

Triplet State E.S.R. Studies of Aryl Cations. Part 2.¹ Substituent Factors influencing Net Stabilisation of the Triplet Level

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E.s.r. study of triplet state aryl cations generated photochemically ($h\nu$ at 77 K) by the process $\text{ArN}_2^+\text{BF}_4^- \rightarrow \text{Ar}^+ + \text{N}_2 + \text{BF}_4^-$ indicates that the lowering of the triplet state energy level of Ar^+ (relative to the almost isoenergetic singlet level) to become the ground state, is promoted by the presence of electron-releasing groups, such as NR_2 , OR, SR, and SAr; the stabilising effect of a given substituent is positionally dependent, viz. $4 > 2 \geq 3$ substitution, whilst for a given site of substitution the stabilisation effect is $\text{NR}_2 > \text{OR} \sim \text{SR} \sim \text{SAr}$. The magnitude of the D parameter reflects both this sequence and the presence of other electron-withdrawing substituents. It is concluded that *ab initio* calculations cannot deal adequately with the subtlety of the effects promoting stabilisation of triplet Ar^+ .

CURRENT interest in aryl cations centres on three areas: (i) *ab initio* calculations of their energy states and geometries,²⁻⁴ (ii) consideration of their role as kinetic intermediates in the thermal and photochemical decomposition of arenediazonium salts,⁵⁻⁸ and (iii) determination of their e.s.r. spectral parameters in those instances where their triplet states are stabilised with respect to the corresponding singlet states.^{1,9,10} The latter measurements have significance for the other areas of study: not only do they offer unequivocal confirmation of the existence of Ar^+ as an isolable intermediate, and the possibility of kinetic studies, but they also allow direct comparison with theoretical predictions⁴ of the stabilising influences of various electron-releasing substituents in different ring positions. In the present study, we report a detailed examination of the stabilising influences of alkylamino-, dialkylamino-, alkoxy-, and alkyl-, and arylmercapto-substituents. While either a single or two OR, SR, or SAr groups fail to stabilise the triplet level sufficiently to make it the ground state of Ar^+ , three such groups, suitably located, render Ar^+ paramagnetic.

EXPERIMENTAL

Materials.—Arenediazonium salts were provided mostly by Mr. P. Pinot de Moira of Ozalid (U.K.) Ltd. and were purified by precipitation methods as follows. (i) In the case of tetrafluoroborate or hexafluorophosphate salts, by adding diethyl ether to an acetone solution and (ii) in the case of tetrachlorozincate salts, by adding HBF_4 or HPF_6 to aqueous solutions. In one case, the minimal quantities available (and precipitated) required successive use of these acids, giving a co-precipitate of the two salts. These procedures were carried out two or three times as required. Other arenediazonium salts were prepared by the diazotisation of the precursor amines, normally by the so-called 'direct method.'¹¹ Microanalyses for C, H, N and (where necessary) P, S, and halogen gave excellent results (Table 1).

E.s.r. Measurements.—These measurements were carried out with a Bruker Spectrospin Ltd. model ER 200 tt X-band instrument. Field positions were calibrated using as a standard a dilute (microcrystalline) solution of 2% $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ as proposed by Andriesen.¹²

Irradiations.—Samples of arenediazonium salts, either as crystalline powders (in most cases) or as solutions either in 9 mol dm^{-3} LiCl in H_2O or in cellulose acetate film (made up as

given previously⁹) were irradiated with the Pyrex-filtered output of a 200 W high-pressure Hg-Xe point source lamp for several hours while immersed in liquid N_2 .

RESULTS

Typical e.s.r. spectra are shown in Figures 1 and 2, together with an outline of the analysis following Kottis and Lefebvre.¹³ In general, good agreement was obtained between these results for D and those obtained using Wasserman's procedure.¹⁴ Not all spectra were as intense or well-resolved as these, with a consequent uncertainty in

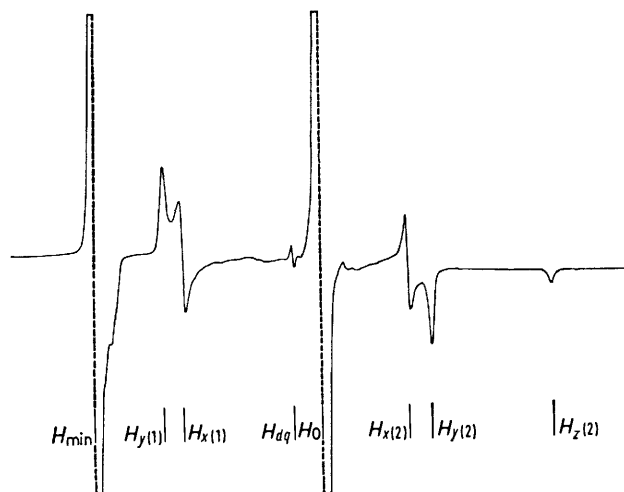


FIGURE 1 E.s.r. spectrum (0–0.7 T) of photoirradiated powdered compound (III) at 77 K. For exact field positions of transitions see Table 2. Note clear $H_{z(2)}$ feature and H_{dq} transition

the resulting evaluation of the D parameter. In many cases, in particular, the weak absorption $H_{z(2)}$ was lost in the noise, and in others the $H_{z(1)}$ peak overlapped with the sharp peak due to the H_{min} component of the $\Delta m = 2$ transition: in these cases the D parameter could be obtained only from the $H_{x(1)}$, $H_{x(2)}$, $H_{y(1)}$, and $H_{y(2)}$ peaks (in one analysis) or the H_{min} peak (in another analysis). Another situation often encountered was the overlapping of the x - and y -components to yield only broad $H_{xy(1)}$ and $H_{xy(2)}$ resonances. For compound (III) the double-quantum transition H_{dq} was apparent slightly to low field of H_0 , its nature being confirmed by its large relative enhancement as the microwave power was increased. The results are summarised in Table 2, together with evaluation of the triplet-state parameters¹³ D , E , D^* , X , Y , and Z , their g -factor components, the inter-

TABLE I
Microanalyses for arenediazonium salts

Compound		C(%)	H(%)		N(%)			
			Calc.	Found	Calc.	Found	Calc.	Found
	(I)	C ₁₀ H ₁₄ N ₃ BF ₄	45.66	45.76	5.36	5.38	15.97	16.01
	(II)	C ₁₀ H ₁₃ ClN ₃ BF ₄	40.37	40.30	4.40	4.38	14.12	14.21
	(III)	C ₁₄ H ₂₁ ClN ₃ BF ₄	47.56	47.35	5.99	5.96	11.89	11.97
	(IV)	C ₉ H ₁₂ N ₃ BF ₄ ⁻ 67.7% C ₉ H ₁₂ N ₃ PF ₆ ⁻ 32.3%	40.37	40.38	4.52	4.49	15.69	15.78
	(V)	C ₁₀ H ₁₁ N ₃ OClBF ₄	38.56	38.70	3.56	3.61	13.49	13.62
	(VI)	C ₁₈ H ₂₈ N ₃ O ₃ BF ₄	51.32	51.19	6.70	6.78	9.98	10.00
	(VII)	C ₁₇ H ₁₈ N ₃ O ₃ BF ₄	51.16	51.05	4.55	4.52	10.53	10.71
	(VIII)	C ₁₄ H ₂₁ N ₂ O ₂ SBF ₄	45.67	45.68	5.75	5.70	7.61	7.79
	(IX)	C ₁₅ H ₁₅ N ₂ O ₂ SBF ₄	48.15	46.18	4.04	3.93	7.49	7.36
	(X)	C ₂₁ H ₁₉ N ₂ O ₂ S ₂ BF ₄	54.09	54.06	4.11	4.14	6.01	6.00
	(XI)	C ₁₆ H ₁₆ N ₄ O ₄ SP ₂ F ₁₂	29.55	30.68	2.48	2.65	8.62	7.94
	(XII)	C ₉ H ₁₁ N ₂ O ₃ PF ₆	31.78	31.87	3.26	3.18	8.24	8.31

spin distance R calculated from a simple point dipole model, the function $(D/D_0)^{2/3}$ [relating to $D_0 = 0.1018$ for compound (X) which has the smallest D parameter and hence the largest R value] and the field position H_0 for the corresponding Ar^+ species. Normally the latter gave a considerably stronger signal than Ar^+ (by a factor of 10^2), but in the case of compound (III) the ratio fell to 10 : 1.

A compilation of compounds *not* giving triplet e.s.r. spectra following prolonged irradiation at 77 K is given in Table 3.

DISCUSSION

From Table 2, which refers to powder samples, the following principal points can be drawn.

(A) *Nitrogen-containing Substituents*.—(i) Any substituent featuring a nitrogen lone-pair and situated at the 4-position is, in itself, sufficient to stabilise the triplet state of Ar^+ . This applies even when the nitrogen is part of an amide group and the stabilising lone-pair is less available, although under these conditions the D parameter is reduced to 0.1725 cm^{-1} .

(ii) The effect of a strongly effective 4-morpholino-group can, however, be nullified by location at the 3-position of a strongly electronegative CF_3 group.

(iii) As previously noted,¹ a 2-morpholino-substituted phenyl cation does not exhibit triplet state resonance, implying a lower efficiency of stabilisation from the 2-position than indicated by *ab initio* calculations.⁴

(B) *Oxygen-containing Substituents*.—Contrary to the predictions of *ab initio* calculations,⁴ the presence of a 4-alkoxy-group is not, in itself, sufficient to stabilise the triplet level of Ar^+ sufficiently to bring it below the alternative singlet $(\pi)^5(sp^2)^1$ configuration. Indeed, none of the dimethoxylated aryl cations are triplets nor are

even certain trimethoxylated aryl cations (Table 3), notably the 2,4,6-trimethoxyphenyl cation which features substituents at all the positions considered⁴ most likely to facilitate stabilisation. Rather surprisingly, therefore, strong resonance was obtained from

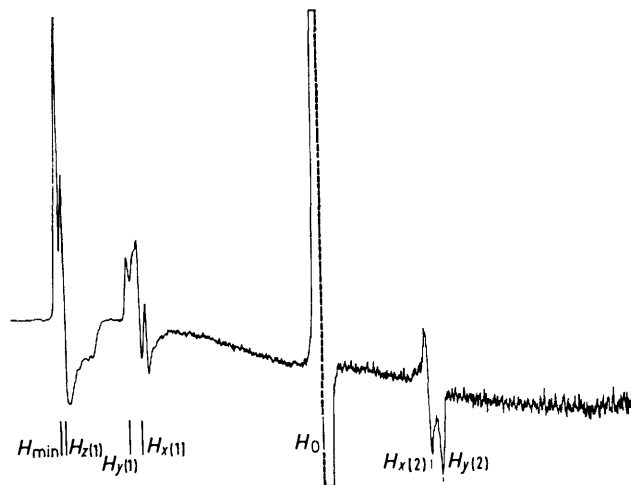


FIGURE 2 E.s.r. spectrum (0–0.7 T) of photoirradiated powdered compound (I) at 77 K. For exact field positions see Table 2. Note generally poor S/N and apparent absence of less-intense components

the 2,4,5-trimethoxyphenyl cation, albeit with a considerably reduced D parameter of 0.1779 cm^{-1} .

(C) *Sulphur-containing Substituents*.—While no calculations have been reported of the stabilising effect of SR groups on phenyl cations in either singlet or triplet configurations, it was anticipated that SR groups might

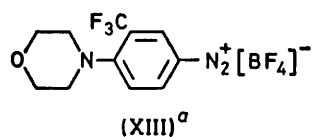
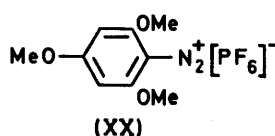
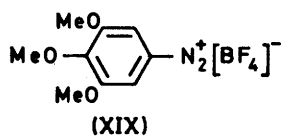
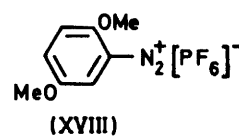
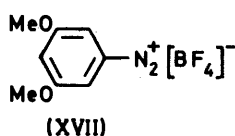
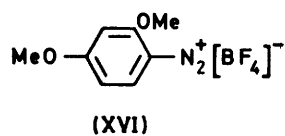
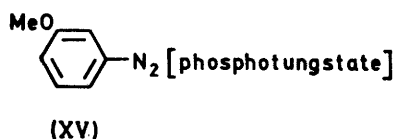
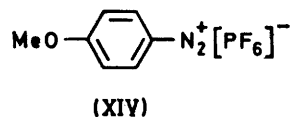
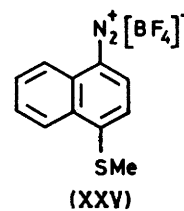
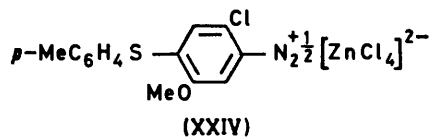
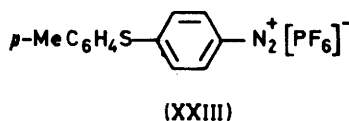
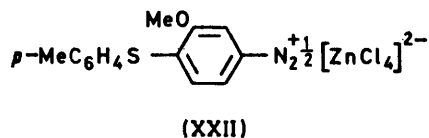
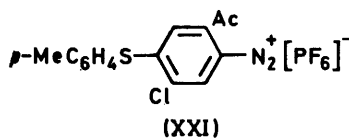
TABLE 2
Triplet state parameters for substituted aryl cations

Compound	$\Delta m = 2$		$\Delta m = 1$ Field position/mT					$\Delta m = 1$ ZFS parameters/ cm^{-1}							R/A	$\left\{ \frac{D}{D_0} \right\}^{2/3}$	H_0/mT	
	H_{\min}/mT	D^*/cm^{-1}	$H_{z(1)}$	$H_{y(1)}$	$H_{z(1)}$	$H_{z(1)}$	$H_{y(2)}$	$H_{z(2)}$	$X_1 Y_1 Z_1 c$	D	$-E$	D^*	g_{xx}	g_{yy}				g_{zz}
(I)	42.1	0.2654	46.7	121.5	135.5	452.7	466.8		$X = 0.08595$ $Y = 0.09355$ $-Z = 0.17950$	0.2693	0.0038	0.2694	2.305	2.303	~ 2.014	2.13	1.913	338.4
(II)	91.4	0.2306	98.2	157.8	184.4	434.1	455.0		$X = 0.07112$ $Y = 0.08387$ $-Z = 0.15499$	0.2325	0.0064	0.2328	2.191	2.211	~ 1.974	2.24	1.734	338.5
(III) ^a	95.1	0.2264		168.5	189.4	430.9	456.2	582.7	$X = 0.06904$ $Y = 0.08283$ $-Z = 0.15187$	0.2278	0.0069	0.2281	2.183	2.168	~ 1.983	2.25	1.711	338.2
(IV)	42.9	0.2652		92.5	123.6	457.9	472.6		$X = 0.08949$ $Y = 0.09888$ $-Z = 0.18837$	0.2826	0.0047	0.2827	2.332	2.399		2.10	1.975	339.0
(V)	111.6	0.2062			199.2 ^b		432.5 ^b		$X = 0.06784$ $Y = 0.06784$ $-Z = 0.13569$	0.2035	0	0.2035	2.146	2.146		2.34	1.587	338.4
(VI)	91.3	0.2306	82.3	174.5		447.3	588.6		$X = 0.07813$ $Y = 0.07813$ $-Z = 0.15646$	0.2346	0	0.2346	2.179	2.179	2.019	2.23	1.745	334.8
(VII)	133.3	0.1686		227.6		420.2			$X = 0.05749$ $Y = 0.05749$ $-Z = 0.11498$	0.1725	0	0.1725	2.024	2.024		2.47	1.421	337.5
(VIII)	133.1	0.1689		226.4	234.3	412.7	423.6	525.9	$X = 0.05313$ $Y = 0.05906$ $-Z = 0.11225$	0.1684	0.0029	0.1685	2.093	2.084	1.914	2.49	1.399	334.4
(IX)	133.2	0.1687		227.0		420.1			$X = 0.05759$ $Y = 0.05759$ $-Z = 0.11518$	0.1728	0	0.1728	2.093	2.093		2.47	1.423	337.5
(X)	156.6	0.1037		267.5	288.8	377.4	399.9		$X = 0.02719$ $Y = 0.04068$ $-Z = 0.06787$	0.1018	0.0067	0.1025	2.034	2.030		2.95	1.000	337.9
(XI)	130.2	0.1749		219.3	233.5	414.1	429.1		$X = 0.05387$ $Y = 0.06266$ $-Z = 0.11653$	0.1748	0.0044	0.1750	2.092	2.089		2.46	1.434	339.5
(XII)	129.6	0.1761		218.3	227.9	416.9	428.2	529.3	$X = 0.05613$ $Y = 0.06250$ $-Z = 0.11863$	0.1779	0.0032	0.1780	2.101	2.096	~ 2.489	2.45	1.451	338.6

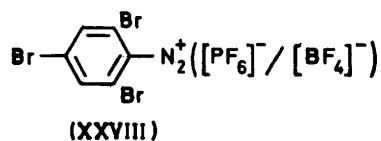
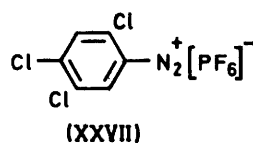
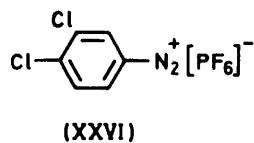
^a Double quantum transition H_{dq} at 3 074 mT. ^b A single entry implies overlapping of the x and y peaks. ^c Signs of X , Y , and Z are relative. ^d Signs of D and E are relative.

TABLE 3

Arenediazonium salts giving no triplet resonance on photolysis at 77 K

N-Substituted*p*-Substituted*S*-Substituted

Halogen-substituted

^a Note added in proof: Compound (XIII) gives a triplet resonance in aqueous LiCl glass at 77 K.

parallel OR in behaviour, and compounds (VIII)—(XI) all show clear triplet resonance on irradiation. In all these, the apparently special 2,4,5-trisubstitution pattern is found, with SR or SAr groups occupying the critical 4-position and OR or SAR groups in the 2- and 5-positions. In compounds (VIII), (IX), and (XI), the D and D^* parameters are in the range 0.168—0.173 cm^{-1} whilst compound (X) features the lowest D parameter (0.1018 cm^{-1}) of the entire series by a considerable margin (whether this be estimated from either $\Delta m = 1$ transitions or H_{min}), which implies extensive migration of the unpaired π electron on to the SAR groups. The smallness of the factors resulting in net stabilisation of the triplet (as opposed to the nearly isoenergetic singlet) state is evident from inspection of the thiol-substituted arenediazonium salts *not* yielding triplet resonance. Compound (XXII) differs from (X) by a single $\text{SC}_6\text{H}_4\text{Me-}p$ group while the presence of a condensed ring in (XXV) does not appear to be effective. The presence of halogen substituents, either singly or in quantity [compounds (XXIV), (XXVI)—(XXVIII)] appears inimical to stabilisation of triplet Ar^+ .

Magnitude of D Parameters.—These are maximal with N-substituents, particularly NHEt and NEt_2 , are slightly less with NBu_2 and morpholino, and are reduced by the presence of electronegative groups on the ring [compound (V)] or the substituent [compound (VII)]. They are rather less with O- and S-substituted cations, and the lowest value is reached ($D^* = 0.1025 \text{ cm}^{-1}$) with compound (X). Since $D \propto R^{-3}$, where R is the inter-spin distance, then the electron–electron repulsion, which is proportional to R^{-2} , must also be proportional to $D^{2/3}$. Taking compound (X) (having the smallest electron–electron interactions) as the standard (denoted D_0), values for $(D/D_0)^{2/3}$ (Table 2) reflect the coulombic repulsion and hence the balancing stabilising effects of the substituents. This is largest for those Ar^+ featuring the best combination of donor substituents and ring substitution, and may be taken as an index of the stabilising effect of electron-releasing substituents.

To summarise, the substituent effects promoting stabilisation of the triplet, as opposed to the singlet level of Ar^+ operate in a subtle way. While a 4-dialkylamino-group produces a ground triplet state, the presence of mildly electronegative groups reduces the D parameter whilst that of a group such as CF_3 makes the singlet state of lower energy. Of all the mono-, di-, and tri-methoxy-phenyl cations examined, only one, with the 2,4,5-substitution pattern exists as a triplet ground state. Various 2,5-dialkoxy-4-alkylthio(or arylthio)phenyl cations are also triplets whilst less highly substituted analogues are singlets. It is doubtful whether even STO–3G calculations are sufficiently accurate to cope with the subtleties of the singlet–triplet splitting, despite their notable prediction of the triplet character of $4\text{-H}_2\text{NC}_6\text{H}_4^+$ as opposed to the singlet state of C_6H_5^+ .

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