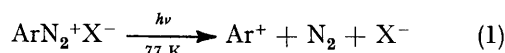


Triplet-state Electron Spin Resonance Studies of Aryl Cations. Part 3.¹ Substituent and Medium Effects for Aminophenyl Cations

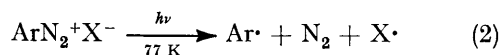
By Hanna B. Ambroz and Terence J. Kemp,* Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The presence of a strong medium effect on the observation of triplet-state Ar⁺ has been noted, enabling extension of our previous studies to further examples of triplet Ar⁺ including that of the parent molecule of the series, *p*-NH₂-C₆H₄⁺ which features a *D* parameter of 0.2967 cm⁻¹ and of the *o*-morpholinophenyl cation (*D* 0.1671 cm⁻¹) which is the first example of Ar⁺ stabilised in its triplet state by a single *ortho*-substituent. The trend, noted earlier, for a large *D* parameter to be associated with a good π-donor in the 4-position, is confirmed by new examples.

In previous parts^{1,2} we have shown that aryl cations suitably substituted with good π-donors exist as ground-state triplets which exhibit characteristic triplet-state e.s.r. resonance at 77 K. The *D* parameter of these species is quite large, covering the range *ca.* 0.102–0.283 cm⁻¹ depending on the position, number, and nature of the substituent groups. Despite the successful characterisation of *ca.* 20 of these novel species by reaction (1) certain examples failed to give triplet state



resonance although photodecomposition was known to have occurred from the accumulation of free radicals *via* the alternative photodecomposition (2). These failures



were attributable either to (i) complete dominance of (2) over (1) or (ii) Ar⁺ existing in the almost isoenergetic singlet state. In the present account we report that some materials failing to undergo reaction (1) under certain matrix conditions do so very effectively under different conditions, which implies that previous failure to observe Ar⁺ simply reflects a matrix-dependence of the contributions of pathways (1) and (2). Of particular interest is the characterisation of what may be regarded as the parent molecule of this series, namely *p*-aminophenyl cation. Measurements on the triplet resonance of several new aminophenyl cations, together with much improved spectra of materials examined earlier,² enable some trends to be discerned.

EXPERIMENTAL

Sample Preparation, Photolyses, and E.S.R. Measurements.—These have been described in earlier parts.^{1,2} LiCl glasses were made by mixing equal quantities of saturated aqueous LiCl with a saturated (or near-saturated) solution of the arenediazonium salt in acetone. Most photolyses were of two hours duration.

Triplet-state Parameters.—The usage of the terms *D**,³ *X*, *Y*, *Z*,^{4,5} *H*_{min},^{4,5} *H*_{dq},^{6,7} *H*_{x(1)}, *H*_{x(2)},⁷ *etc.* and *R*⁸ follows that of the literature.

Computer Simulation.—This was performed by Dr. J. Baranowski in the Department of Chemistry, University of Wrocław, Poland, by arrangement with Professor B. Jezowska-Trzebiatowska, and was based on 20 000 orientations. Details of the program have been published.⁹

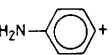
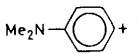
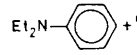
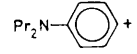
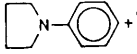
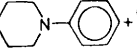
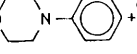
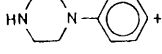
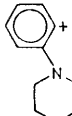
Materials.—Arenediazonium salts were prepared by Mr. P. Pinot de Moira, Ozalid (UK) Ltd., to whom we express our thanks. Further purification was carried out by precipitation methods as described before.^{1,2}

RESULTS

These are summarised in Table 1 for monosubstituted Ph⁺ and in Table 2 for disubstituted Ph⁺ and one naphthalene analogue. No entry for *D** (*Δm* = 1) is given in either Table because of the comparative minuteness of the *E* parameter, and no entry for *H*_{x(1)} is given because of its being obscured by the strong *H*_{min} feature (*e.g.* see Figure 1 of Part 2¹). The spectrum of the 'parent' of this series, namely 4-aminophenyl cation, is presented in the Figure, together with a computer simulation giving good agreement with both field positions and line shapes: previous attempts to generate this species in microcrystalline powder [which is very often the *best* medium for obtaining reasonable concentrations of Ar⁺ following the photolysis (1)] had failed, but irradiation in a LiCl glass proved successful. The spectrum differs from those we described in Part 2 in that the *H*_{x(1)} and *H*_{y(1)} features have merged into a single broad peak whereas *H*_{x(2)} and *H*_{y(2)} features remain distinct. The *H*_{z(2)} feature is very weak, but was quite reproducible. Resonance from *p*-Me₂NC₆H₄⁺ was also obtained in a LiCl glass, whereas a microcrystalline sample of the parent diazonium salt gave no triplet signal on irradiation. On several occasions^{1,2} we have made a painstaking search for triplet resonance from irradiated 2-morpholinobenzene-diazonium tetrafluoroborate without avail, but prolonged photolysis of a solution in LiCl glass yielded small but definite peaks of unmistakably characteristic pattern for a triplet state. The prediction of Pople *et al.*¹⁰ that a 2-amino-group should stabilise the triplet state sufficiently to render it of lower energy than the corresponding singlet is therefore vindicated. 3-Trifluoromethyl-4-morpholinophenyl cation could also be prepared in a LiCl glass in contrast to a microcrystalline powder.

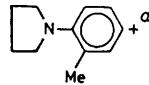
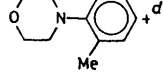
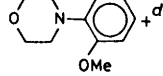
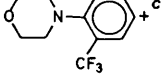
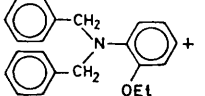
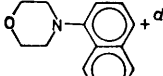
The double quantum transition *H*_{dq} was apparent in many of the spectra to low field of *H*₀ (Table 1), and was identified from the sharp dependence of its relative intensity upon microwave power level. The assignment is confirmed by calculation of *D** from the field position of *H*_{dq},^{6,7} which is in good agreement with values of *D** calculated from *H*_{min}.³⁻⁵ and the *Δm* = 1 transitions³⁻⁷ (see Table 1), except in the notable case of *p*-aminophenyl cation where there is a large discrepancy which we cannot explain: thus *D** calculated from *H*_{dq} is 0.136 8 cm⁻¹ whilst that from *H*_{min} is 0.272 0 cm⁻¹.

TABLE 1
Triplet state parameters and field positions for monosubstituted aryl cations and radicals

Compound	$\Delta m = 2$		$\Delta m = 1$								ZFS parameters/cm ⁻¹			<i>R</i> /Å
	$H_{\min.}/$ mT	$D^*/$ cm ⁻¹	Field position/mT					H_0	X, Y, Z^b	D^b	$-E^b$			
			$H_{xy(1)}$	$H_{x(2)}$	$H_{y(2)}$	$H_{z(2)}$	H_{dq}							
	19.48	0.2720	87.31 ^a	464.5	478.2	660.1	327.5	338.0	$X = 0.095\ 93$ $Y = 0.101\ 85$ $Z = 0.1978$	0.2967	0.0030	2.062		
	71.55	0.2485	153.4	449.1	458.9	612.1	301.6	339.9	$X = 0.082\ 03$ $Y = 0.086\ 09$ $Z = 0.1681$	0.2522	0.0020	2.176		
	68.43	0.2506	151.7	449.9	461.1	617.4	298.4	337.9	$X = 0.082\ 59$ $Y = 0.087\ 32$ $Z = 0.016\ 99$	0.2549	0.0024	2.169		
	70.64	0.2493	153.9	447.7	460.2	615.2	300.1	338.0	$X = 0.081\ 30$ $Y = 0.086\ 54$ $Z = 0.1678$	0.2518	0.0026	2.177		
	71.62	0.2485	155.1	448.9	459.2	614.0	300.1	338.2	$X = 0.081\ 67$ $Y = 0.085\ 97$ $Z = 0.1676$	0.2515	0.0021	2.178		
	74.47	0.2463	160.0	448.5	456.5	606.8	301.6	338.5	$X = 0.080\ 73$ $Y = 0.084\ 13$ $Z = 0.1649$	0.2474	0.0017	2.190		
	68.74	0.2506	153.5	449.6	460.1	615.9	299.7	338.6	$X = 0.082\ 18$ $Y = 0.086\ 56$ $Z = 0.1687$	0.2531	0.0022	2.174		
	69.43	0.2502	151.7	452.3	461.4	613.7		338.0	$X = 0.083\ 54$ $Y = 0.087\ 33$ $Z = 0.1709$	0.2563	0.0019	2.165		
	135.0	0.1615	233.4		417.6 ^a			335.1	$X = 0.055\ 69$ $Y = 0.055\ 69$ $Z = 0.1114$	0.1671	0	2.496		

^a A single entry implies overlapping of the *x* and *y* peaks. ^b Signs are relative. ^c In Part 1² it was found that no triplet resonance occurs in microcrystalline powder. ^d Parameters for microcrystalline powder are given in Part 2.¹ ^e Noted in Part 1² as a triplet, but without zero-field splitting parameters.

TABLE 2
Triplet-state parameters and field positions for disubstituted aryl cations and radicals

	$\Delta m = 2$		$\Delta m = 1$										$R/\text{\AA}$	
	$H_{\min.}/$ mT	$D^*/$ cm^{-1}	Field positions/mT					ZFS parameters/ cm^{-1}						
			$H_{xy(1)}$	$H_{x(2)}$	$H_{y(2)}$	$H_{z(2)}$	H_{drl}	H_0	X, Y, Z^b	D^b	$-E^b$			
	81.27	0.2376	165.9 ^a		443.1 ^a	594.8	301.7	335.1			$X = 0.078\ 41$ $Y = 0.078\ 41$ $Z = 0.1568$	0.2352	0	2.228
	99.00	0.2914	183.7		440.0	576.5		335.5			$X = 0.074\ 23$ $Y = 0.074\ 23$ $Z = 0.1485$	0.2227	0	2.268
	115.7	0.1967	204.4		430.3	549.2	312.3	335.0			$X = 0.066\ 62$ $Y = 0.066\ 62$ $Z = 0.1332$	0.1998	0	2.352
	108.8	0.2068	198.1		432.7	557.5		335.3			$X = 0.068\ 74$ $Y = 0.068\ 74$ $Z = 0.1375$	0.2062	0	2.327
	113.3	0.2004	202.0		432.7	552.2	311.4	335.1			$X = 0.068\ 00$ $Y = 0.068\ 00$ $Z = 0.1360$	0.2040	0	2.336
	66.20	0.2476	149.8	442.2	463.1	616.9	295.8	335.0			$X = 0.080\ 98$ $Y = 0.089\ 81$ $Z = 0.1708$	0.2562	0.0044	2.165

^a A single entry implies overlapping of the *x* and *y* peaks. ^b Signs are relative. ^c In Part 1² it was found that no triplet resonance occurs in microcrystalline powder. ^d Noted in Part 1² as a triplet, but without zero-field splitting parameters.

DISCUSSION

Medium Effects.—One feature emerging from a comparison of the present results with those of Parts 1 and 2 is the importance of the medium in achieving the appearance of triplet Ar^+ on photolysis of $\text{ArN}_2^+\text{BF}_4^-$. Use of a LiCl glass has enabled the successful charac-

are preferentially formed in a powder simply because of the concentration effect; this consideration is less significant when Ar^+ can react with neighbouring diazonium cations.

Magnitude of the D Parameter.—The D parameter for $p\text{-H}_2\text{NC}_6\text{H}_4^+$ of $0.296\ 7\ \text{cm}^{-1}$ is the largest we have found in the Ar^+ series, being considerably larger (by *ca.*



(a) E.s.r. spectrum of $p\text{-NH}_2\text{C}_6\text{H}_4^+$ in LiCl glass at 77 K. H_0 , radical absorption of $p\text{-NH}_2\text{C}_6\text{H}_4^+$; inserts A, B, regions of H_{dq} and $H_{z(2)}$ absorption; Q, quartz signal. (b) Computer simulation of (a) based on 20 000 orientations with accuracy $\pm 0.9\ \text{mT}$

terisation of three new triplet states including two of particular theoretical interest where previously the use of microcrystalline powders had failed (whereas normally the use of the latter results in enhanced signal levels compared with solution samples). The reasons for this medium effect are unclear: factors of importance with aqueous glasses are likely to be increased transmission of irradiation, promotion of a heterolytic, as opposed to a homolytic, photodissociation, and stabilisation of the extremely reactive Ar^+ at 77 K by a (relatively) inert saline aqueous medium. Possibly the *less* reactive Ar^+

($0.04\ \text{cm}^{-1}$) than the figures for a number of $p\text{-R}_2\text{NC}_6\text{H}_4^+$ species. This conforms with our previous generalisation^{1,11} that the D parameter increases with the electron-donor ability of the substituent group. What parameter to adopt as a measure of the donor ability in the present situation is uncertain: the *ab initio* calculations of Pople *et al.*¹⁰ suggest that the stabilisation of C_6H_5^+ by substituent groups derives from both σ - and π -effects, with (i) the σ effect decreasing through the series $o \sim m > p$ (and with NH_2 acting as a σ -acceptor) and (ii) the π effect decreasing similarly, and in the sequence

$\text{NH}_2 > \text{OH} > \text{F}$. Consequently, in making comparisons between *para*-substituents not covered by Pople *et al.* we have selected the (*para*) $\sigma_{\text{R(A)}}^-$ values of Taft *et al.*¹² The correlation between *D* and $\sigma_{\text{R(A)}}^-$ is inherently rather limited as singly-alkoxy or thiol-substituted Ar^+ do not give triplet resonances, and no $\sigma_{\text{R(A)}}^-$ value is

TABLE 3

Sequence of *D*-parameters related to corresponding

Substituent	$\sigma_{\text{R(A)}}^-$ value		Reference to <i>D</i>
	<i>D</i>	$\sigma_{\text{R(A)}}^-$ ¹²	
<i>p</i> -O ⁻	0.3179		13
<i>p</i> -NH ₂	0.2967	-0.48	This work
<i>p</i> -NMe ₂	0.2522	-0.34	This work
2,4,5-(OMe) ₃	0.1779	-0.45 ^a	1
4-SBu ⁿ -2,5-(OEt) ₂	0.1684	-0.14 ^a	1

^a Note that this material bears an *o*-alkoxy-group, which is likely to exert a strong inductive effect, e.g. σ_I for *p*-OMe is +0.27.¹²

listed for the strong π -donor -O⁻, but a trend is clearly apparent that substituents increasing the π -density in the ring afford larger *D* parameters, *i.e.* reduced electron-electron distances.

Inspection of the *D* parameters for 3-substituted-4-morpholinophenyl cations reveals a complex of effects, *viz.*

3-Substituent	H	Me	CF ₃	Cl ¹	OMe
<i>D</i> parameter/cm ⁻¹	0.2531	0.2227	0.2062	0.2035	0.1998

All substituents give a reduced *D* parameter: Me is a good σ -donor¹² and is acting presumably by steric inhibition of the π -donor action of the morpholino-group, while the other substituents act both sterically and by σ -withdrawal. Similarly a 3-chloro-substituent¹ reduces the *D* parameter of *p*-dimethylaminophenyl cation from 0.254 9 to 0.232 5 cm⁻¹. This effect of chloro-substituents contrasts with that reported by Wasserman *et al.*¹³ for dichloro-substituted-*p*-phenoxide aryl cation, when *D* is increased. The effect of placing a benzene ring in the 2,3-positions in the *p*-morpholinophenyl cation (*D* increased from 0.253 1 to 0.256 2 cm⁻¹) parallels that found in Wasserman's series of triplets (*D* increased from 0.317 9 to 0.333 3 cm⁻¹).¹³

The most radical change in the *D* parameter is that occasioned by placing a morpholino-substituent at the *ortho*- (*D* 0.167 1 cm⁻¹) rather than the *para*-position (0.253 1 cm⁻¹), which implies a much larger spin-spin separation, *R*, in *o*-morpholinophenyl cation (see Table 1). We have embarked on *ab initio* calculations of *ortho*- and *para*-aminophenyl cations in order to illuminate the remarkable difference in *R* between the two species. Strong differentiation between *ortho*- and *para*-morpholino-substituents was apparent in the parent arene-diazonium salts: the *ortho*-substituted compound was much more stable to irradiation at 77 K and required prolonged photolysis to achieve even a fractional level of Ar^+ and Ar^\bullet production, and then only under precise matrix conditions (LiCl glass).

Small but distinct changes in *D* resulted from alteration of the *p*-amino-substituent, *viz.*

Substituent	NH ₂	Piperaziny	NEt ₂	Morpholino
<i>D</i>	0.2967	0.2563	0.2549	0.2531
Substituent	NMe ₂	NPr ₂	Pyrrolidino	Piperidino
<i>D</i>	0.2522	0.2518	0.2515	0.2474

NH₂ provides a special π -donor effect as indicated by its $\sigma_{\text{R(A)}}^-$ value;¹² otherwise the π -donor effect falls systematically with increase in the number of carbon atoms bonded to the donor nitrogen-atom (with the exception of NMe₂). Rather peculiar is the sequence for *D* of piperazino > morpholino > piperidino which is clearly not based simply on the σ -withdrawal effect of the group in the 4-position of the saturated ring. Finally, one might note in Table 1 the level of discrepancy between values for *D** calculated from the $\Delta m = 1$ transition (which is virtually the same as the value for *D* listed) and those of *D** calculated from the $\Delta m = 2$ transition.^{3,4} This is reasonably small for all the phenyl cations listed with the exception of *p*-aminophenyl cation for which it is much larger than normally found;^{6,14-16} indeed, the values of *D* and *E* obtained from the $\Delta m = 1$ transition predict a vanishing value for $H_{\text{min.}}$, whereas we find $H_{\text{min.}}$ at 19.48 mT: presumably this reflects on the theoretical basis of the relevant equations.

Intensity of Triplet Resonance.—Assuming that the trapping efficiencies of Ar^+ and Ar^\bullet are not dissimilar, the ratio of the two pathways (1) and (2) is indicated roughly by the intensity ratio of the two transitions $H_{\text{min.}}$ and H_0 . In most of our work we have found this ratio $\ll 1.0$; where the ratio could be assessed, the following figures were obtained (at 3 dB power level):

Substituent(s)	3-Methoxy-4-morpholino	<i>p</i> -Pyrrolidino	<i>p</i> -NH ₂	<i>p</i> -Morpholino
Intensity ratio: $H_{\text{min.}}/H_0$	4	2.1	1.3	1.2
Substituent(s)	3-Methyl-4-morpholino	3-Methyl-4-pyrrolidino	<i>p</i> -NPr ₂	
Intensity ratio: $H_{\text{min.}}/H_0$	1	1	0.6	

We thank the S.R.C. for grants to purchase the e.s.r. spectrometer and for the support of H. B. A., and Professor B. Jezowska-Trzebiatowska for arranging the computer simulation in the Figure. H. B. A. thanks the Institute of Nuclear Research, Warsaw, Poland for leave.

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