Electron Spin Resonance Characterization of Ground State Triplet Aryl Cations Substituted at the 4 Position by Dialkylamino Groups

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Abstract: UV irradiation at 77 K of arenediazonium salts substituted at the 4 position by dialkylamino groups yields ESR spectra comprised of three principal, broad peaks at ca. 800, 1500, and 4400 G, together with a resonance at $g \sim 2.0$. The low- and high-field absorptions are assigned to the aryl cation, Ar^+, which appears to be stabilized in its triplet configuration by the $-NR_2$ group in accordance with recent ab initio calculations. The D parameter for these unusual triplet states is ca. 0.24 cm^{-1}, indicating a high π spin density on C_1. The triplet states were produced from powders and solutions in both polymer films and a 9 M LiCl aqueous glass, and constitute irrefutable evidence for the existence of these carbonium ions.

The aryl cation Ar^+ has long been regarded[2a] as the probable key intermediate in both the thermal[2a] and photochemical[2b] decomposition of arenediazonium salts in aqueous solution:

$$ArN_2^+ \xrightarrow{\Delta \text{ or } h\nu} Ar^+ + N_2 \qquad (1)$$

While there have been suggestions (summarized in Zollinger's review[2c]) that the departure of N_2 may coincide with arrival of a water molecule or other nucleophile,[3] this view has been strongly contested.[2c,4] The extremely high reactivity of the supposed Ar^+ is implied both by its lack of selectivity toward nucleophiles[3b] and its apparent ability to reverse reaction 1 as evinced both by scrambling of $^{15}N-^{14}N$ in partially decomposed $ArN_2^+X^-$ and by incorporation of N_2 when dediazoniation is carried out under high pressures of nitrogen.[5] The recent intensified interest in Ar^+ has focused upon (1) its detection and role as an intermediate in gas-phase studies involving mass spectrometry,[6a] ion cyclotron resonance,[6b] and crossed molecular beams,[6c] and (2) theoretical approaches to its structure, dimensions, and spin multiplicity.[7,8] In the latter context, Taft's early proposal[9] (modified by Abramovitch[10]) that Ar^+ is a triplet ground state, based on anomalously large accelerating effects of substituent groups such as m-OMe on the thermal decomposition of ArN_2^+ (an argument since criticized[4a]), has been developed by several groups using semiempirical methods[4b,7] and most recently by ab initio calculations of Pople et al.[8] The latter approach suggests that of the two alternative electronic configurations for Ar^+, the "Taft configuration" $(\pi)^5 (sp^2)^1$ is especially stabilized[8c] by a p-NH_2 group; otherwise the $(\pi)^6 (sp^2)^0$ configuration, albeit highly distorted with $\angle C_6C_1C_2 \sim 145°$, is the more stable form by a considerable margin (e.g., 20.1 kcal mol^{-1} for $C_6H_5^+$ itself).[8b] Other "triplet-stabilizing" influences are substitution at the ortho positions (by NH_2 or OH) and at the para position by OH (although only the latter feature gave per se a resultant triplet ground state apart from p-NH_2, and then only as a small difference between two large figures). Another group[11] has argued that the greater selectivity of p-$O_2NC_6H_4^+$ toward attack on arenes (compared with $C_6H_5^+$) is best understood in terms of both species existing as triplets, with the NO_2 substituent exercising additional stabilization of the triplet level.

In this paper we report definitive characterization of the triplet character of p-$R_2NC_6H_4^+$ for a variety of p-NR_2 groups by means of ESR spectroscopic identification of the expected transitions, enabling estimation of the D and E parameters and hence some conclusions about the spin density distribution. This has been accomplished under the following experimental conditions: crystalline powders, solutions in a transparent polymer film, solutions in an aqueous (9 M LiCl) glass, and in a single crystal. Apart from our preliminary note,[12] the only previous claim[13] to have identified Ar^+ was based on optically detected transient absorptions in the microsecond flash photolysis of aqueous solutions of ArN_2^+; we have been unable to reproduce these results using laser flash photolysis (λ_{excit} 347 nm).

Experimental Section

ESR measurements were performed at or near 77 K using X-band instrumentation. (The spectra in Figures 1 and 2 were recorded with a Bruker Spectrospin Model ER-200tt). The solutions in polymer film were made by drawing out across a glass plate a viscous acetone solution of cellulose acetate containing the requisite quantity of arenediazonium salt by means of a glass rod. This procedure gave films of high optical quality and having a reproducible thickness of ca. 0.02 mm on evaporation of the solvent. Irradiations were carried out using a focused 200-W high-pressure point-source Hg lamp. Certain of the arenediazonium salts investigated are marketed by Ozalid (U.K.) Ltd., Loughton, Essex, and we acknowledge gifts of assayed samples. Other salts were synthesized and purified by standard procedures (normally as the fluoroborates), and their purity was checked both by UV-visible spectrophotometry and by nitrometer analysis of released N_2. Single crystals (as 3 × 1 mm prisms) of 4-morpholinobenzenediazonium tetrafluoroborate were grown by allowing a saturated ethanolic solution containing a small percentage of acetone partly to evaporate overnight at room temperature.

Results and Discussion

As indicated in our preliminary note,[12] photolysis of solutions in polymer films of a number of arenediazonium salts at 77 K yielded strong resonances at four field positions (Figure 1a and Table I), i.e. (very approximately), 900 (peak A), 1500 (peak B), 3300 (peak R), and 4400 G (peak C). Warming samples to 120 K resulted in a gradual decay of the peaks A, B, and C, leaving R relatively unaffected. Photolysis of 2,5-di-n-butoxy-4-morpholinobenzenediazonium tetrafluoroborate in a frozen 9 M LiCl-H_2O glass at 77 K led to production of A, B, and C but practically no R peak (Figure 2). We conclude that R is due to a normal organic radical (i.e., with $g \sim 2.0$), probable the aryl radical formed in the reaction

$$ArN_2^+X^- \xrightarrow{h\nu} Ar\cdot + N_2 + X^\cdot \qquad (2)$$

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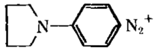
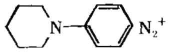
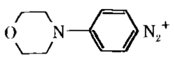
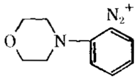
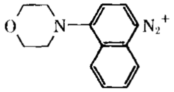
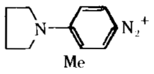
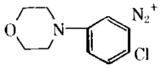
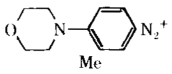
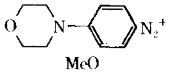
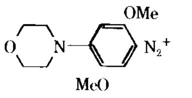
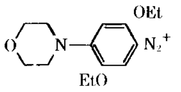
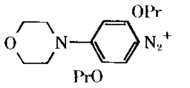
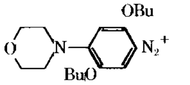
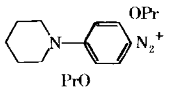
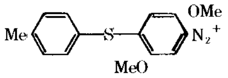
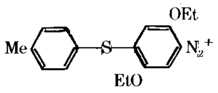
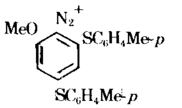
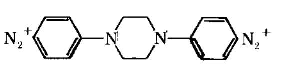
Table I. Field Positions of First Three Resonances in the Triplet ESR Spectrum of Substituted Phenyl Cations

arenediazonium cation	anion	matrix	field positions of peaks[a]			H_0[b]
			A	B	C	
		A. Monosubstituted $ArN_2^+X^-$ Salts				
$4\text{-}Me_2NC_6H_4N_2^+$	BF_4^-	CA[c]		no resonance		3265
$4\text{-}(n\text{-}Bu)_2NC_6H_4N_2^+$	BF_4^-	CA	1000	1660	*d*	3272
$4\text{-}(PhCH_2)_2NC_6H_4N_2^+$	BF_4^-	CA		no resonance		3266
	BF_4^-	CA	647	1287	4667	3270
	BF_4^-	CA	663 ± 25	1328 ± 36	4618 ± 3	3269
	BF_4^-	CA	680 ± 11	1267 ± 45	4600 ± 5	3264
		Epikote	916	1662	4478	
		MeOH		no resonance		3263
		CD_3OD		no resonance		3264
		SiO_2		no resonance		3263
	BF_4^-	CA		no resonance		
	BF_4^-	CA	550	1200	4325	3259
		B. $ArN_2^+X^-$ Salts Bearing Two Substituents				
	BF_4^-	CA	1010	1775	4625	
	BF_4^-	CA		no resonance		
	BF_4^-	CA	940	1675	4250	
	BF_4^-	CA	1110	1870	4200	

The small [R·] found in the aqueous glasses accords with the view that in media promoting separation of ArN_2^+ and X^-, only heterolysis is significant, while homolysis becomes important under poorly solvating conditions as in polymer films, organic glasses (in which we rarely found the A, B, C peaks; see Table I), and in powders (Figure 1b). The fairly constant intensity ratio of A, B, and C in different media (compare Figures 1a and 1b and Figure 2) and in warming experiments indicates that they are due to a single species. The field positions indicate a spin system other than $S = 1/2$, and we propose that the three resonances are the first three of the four components expected of an isotropic $S = 1$ (or triplet state) expected of a phenyl cation, $(\pi)^5$ (sp^2).[1] Our assignment of the individual resonances follows Wasserman et al.[14] and is set out in Figure 2, which also depicts our search at $H > 5$ kG for the expected very weak fourth transition, which is just apparent at 5870 G. Our assignment is summarized in Table II. The weak absorption of Figure 2 denoted dq was considerably en-

Table I (*Continued*)

arenediazonium cation	anion	matrix	field positions of peaks[a] A	B	C	H_0[b]
			C. $ArN_2^+X^-$ Salts Bearing Three Substituents			
	BF_4^-	CA	851		4497	3265
	BF_4^-	CA	875	1594	4461	3265
		SiO_2	789	1480	4538	
		t-BuOH		no resonance		3263
		$PhCH_2OH$	851	1588	4508	
		$PhCH_2CH_2OH$	856	1598	4491	
	PF_6^-	CA	930	1545	4428	3264
		MTHF[e]		no resonance		3263
		polystyrene[f]	881		444	
	0.5 $ZnCl_4^{2-}$	CA[f]	808		4482	3265
	CNS^-	CA		no resonance		3263
	BF_4^-	CA	880 ± 110	1651	4387 ± 100	3265
	BF_4^-	CA	928 ± 25	1630 ± 10	4372 ± 100	3265
		MF[g]	804	1460	4259	3262
	BF_4^-	CA	879	1581	4360	3269
	BF_4^-	CA		no resonance		3263
	0.5 $ZnCl_4^{2-}$	CA		no resonance		3264
	BF_4^-	CA		no resonance		3263
	0.5 $ZnCl_4^{2-}$	CA		no resonance		3262
	PF_6^-	CA		no resonance		3262
	BF_4^-	CA		no resonance		3253
			D. Bisdiazonium Salt			
	$2BF_4^-$	CA		weak singlet 1650 G		3305

[a] Recording of these as follows: peak A at crossover, B at upward peak, C at downward peak (all data in G). [b] Field position of Ar$^\cdot$, i.e., approximate free spin value (a nil entry means no measurement was made). [c] CA = cellulose acetate. [d] Peak too weak for accurate determination. [e] MTHF = 2-methyltetrahydrofuran. [f] Weak resonances. [g] MF = Melanex film, i.e., basically a cellulose propionate.

hanced relative to A, B, and C when the attenuation was reduced from 10 to 3 dB, in conformity with an assignment to the double quantum transition, the intensity of which depends on the square of the microwave power intensity.

From our assignments, it was possible to evaluate the characteristic triplet state parameters: the lack of splitting of any of the components enables an upper limit of 30 G to be placed on E'. The positions of the z components relative to the H_0 position (3342 G in Figure 2) yield two values for D', i.e., 2537 and 2533 G, while the two field values for H_{xy} give, following Wasserman's equations,[14] $D' = 2500$ G. A further value for D' of 2360 G can be extracted from the relative positions of the double quantum transition at 3050 G and H_0. Of these various figures, which are in fair agreement considering the line widths (thereby supporting our overall assignment), those deriving from the values of H_z are considered the most reliable; these yield $D = 0.237$ cm^{-1}. The single crystal data, while wholly consistent with our analysis, were disappointing in that,

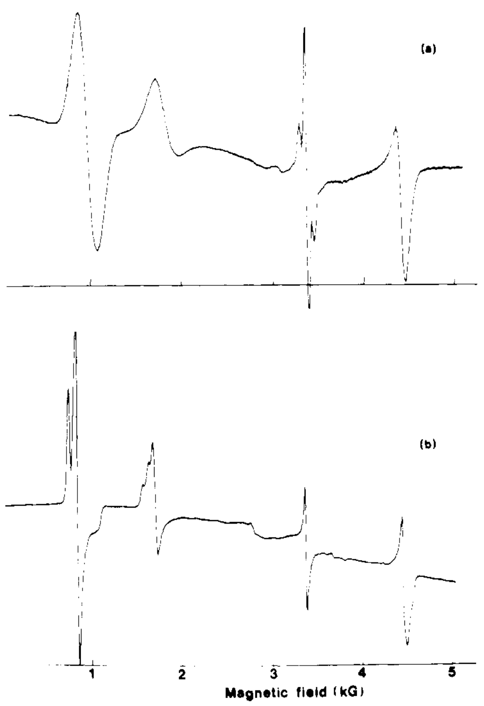
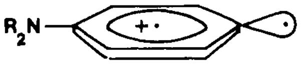


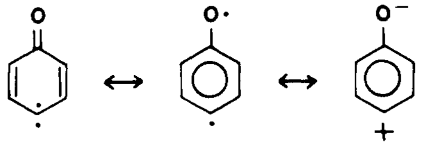
Figure 1. Triplet ESR spectra of Ar^+ produced in the photolysis ($\lambda > 300$ nm) of 2,5-di-*n*-butoxy-4-morpholinobenzenediazonium tetrafluoroborate at 77 K: (a) in (shredded) cellulose acetate film; (b) as powdered crystalline salt.

while the field positions of the resonances changed with crystal orientation as expected, the high-field lines were often very weak, preventing a full analysis.

The value for D, which provides the first unequivocal spectroscopic parameter relating to a phenyl cation, implies a spin separation of 2.8 Å in a simple point dipole model. A model, based on I (i.e., a $(\pi)^5\ (sp^2)^1$ configuration), featuring one electron localized in a sp^2 hybrid orbital and the other present in the π system, recalls that utilized by Wasserman et al.[15] for species II: the latter yielded $D = 0.3179$ and $E = 0.0055\ cm^{-1}$, the D value being taken to indicate $\rho(C_1) \sim 0.4$, cf. a phenoxyl radical, implying that for I $\rho(C_1) \sim (0.237/0.318) \times 0.4 \simeq 0.3$. The value for E in I is even less than the low figure recorded for II, implying a degree of cancellation of the effect of spin density at C_1 by those at C_2 and C_6. Pople's calculations[8b] on the $^3B_1$ state of $C_6H_5^+$ place a large spin density ca. +0.5 on C_1, with sizable values on C_2 and C_6, in tolerable agreement with our picture.



I



II

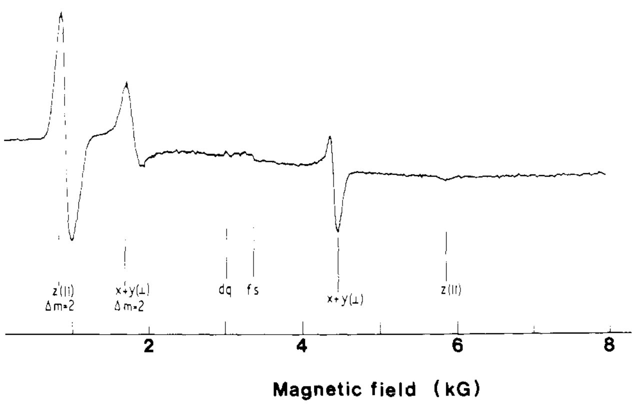


Figure 2. Extended field ESR spectrum of Ar^+ produced in the photolysis ($\lambda > 300$ nm) of 2,5-di-*n*-butoxy-4-morpholinobenzenediazonium tetrafluoroborate at 77 K in a (glassy) medium of 10% acetone–90% aqueous (9 M) LiCl.

Table II. Summary of Assignments in ESR Spectrum (Figure 2)

line position, G	assign-ment	comments
805 5870	H_z	parallel features: 5870-G line extremely weak and broadened as expected; low field component combined with $\Delta m = 2$ transition
1700 4467	H_{x+y}	perpendicular features; low field component combined with $\Delta m = 2$ transition
3050	dq	intensity increased by increase of microwave power
3342	Ar·	taken as free spin value for calculation

Thus far, we have been unable to detect triplet resonance with any aryl cation other than one bearing a 4-amino substituent; even 2-morpholino or 4-methoxy substitution is ineffective, indicating the problems of theoretical prediction of small stabilizing effects on two energy levels of large and similar magnitudes; we have, however, wholly confirmed Pople's view[8c] of the special stabilization of the triplet phenyl cation by a 4-amino group, but are as yet unable to support his prediction of the much smaller net triplet-stabilizing effect of a 4-hydroxy substituent. The principal significance of our study is the confirmation of at least one variety of aryl cation as a true, isolable intermediate in the condensed phase, particularly in an aqueous glass.

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An Electron Spin Resonance Study of the Association of a Surfactant Nitroxyl Radical with a Cationic Micelle Using Spin-Intensity Measurements and Hyperfine Structure Analyses

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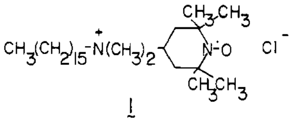
Abstract: The association constant, $K = (3.2 \pm 0.2) \times 10^5\ M^{-1}$, for incorporation of 4-[*N,N*-dimethyl-*N*-(*n*-hexadecyl)ammonium]-2,2,6,6-tetramethylpiperidinyl-*N*-oxy chloride (**1**) into the hexadecyltrimethylammonium chloride micelle was determined from analyses of composite spectra made up of free **1** and singly bound **1** and spin-intensity measurements. The hyperfine structure observed in the ESR spectrum of free **1** in water is lost upon binding with the micelle. The severe line broadening (5–10 G) in the spectrum of **1** located in multiply occupied micelles leads to apparent intensity loss in peak to peak measurements of the unbroadened 1.7-G middle-field line of **1** from both free and singly bound **1**. The data are analyzed in terms of a multiple-step equilibrium model for the incorporation of **1,** which provides a critical micelle concentration of 4×10^{-3} M and a number-average aggregation number of 59 ± 7 for the hexadecyltrimethylammonium chloride micelle.

Introduction

Nitroxyl radicals have been widely used for a number of years for studying the properties and reactivities of assemblies such as bilayers and micelles.[1] We describe an ESR method, based on the measurements of both signal intensity and change in hyperfine structure, for studying the association of surfactant nitroxyl radicals with micelles.

Most previous studies that qualitatively[2] and quantitatively[3] studied the association of nitroxyl radicals with micelles were based on the difference in field position observed for the high-field line of the bound and free nitroxyl radicals. This approach is limited to cases where the resulting field shift, due to changes in g values and nitrogen splitting for the bound and free spin labels, is large enough to be distinguished.

Our approach, which does not have this limitation, provides the K for association of the nitroxyl radical with the micelle structure, as well as association information on the micelle itself (critical micelle concentration, i.e., CMC, and aggregation number). This methodology is demonstrated with the surfactant nitroxyl radical **1**/hexadecyltrimethylammonium chloride (more commonly called cetyltrimethylammonium chloride or "CTAC") system. Further, we analyzed the ESR data in terms of a multiple-step equilibrium model for incorporating the spin label into the micelle structure.[4]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Results and Discussion

4-[*N,N*-Dimethyl-*N*-(*n* - hexadecyl)ammonium] - 2,2,6,6-tetramethylpiperidinyl-*N*-oxy chloride (**1**) was prepared by conventional procedures as described in the Experimental Section.

In pure water at ~10^{-5} M, **1** shows the typical three-line nitrogen-splitting pattern ($a_N = 16.9$ G) of nitroxyl radicals. Degassed solutions reveal hydrogen hyperfine structure (~0.5 G)[5] which is particularly noticeable in the low- and middle-field lines. (Figure 1). Although these hyperfine structures were previously reported,[6] they have not been used for diagnostic purposes.

We find these structures to be sensitive to the microenvironment of **1**. Figure 2, series A, shows representative spectra of the middle-field line. The top spectrum was recorded in pure water, while the bottom spectrum was observed in the presence of 4.0×10^{-2} M CTAC. The latter is well above the CMC point of CTAC, generally estimated to be ~1.0×10^{-3} M.[7] We assume that the bottom spectrum in series A corresponds to **1** singly bound to the CTAC micelle.[8] The loss of the hydrogen hyperfine structure for singly bound **1** may be associated with a slower tumbling rate for **1** in the micelle environment.[2,9]

As pointed out by Oakes,[2a] above the CMC point the ESR spectrum of a nitroxyl radical usually is a superposition of two individual spectra weighted according to the respective concentrations of the aqueous and micellar states.[10] Indeed, a series of spectra in the range $5\text{–}7 \times 10^{-3}$ M CTAC could be computer simulated as a composite of the free (top) and bound (bottom) states of **1;** see Figure 2. Figure 2, series B, shows representative simulated spectra for two intermediate CTAC concentrations. Note that this matchup between the experimental and simulated spectra is based on the details in the hyperfine structure in addition to the slight differences in g and a_N values of nitroxyl radicals in aqueous and micellar environments as used by previous studies.[3] Further, our approach is not jeopardized by the superposition of a severely broadened ($\gtrsim 5$ G) spectrum of **1** in multiply occupied micelles which is described below.

Since the composite spectra could be simulated using the line width of **1** in pure water, we estimate the broadening of free

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