

Proton Hyperfine Coupling Constants in the Tri-*p*-anisylaminium Cation Radical from Proton and Deuterium Contact Shifts

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Abstract: Proton sideband spectrum deconvolution NMR and deuterium pulse Fourier transform spectra have been obtained for the stable tri-*p*-anisylaminium cation free radical and for its 2,6,2',6',2'',6''-*d*₆, 2,3,5,6,2',3',5',6',2'',3'',5'',6''-*d*₁₂, and methyl-*d*₉ derivatives. The proton or deuterium line separations so obtained permit the unambiguous assignment of electron-proton hyperfine coupling constants for this radical: $a_{\text{ortho}} = -1.76 \pm 0.10$, $a_{\text{meta}} = 0.61 \pm 0.02$, and $a_{\text{methyl}} = 0.65 \pm 0.02$ G. These assignments neglect possible isotope effects on the spin distribution and coupling constants; if present, these effects are too small to evaluate reliably with data of the precision currently available.

The ESR spectrum of tri-*p*-anisylaminium ion has been studied by a number of groups,²⁻⁴ and electron-nuclear hyperfine coupling constants have been assigned in the usual way by optimizing the fit of a calculated to the observed ESR spectrum. However, there are some difficulties with the assignment of proton hyperfine couplings based upon this experimental spectrum, which contains only about 60 lines of the theoretically possible 1470. The small number of observed lines can be accounted for in part by assuming that some coupling constants are accidentally equal to one another. In addition, the number of lines observed in the outer wings of the spectrum (for which nitrogen spin $I_N = \pm 1$) is so small that one is forced to choose all proton coupling constant ratios as small integers. Both of these possibilities have been exploited in assigning the published values^{3,4} for proton hyperfine couplings for this radical: $a_{\text{ortho}} = 1.22$ G; $a_{\text{meta}} = a_{\text{methyl}} = 0.61$ G. However, it is not easy to obtain evidence upon which to base an unambiguous choice of the integer ratio to use. In place of this ortho/meta ratio of two, the ratio three, which leads to $a_{\text{ortho}} = 1.82$ G, has recently been proposed by Neugebauer and co-workers⁵ based upon ESR studies, but no details of the reasons for their choice are given by them.

Either of these assignments requires an improbable number of coincidences for which one would like to have more direct evidence. Our reservations about these matters were confirmed when we studied the proton sideband spectrum deconvolution NMR of this compound; the results require a reassignment of the earlier value for a_{ortho} . We have also directly confirmed that a_{meta} and a_{methyl} are nearly (but not exactly) equal by observing the proton NMR and the deuterium pulse Fourier transform NMR spectra of appropriate compounds with specific deuterium labels. Furthermore, these results, which overlap the data obtained from proton NMR spectra, afford a desirable independent check of the precision of the proton NMR studies and of the validity of the methods used to analyze those spectra. These experiments required the synthesis of tri-*p*-anisylamine, I, and its 2,6,2',6',2'',6''-*d*₁₂ (hereafter called ortho-*d*₆), II, 2,3,5,6,2',3',5',6',2'',3'',5'',6''-*d*₁₂ (hereafter called the ring-*d*₁₂), III, and tri(methoxy-4,4',4''-*d*₃) triphenylamine (hereafter called the methyl-*d*₉) IV, derivatives.

Experimental Section

Methods for the synthesis of I⁶ and of II⁷ have been described. Deuterium exchange in II was estimated at 90–95% from its NMR spectrum;⁷ the mass spectrum shows the molecular ion to have a mass of 341 daltons (calcd for C₂₁H₁₅D₆NO₃: 341), with approximately 32% *d*₅ and 11% *d*₄ molecules, at 91% label.

Synthesis of III. I (4.8 g) was exchanged with D₂O (120 mL) con-

taining 0.8 mL of 38% DCl in a degassed and sealed tube for 220 h at 200 °C by the method described by Werstuijk.^{8,9} The product, recovered in 40% yield, melts at 94–96 °C. Its NMR spectrum shows that exchange is complete at the ortho positions and 65–70% complete at the meta positions: the single aromatic proton NMR line (located at the upfield half of the original A₂B₂ aromatic proton pattern) has an integral value equal to 23% of the integral for the three methoxy protons, and this represents 0.69 proton remaining per ring. The mass spectrum confirms 85% overall exchange.

Synthesis of 4,4',4''-Trihydroxytriphenylamine (V). Reagents were prepared by dissolving 5.0 g of I in 100 mL of methylene chloride and 15.5 g of boron tribromide¹⁰ in 60 mL of that solvent. These solutions were cooled to –80 °C, mixed, and allowed to stand overnight at this temperature. The deep blue solution thus produced was allowed to warm to room temperature and 60 mL of water was added cautiously. Crude product precipitated in the organic layer and was recovered in 90% yield. (Little additional product was recovered by workup of the deep blue aqueous layer, despite its intense color.) The crude material from two runs was dissolved in 50 mL of methanol, boiled with zinc dust to reduce oxidized amine, and filtered. Dropwise addition of water (48 mL) to the refluxing methanol solution (now 41 mL) gave 5.6 g of 4,4',4''-trihydroxytriphenylamine, V. Recrystallization of a small sample from acetonitrile–water gave colorless needles, mp 238–241 °C. The NMR spectrum of this intermediate is unsatisfactory in the aromatic region because of line broadening by small amounts of the aminium radical formed by rapid air oxidation. The peak due to methoxy protons is sharp but quite weak.

Deuteriomethylation of V. The phenol was deuteriomethylated by the method of Gillis.¹¹ Sodium hydroxide pellets (5.0 g) were crushed under 20 mL of dimethyl sulfoxide and washed into one arm of an inverted U-tube with an additional 10 mL of solvent. V (3.0 g) was dissolved in 30 mL of DMSO and 10 g of methyl-*d*₃ iodide was added, and this solution was rinsed into the second arm of the U-tube with another 30 mL of solvent. Both arms of the U-tube were degassed through 3 freeze-pump-thaw cycles, and the system was sealed under vacuum. The solution of V was then poured into the sodium hydroxide suspension and stirred 12 h at room temperature. Water (90 mL) was added to the opened U-tube, and the product was extracted into carbon tetrachloride, washed with water, dried, and evaporated to dryness. Recrystallization from hexane gave 2.6 g of IV (74%), mp 92–95 °C. Both the NMR and the mass spectra indicate complete deuteration: the NMR line for methoxy at δ 3.8 ppm has negligible intensity, and the molecular ion has a mass of 344 daltons.

Preparation of the Radicals. Each of the labeled trianisylamines was converted into the crystalline aminium perchlorate by a modification of the published method.⁶ The crude radical (ca. 1.25 g; prepared by oxidation with silver perchlorate in ether solution) was redissolved in ca. 30 mL of methylene chloride and filtered to remove silver metal. Then 250 mL of anhydrous ether was dropped into the stirred solution over 30 min, and the mixture was cooled overnight in the freezer. This produced a granular solid which is more easily filtered and dried than that obtained by the older procedure. Samples for study of the NMR spectra were prepared as described earlier.¹² All concentrations were close to 1.0 M, which is near the solubility limit for this salt.

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

1. Labeled sites in sample ^a	2. Isotope giving spectrum ^b	3. Data analysis method ^c	4. Calcd no. of protons per ring ^d	5. Obsd. freq of line center, kHz ^e	6. Calcd/chem shift, ppm vs TMS	7. Calcd coupling const, G ^g	8. <i>R</i> ^h	9. Line width, full width at half ht, kHz ⁱ	10. Heisenberg eln. spin exch rate, s ⁻¹ × 10 ⁻⁹
	Ortho position								
None/ ^j	H	CONFIT	2.38	4.150	-122.3 ± 6.4	-1.735 ± 0.085	0.028	8.26	5.7
None/ ^j	H	DECON		11.79	-123.7 ± 5.6	-1.753 ± 0.073		7.09	5.9
Methyl- <i>d</i> ₉	H	CONFIT	2.06	10.96	-119.7 ± 11.	-1.699 ± 0.15	0.067	13.93	2.6
Methyl- <i>d</i> ₉	H	DECON		11.75	-123.3 ± 8.2	-1.747 ± 0.11		10.63	3.5
Ortho- <i>d</i> ₆	D	DPFT		1.875	-128.4 ± 2.7	-1.816 ± 0.036		(23.7)	(1.7)
Ring- <i>d</i> ₁₂	D	DPFT	2.30	1.886	-129.2 ± 2.6	-1.827 ± 0.035		(23.2)	(1.8)
	Meta position								
None/ ^j	H	CONFIT	2.31	-11.82	55.17 ± 0.86	0.642 ± 0.011	0.028	1.17	4.1
None/ ^j	H	DECON		-4.27	54.80 ± 0.88	0.637 ± 0.012		1.22	4.1
Ortho- <i>d</i> ₆	H	CONFIT		-0.193	52.50 ± 1.2	0.606 ± 0.016	0.047	1.57	2.9
Ortho- <i>d</i> ₆	H	DECON		-4.035	52.16 ± 1.1	0.602 ± 0.015		1.57	2.9
Methyl- <i>d</i> ₉	H	CONFIT	1.94	-4.535	52.49 ± 1.1	0.606 ± 0.015	0.067	1.54	2.9
Methyl- <i>d</i> ₉	H	DECON		-4.075	52.61 ± 1.1	0.608 ± 0.015		1.57	2.8
Ring- <i>d</i> ₁₂	D	DPFT	1.70	-0.610	51.52 ± 0.54	0.594 ± 0.007		(5.85)	(0.8)
	Para position								
None/ ^j	H	CONFIT	2.31	-11.82	55.17 ± 0.83	0.686 ± 0.011	0.028	1.17	4.8
None/ ^j	H	DECON		-4.27	54.80 ± 0.88	0.681 ± 0.012		1.22	4.7
Ortho- <i>d</i> ₆	H	CONFIT		-0.193	52.50 ± 1.2	0.650 ± 0.016	0.047	1.57	3.3
Ortho- <i>d</i> ₆	H	DECON		-4.035	52.16 ± 1.1	0.645 ± 0.015		1.57	3.3
Ring- <i>d</i> ₁₂	H	CONFIT		1.771	48.22 ± 1.5	0.593 ± 0.020	0.080	1.92	2.3
Ring- <i>d</i> ₁₂	H	DECON		-4.075	52.61 ± 1.4	0.651 ± 0.019		1.97	2.7
Methyl- <i>d</i> ₉	D	DPFT		-0.616	51.88 ± 0.4	0.642 ± 0.006		(4.46)	(1.1)

^a All samples were prepared by dissolving crystalline aminium perchlorate in trifluoroacetic acid with the appropriate label. Solutions were close to 1.00 M. See Experimental Section for details. ^b Proton positions are given relative to the position at which the amine nitrogen is bonded to the aromatic ring. ^c CONFIT and DECON are described in ref 12 and 13. DPFT entries are calculated for hydrogen from the data (averaged for two runs) obtained from the deuterium PFT spectra. See text. ^d Calculated from the fraction contributed by a given line to the total integrated intensities of all lines due to protons on paramagnetic sites, multiplied by the total number of protons per ring. ^e Frequencies are given relative to the diamagnetic line in the centerband of each sideband spectrum. They are measured relative to the diamagnetic reference line in the deconvoluted and the DPFT spectra. ^f Reference proton chemical shifts were measured for trianisylamine in deuteriotrifluoroacetic acid solution after reduction by heating with zinc dust: ortho = 7.36, meta = 7.17, and methyl = 3.92 ppm. ^g Coupling constants are calculated from the observed chemical shifts with eq 2 or 3. Observed deuterium coupling constants from the DPFT spectra multiplied by $(\gamma_H/\gamma_D) = 6.514$ give the corresponding proton coupling constants listed. ^h The use of *R* values as a criterion for reliability of the least-squares fit of the calculated to the observed sideband spectrum is discussed in ref 13b and 14. ⁱ Widths of the lines from DPFT spectra multiplied by $(\gamma_H/\gamma_D)^2 = 42.4$ give the widths of lines due to protons. ^j These data are from a single-scan spectrum, rather than a phase-corrected linear combination of several scans. See ref 12.

Spectral Acquisition and Analysis. The instrumentation and procedures for recording and deconvoluting the proton sideband NMR spectra have been reported.¹² Our reasons for preferring these techniques, given the limitations imposed by available instrumentation, to the conventional broad-line (low-frequency modulation with phase-sensitive detection) or Fourier transform spectra have also been discussed.¹² Deuterium Fourier transform spectra can be obtained, since the ratio $(\gamma_D/\gamma_H)^2$ of the squares of the magnetogyric ratios for these two nuclei reduces line widths by nearly the theoretical factor 1/42.3. These spectra were run at 13.8155 MHz with the sampling rate of the free induction decay chosen to give a 10-kHz scan in the frequency domain. The spectrometer used was the Bruker B-KR 322S.

In order to maximize signal intensity with minimum use of sample, these spectra were run in 7.5 mm sample tubes. The corresponding probe has no provision for field lock. Consequently, field drifts during the 2000 pulses ordinarily used to obtain the time-averaged spectra probably produced significant broadening of all of the lines of the spectra. In addition, we assumed that it was unnecessary to spin samples which give lines as broad as these. Both of these factors may have contributed to the observed line widths, which were about 90 Hz for the diamagnetic protons and 700 Hz for ortho and 160 Hz for the meta or methyl lines due to the radicals.

Results

The proton sideband NMR spectra of I and its deuterated derivatives are shown in the upper halves of Figures 1-4. These

spectra are simplified by direct deconvolution^{13a} to give the contact-shifted NMR spectra in the lower parts of these figures. Direct measurement of line positions and widths in these deconvoluted spectra gives the data in the rows marked DECON in Table I. The alternate procedure involving least-squares fit of a calculated NMR sideband spectrum to the experimental convoluted spectrum gives the data in the lines marked CONFIT.^{13b} The availability of deuterium-labeled compounds affords an independent set of spectra in which the lines due to meta and to methyl protons can be identified unambiguously. Furthermore, these compounds can be used for deuterium pulse Fourier transform spectra (in Figure 5) which provide still another set of independent data; these afford a useful check of the validity of the results obtained from the little-used deconvolution method.

Figures 3 and 4 indicate qualitatively that the NMR peaks due to the meta and methyl protons overlap. The absence of structure in the combined peak in Figures 1 and 2 indicates that the overlap is quite precise, so that the assumption that $a_{\text{meta}} = a_{\text{methyl}}$ is at least approximately correct. Finally, the separations of the ortho and the meta/methyl peaks from the reference line positions in Figures 1 and 3 are close to the ratio 3:1, rather than the ratio 2:1 given in the earlier literature.^{3,4} All of these qualitative results are confirmed by the three deuterium spectra reproduced in Figure 5.

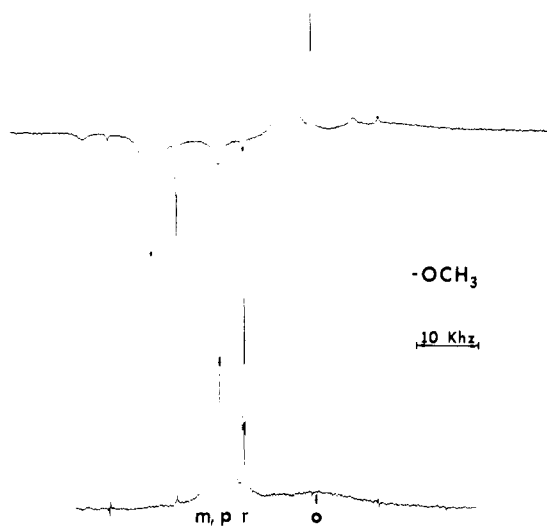


Figure 1. Experimental sideband spectrum (upper) and calculated deconvoluted proton NMR spectrum of tri-*p*-anisylaminium cation. The sideband spectrum is a phase-corrected linear combination of five scans.

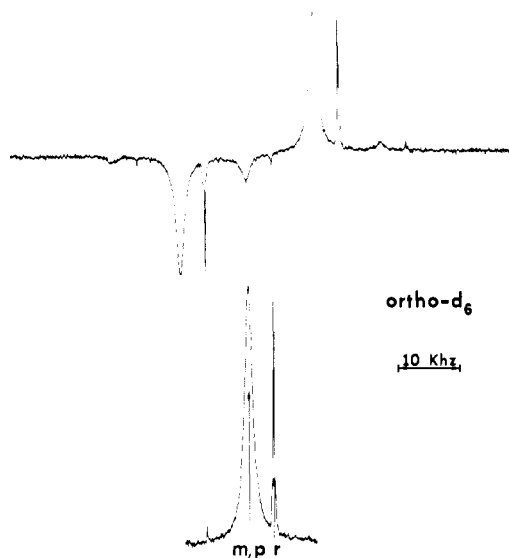


Figure 2. Experimental sideband and calculated deconvoluted proton NMR spectra of tri-*p*-anisylaminium-2,6,2',6',2'',6''- d_6 cation. The single peak is due to both meta and methoxy protons. The sideband spectrum is a phase-corrected linear combination of three scans.

The quantitative results extracted from these spectra are in Table I. There we show data for each of the three sets of protons obtained from each of the spectra capable of yielding data for that set. All of the sideband spectra are analyzed by both the CONFIT and DECON procedures. Hyperfine coupling constants a_i in column 7 are calculated from the chemical shifts by the equation

$$a_i = (\Delta H_i/H_0)(\gamma_i/\gamma_c)(4kT/g_c\beta_c) \quad (1)$$

This reduces to:

$$a_i = 0.013328(\Delta H_i/H_0) \quad (2)$$

for protons, and

$$a_i = 0.002046(\Delta H_i/H_0) \quad (3)$$

for deuterons. In all of these equations, a_i is in gauss and the chemical shift ($\Delta H_i/H_0$) is in ppm relative to the NMR line

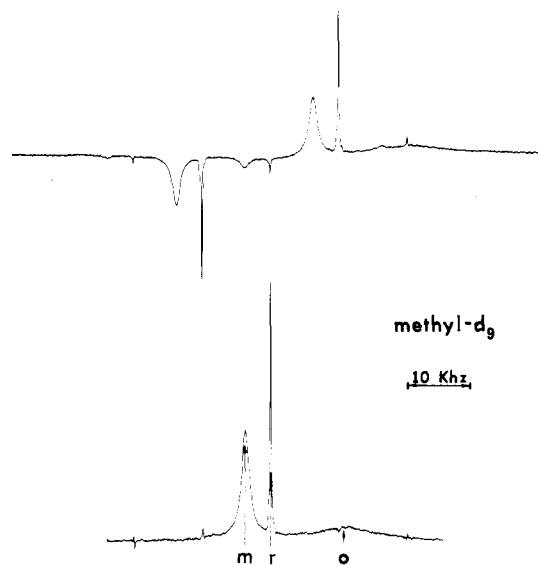


Figure 3. Experimental sideband and calculated deconvoluted proton NMR spectra of tri-*p*-anisylaminium-tri(methoxy-4,4',4''- d_3)triphenylamine cation. The sideband spectrum is a phase-corrected linear combination of five scans. The downfield peak is now due only to meta protons.

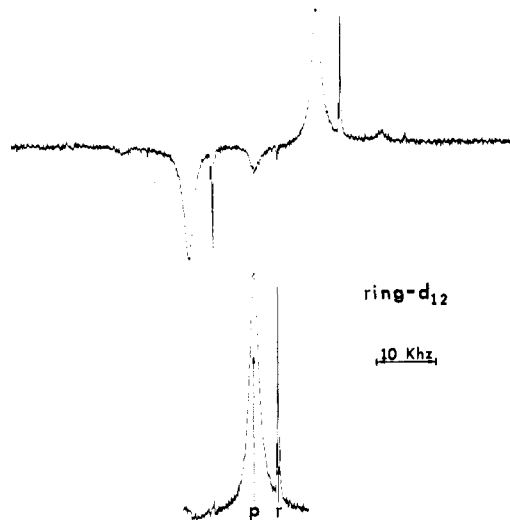


Figure 4. Experimental sideband and calculated deconvoluted proton NMR spectra of tri-*p*-anisylaminium-2,3,5,6,2',3',5',6',2'',3'',5'',6''- d_{12} cation. The sideband spectrum is a phase-corrected linear combination of three scans. The downfield peak is now due only to methoxy protons.

for the corresponding proton in the free amine. Error ranges in the table are calculated to \pm one standard deviation.

Average values for the hyperfine coupling constants, calculated from the (more precise) CONFIT data only, are: ortho = -1.72 ± 0.10 , meta = $+0.62 \pm 0.12$, and methyl = $+0.65 \pm 0.02$ G. The data (in parentheses) on coupling constants from deuterium contact shifts are excluded from these averages. Since the same observed NMR line position is used for both of the latter protons, the difference between a_{meta} and a_{methyl} is entirely due to the difference in positions of the reference NMR lines measured for the corresponding protons of the free amine in trifluoroacetic acid- d : ortho = 7.36, meta = 7.17, and methyl = 3.92 ppm. Problems associated with the determination of this parameter for this easily oxidized amine have already been considered.¹²

The coupling constants in Table I generated from the proton and the deuteron spectra differ slightly. It is possible that this difference is due to changes in spin distribution in the radical

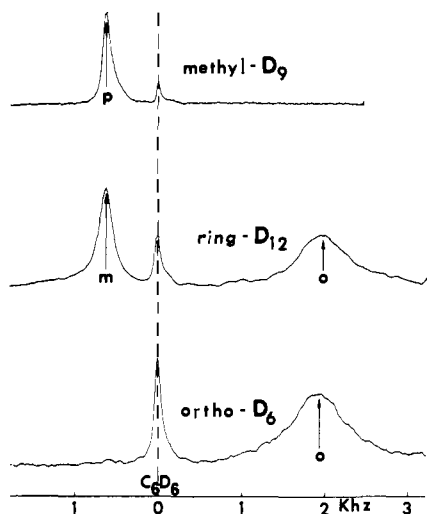


Figure 5. Deuterium pulse Fourier transform spectra of three labeled tri-*p*-anisylaminium cations. All lines are broadened by lack of field lock and possibly by absence of spin. Widths of reference peaks (under dashed line) ca. 90 Hz.

as a result of deuterium substitution, of the type reported by Lawler et al. for the naphthalene negative ion.¹⁴ This is difficult to check with results of our precision, particularly since the extent of deuterium substitution, and with it the possible effect on spin distribution, varies in compounds II, III, and IV.

The *R* values^{13a,15} listed in column 8 in Table I afford an indication of the goodness of fit of the calculated to the sideband spectra. All of these values are within an acceptable range.

The line widths recorded in column 9 are obtained in a straightforward way from CONFIT and DECON spectra. Values in parentheses were obtained from the deuterium spectra by multiplication of the observed deuterium line widths by the factor $(\gamma_u/\gamma_D)^2 = 42.3$. All of the values so calculated are 2.5 to 4.0 times larger than those obtained directly from the proton sideband spectra. We attribute this additional broadening of the deuterium spectra to the measurement conditions already discussed plus the operation of an additional mechanism for fast relaxation in the deuterium spectra through coupling with the deuterium quadrupole moment. As before,¹² the line widths can be used to calculate a rough upper limit for the second-order Heisenberg spin exchange rate constant for these radicals; in this case the result, based only upon the (narrower) proton line widths, is 4.9×10^9 L/mol s.

The coupling constants reported above for trianisylaminium ion check reasonably well with the corresponding data for the meta and methylene positions in the tris (*p*-ethoxyphenyl)aminium ion,¹² for which we expect very much the same

spin distribution. Data for the ortho positions are quite different, but the ortho peak in the anisyl spectra is much better resolved than it is in the spectra for the ethoxy analogue. We believe that the results reported here are correct and that it is likely that the ortho coupling constant obtained from the very low amplitude peak in the proton sideband spectra for the ethoxy compound is incorrect.

We turn now to the question of deviations of our coupling constants from exact integral multiples. In our ESR spectra of the radical from I, we have never been able to resolve significantly more lines than are shown in the published spectrum.³ These lines are not sharp; line widths exceed 0.20–0.25 G in this spectrum. This is at least five times wider than the lines in our best spectra of triarylammonium ions with other substituents. A stick spectrum simulated with the average values of the coupling constants in Table I shows groups of closely spaced lines at the positions of the single lines observed in the experimental ESR spectrum. If the coupling constant ratios were precisely equal to integers, sharp lines would be expected at the same positions. We conclude that the broad lines in the experimental ESR spectrum are due to groups of closely spaced lines which cannot be resolved with our spectrometer and that small deviations from integral ratios must exist to account for the ESR line widths observed.

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