from the bulk (where symmetry of forces exists), the molecule will become polarized. Frohlich[3] has considered the general case of a dielectric in a field. He consideres one molecule to be contained in a spherical volume element, V, of a dielectric which polarizes to yield a dipole $\mathbf{m} = (-e)\mathbf{r}$. There will then be an interaction between the polarized sphere and the surroundings, giving rise to an interaction free energy, $F_e = -(4\pi/3)(M^2/V)[(\epsilon_s - 1)/(2\epsilon_s + 1)]$. We suggest that the energy per unit area, γ, arises from Frohlich's F_e, the energy per molecule, created when molecules are brought into the surface and thereby polarized. This is concordant with the usual assumption of the role of London dispersion forces in surface tension. The rather remarkable result is that there is an intimate correlation between the surface tensions of such diverse dielectric liquids. These correlations may be used to estimate reasonable values of γ from n for non-hydrogen-bonded polar liquids and fairly accurate values for nonpolar liquids.

(3) H. Frohlich, "Theory of Dielectrics," Oxford University Press, London, 1958.

Electronic Structures of Substituted Aryl Cations

E. M. Evleth* and P. M. Horowitz

Contribution from the Division of Natural Science, University of California, Santa Cruz, California 95060. *Received February 11, 1971*

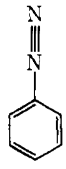
Abstract: INDO calculations of the electronic structures of the phenyl cation and the 4-aminophenyl cation indicate that the relative energies of the filled-shell singlet and open-shell triplet are strongly substituent dependent. For the case of the phenyl cation, the ground state is predicted to be a singlet σ cation with the nearest triplet being at much higher energies. In the 4-aminophenyl cation, the lowest triplet is predicted to be a π cation, while the singlet is a filled-shell σ cation. Both these states have nearly the same energy. Test calculations on the phenyl radical, the 4-aminophenyl radical, pyridine, and pyridine cation indicate that the INDO predictions are not completely reliable and therefore the results on the phenyl cation calculations are in question.

The thermal solvolysis of arenediazonium cations in acidic aqueous or alcoholic media is mechanistically complex. The exact nature or even existence of distinct intermediates in either the thermal or photochemical solvolyses of these materials is not known. Earlier work proposed the phenyl cation ($C_6H_5^+$, I) as a distinct intermediate in the solvolysis of benzenediazonium cation (II).[1,2] This is still in doubt.[3] That radical intermediates exist in the thermal acidic solvolysis of arenediazonium cations in methanol seems likely.[4]

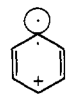
Not only is the possible existence of distinct intermediates in doubt, but the electronic character of the transition state of arenediazonium cation thermal solvolysis is confusing. The substituent effect[1,2] on solvolysis cannot be easily analyzed within the context of a normal or an acceptably modified Hammett σ–ρ relationship.[5] The conclusions drawn for this anomaly are that either a mechanistic change occurs which is substituent dependent or there is something unusual about the electronic character of the transition state compared to those systems which give normal Hammett σ–ρ relationships. Taft argues[6] that the strong meta-substituent effects on this reaction indicate some biradical character[7] in the transition state. Such an argument does not depend on the actual kinetic existence of a phenyl or substituted-phenyl cation. However, the possible biradical character of the phenyl or substituted-phenyl cation implies that such an intermediate might undergo radical-like reaction processes in nonaqueous media.

This paper addresses itself to the theoretical acceptability of the possible biradical ground-state character of aryl cations. A preliminary qualitative analysis[8] of this problem came to the conclusion that it was likely that the corresponding singlet and triplet forms (III) of the phenyl π cation are more stable than the σ cation form I. This qualitative argument is based on the localized orbital view that the positive charge in ion I is located mainly on the carbon having the "empty" sp^2 orbital. Since the pure p orbital has a lower


I



II



III

(one resonance form)

(1) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1949).

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 1st ed, Cornell University Press, Ithaca, N. Y., 1953, pp 799–802.

(3) (a) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Amer. Chem. Soc.*, **91**, 419 (1969); (b) E. S. Lewis and R. E. Holliday, *ibid.*, **91**, 426 (1969); (c) E. S. Lewis, R. E. Holliday, and L. D. Hartung, *ibid.*, **91**, 430 (1969), and references cited in these papers.

(4) T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970).

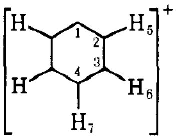
(5) D. Schulte-Frohlinde and H. Blume, *Z. Phys. Chem. (Frankfurt am Main)*, **59**, 299 (1968). These authors obtained a rough correlation between log (solvolysis) *vs.* the sum of σ(inductive) + σ(mesomeric) for para substituents and the sum of σ(inductive) + 0.33σ(mesomeric) for meta substituents. The theoretical interpretation of even this rough correlation escapes us.

(6) R. W. Taft, *J. Amer. Chem. Soc.*, **83**, 3350 (1961).

(7) (a) R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965); (b) R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc. B*, 479 (1968). Reference 7a quotes unpublished work of I. Absar and K. L. McEwen on calculations of the electronic state of the phenyl cation. No quantitative information is given.

(8) R. J. Cox, R. Bushnell, and E. M. Evleth, *Tetrahedron Lett.*, 207 (1970).

Table I. Calculated Electronic Structures of the Lowest Singlet and Triplet of the Phenyl Cation



		Singlet		Triplet			
Atom	Atomic orbital[a]	Electron densities	Total	Electron densities	Total	Spin densities[b]	Hyperfine coupling constant
1	s	1.158		1.221		0.178	146
	$p_x + p_y$	1.409	3.688	1.719	3.907	0.793	
	p_π	1.121		0.967		0.067	
2	s	1.052		1.055		−0.018	−14
	$p_x + p_y$	1.908	3.952	1.858	3.927	0.075	
	p_π	0.992		1.014		−0.043	
3	s	1.039		1.053		−0.002	−1.5
	$p_x + p_y$	1.887	3.909	1.871	3.929	0.094	
	p_π	0.983		1.005		0.027	
4	s	1.045		1.054		−0.009	−7.2
	$p_x + p_y$	1.973	3.946	1.848	3.898	0.126	
	p_π	0.929		0.996		−0.034	
5	s		0.911		0.876	0.168	90.9
6	s		0.942		0.888	0.139	75.0
7	s		0.940		0.958	−0.001	−0.4
Energy	−44.2496			−44.1222			
Symmetry	$^1A_1$ (σ)			$^3B_2$ (σ)			

[a] s = 2s orbital, $p_x + p_y$ = in-plane 2p orbitals, p_π = p orbital perpendicular to the molecular plane. Energies given in atomic units (au).
[b] Atomic orbital spin densities.

valence-state ionization potential[8] than the sp^2 hybrid, it was argued that it would be energetically downhill for ion I to convert to ion III. In this view ion I is an excited state of either the singlet or triplet forms (III) of the phenyl cation. That this is not computationally true within the context of INDO semiempirical molecular orbital calculations will be shown for the phenyl cation. However, this simplistic view is fulfilled in the case of the *p*-aminophenyl cation.

As the first computational step in a theoretical analysis of the problem of the thermal and photochemical solvolysis reaction of arenediazonium cations, we have done INDO calculations on the electronic structures of the lowest energy filled-shell singlet and triplet states of phenyl cation and *p*-aminophenyl cation. In an attempt to test the possible validity of these calculations we have also investigated the electronic structures of phenyl radical, the *p*-aminophenyl radical, pyridine, and the pyridine cation.

Method of Calculation

The calculations reported here were done using the Quantum Chemistry Program Exchange (Bloomington, Ind.) Program No. 141. The program was used in the standard INDO open-shell mode for the doublet and triplet states and the INDO closed-shell mode for the singlet states. The formalism of the CNDO–INDO calculations is reported in a number of references[9,10] and will not be repeated here. The geometries of the molecules were calculated from standard bond length.[11] Since an unreparameterized form of the CNDO–INDO calculation is known not to give good estimates of spectroscopic transition energies,[10] our results can only be used as semiquantitative guides as to the relative energies of the lowest fillled-shell singlet and open-shell triplet states of aryl cation. A more complete analysis of the spectral features of arenediazonium cations and aryl cations has only just been initiated. Nevertheless, the results we have obtained are interesting in their own right insofar as they establish that substituted aryl cations might have biradical ground-state character.

Results and Discussion

The Phenyl Cation. As seen by inspecting Table I, the lowest singlet and triplet states of the phenyl cation are predicted to have σ structures ($^1A_1$ and $^3B_2$, respectively). This result is contrary to the qualitative prediction[8] which argued that the ground state should be a π triplet. The separation between the ground-state filled singlet and the triplet state is about 3.5 eV. The sequence of highest filled orbital symmetries and energies (eV) for the closed-shell singlet cation is b_1 (−20.9), a_2 (−20.6), b_2 (−20.6). The two lowest unoccupied orbital symmetries and energies are a_1 (−8.2) and b_1 (−3.2). Thus the two highest filled MO's are accidently degenerate. Even without knowing the values of the molecular Coulomb and exchange integrals, it seems likely that the calculated lowest energy π–σ^* and σ–σ^* singlet–triplet transitions would have similar values. In addition the lowest σ^* unfilled orbital (a_1) is largely localized (*ca.* 70%) on the electron-deficient carbon atom (1). Thus it also seems likely that the corresponding cation π triplet of $^3A_2$ symmetry has a structure approaching the biradical structure. In any case, the calculation indicates both the σ and π triplets to have energies much higher than the filled-shell singlet.

The 4-Aminophenyl Cation. In contrast with the above results on the phenyl cation, the calculation of the 4-aminophenyl cation IV predicts (Table II) a near degeneracy of the π-cation triplet state ($^3A_2$) and the σ filled-shell cation singlet ($^1A_1$). The triplet state is pre-

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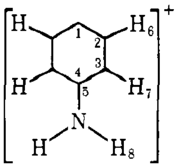
(9) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
(10) H. H. Jaffé, *Accounts Chem. Res.*, 2, 136 (1969).
(11) Reference 9, Table 4.16, p 111.

Table II. Calculated Electronic Structures of the Lowest Singlet and Triplet of the 4-Aminophenyl Cation

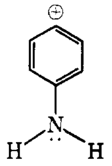


		Singlet		Triplet			
		Electron densities		Electron densities			Hyperfine
Atom	Atomic orbital[a]		Total		Total	Spin densities[b]	coupling constant
1	s	1.149		1.211		0.197	161
	$p_x + p_y$	1.377	3.738	1.868	3.929	0.668	
	p_π	1.212		0.850		0.267	
2	s	1.050		1.037		−0.009	−7.5
	$p_x + p_y$	1.911	3.923	1.940	3.944	−0.023	
	p_π	0.962		0.968		−0.123	
3	s	1.037		1.044		0.023	18.9
	$p_x + p_y$	1.878	3.996	1.941	3.947	0.046	
	p_π	1.081		0.962		0.188	
4	s	1.012		1.016		−0.009	−7.2
	$p_x + p_y$	1.901	3.778	1.841	3.855	−0.034	
	p_π	0.865		0.998		−0.047	
5	s	1.272		1.345		0.043	16.3
	$p_x + p_y$	2.097	5.206	2.325	4.962	0.062	
	p_π	1.837		1.291		0.650	
6	s		0.920		0.960	0.035	18.8
7	s		0.944		0.976	0.000	
8	s		0.856		0.798	−0.035	−19.1
Energy	−56.2282			−56.2395			
Symmetry	$^1A_1$ (σ)			$^3A_2$ (π)			

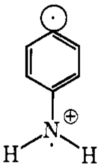
[a] For orbital designation, see footnote *a* Table I. [b] Atomic orbital spin densities.

dicted to be slightly more stable than the lowest filled-shell singlet. This result fulfills expectations as to the possibility of a low-lying triplet state for aryl cations having electron-donating substituents.

Comments on the Electron and Spin Densities of the Phenyl and 4-Aminophenyl Cations. Examination of the spin and electron densities of the triplet state of the 4-aminophenyl cation (Table II) shows that the π-electronic structure is approximated to a large degree by the valence-bond structure IV–VB. Qualitatively, IV–VB looks like a biradical in that the spins are largely localized on the 1-carbon atom (σ) and the nitrogen π orbital. The ground-state singlets IV and I only have a fraction of their total positive charge localized on the "electron-deficient" carbon atom 1 (*ca.* 30%). No simple VB structures rationalize this, but the result is not unexpected. It also occurs in calculations on aliphatic carbonium ions.[12] Even greater charge delocalization occurs in the triplet σ cation (Table I). This result is anticipated to be greater for the triplet because of desire of like spins to be polarized away from one another.



IV



IV-VB

Comments on the Energetic Reliability of These Calculations. In order to analyze the reliability of these results, comparative calculations were performed on the phenyl radical, the 4-aminophenyl radical, pyridine, and pyridine cation. Kasai and coworkers[13] found that INDO calculations on the phenyl radical, the napthyl radical, and a number of related radicals of aromatic hydrocarbons correctly predicted the spin densities in these radicals. In addition, the calculations also reflected the σ-radical structures of these aromatic radicals. Kasai and coworkers had anticipated that in large aromatic radical systems the π molecular orbitals would become higher in energy than the σ orbitals and that eventually a crossover would occur in which a π-radical structure would become more stable than the σ-radical structure. This did not occur either experimentally or theoretically for the systems studied. Thus, the INDO calculations were adequate for these systems. We repeated the calculation on phenyl radical and obtained the same results as Kasai and coworkers. We also found that 4-aminophenyl radical is also predicted to be a σ structure. Thus, the amino group does not sufficiently enrich the π orbitals of the phenyl radical to allow for the demotion of an electron from the π system to the half-filled sp^2 orbital to generate a π radical analogous to the case in the corresponding 4-aminophenyl cation. The qualitative arguments[14] against such a demotion in the case of the radical are twofold. First, such a demotion would localize the electron pair in the sp^2 orbital which has a higher value for the one-centered molecular repulsion integral than the more delocalized π orbital. Second, the zwitterionic resonance structures possible for such a π radical are coulombically unfavorable.

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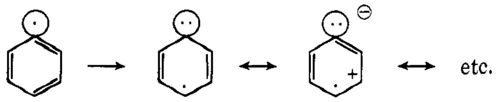
(12) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(13) P. H. Kasai, P. A. Clark, Jr., and E. B. Whipple, *J. Amer. Chem. Soc.*, 92, 2640 (1970).

(14) This is not explicitly argued from resonance structures in ref 13, but Dr. Kasai presented a similar argument during a seminar given at the University of California, Santa Cruz, in 1969.



In the corresponding aminophenyl cation π-electron demotion plus the role of isovalent resonance structures tend to work toward the demotion of the π electron into the σ framework. Thus, the apparent correctness of the calculation in the case of phenyl and substituted-phenyl radicals does not directly reflect on the analogous case of the substituted-phenyl cation. From the energy difference between the phenyl radical and the phenyl cation we calculated directly (Koopmans' theorem does not apply to open-shell systems) the ionization potential of the phenyl radical, 9.7 eV. Although this is not far from the experimental value[15] of 9.2 eV, theoretical ionization potential energies are mainly dependent on the atomic work-function (Coulomb) parameters incorporated in the calculations. They are not good indicators of the reliability of the calculations unless large numbers of theoretical values correlate well with experimental values. The corresponding calculated ionization potential of the ionization of 4-aminophenyl radical to give the 4-aminophenyl cation triplet is 9.1 eV, not an unreasonable number. This still does not reflect on the possible accuracy of the prediction that the 4-aminophenyl cation triplet and singlet have about the same energy.

A final set of calculations was done on pyridine and the pyridine cation. All experimental information[16–18] indicates that the lowest ionization potential of pyridine occurs from π orbitals yielding a π cation. Bertus and McGlynn[19] have analyzed this problem also using a semiempirical method and obtained the apparently correct orbital sequence for the three highest filled MO's: a_1 (−10.46 ev), b_1 (−9.37), a_2 (−9.35). The a_1 orbital is σ (highly nitrogen localized) and the latter two are π orbitals. This orbital sequence is not equivalent to the *ab initio* limited-basis-set calculations of Clementi.[20] Both sets of workers predict a π-cation structure for the pyridine cation.

Two sets of CNDO calculations on pyridine predict, on the basis of Koopmans' theorem, that pyridine cation should have a σ structure.[21,22] Our INDO sequence for the top three filled highest occupied orbitals in pyridine are b_1 (−13.8 ev), a_2 (−13.5), and a_1 (−11.6). Thus, from Koopmans' theorem, the INDO calculation also predicts a σ structure for the cation. Direct open-shell INDO calculation also yields a predicted σ structure for the pyridine cation ($^2A_1$). The calculated INDO ionization potential of pyridine, as obtained from Koopmans' theorem, is 11.6 eV. However, direct calculation of the ionization potential based on the difference in the calculated energy of pyridine and pyridine cation is 9.8 eV, much closer to the experimental value of 9.3 eV.[16,17] This represents a considerable divergence from the Koopmans' theorem value. The open-shell INDO calculation is unprojected, and the calculated energy for the pyridine cation is not for a true doublet species. Del Bene and Jaffé predict[23] on the basis of their CNDO–CI calculations and Koopmans' theorem a π cation. The ionization potential for pyridine is predicted to be about 1.5 eV higher than observed.

The INDO method yielded adequate calculations in the case of aromatic radicals, but failed in the case of pyridine and pyridine cation. The degree of success in the former case and failure in the latter case is unknown unless calculations of possibly low-lying excited states can be analyzed. This has not been done yet. Del Bene and Jaffé's results show that parameter changes scramble orbital levels in pyridine to a sufficient degree to yield "correct" results. Our results show that the ionization potential energies predicted by direct calculation and from Koopmans' theorem are significantly different. Thus, it is not clear what constitutes a "correct" orbital sequence in a closed-shell calculation.

Our calculations do not address themselves to the relative energy of the singlet form of the biradical. Because of the large spatial separation of the electrons involved in the π biradical, it can be assumed that there is not a large energy difference between the singlet and triplet forms of the biradical, somewhat analogous to the case of the low splitting between n–π* singlets and triplets. However, if this is the case and there is a low energy separation between the singlet filled-shell σ cation and singlet open-shell biradical cation, the danger exists that the single-determinate wave function badly breaks down because of the lack of inclusion of configuration interaction.

Conclusion

The results cast doubt on the relative energetic reliability of the calculations. However, it is established that the aryl cation calculations are very sensitive to the effect of an electron-donating substituent. The energy gap of 3.5 eV between the filled-shell singlet and lowest triplet in phenyl cation is removed on the substitution of an amino group. Along with Taft's analysis,[6] these results are suggestive of the possibility of the presence of more than one electronic species in arenediazonium cation thermal chemistry. We have already commented[8] on the orbital symmetry problem of correlating the ground and excited states of arenediazonium cations with those of the aryl cations.

Acknowledgments. The authors thank both NASA and the Faculty Research Committee of the University of California, Santa Cruz, for their aid.

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(15) I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, **86**, 2741 (1964).

(16) M. A. El-Sayed, M. Kasha, and Y. Tanaka, *J. Chem. Phys.*, **34**, 334 (1961).

(17) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

(18) M. R. Basila and D. J. Clancy, *J. Phys. Chem.*, **67**, 1551 (1963).

(19) B. S. Bertus and S. P. McGlynn, "Sigma Molecular Orbital Theory," O. Sinanoğlu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, pp 293–300.

(20) E. Clementi, *J. Chem. Phys.*, **46**, 4731 (1967).

(21) A. Pullman in ref 19, p 285.

(22) J. E. Bloor and D. L. Breen, *J. Amer. Chem. Soc.*, **89**, 6835 (1967).

(23) J. Del Bene and H. M. Jaffé, *J. Chem. Phys.*, **50**, 563 (1969).