Aryl Cations – New Light on Old Intermediates

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1 Introduction

The comparative instability of simple arenediazonium salts with respect to thermal loss of molecular nitrogen (a process termed dediazoniation[1]) either in the solid state or in solution (aqueous or organic) has long been known,[2] and soon after the development of the concept of the S_N1 mechanism of nucleophilic substitution at carbon (sp^3) centres came extension to the solvolysis of ArN_2^+ salts in hydroxylic media,[3] *viz.*

$$ArN_2^+ \xrightarrow{k_1} Ar^+ + N_2 \tag{1}$$

$$Ar^+ + H_2O \xrightarrow{k_2} ArOH + H^+ \tag{2}$$

with $k_2 \gg k_1$. In saline media, *e.g.* in the presence of chloride ion, appreciable ArCl is formed,[4] indicating a low degree of selectivity of the Ar^+ intermediate, *i.e.* a high reactivity. A similar reduced selectivity is apparent when the supposed Ar^+ intermediate is allowed to attack the ring positions of substituted benzenes, *e.g.* nitrobenzene, when the partial rate factors are lower than when either other electrophiles[5] or aryl radicals $Ar\cdot$ are the reactive species.[6] A particularly striking instance of the 'hyper-reactivity' of Ar^+ has come from isotopic labelling studies of dediazoniation.[7] These experiments have taken two forms: in one, labelled $C_6H_5\overset{+}{N}{\equiv}{}^{15}NBF_4^-$ is allowed partly to decompose and the ^{15}N content of recovered unreacted material determined after conversion to $C_6H_5NH_2$.[8] The demonstration of $\sim 8\%$ of ^{15}N incorporation into the aniline implies reversibility of equation (1), *viz.*

$$ArN_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar^+ + N_2 \tag{3}$$

and this is confirmed by the second series of experiments[8] in which decomposition

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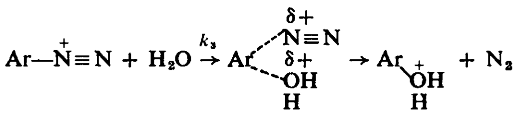
[1] H. Zollinger, *Accounts Chem. Res.*, 1973, **6**, 335.
[2] K. H. Saunders, 'The Aromatic Diazo Compounds and their Technical Applications', Edward Arnold, London, 1949, vol. 2.
[3] W. A. Waters, *J. Chem. Soc.*, 1942, 266.
[4] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, 1951, **49**, 273.
[5] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds', Elsevier, New York, 1965.
[6] N. Kamigata, M. Kobayashi, and H. Minato, *Bull. Chem. Soc. Japan*, 1972, **45**, 2047.
[7] H. Zollinger, *Angew. Chem. Internat. Edn.*, 1978, **17**, 141.
[8] R. G. Bergstrom, R. G. M. Landells, G. H. Wahl, jun., and H. Zollinger, *J. Amer. Chem. Soc.*, 1976, **98**, 3301.

of ^{15}N-enriched benzenediazonium tetrafluoroborate is allowed to decompose thermally under 300 atmospheres pressure of normal nitrogen when accelerated loss of ^{15}N occurs from undecomposed diazonium salt, signifying N_2-exchange prior to decomposition.

Clearly then, Ar^+ is now accepted as a genuine intermediate albeit of exceptional reactivity. This situation was not clearly established, however, until quite recently, another view maintaining that dediazoniation was an S_N2-type process in which the departure of N_2 was synchronous with bond-formation with an incoming solvent (nucleophile)[9] *viz.*



$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N + H_2O \xrightarrow{k_3} Ar\begin{smallmatrix}\overset{\delta+}{\cdots N{\equiv}N}\\ \delta+\\ \cdots \underset{H}{O}H\end{smallmatrix} \rightarrow Ar{-}\overset{+}{\underset{H}{O}}H + N_2} \qquad (4)$$

The evidence enabling discrimination between equations (2), (3), and (4) is given below. Two further points of contemporary interest surrounding Ar^+ are its electronic structure and configuration: Taft's original suggestion[10] of a biradical structure for $C_6H_5^+$ has stimulated several theoretical approaches by both semi-empirical and *ab initio* methods and these have been augmented by efforts by both optical and e.s.r. spectroscopists to characterize this elusive species. These various investigations, all made in the last decade, form the basis of this review.

2 Kinetic Evidence concerning Ar^+

That the principal mode of thermal decomposition of $ArN_2^+X^-$ (X = Cl, BF_4, PF_6, *etc.*) is heterolytic, at least in aqueous solution, is indicated by the product of reaction. In water or dilute aqueous acid, this is ArOH in high (>95%) yield, and no coupled products suggestive of the intermediary of Ar· are evident. The same pattern is found[11] for the photolytic decomposition of $ArN_2^+X^-$. The kinetics for decomposition of ArN_2^+ in water are first-order, but this is compatible with the various mechanisms (1), (3), and (4). The leading evidence in favour of (4) would be demonstration of a dependence of k_3 upon nucleophile (either as a different solvent, a co-solvent, or added anion). Several instances of such a dependence have been cited in the literature,[12–15] mainly by Lewis and co-workers who report acceleration of the rate of thermolysis in the presence of Br^- or SCN^- ions. In a particularly detailed kinetic study[9] of the decomposition of $C_6H_5N_2^+PF_6^-$ in dilute sulphuric acid (0.01 mol dm^{-3}), Lewis *et al.* report the effects of added salts to concentrations ≥ 1.00 mol dm^{-3}. Added HSO_4^- ions *retard* decomposition by up to 20% (attributed to effective removal of free, weakly nucleophilic H_2O), while Cl^- and Br^- ions leave the rate unaffected within 7%.

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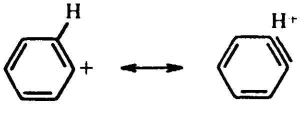
[9] E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Amer. Chem. Soc.*, 1969, **91**, 419.
[10] R. W. Taft, *J. Amer. Chem. Soc.*, 1961, **83**, 3350.
[11] W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Amer. Chem. Soc.*, 1961, **83**, 1928.
[12] E. S. Lewis and M. D. Johnson, *J. Amer. Chem. Soc.*, 1960, **82**, 5408.
[13] E. S. Lewis and W. H. Hinds, *J. Amer. Chem. Soc.*, 1952, **74**, 304.
[14] E. S. Lewis and J. E. Cooper, *J. Amer. Chem. Soc.*, 1962, **84**, 3847.
[15] E. S. Lewis and J. M. Insole, *J. Amer. Chem. Soc.*, 1964, **86**, 34.

The latter result is interpreted as a combination of the retarding effect of Na^+ combined with an accelerating effect of Cl^- and Br^-. These results,[9] combined with those of ref. 14, indicate the accelerative effects of the added ions to be $SCN^- > Br^- > Cl^- > HSO_4^-$, *i.e.* the sequence of their nucleophilicity. It must be remarked that these kinetic effects are comparatively small and that the very low selectivity for nucleophiles (evident both from kinetics and product distribution) is much more in accord with an intermediate like $C_6H_5^+$ than the stable $C_6H_5N_2^+$. Swain *et al.*[16] found only a two-fold variation in the thermolysis rate of $C_6H_5^+BF_4^-$ in a variety of media including 10^{-4} mol dm^{-3} aqueous H_2SO_4, 1.0 mol dm^{-3} aqueous H_2SO_4, 21.0 mol dm^{-3} H_2SO_4, pure acetic acid, and CH_2Cl_2 (the results in the sulphuric acid solutions in particular reflecting virtual constancy of k_1 despite a 10^5-fold change in the activity of water). Swain[16] also notes that the absence of a solvent (H_2O/D_2O) isotope effect is more in accord with reaction (1) than reaction (4) for the latter involves (with H_2O as nucleophile) *two* $^+O—H$ centres in the transition state. Finally, $\Delta S^{\ddagger}$ for the decomposition of $C_6H_5N_2^+Cl^-$ in water[17] (298 K) is 43.0 ± 4.2 J mol^{-1} K^{-1}, which is close to that (51 J mol^{-1} K^{-1}) for hydrolysis of t-C_4H_9Cl (where H_2O is *not* covalently bound in the transition state)[18] while it is ~85—100 J mol^{-1} K^{-1} higher than $\Delta S^{\ddagger}$ for the hydrolysis of methyl or benzyl halides[19,20] where H_2O *is* bound to carbon in the transition state.

Another line of argument has centred around kinetic isotope effects in the decomposition of arenediazonium salts: for those of $C_6H_5N_2^+BF_4^-$ in aqueous H_2SO_4, CH_3CO_2H, or CH_2Cl_2 at 298 K, the (secondary) deuterium isotope effects are[21] (for each single position):

2-position 1.22 ± 0.01 3-position 1.08 ± 0.01 4-position 1.02

The *ortho* effect is exceptionally large for aromatic substitution, ranking with the largest isotope effects observed per β-deuterium atom in established S_N1 solvolyses, and imply substantial hyperconjugation of the type



It may be taken as further evidence for the role of Ar^+ as the crucial intermediate in dediazoniation.

Several groups have determined ^{15}N-^{14}N kinetic isotope effects. Lewis and Insole[15] found $k_{14}/k_{15} = 1.019 \pm 0.004$ at 322 K for the decomposition of

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[16] C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Amer. Chem. Soc.*, 1975, **97**, 783.

[17] M. L. Crossley, R. H. Kienle, and C. H. Benbrook, *J. Amer. Chem. Soc.*, 1940, **62**, 1400.

[18] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[19] R. L. Hepolette and R. E. Robertson, *Proc. Roy. Soc. (London)*, 1959, **A252**, 273.

[20] R. E. Robertson and J. M W. Scott, *J. Chem. Soc.*, 1961, 1596.

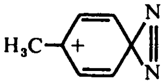
[21] C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Harbison, *J. Amer. Chem. Soc.*, 1975, **97**, 791.

toluene-*p*-diazonium-α-^{15}N tetrafluoroborate in aqueous HCl, using direct kinetic methods. Brown and Drury[22] measured k_{14}/k_{15} by determining isotopic fractionation (from natural-abundance material) in evolved N_2 mass-spectrometrically: they derived systematically higher values than Lewis and Insole, *e.g.* 1.043 ± 0.004 for both *m*-chlorobenzenediazonium and toluene-*p*-diazonium tetrafluoroborates at 371.5 K. The latter values are in good agreement with that of 1.039 predicted from infrared measurements on ^{15}N-labelled materials, but involve the assumption that *only* the α-N atom exerts any effect on the $^{28}N_2/^{29}N_2$ ratio (which was 1.022 ± 0.002). Swain *et al.*[23] found $^{28}N_2/^{29}N_2$ to be 1.0245 ± 0.0005 (298 K), but regarded the leaving group as being of mass 28 (or 29) rather than just 14 (or 15), yielding a lower isotope effect of 1.023. To clarify the situation, Swain *et al.*[23] measured the β-nitrogen isotope effect separately (as 1.0106 ± 0.0003) and thereby segregated the overall isotope effect into its α- and β-components, *i.e.* k_{14}/k_{15} (α-N) is 1.0384 at 298 K. This is very large, indicating that the C—N bond is very much attenuated at the transition state, corresponding to almost complete formation of Ar^+.

Quite separate from these ^{15}N measurements are those concerned with scrambling of ^{15}N between the α and β positions. This was first noted by Lewis and Insole[24] as follows:

$$[\mathrm{Ar{-}^{15}\overset{+}{N}{\equiv}N}] \rightleftharpoons [\mathrm{Ar{-}\overset{+}{N}{\equiv}^{15}N}] \tag{5}$$

Rearrangement was *slower* than hydrolysis by a factor of 0.014 for Ar = C_6H_5 and 0.029 for Ar = *p*-MeC_6H_4. The authors ruled out the forward or reverse steps of equation (3) because the decomposition of $C_6H_5N_2^+BF_4^-$ under high pressures of CO led to no detectable benzoic acid (resulting from capture of CO by $C_6H_5^+$), preferring instead a spirodiazirine intermediate (1) to account for the scrambling



(1)

The scrambling reaction plays a minor role in the aqueous chemistry of arenediazonium salts (amounting to only 2.3% at 80% decomposition of $C_6H_5N_2^+$) and was considered[25] at one point to be an artefact, but it was carefully confirmed with $k_{\mathrm{rearr}}/k_{\mathrm{hydrolysis}}$ ~0.016.[8,23,26] When the polar, but essentially non-nucleophilic solvent 2,2,2-trifluoroethanol is used, decomposition of ^{15}N-labelled $C_6H_5N_2^+BF_4^-$ proceeds with ~8% isotopic rearrangement.[8] In the same solvent, β-^{15}N labelled material was allowed to dediazoniate under various pressures (up to 1000 atm) of 'normal' N_2 (0.4% ^{15}N); as the pressure is increased, larger

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[22] L. L. Brown and J. S. Drury, *J. Chem. Phys.*, 1965, **43**, 1688.
[23] C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Amer. Chem. Soc.*, 1975, **97**, 796.
[24] E. S. Lewis and J. M. Insole, *J. Amer. Chem. Soc.*, 1964, **86**, 32.
[25] A. K. Bose and I. Kugajevsky, *J. Amer. Chem. Soc.*, 1966, **88**, 2325.
[26] R. G. Bergstrom, G. H. Wahl, jun., and H. Zollinger, *Tetrahedron Letters*, 1974, 2975.

amounts of ^{15}N are lost from unreacted diazonium salt.[8] At 300 atm of N_2 (298 K), 2.46 ± 0.40% of external nitrogen is incorporated at 70% dediazoniation. Again,[8] under 320 atm of CO, 5.2% of 2,2,2-trifluoroethyl benzoate is found, implying capture of CO by $C_6H_5^+$.

To summarize, the weight of kinetic evidence, both direct and that involving isotopic labelling, supports equation (3) as the key reaction and Ar^+ as the key intermediate in thermal decomposition of arenediazonium salts.[7] Points of detail remain to be settled, however, such as the greater extent of intramolecular ^{15}N-isotopic rearrangement of decomposing ArN_2^+ in solution as compared with its exchange with dissolved N_2.[26] This may involve rearrangement within a solvent cage,

$$\mathrm{Ar{-}^{15}\overset{+}{N}{\equiv}N} \rightarrow [\mathrm{Ar^{+}\,^{15}N{\equiv}N}] \rightleftharpoons [\mathrm{Ar^{+}N{\equiv}^{15}N}] \rightarrow \mathrm{Ar{-}\overset{+}{N}{\equiv}^{15}N} \qquad (6)$$

rather than displacement of solvent from 'free' Ar^+ by 'free' N_2.[27]

3 Ar^+ as Gas-phase Intermediates

The key reaction in the production of Ar^+ in the gas phase is of the general type

$$C_6H_5X \rightarrow C_6H_5^+ + X\cdot + e^- \qquad (7)$$

The appearance potentials of $C_6H_5^+$ are 12.81 (X = Cl), 11.82 (X = Br), and 11.34 eV (X = I)[28] leading to a mean ΔH_f^{420} of $C_6H_5^+$ of 1146 kJ mol^{-1}, which agrees well with the figure of 1152 kJ mol^{-1} obtained from reaction (8)[28]

$$C_6H_5CO_2CH_3^{+\cdot} \xrightarrow{-\,MeO\cdot} C_6H_5CO^+ \xrightarrow{-\,CO} C_6H_5^+ \qquad (8)$$

and that of 1166 kJ mol^{-1} obtained from reaction (9)[28]

$$C_6H_5COCH_3 \rightarrow C_6H_5^+ + CO + CH_3\cdot + e^- \qquad (9)$$

One problem is that the $C_6H_5^+$ species produced here may not have the phenyl cation structure; the ΔH_f value yields an ionization potential for $C_6H_5\cdot$ of 8.80 eV, which is somewhat lower than the directly measured value of 9.2 eV.[29] However, support for true 'tolyl' ions as relatively stable intermediates has come from collisional activation spectra of *m*- and *p*-MeC_6H_4X (X = NO_2, I, COMe, COC_6H_5, COC_6H_4Me, or CO_2Me).[30] Gaspar *et al.*,[31] using ion-cyclotron resonance spectroscopy, have reported dehalogenation of ArX assisted by a variety of small ions (H_2^+, H_3^+, CH_3^+, CH_4^+, CH_5^+ and their deuteriated analogues), with particularly good yields of Ar^+ induced by H_n^+, *viz.*

$$H_n^+ + X{-}Ar \rightarrow H_{n-1} + H{-}\overset{+}{X}{-}Ar \xrightarrow{-\,HX} Ar^+ \qquad (10)$$

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[27] D. J. Raber, J. M. Harris, and P. von R. Schleyer, 'Ions and Ion-pairs in Organic Reactions ed. M. Szwarc, Wiley-Interscience, New York, 1973, Vol. II.

[28] R. A. W. Johnstone and F. A. Mellon, *J.C.S. Faraday II*, 1972, **68**, 1209.

[29] I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, 1964, **86**, 2741.

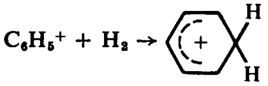
[30] F. W. McLafferty and J. Winkler, *J. Amer. Chem. Soc.*, 1976, **96**, 5182.

[31] M. Speranza, M. D. Sefcik, J. M. S. Henis, and P. P. Gaspar, *J. Amer. Chem. Soc.*. 1977, **99**, 5583.

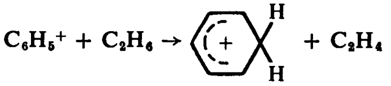
Ar^+ is found to be a highly electrophilic gas-phase species, attacking both π-systems

$$C_6H_5^+ + C_6H_5X \rightarrow C_6H_5{-}C_6H_4^+ + HX\ (X = Cl\ \text{or}\ F) \qquad (11)$$

and σ-systems, *e.g.*


(12)

$$C_6H_5^+ + CH_4 \rightarrow C_7H_9^+, C_7H_7^+ \qquad (13)$$


(14)

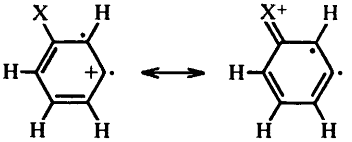
Reaction between crossed molecular beams of Cs^+ ions and ArX also leads to Ar^+, *viz.*[32]

$$Cs^+ + C_6H_5Cl \rightarrow CsCl + C_6H_5^+ \qquad (15)$$

The Ar^+ produced is deduced to be singlet in character, and to lie *ca.* 1.5 eV above the ground electronic state, which is considered therefore to be possibly of triplet type.

4 Theoretical Approaches to Ar^+

The original suggestion that $C_6H_5^+$ might not be a singlet state species came from Taft,[10] who noted strong *meta*-group activation of reaction (1). This he interpreted as follows:


(2) (3)

i.e. Ar^+ was regarded as a ground-state triplet of configuration $(\pi)^5(sp^2)^1$ and the stabilizing effect of X was believed to be due to its participation in structure (3) (with MeO > OH > C_6H_5 > Me > Cl). Enhanced *meta*-substituent effects on rates had previously been noted[33] for several reactions involving radical-ion formation, *e.g.* the polarographic oxidation of substituted anilines. Abramovitch[34–36] modified the Taft model, regarding the biradical cation form as an isomer of the initially-produced (singlet) Ar^+ largely on the basis of its activity as a phenylating agent for aromatic rings. (This view has since been criticized and the results reinterpreted.[16]) Isomer distributions and partial rate factors (*f*) for the arylation of anisole, chlorobenzene, and nitrobenzene by phenyl and *p*-nitrophenyl cations indicate the latter always exhibits greater *f*-values, *i.e.* is more selective and hence less reactive than $C_6H_5^+$ itself, an

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[32] R. C. Horvat, G. D. Miller, and S. A. Safron, *J. Amer. Chem. Soc.*, 1976, **98**, 8274.

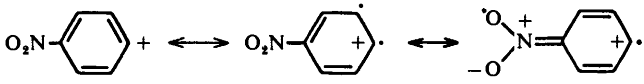
[33] R. W. Taft, I. R. Fox, and I. C. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 3349.

[34] R. A. Abramovitch, W. A. Hymers, J. B. Rajan, and R. Wilson, *Tetrahedron Letters*, 1963, 1507.

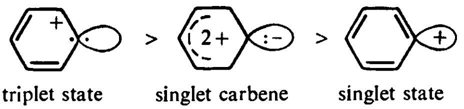
[35] R. A. Abramovitch and G. Tertzakian, *Canad. J. Chem.*, 1965, **43**, 940.

[36] R. A. Abramovitch and J. G. Saha, *Canad. J. Chem.*, 1965, **43**, 3269.

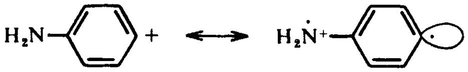
observation suggesting stabilization by the nitro group of a biradical cation structure:[6]



These intuitive approaches have given way to a variety of purely theoretical attempts to resolve the structure and multiplicity of Ar^+. Preliminary MO calculations by Absar and McEwen[37] indicated a sequence of stability as:



INDO calculations on both C_6H_5 and p-$H_2NC_6H_4^+$ indicate the relative energies of the singlet $(\pi)^6(sp^2)^0$ and triplet $(\pi)^5(sp^2)^1$ configurations of Ar^+ are strongly substituent-dependent.[38] For $C_6H_5^+$, the singlet is clearly more stable than the triplet level (by ~3·5 eV), whilst for p-$H_2NC_6H_4^+$ there is a near-degeneracy of the π-cation triplet ($^3A_2$) and the cation singlet ($^1A_1$), with the former situated slightly lower. The stabilizing effect of the p-NH_2 group can be visualized in valence-bond terms thus:



Extended Hückel MO calculations also concur with the view that for $C_6H_5^+$ itself, the $^1A_1$ state is of lower energy than the $^3A_2$ state by a considerable margin.[39]

A series of *ab initio* calculations of aryl cations using STO-3G and 4-31G Gaussian basis sets have been performed very recently by Pople and colleagues. Energies and geometries were derived[40] for the singlet and triplet ($^3B_1$) and triplet ($^3A_2$) configurations of $C_6H_5^+$. It was established that of the alternative triplet state configurations, the $^3B_1$ level is lower in energy by 11.3 kJ mol^{-1} (as indicated by semi-empirical methods). The 4-31G energies place the $^3B_1$ level 31.4 kJ mol^{-1} *below* the $^1A_1$ level, but this is an overestimate typical of UHF methods, and a correction by 115 kJ mol^{-1} (the over-estimate recognized for CH_2:) results in the $^1A_1$ state appearing 84.1 kJ mol^{-1} *below* the $^3B_1$ level. The STO-3G geometry for the $^1A_1$ state is most intriguing (Figure 1), revealing much flattening of the angle at C-1 and shortening of the bonds to C-1 in order to feed charge

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[37] I. Absar and K. L. McEwen, cited in R. A. Abramovitch in 'Advances in Free Radical Chemistry', ed. G. H. Williams, Academic Press, London, 1967, vol. 2, p. 116.

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

[39] R. Gleiter, R. Hoffmann, and W. D. Stohrer, *Chem. Ber.*, 1972, **105**, 8.

[40] J. D. Dill, P. von R. Schleyer, J. S. Binkley, R. Seeger, J. A. Pople, and E. Haselbach, *J. Amer. Chem. Soc.*, 1976, **98**, 5428.

from the σ-framework of the ring into the vacant σ-orbital. (This distortion results in a reduction in energy of 105 kJ mol^{-1} over the standard benzenoid geometry.)

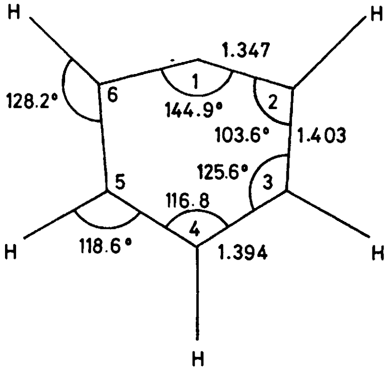


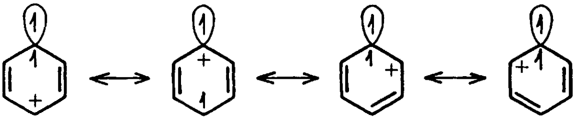
Figure 1 *Optimized geometry of* $C_6H_5^+(^1A_1)$ *using an* STO-3G *Gaussian basis set*[40]

STO-3G calculations were then[41] applied to the aryl cations X—$C_6H_4^+$ where X = (*o*, *m*, *p*) Li, HBe, H_2B, H_3C, H_2N, HO, or F. Benzene geometries were assumed which, while rather invalidating absolute energies, should not affect the ordering of singlet and triplet levels which was the principal point of interest. Stabilization by both π and σ interactions, respectively, was revealed by π-electron densities in the ring and the total charges on the hydrogen atoms (compared with those in C_6H_6) for the $^1A_1$ state of $C_6H_5^+$. 'Stabilization energies' of X—$C_6H_4^+$ were defined by equation (16).

$$X\text{—}C_6H_4^+(\text{singlet}) + C_6H_6 \rightarrow C_6H_5^+(^1A_1) + X\text{—}C_6H_5 \quad \Delta H^\circ \qquad (16)$$

and the results are summarized in Table 1. The strongly stabilizing inductive effect of Li (and to a lesser extent, HBe) falls off with distance from C-1, as does the destabilizing inductive effect of F. OH destabilizes inductively at the *o*- and *m*-positions, but stabilizes *via* a π-effect at the *p*-position. The other principal feature is the strongly stabilizing effect of (co-planar) NH_2 in the *p*-position. Me is weakly π-stabilizing (through hyperconjugation) and weakly destabilizing through σ-withdrawal (relative to H).

As regards the triplet-singlet splitting, the triplet states of X—$C_6H_4^+$, which could be distinguished clearly as $^3B_1$ and $^3A_2$ in $C_6H_5^+$, are less readily recognized as such, but '$^3B_1$-like' states were selected for study. These may be depicted in valence-bond form:



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[41] J. D. Dill, P. von R. Schleyer, and J. A. Pople, *J. Amer. Chem. Soc.*, 1977, **99**, 1.

Table 1 *Singlet stabilization energies for* X—$C_6H_4^+$/kJ mol^{-1}

X	*Ring site* *ortho*	*meta*	*para*
Li	227	158	120
HBe	48.5	28.5	15.5
H_2B (co-planar)	8.3	8.8	−8.3
(orthogonal)	20.5	15.1	16.7
H_3C (*syn*)	14.6	16.7	17.6
(*anti*)	16.3	15.9	17.6
H_2N (co-planar)	20.1	20.5	47.3
(orthogonal)	15.5	28.0	13.4
HO (*syn*)	−31.0	−5.4	11.3
(*anti*)	−1.7	−9.6	11.3
F	−36.0	−25.5	−14.6

and π-donors should be most effective at stabilizing this state at the *o*- and *p*-positions. This simple prediction is confirmed by 'triplet stabilization' energies defined by analogy with equation (16) and given in Table 2. Generally, inductive effects seem less important in stabilizing triplet (compared with singlet) Ar^+, while π-donor effects dominate.

Table 2 *Triplet stabilization energies for* X—$C_6H_4^+$/kJ mol^{-1}

X	*Ring site* *ortho*	*meta*	*para*
Li	202	160	193
HBe	27.2	22.6	12.6
H_2B (co-planar)	−4.2	12.1	−19.7
(orthogonal)	49.8	36.0	54.4
H_3C	20.9	39.7	55.2
H_2N (co-planar)	23.5	152	236
(orthogonal)	31.0	32.6	22.6
HO (*syn*)	125	63.2	127
(*anti*)	123	55.2	127
F	31.4	12.1	41.0

The singlet-triplet splittings, given in Table 3, predict the triplet state always to be lower in energy. However, as pointed out in Section 2, this reflects firstly the tendency of UHF methods to place triplets artificially low: secondly, benzene-like geometries (rather than optimized geometries) have been used throughout. The latter simplification is known to reduce the $^1A_1$–$^3B_1$ separation for $C_6H_5^+$ from 160 to 31 kJ mol^{-1}. The two sources of error combined should change the singlet–triplet splitting by $115 + (160-31) = 244$ kJ mol^{-1}, and this

Table 3 *Singlet–triplet splittings in* $X—C_6H_4^+$, ΔE_{ST}/kJ mol^{-1}

X	*Preferred isomer* *Singlet*	*Triplet*	ΔE_{ST} (*uncorrected*)	ΔE_{ST} (*corrected*)
Li	*ortho*	*ortho*	126	−118
HBe	*ortho*	*ortho*	138	−106
H_2B	*meta* (co-planar)	*para* (*ortho*)	176	−68
H_3C	*para*	*para*	198	−46
H_2N	*para* (co-planar)	*para* (co-planar)	348	+104
HO	*para*	*para*	276	+32
F	*para*	*para*	216	−28

figure has been subtracted from column three of Table 3 to yield column four. Only the *p*-amino substituent shows a degree or stabilization clearly indicating the triplet to be the ground state, although the *p*-OH and *p*-F substituents exert sufficient stabilization to leave the multiplicity of the ground state of *p*-$HOC_6H_4^+$ and *p*-$FC_6H_4^+$ an open question. In the next section we shall deal with the experimental vindication of Pople's predictions.

5 Spectroscopic Detection of Ar^+

Assuming that Ar^+ is an extremely reactive and therefore very short-lived species, its detection might be expected to be based either on matrix isolation or some type of fast reactions method. Undoubtedly the most sensitive cryogenic method would be electron spin resonance spectroscopy in those possibly rare cases when Ar^+ is a ground triplet state. Otherwise, u.v-visible spectroscopy of a flash- or electron pulse-irradiated solution would seem to offer the best chance of detecting Ar^+. Noting Pople's prediction of special stabilization of triplet Ar^+ by a *p*-NH_2 substituent, the present authors and colleagues[42–45] irradiated a series of *p*-dialkylamino-substituted arenediazonium salts in a variety of matrices (powders, single crystals, solutions in aqueous glasses, and polymer films) all at 77 K [equation (17)]. In all cases an e.s.r. spectrum, of which Figure 2 is typical, was obtained, featuring the resonances H_{min}, $H_{x(1)}$, $H_{y(1)}$, $H_{x(2)}$, $H_{y(2)}$ and sometimes $H_{z(2)}$ so typical of triplet state species. In later work,[44,45] they were also able to detect triplet state resonance from irradiated arenediazonium salts substituted with several alkoxy or mercapto groups. In these cases, the pattern of substitution is quite critical; 2,4,5-trisubstituted Ar^+ always yields a triplet resonance while any other trisubstitution pattern (or any disubstitution) is in-

$$ArN_2^+ + BF_4^- \xrightarrow[77\ K]{h\nu} Ar^+ + N_2 + BF_4^- \qquad (17)$$

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[42] A. Cox, T. J. Kemp, D. R. Payne, M. C. R. Symons, D. M. Allen, and P. Pinot de Moira, *J.C.S. Chem. Comm.*, 1976, 693.

[43] A. Cox, T. J. Kemp, D. R. Payne, M. C. R. Symons, and P. Pinot de Moira, *J. Amer. Chem. Soc.*, 1978, **100**, 4779.

[44] H. B. Ambroż and T. J. Kemp, *J.C.S. Perkin II*, 1979, 1420.

[45] H. B. Ambroż and T. J. Kemp, *Polish J. Chem.*, in the press.

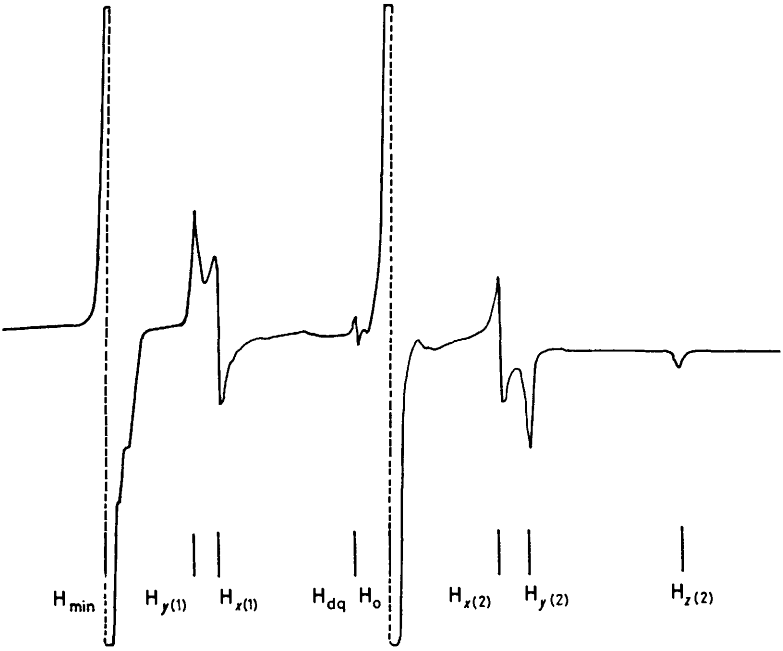
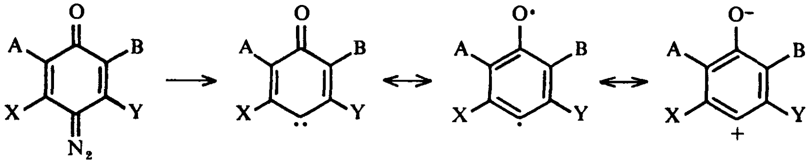


Figure 2 *Triplet e.s.r. spectrum of u.v.-irradiated* 3-chloro-4-di-*n*-butylamino benzenediazonium tetrafluoroborate (*microcrystalline powder*). *Resonance positions occur as indicated in Table* 4: *additionally* H_0 *is at* 3382 G, $H_{\text{double quantum}}$ *at* 3074 G[44]

effective. Particularly noteworthy is the triplet resonance from 2,4,5-trimethoxyphenyl cation, but the absence of resonance from 2,4,6-trimethoxyphenyl cation which is presumably singlet in character. In Table 4 are summarized representative examples of these studies, including the triplet state D and E parameters; the D parameters in particular show a dependence on the various π-stabilizing and σ-stabilizing influences of various substituents on the ring. It is of interest to note the early claim of Wasserman *et al.*[46] (and later of Koser[47]) to have prepared a type of aryl cation in the photolysis of diazo-oxides, *viz.*

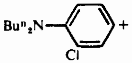
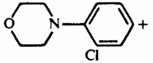
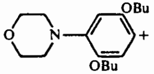
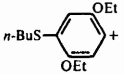
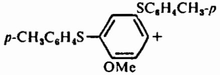
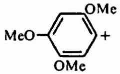


(18)

A, B, X, Y = H	$D = 0.3179$,	$E = 0.0055\ \text{cm}^{-1}$	(ref. 46)
A, B = Cl; X, Y = H	$D = 0.3284$,	$E = 0.0086\ \text{cm}^{-1}$	(ref. 46)
A, B = H; X, Y = Cl	$D = 0.3470$,	$E = 0.0010\ \text{cm}^{-1}$	(ref. 46)
A, X = C_4H_4; B, Y = H	$D = 0.3333$,	$E = 0.0112\ \text{cm}^{-1}$	(ref. 46)
A, B = Bu^t; X, T = H	$D = 0.3141$,	$E = 0.0051\ \text{cm}^{-1}$	(ref. 47)

[46] E. Wasserman and R. W. Murray, *J. Amer. Chem. Soc.*, 1964, **86**, 4203.
[47] G. F. Koser, *J. Org. Chem.*, 1977, **42**, 1474.

Table 4 *Triplet state resonance from Ar^+: field positions and triplet state parameters*/G [1 mT = 10 G]

Ar^+	H_{min}	$H_{z(1)}$	$H_{y(1)}$	$H_{x(1)}$	$H_{x(2)}$	$H_{y(2)}$	$H_{z(2)}$	D/cm^{-1}	$-E$/cm^{-1}
p-$Et_2NC_6H_4^+$	421	467	1215	1355	4527	4668	—	0.269	0.0038
	951	—	1685	1894	4309	4562	5827	0.2278	0.0069
	1116	—	1992^a		4325^a		—	0.204	*ca.* zero
	913	823	1745^a		4473^a		5886	0.235	*ca.* zero
	1331	—	2264	2343	4127	4236	5259	0.168	0.0029
	1566	—	2676	2888	3774	3999	—	0.102	0.0067
	1296	—	2183	2279	4169	4282	5293	0.178	0.0032

^{a}Unresolved peak H_{xy}

The relatively large values of *D* in this series reflects the very strong π-stabilizing character of the —O⁻ substituent.

The other principal claim to have identified Ar^+ spectroscopically is due to Becker's group[48] who subjected various ArN_2^+ salts in water to flash photolysis, obtaining visible spectra of transient species absorbing in the region 400—500 nm. However, this claim has subsequently been withdrawn,[49] an assignment to phenoxy-radicals being preferred. Payne[50] has recorded u.v.-visible spectra of photolysed solutions of $ArN_2^+BF_4^-$ at 77 K under conditions when these are *known* to give triplet e.s.r. resonance of Ar^+; however, $Ar^\cdot$ is always produced with Ar^+ and it is not clear to which of these transient species his spectra should be assigned.

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[48] H. Böttcher, H. G. O. Becker, V. L. Ivanov, and M. G. Kusmin, *Chimia*, 1973, **27**, 437.

[49] H. G. O. Becker, E. Fanghänel, and K. Schiller, *Wissenschaftliche Zeitschrift Techn.-Hochsch. Leuna-Merseburg*, 1974, **16**, 322.

[50] D. R. Payne, Ph.D Thesis, University of Warwick, 1978.