally equivalent set of protons in the paramagnetic sample, multiplied by the total number of protons at all sites on the aromatic ring, gives the calculated number of protons per ring which contribute to each NMR line listed in column 4 in the table. These numbers should be compared with the 2, 2, 1, and 2 or 3 protons at the ortho, meta, para, and para-substituent positions in each aromatic ring which contribute to the intensities of these lines. They show that values of the integrated intensities obtained from CONFIT have a precision of ±15% except for the very weak line due to ortho protons in the spectrum of the ethoxy-substituted radical. Some special difficulties in fitting this line will be considered below. We made no effort to repeat this calculation with our less precise data from the DECON spectra.

Other input data in Table I are the frequencies at line centers and reciprocal half-widths of the radical NMR lines in columns 5 and 10. These data are obtained directly from the sideband spectra during operation of the CONFIT program, by optimizing the fit of Lorentzian lines to all sidebands of each absorption peak. Corresponding data are obtained (with lower precision) from the deconvoluted spectra by direct measure-

Calcd coupling constant, G[g]	R	Obsd recip half-width, kHz^{-1}	Heisenberg eln spin exch rate,[h] s^{-1} × 10^{-9}	Rate const,[i] L/mol s × 10^{-9}
−2.06 ± 0.12	0.044	0.1788	8.7 ± 0.8	3.7 ± 0.2
−2.08 ± 0.11		0.192		
1.014 ± 0.019		0.967		
1.012 ± 0.019		0.943		
−2.103 ± 0.067	0.019	0.3074	16.8 ± 1.0	13.2 ± 0.4
−2.117 ± 0.057		0.350		
1.067 ± 0.017		1.199		
1.071 ± 0.016		1.129		
−2.04 ± 0.13	0.061	0.1650	8.1 ± 0.7	7.1 ± 0.3
−2.06 ± 0.12		0.1752		
1.080 ± 0.030		0.672		
1.092 ± 0.029		0.677		
−2.055 ± 0.081	0.057	0.253	14.7 ± 1.3	7.1 ± 0.3
−2.061 ± 0.074		0.274		
1.032 ± 0.017		1.131		
1.040 ± 0.017		1.104		
3.89 ± 0.22		0.0967		
3.75 ± 0.23		0.0907		
−2.54 ± 0.16	0.065	0.128	3.6 ± 0.6	k
0.632 ± 0.044		0.470		
0.613 ± 0.042		0.479		
0.676 ± 0.044		0.470		
0.657 ± 0.042		0.479		
−0.025 ± 0.002		9.12		
−0.020 ± 0.002		7.70		
−1.86 ± 0.100	0.055	0.2072	8.9 ± 0.2	8.6 ± 0.1
−1.84 ± 0.098		0.2117		
0.919 ± 0.024		0.832		
0.928 ± 0.024		0.847		
−0.566 ± 0.010		1.930		
−0.580 ± 0.014		1.411		
0.223 ± 0.003		6.147		
0.230 ± 0.003		5.080		
−0.639 ± 0.014		1.370		

of each deconvoluted spectrum. [f] From analysis of the NMR spectrum of the corresponding amine in DTFAA solution; see text. [g] Calculated using eq 2. [h] See text for this calculation. [i] Second-order rate constant for the Heisenberg spin exchange. [j] This peak is too broad and weak to measure accurately its position or line width on the deconvoluted spectrum. [k] The result is unreliable in this case due to difficulties (discussed in the text) with the determination of the line width of the ortho peak. [l] This peak is indistinguishable from the ortho′ peak in the deconvoluted spectrum; the same parameters apply to both.

ment. In addition to these data from the free-radical NMR spectra, it is necessary to have the chemical shifts of the amine protons given in column 7.

The observed frequencies at line centers (given relative to different reference positions in the sideband and the deconvoluted spectra, see footnote *e* to Table I) were used to calculate the chemical shifts relative to tetramethylsilane in column 6, with error ranges given to ± one standard deviation. These results, together with the amine chemical shifts in column 7, were used with eq 2 to calculate the hyperfine coupling constants, a_i, in column 8; error ranges again are given to ± one standard deviation. Agreement between the results obtained by the two schemes for data analysis is excellent. Since both CONFIT and DECON are based upon the same data, good agreement is expected and simply verifies that the deconvolution procedure, which is much faster than CONFIT, is reliable.

The reciprocal half-widths in column 10 were used, together with the corresponding coupling constants, to compute the approximate Heisenberg spin exchange rates in column 11. From eq 3, the slope of a plot of $(\gamma_e^2 a_i^2/4)$ against $(w_i/2)$ for all lines in the spectrum gives an approximation to the Heisenberg spin-exchange rate. Note that the Heisenberg exchange rate is half the spin flip rate, since two spins flip at each exchange step. The second-order rate constants in the table were calculated directly from these exchange rates and the known radical concentrations and should therefore be regarded as approximate upper limits to the true rate constants. The second-order rate constants for Heisenberg exchange for these propeller-shaped cation radicals fall in the range (3.7 to 13.2) × 10^9 L/mol s, unexpectedly similar to the value (k = 3.7 × 10^9) reported for the almost spherical neutral radical di-*tert*-butyl nitroxide.[14]

Results (not reported) from the analysis of duplicate spectra in most cases agree with the data reported within the limits listed in Table I, that is, within a range of ± one standard deviation. In those cases where an identifiable diamagnetic reference other than HTFAA is present in a spectrum, the data have been recalculated for each of these diamagnetic lines (benzene or acetonitrile) taken in turn as the reference; results are independent of the reference line selected. The hyperfine coupling constants reported in Table I agree well, with an exception discussed later, with the values we have been able to obtain from ESR spectra.[15]

The R values[9b] tabulated in column 9 indicate the reliability of the least-squares fit of the calculated spectra produced by

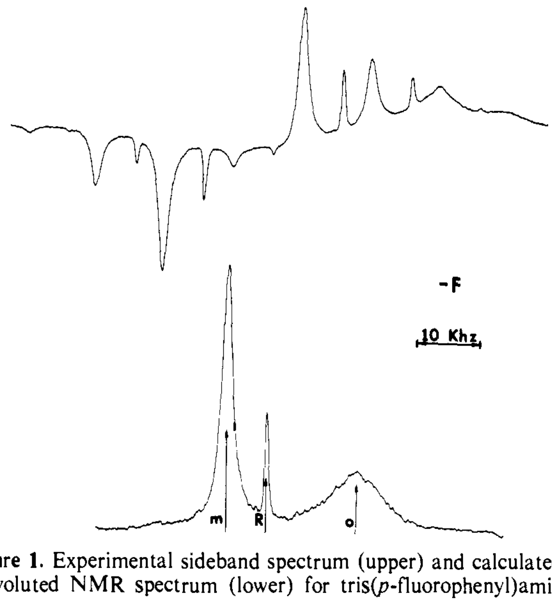

Figure 1. Experimental sideband spectrum (upper) and calculated deconvoluted NMR spectrum (lower) for tris(*p*-fluorophenyl)aminium cation. The sideband spectrum is a phase-corrected linear combination of three scans.

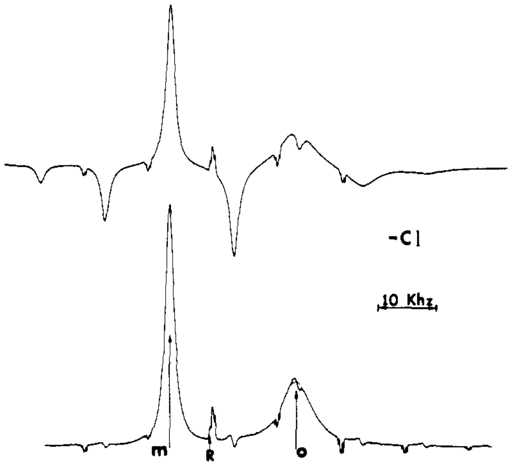

Figure 2. Experimental sideband and calculated deconvoluted NMR spectra for tris(*p*-chlorophenyl)aminium cation. The sideband spectrum is a single scan with only instrumental phase correction. The feature at the maximum of the ortho peak is discussed in the text.

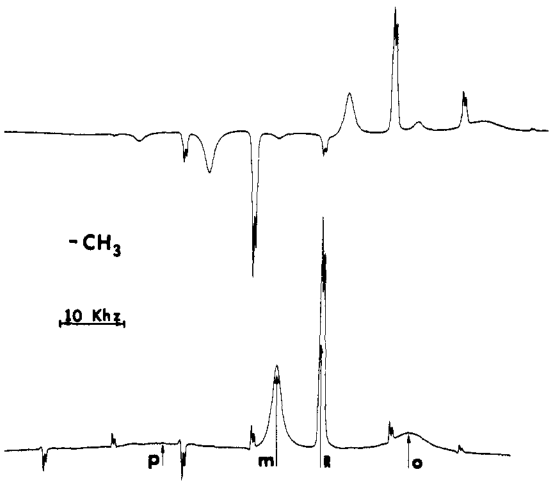

Figure 3. Experimental sideband and calculated deconvoluted NMR spectrum for tri-*p*-tolylaminium cation. The sideband spectrum is a single scan with only instrumental phase correction.

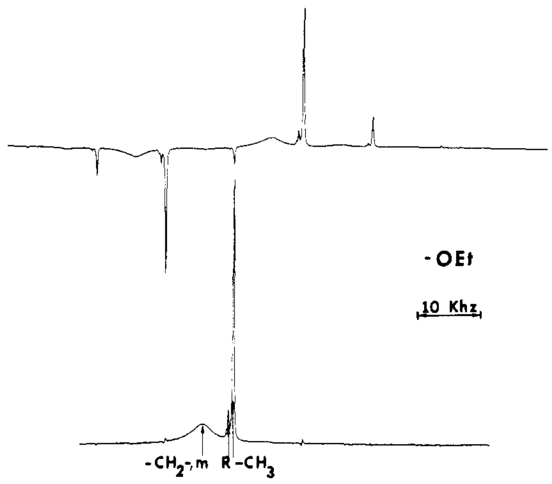

Figure 4. Experimental sideband and calculated deconvoluted NMR spectra for tris(*p*-ethoxyphenyl)aminium cation. The sideband spectrum is a phase-corrected linear combination of three experimental spectra.

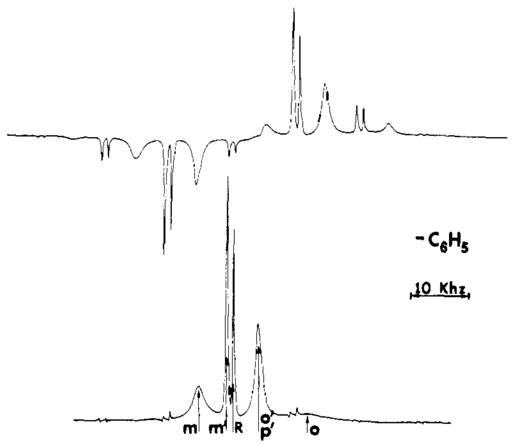

Figure 5. Experimental sideband and calculated deconvoluted NMR spectra of tri-*p*-biphenylylaminium cation. The sideband spectrum is a phase-corrected linear combination of three experimental spectra.

CONFIT and the experimental spectra.[16] Crystallographers generally accept a value of the order of 0.05 as evidence for excellent fit of a crystal structure to x-ray diffraction data. Spectra in which lines are broadened as a result of our use of special home-built modulation coils with no provision for field shim gave *R* values which average 0.10, with considerable scatter.

The three halogen-substituted aminium ions give the spectra in Figures 1 and 2 and ref 9a and the data entered in the top three sections of Table I. Hyperfine coupling constants for the fluorine-substituted radical are close to our unpublished assignments from the ESR spectrum. Results for the chlorine-substituted radical are not consistent with the ESR data reported by either Mohammad and Sundheim[17] or Seo, Nelson, Fritsch, Marcoux, Leedy, and Adams.[18] As far as we are aware, the ESR spectrum of the bromine-substituted radical has never been resolved. There is no regular trend in the estimated Heisenberg exchange rates through this series of three halogen-substituted radicals.

The spectrum shown in Figure 1 is a linear combination of three scans which shows two undesirable features. The reference line has a width of 0.6 kHz, about three times the normal value, and this spectrum was recorded at a time when the spectrometer was unusually noisy. The line broadening is the result of operation with the special modulation coils already mentioned. In spite of these problems, the parameters derived from this spectrum by both CONFIT and DECON agree (within the error limits given) with those obtained from another spectrum of this radical in which line widths and noise were normal.

The spectrum in Figure 2 is a single scan which was not phase corrected by the linear combination procedure. A small feature appears superimposed upon the deconvoluted spectrum at intervals equal to the modulation frequency on either side of the peak due to the meta protons. Evidently this arises from incomplete correction for the meta peak in the 2+ sideband, which happens in this sideband pattern to be superimposed upon the ortho peak in the center band. One of these features accidently appears at the tip of the ortho peak in the deconvoluted spectrum. The corrected peak used in calculating the DECON values in Table I is dotted in.

The NMR data for the tri-*p*-tolyaminium ion give coupling constants in excellent agreement with our ESR data. In this case we were fortunate that the aminium perchlorate is more soluble in DTFAA than are most of our samples. It was possible to study this sample at 1.44 M concentration, where the exchange is fast enough that the broad line due to the methyl protons is adequately resolved by the CONFIT procedure.

For the radical substituted by ethoxy groups, three individual spectra give the rather scattered values −2.5, −2.35, and −2.48 G for the ortho coupling, with standard deviations of ±0.16, 0.21, and 0.19 G, respectively. In this case, considerable variation in the data is expected because the spectrometer must be operated at quite low rf power levels (rf power attenuation was 40–50 dB greater than used for other spectra) in order to avoid distortion of the slightly shifted, and consequently very narrow and high-amplitude, line due to the methyl protons in the substituents. This restriction is basically due to limitations imposed by the dynamic range of the digitizer and the spectrometer amplifiers. Under these conditions, the strongly shifted and broad peak due to the ortho protons has a very low amplitude, as can be seen in Figure 4. In this situation, small residual phase errors in the high-amplitude methyl peak produce errors in its wings which could be comparable to the magnitude of the ortho peak on its upfield side, and thus substantially shift the apparent position of the latter. Consequently, one expects a large error in the determination of the position of this line by CONFIT. It is too broad to estimate its position in the deconvoluted spectrum.

We doubt that a better value for this coupling constant can be obtained by the proton NMR technique, but improvement would be possible by studying the deuterium NMR of a labeled sample, where the lines would be narrower. The ESR spectrum of this radical can be accounted for about equally well by an ortho coupling close to 2.5 or 1.8 G. The differences in the spectra computed for these two values are so subtle that we have been unable to satisfy ourselves which value is required by the experimental ESR spectra. Consistency with the general trend of ortho coupling constants in a series of these radicals would require the smaller value.[19] No indication at all of the very small coupling with the methyl protons in the ethoxy substituents can be seen in the ESR spectrum.

Coupling constants have been assigned in the phenyl-substituted radical on the basis of expected intensities and chemical shifts of the NMR lines. We assume that the farthest upfield and farthest downfield lines would arise from the ortho and meta protons in the disubstituted rings. The somewhat unsymmetrical peak with higher intensity is assigned to the ortho′-para′ protons in the monosubstituted ring. This leaves the peak at chemical shift 24.3 ppm for the meta′ protons of this same ring. It is possible that assignments of the ortho′ and para′ peaks have been interchanged, but we believe that all of the others are correct. There are no independent data against which to check the parameters reported for this case. Figure 5 shows the spectra for this compound. The most interesting feature is the slight asymmetry in the peak attributed to the o′,p′ protons. CONFIT is capable of resolving this into two lines with the intensity ratio 1.81/1.24, reasonably close to the ratio 2.0 expected for ortho′/para′ protons. Note that the coupling constants assigned for this compound confirm that alternation in algebraic signs extends into the second ring. Since there are five unrelated electron–proton coupling constants in addition to the nitrogen coupling in this radical, the simulated ESR spectrum is such a thicket of lines that it would not be expected to be resolvable with currently available instruments. Errors in the chemical shifts roughly assigned for the amine are unlikely to be large enough to affect the calculated hyperfine coupling constants which we report.

The radicals substituted by ethoxy and by phenyl groups were observed over a temperature range of 25 °C. In neither case do the data provide unambiguous evidence for temperature effects on the contact interaction; the changes in coupling constants over this temperature range lie outside our normal error range but are not sufficiently large to afford convincing evidence of a real effect.

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Appendix

We offer here further justification for the approximations used to arrive at eq 3. For convenience, we use coupling constants a_i and half-widths $(w_i/2)$ in radians/second, to be consistent with the equations in the references cited below. We divide the contributions to the half-width of any selected proton line into an intramolecular Fermi contact term, an intramolecular electron–nuclear dipolar term, and a term which includes all intermolecular electron–nuclear interactions:

$$T_2^{-1} = (T_2^{-1})_{\mathrm{FC}} + (T_2^{-1})_{\mathrm{D}} + (T_2^{-1})_{\mathrm{I}} \qquad (4)$$

Expressions for the intramolecular contact and dipolar terms have been given:[20]

$$(T_2^{-1})_{\mathrm{FC}} = \tfrac{1}{4}a^2\tau_e[1 + 1/(1 + \omega_e^2\tau_e^2)] \qquad (5)$$

$$(T_2^{-1})_{\mathrm{D}} = \tfrac{1}{120}\,\mathrm{tr}\,\mathbf{T}^2\,\tau_d[7 + 13/(1 + \omega_e^2\tau_d^2)] \qquad (6)$$

Here, τ_e is the electron spin relaxation time, ω_e is the electron angular frequency, $\mathbf{T}$ is the anisotropic dipolar tensor, and τ_d is the dipolar correlation time, given by

$$\tau_d^{-1} = \tau_e^{-1} + \tau_r^{-1} \qquad (7)$$

where τ_r is the molecular tumbling correlation time. For free-radical samples of the types studied in this paper,

$$T_2^{-1} \approx \tfrac{1}{4}a^2\tau_e + (T_2^{-1})_{\mathrm{I}} \qquad (8)$$

If $(T_2^{-1})_{\mathrm{I}}$ is assumed, following Davis and Kreilich,[20b] to have the same value for all protons in a given sample, then:

$$\tau_e^{-1} \simeq \tfrac{1}{4}[\partial(a^2)]/[\partial(T_2^{-1})] \qquad (9)$$

This is essentially the Heisenberg spin exchange rate if all other contributions to electron spin relaxation are negligible. It is identical with eq 3, where a_i is in gauss.

We now justify the approximations used in deriving eq 8. Since $\omega_e = 3.7 \times 10^{11}$ at our spectrometer operating conditions, and the τ_e values for our samples fall in the range (3 to 17) × 10^{-9}, the second (frequency-dependent) term in eq 5 is negligible. Consideration of the contribution of $(T_2^{-1})_{\mathrm{D}}$ requires an estimate of the value of the dipolar hyperfine tensor. For

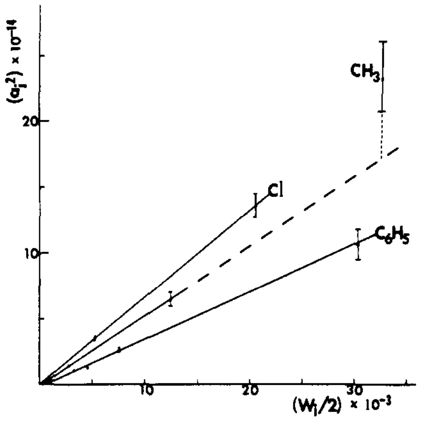

Figure 6. Test of the validity of eq 3 and 9. Square of the proton hyperfine coupling constant plotted against the half-width of the NMR line for various aminium cations; both a_i and $(W_i/2)$ are in radians/second. The lines for the Cl- and the C$_6$H$_5$-substituted radicals represent the extreme range of observed slopes. Both coordinate values are halved for all points for the methyl-substituted radical in order to retain a compact coordinate system. Estimated errors in the magnitude of (a_i^2) are indicated by the lengths of the vertical range bars. These errors are largely dependent upon the widths of the NMR lines; for the narrower lines toward the left of the figure, the errors are within the diameters of the points plotted.

aromatic π radicals in an appropriate coordinate system, the hyperfine tensor has the form:

$$\mathbf{T} \approx (a/2)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad (10)$$

Thus,

$$(T_2^{-1})_{\mathrm{D}}/(T_2^{-1})_{\mathrm{FC}} \approx 0.117[\tau_r/(\tau_e + \tau_r)] \times [1 + 1.857/(1 + \omega_e^2\tau_d^2)] \qquad (11)$$

This ratio can vary between 0.00 and 0.117 for our samples, as τ_r^{-1} ranges from zero to infinity. From this, we can estimate that neglect of the intramolecular dipolar terms introduces an error (τ_e^{-1} too small) of magnitude $\leq$12% into eq 9. Exceptions could arise when the ratio of dipolar to contact hyperfine interactions is greater than that for π radicals. That is, deviations from eq 7 would be expected only for aliphatic protons present in some substituents on the π systems.

The validity of the approximate eq 3 or 9 for protons directly attached to the π-carbon framework in our radicals is confirmed in Figure 6. Here, the five sets of protons on the aromatic carbon atoms in the tri-*p*-biphenylylaminium cation lie on a good straight line; one-fourth the slope gives the Heisenberg exchange rate. The aromatic protons on the radicals substituted by fluoro, bromo, or methoxy groups lie on closely spaced lines (not shown) with nearly the same slope. Thus, differences in the calculated second-order rate constants for Heisenberg exchange in these samples are due almost entirely to variations in the concentrations of these samples. The two sets of protons in tris(*p*-chlorophenyl)aminium cation give quite a different line which illustrates the maximum range of the observed slopes. This slope is reproduced well by data from duplicate spectra and reflected in the high rate constant for Heisenberg exchange for that radical. Tri-*p*-tolylaminium cation does not give a linear correlation of these parameters; the point for the methyl protons (this point is labeled in the figure) is well off the extension of the line defined by the aromatic protons. This is the type of system for which we have already predicted deviations from eq 9. Tris(*p*-ethoxyphenyl)aminium cation also gives a poor correlation, but in this case the assignment of the group which deviates from the linear correlation expected for the aromatic protons is uncertain because of problems (already discussed) with the determination of the position and width of the line for the ortho protons. It is interesting that the methylene protons in this compound and the methyl protons in tri-*p*-anisylaminium cation do fall on the line for the aromatic protons, although they are not directly attached to carbon atoms in the π system but instead are on carbon atoms bonded to the ether oxygen atoms.

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