Electron Spin Resonance of Ground-state Triplet Aryl Cations in the Photolysis of Substituted Arenediazonium Salts at 77 K

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Summary Suitably substituted arenediazonium salts undergo photolysis in a polymer film at 77 K to yield e.s.r. spectra characteristic of triplet states which are assigned to the corresponding aryl cations of configuration $(\pi)^5(sp^2)^1$.

WHILST Taft[1] has suggested that the ground-state electronic configuration of the phenyl cation is of triplet character, *viz.* $(\pi)^5(sp^2)^1$, only Wasserman and Murray[2] have been successful in obtaining the e.s.r. spectrum of such a species and then only in the case of the photolysis of 1,4-diazo-oxides to a 4-phenoxylphenyl triplet species, which can be regarded as a phenyl cation substituted by O^- at the 4-position. We report here that a number of arenediazonium salts are readily photolysed ($\lambda > 300$ nm) in a cellulose acetate film at 77 K to yield very broad spectra comprising three principal peaks together with the corresponding aryl radical centred near $g = 2$ (Figure and Table). It was possible in the case of 2,5-di-n-butoxy-4-morpholinobenzenediazonium tetrafluoroborate to obtain triplet state resonance on irradiation in organic matrices of ethoxybenzene, benzyl alcohol, and 2-phenylethanol, in addition to solutions in polymer films of polystyrene and the polymer of the diglycidyl ether of bisphenol-A, but unfortunately the features remained broad.

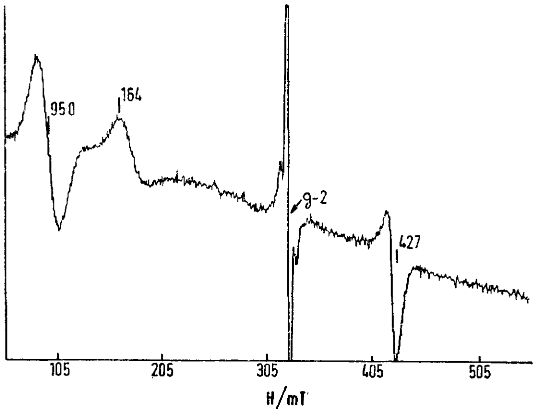
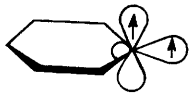


FIGURE. E.s.r. spectrum of irradiated 2,5-di-n-butoxy-4-morpholinobenzenediazonium fluoroborate in cellulose acetate film at 77 K.

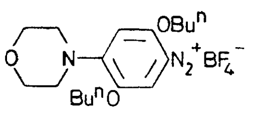
Our attempts to obtain triplet state resonance of less highly substituted aryl cations by analogous experiments with simple arenediazonium salts have been unsuccessful. The stability of the substituted aryl cations may result from a combination of several effects, *viz*, (i) delocalisation of the odd π-electron on to substituent groups to give contributions of the type $^{\bullet}X\text{–}C_6H_4^{\bullet}$ (ii) general steric effects of the bulky substituents, and (iii) 'locking' of the important 4-amino group by the matrix into a conformation maximising conjugation with the π-system. Evleth and Horowitz[3] have calculated the ground state of 4-aminophenyl cation to be a triplet, while that of phenyl cation is predicted to be singlet in character.

Although the features are broader than those usually observed for ground-state organic triplets, they have the correct form and relative intensities, and occur at the correct field positions for species with *D ca.* $0{\cdot}25\ \text{cm}^{-1}$ and $E \leqslant 0{\cdot}004\ \text{cm}^{-1}$. These parameters are in accord with the structure (**1**) rather than a triplet of the type $R_2\overset{+\bullet}{N}\text{–}C_6H_4^{\bullet}$,

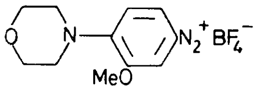


(1)

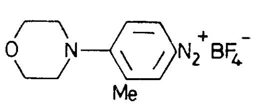
for which the couplings would be an order-of-magnitude smaller.† Only the high-field z components, which are expected to occur in the 600 mT region, were not detected. Since these should be broad and of an intensity *ca.* 0·02 of the stronger lines, our inability to detect them is not surprising.



(2)



(3)



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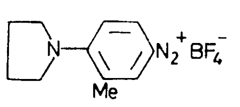

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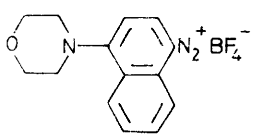

(6)

$(PhCH_2)_2N\cdot C_6H_4\cdot N_2^+BF_4^-$

(7)

TABLE

Field positions of resonances of Ar^+ formed in the photolysis of arenediazonium salts in cellulose acetate film at 77 K

Diazonium salt	Peak positions[a]/mT		
	First	Second	Third
(2)	95	164	427
(3)	111	187·5	420
(4)	94	167·5	425
(5)	101	177·5	462·5
(6)	55	120	432·5
(7)		no resonance	

[a] Recording of these as indicated in the Figure, *i.e.* the first transition taken at crossover, the second at upward peak, the third at downward peak.

Compared with the data for the triplet species obtained from 1,4-diazo-oxides,[2] (D *ca.* 0·32 cm^{-1} and E = 0·001—0·011 cm^{-1}) these aryl cations have a reduced value of D, and rather small E values. Since D stems mainly from the structure (**1**), this implies a somewhat reduced spin-density for the π-spin on C(1). Unfortunately, the lines were too broad to give resolved components for the proton hyperfine coupling expected from the proton(s) adjacent to the σ-electron.

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† We thank a referee for the suggestion of the $R_2\overset{+\bullet}{N}-C_6H_4\cdot$ structure.

[1] R. W. Taft, *J. Amer. Chem. Soc.*, 1961, **83**, 3350.

[2] E. Wasserman and R. W. Murray, *J. Amer. Chem. Soc.*, 1964, **86**, 4203.

[3] E. M. Evleth and P. M. Horowitz, *J. Amer. Chem. Soc.*, 1971, **93**, 5636.