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Unusual features in the triplet state EPR spectrum of 3,5-dichloro-4-aminophenyl cation [1]

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Abstract

The triplet ground state of the 3,5-dichloro-aminophenyl cation ($^3Ar^+$), generated by photolysis at 77 K of the parent arenediazonium salt, exhibits the strongest dipolar interaction in its EPR spectrum ($D > 0.3$ cm^{-1}) found so far for any known aryl cation. It also shows high-energy site splitting, as detected by EPR for several other cations, producing two distinct forms (type A with $D = 0.3066$ cm^{-1} and type B with $D = 0.3410$ cm^{-1}). $^3Ar^+$ and certain other aryl cations also show electronic absorption spectra composed of two or three distinct bands.

Keywords: 3,5-Dichloro-4-aminophenyl cation; Triplet state EPR spectroscopy

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1. Introduction

The simplest aromatic cation, the aryl cation (Ar^+), can be observed spectroscopically only when its electronic ground state is triplet in character, $^3Ar^+(sp^2)^1(\pi)^5$, and the only unambiguous method of detection is low-temperature magnetic resonance, i.e. EPR and ENDOR [1–4]. Although postulated and subject to theoretical study, the singlet aryl cation $^1Ar^+$ [5,6] has never been observed directly, and certain experimental results suggest that it is not stabilized at 77 K [7], i.e. at the temperature which affords the generation and detection of over 35 amino-, alkoxy- and thio-substituted triplet aryl cations [1,2] (the unsubstituted phenyl cation is considered to exist as a singlet ground state species [5]). The electronic structures of $^1Ar^+$ and $^3Ar^+$ (trisubstituted) are depicted in Fig. 1.

In this paper, we describe two new species which exhibit very strong dipolar interaction, i.e. their D parameters are of an energy close to, or higher than, the microwave energy of an X-band EPR spectrometer. To interpret these results, we have recalled our previous discussions concerning several aryl cations [1,2], reappraising our former conclusions.

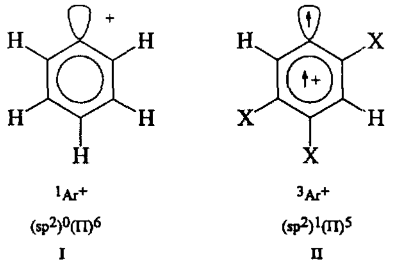

Fig. 1. Electronic configurations of the singlet $^1Ar^+$ (I) and triplet (triply substituted) $^3Ar^+$ (II) aryl cations. The real geometries of I [5] and II (see text) are far from perfectly hexagonal. X ≡ $-NH_2$, $-NR_2$, –OR or –SR.

2. Results and discussion

We have generated, by photolysis at 77 K of the parent arenediazonium salt, two distinct forms of the triplet aryl cation 3,5-dichloro-4-aminophenyl cation or $^3Ar^+$ (Figs. 2 and 3, Table 1) in a matrix of the parent microcrystalline diazonium salt. Both of the triplets feature a D parameter energy of over 0.3 cm^{-1}, the highest reported so far for substituted aryl cations [1,2]. One of the species, B, with a higher value of the zero field splitting (ZFS) parameters, exhibits an EPR spectrum without H_{min}, which is characteristic of the situation in which the value of the D parameter is close to the microwave energy. The other triplet, denoted A, having a slightly lower D value, allows H_{min} to be observed due to the non-linear pattern of energy levels found when the external magnetic field approaches zero.

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[1] Dedicated to Professor Fabian Gerson to mark his retirement after many years of fruitful activity in EPR spectroscopy.

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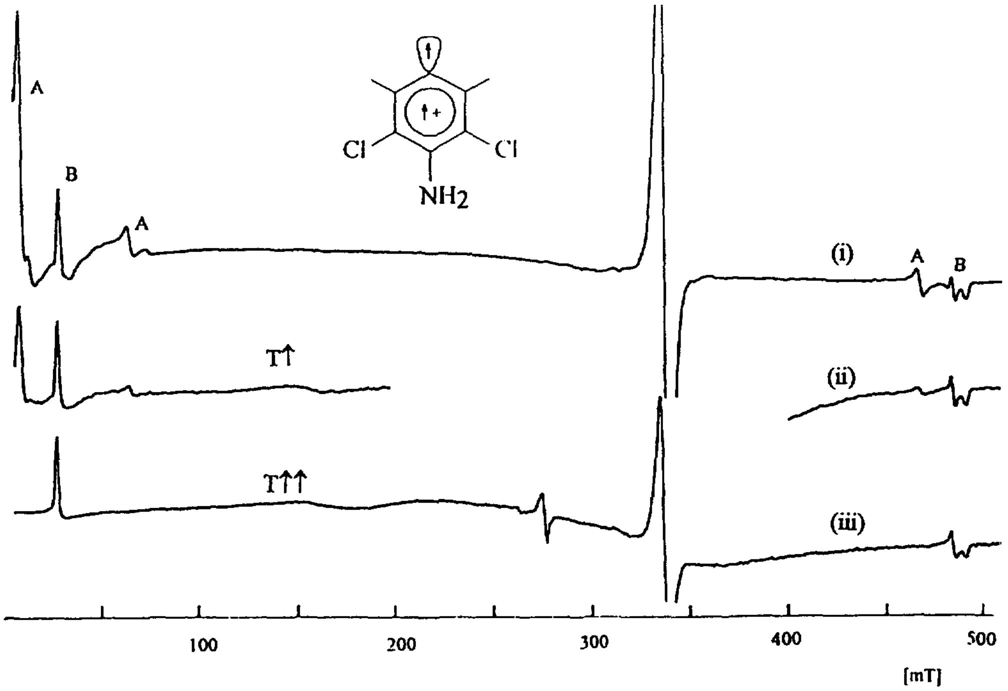

Fig. 2. Triplet EPR spectrum of the 3,5-dichloro-4-aminophenyl cation: species A and B. Line positions are given in Table 1. (i) Initial spectrum at 77 K. (ii) On warming and recooling to 77 K. (iii) On subsequent warming and recooling to 77 K.

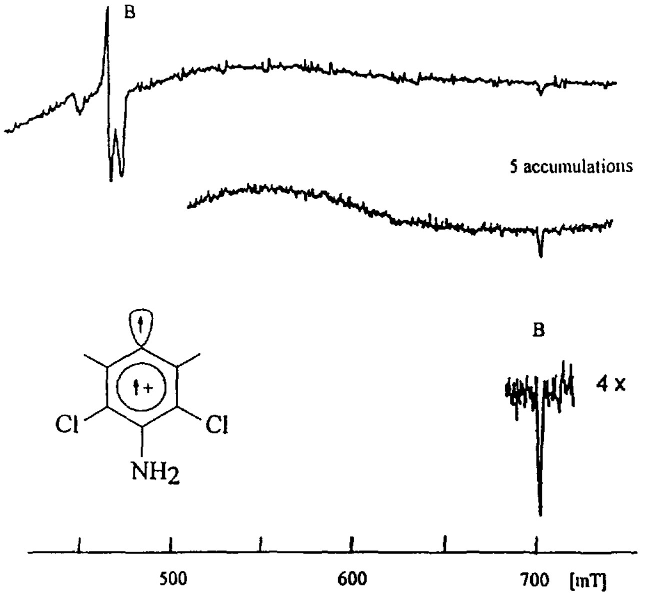

Fig. 3. As in Fig. 2(i). High-field part of the spectrum in which the H_{z2} absorption of B is shown (see Table 1).

The distinctive character of these results is as follows. The so-called "no H_{min}" spectrum of ^{3}Ar$^+$ has been recorded for the first time for an aryl cation. This suggests that species B exhibits the strongest electron–electron interaction found so far for these species, i.e. even stronger than that of the parent 4-aminophenyl cation (Table 2). An accurate comparison of the D values (B, Table 1; 4-NH$_2$C$_6$H$_4^+$, Table 2) is difficult because of the different matrices involved. We have found previously that the low-field transitions are strongly distorted in an LiCl glass, since the lines form an envelope of all the low-energy triplets possible in microcrystalline samples; accordingly, the lines in glasses are broad and cover the whole region of the resolved lines detected in Shpolskii sites in microcrystals. However, despite the matrix effect, the spectrum of 4-NH$_2$C$_6$H$_4^+$ indicates a weaker interaction, as the undistorted high-field peaks H_{x2} at 464 mT and H_{y2} at 478 mT appear at lower fields than in the spectrum of species B (483 and 489 mT respectively) (Table 1). The radical absorptions for these two species are very close to each other at 335 and 338 mT.

By contrast, results obtained under the same experimental conditions show that one chlorine substituent at the meta position of certain triplet aryl cations, e.g. 4-diethylaminophenyl and 4-morpholinophenyl cations, decreases the value of the D parameter (Table 2).

The chloro substituent is a strong π donor and a very strong σ electron acceptor, and both π and σ effects are important in stabilizing triplet aryl cations. Electron donor substituents always increase the spin density within the ring, thus stabilizing the cation; of these the best are π electron donors at the para$\sim$ortho$>$meta positions [6]. If one meta chlorine lowers the value of D via the overwhelming electron-withdrawing effect, then two meta chlorines should be even more influential in decreasing the spin density in the ring. As this is evidently not the case for ^{3}Ar$^+$, the reason must lie in the geometries of the two species (mono- and di-substituted 4-aminophenyl cations). The latter, having two bulky substituent chlorine atoms near the para amino group, must induce a geometrical distortion (bending) of the species, which promotes π electron interaction and reduces the effect of σ electrons. Obviously, a species like ^{3}Ar$^+$, having only five π

Table 1
Spectroscopic data of 3,5-dichloro-4-aminophenyl cation, species A (δ=9.4444 GHz) and B (δ=9.44492 GHz)

	A		B	
	Observed	Calculated [a]	Observed	Calculated [a]
H_{min} (mT)	10	–	–	–
H_{z1} (mT)	–	9.9	27.4	27.9
H_{y1} (mT)	–	–[b]	–	–
H_{x1} (mT)	65.9	64.7	–	–
H_{dq} (mT)	–	–	273.5	263.1[c]
H_{x2} (mT)	467.9	468.3	482.8	483.1
H_{y2} (mT)	478.8	479.0	489.2	489.7
H_{z2} (mT)	–	665.6	702.1	702.1
D (cm^{-1})	0.3066		0.3410	
E (cm^{-1})	0.0029		0.0019	

[a] Calculated using a spectrum simulation program TRIPLET EPR supplied by Andrew Ozarowski of the University of California at Davis, in which resonance fields are calculated using analytical formulae derived by Baranowski et al. [8].

[b] Slight undulation observed, but too broad to permit extraction of canonical line unambiguously.

[c] Calculated using D = 0.3410 cm^{-1} and the Wasserman formula.

Table 2
ZFS parameters of triplet state 4-aminophenyl and 3-chloro-4-aminophenyl cations

Substituent	Matrix			
	Microcrystalline powder		LiCl glass [a]	
	D (cm^{-1})	E (cm^{-1})	D (cm^{-1})	E (cm^{-1})
4-Amino			0.2967	0.0030
4-Diethylamino	0.2693	0.0038	0.2549	0.0024
3-Chloro-4-diethylamino	0.2325	0.0064		
4-Morpholino	0.2626	0.0043	0.2531	0.0022
3-Chloro-4-morpholino	0.2035	0[b]		

[a] Sample preparation given elsewhere [2].

[b] Below resolution.

electrons, may not completely parallel the behaviour on substitution of normal aromatic compounds. The geometry of the ^{3}Ar$^+$ species may not be strictly planar, and the possibility of various conformations of low-energy triplet aryl cations has been noted previously [9]. We believe that the difference in geometry of the species is the reason why we are able to observe up to four distinct triplets of different ZFS, which can be unambiguously identified by their different thermal stability and which reproduce their spectral parameters with high accuracy. However, this does not provide proof that, in a glassy matrix, the same set of triplet configurations is reproduced. We now believe that the glassy matrix can disperse energy levels, especially around zero field, which creates a further triplet species with less precisely determinable parameters.

The electronic absorption of ^{3}Ar$^+$ provides an additional source of information about triplet cations. We have observed composite absorption bands for several triplet aryl cations, which indicate the presence of more than one low-energy triplet as detected by EPR [7,10,11]. For example, the low-temperature optical spectrum of 3,5-dichloro-4-aminophenyl cation features at least two bands (Fig. 4). 2,4,5-Trimethoxyphenyl cation, having three or four (depending on sample preparation) low-energy triplets in a microcrystalline medium (Fig. 5), exhibits three distinct maxima in its optical absorption spectrum (Fig. 6). The resolution of two lines in the electronic spectrum of the 2,5-diethoxy-4-*n*-butylthiophenyl cation is reflected in the site splitting of its EPR tran-

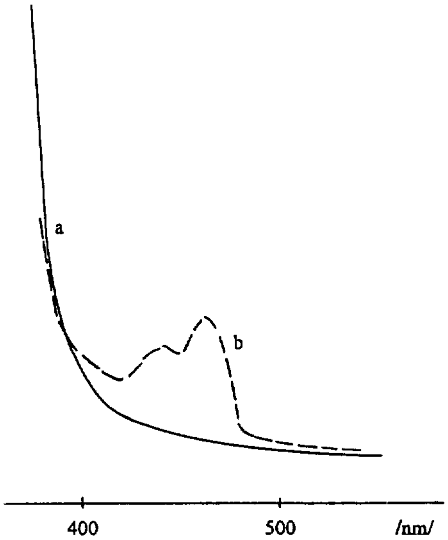

Fig. 4. Electronic spectra of 3,5-dichloro-4-aminobenzenediazonium salt (a) and aryl cation (b) (λ_{max}=445 nm and 463 nm).

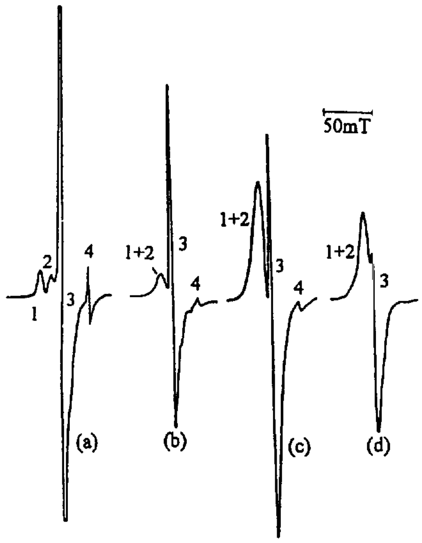

Fig. 5. Triplet EPR H_{min} transition of various samples of 2,4,5-trimethoxyphenyl cation (a, b). (c, d) Sample (b) on successive warming and recooling.

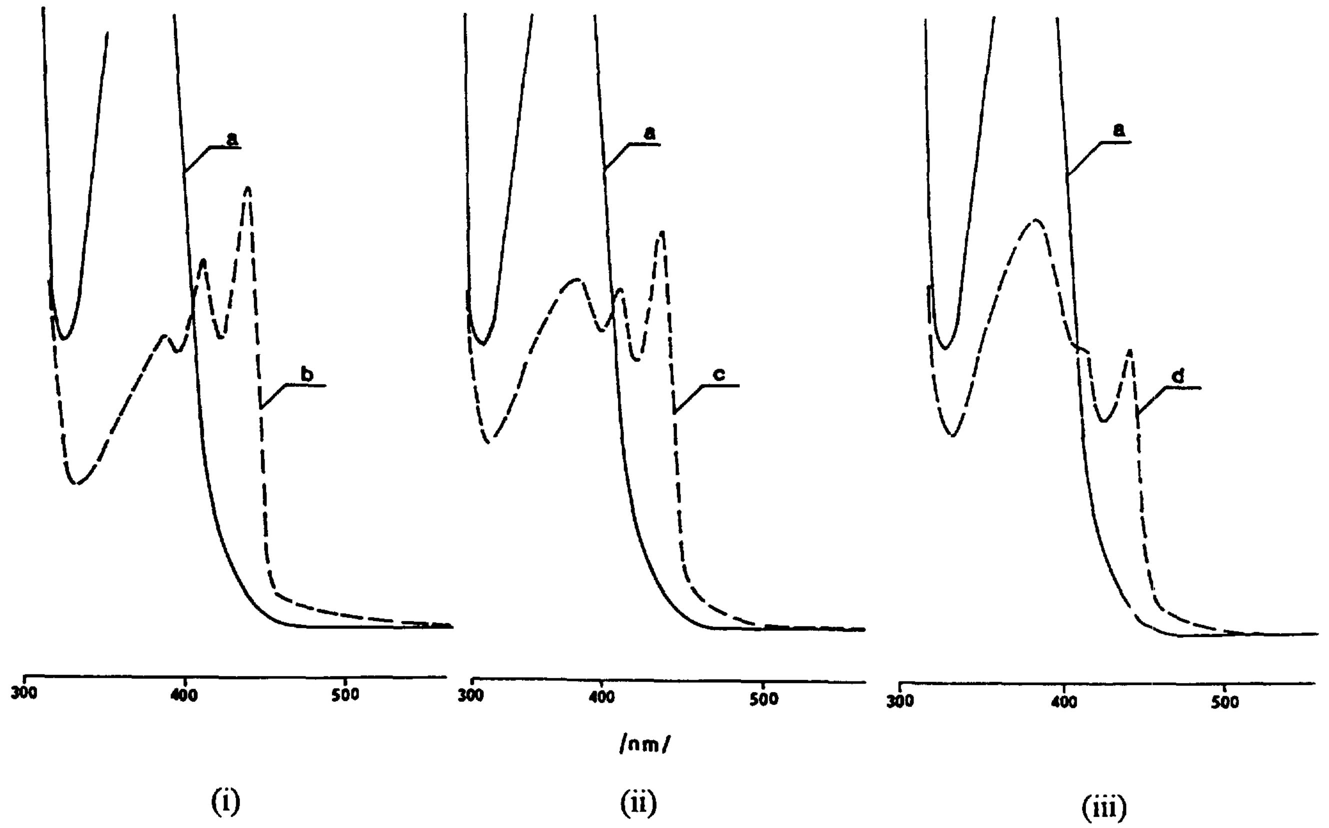

Fig. 6. Initial electronic spectra of: (i) 2,4,5-trimethoxybenzenediazonium cation (a) and 2,4,5-trimethoxyphenyl cation (b); (ii), (iii) double warming and recooling to 77 K (c,d).

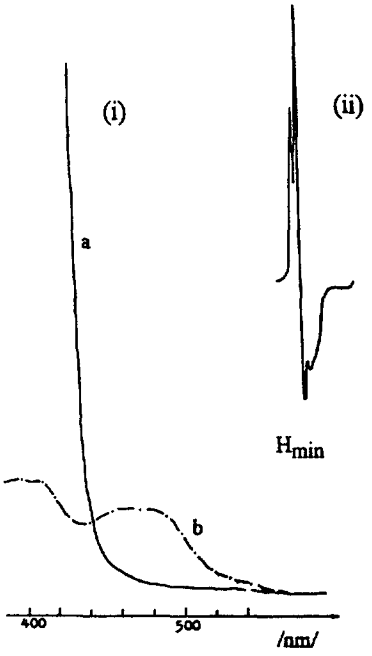

Fig. 7. Electronic spectrum (i) (b) and triplet EPR H_{min} line (ii) of 2,5-di-*n*-butoxy-4-morpholinophenyl cation. (a) Spectrum of parent diazonium salt.

sitions [7,9]. The two close-lying EPR triplets of 2,5-di-*n*-butoxy-4-morpholinophenyl cation probably correspond to the composite peak in the electronic absorption of this cation (Fig. 7) [9,11]. However, despite many experiments, we were unable to detect any differential thermal stability of particular absorption lines in the electronic spectra (Fig. 6: (i), (ii) and (iii)). Double warming–recooling experiments do not allow changes to be observed in the relative peak intensities (b, c, d) because of the growing absorption of the 2,4,5-trimethoxydiazonium cation. This contrasts strongly with the EPR experiments in which the intensities of particular transitions depend unambiguously on the temperature (Fig. 5). On the other hand, certain triplet cations, e.g. 4-diethylamino, 3-chloro-4-diethylamino and 3,5-dichloro-4-aminophenyl cations, featuring high-energy site splitting as detected by EPR, yield only a single optical absorption band. It is necessary to note that the EPR experiments cited above were performed in microcrystalline matrices of the parent diazonium salts, whereas optical measurements were undertaken in acidic glassy media. This may indicate that the optical transitions detected are not influenced by matrix effects or that they are not related to the different geometries of $^3Ar^+$. The assignment of the optical absorption lines to the triplet aryl cations is unambiguous [10]. Glassy matrices, which are softer than microcrystalline media, produce different triplet EPR transitions, especially at low magnetic field, than those generated in crystals, which are sharp multiplets.

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