

AB INITIO STUDIES OF AMINOPHENYL CATIONS

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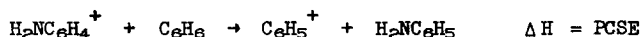
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Attempts to generate phenyl or substituted phenyl cations by solvolysis of aryl triflates have to date met with no success.¹ Although there is evidence for phenyl cations derived from decomposition of benzenediazonium ions,² it is clear from available data that the phenyl cation is a highly unstable species.³ Can substituents alter this situation? Ab initio molecular orbital calculations provide an excellent and time saving probe of stabilizing possibilities. In this paper, we make such an investigation of the influence of a simple stabilizing group, NH₂, attached to the singlet phenyl cation in various positions and orientations.⁴

Calculations were performed at the STO-3G level of approximation, using standard geometrical models.⁵ For ortho, meta, and para isomers, four conformations of the amino group were considered trigonal planar having HNH either coplanar with the ring plane or orthogonal to it (Table I, "planar" and "perpendicular" forms), or pyramidal with the nitrogen lone-pair in the plane of the ring. In the latter cases, the HNH plane is tilted either toward ("cis") or away from ("trans") the positively charged carbon, for para isomers, only one such form is possible ("bent"). In order to assess the stabilizing influence of the substituent, we list in Table I the "phenyl cation stabilization energies" defined by



A positive PCSE value indicates the aminosubstituted cation to be stabilized relative to C₆H₅⁺.⁷ The neutral H₂NC₆H₅ species are calculated in the same conformations as the cations H₂NC₆H₄⁺.

Before examining trends of interest, we consider the predicted magnitudes of amino stabilization. Of greatest effectiveness is para, planar substitution; an amino group in this arrangement stabilizes the phenyl cation by 11.3 kcal/mole. This value may be calibrated by comparing

phenyl with other cations. For example, the reaction $R^+ + C_6H_6 \rightarrow C_6H_5^+ + R-H$ is endothermic even for such unstable R^+ as the ethyl cation, experimental reaction energies³ are +10.9 for R = ethyl, +29.1 for allyl, and +33.4 for isopropyl. Clearly the 11.3 kcal stabilization afforded by amino substitution is insufficient to produce a phenyl cation even loosely classified as stable. .

Table I. Energies

		Total Energy, Hartrees	Relative Energy, ^a kcal/mole		PCSE, kcal/mole
Aminophenyl Cations					
Ortho	Planar	-281.26604	6.5	0.0	4.7
	Trans	-281.25543	13.2	6.7	2.7
	Perpendicular	-281.24722	18.4	11.8	3.7
	Cis	-281.24660	18.7	12.2	-2.9
Meta	Planar	-281.26626	6.4	0.0	4.9
	Cis	-281.25651	12.5	6.1	3.3
	Trans	-281.25492	13.5	7.1	2.3
	Perpendicular	-281.25209	15.3	8.9	6.7
Para	Planar	-281.27647	0.0	0.0	11.3
	Bent	-281.25298	14.7	14.7	1.1
	Perpendicular	-281.24656	18.8	18.8	3.2
Phenyl Cation		-226.94399			0.0
Benzene		-227.89006 ^b			
Anilines					
	Planar	-282.20458 ^b		0.0	
	Bent	-282.19727		4.6	
	Perpendicular	-282.18746		10.7	

^a First column is for entire series. ^b Ref. 9

The general problem of stabilizing a phenyl cation has been considered previously by Gleiter, Hoffmann and Stohrer⁸ using extended Huckel theory. They considered two mechanisms. one a "through-bond" interaction between the formally empty orbital on the charged carbon (the $p(C^+)$)

orbital) and the lone pair orbital (in conformations with the lone pair axis in the phenyl plane) and the other a destabilizing inductive effect, the magnitude of which decreases with increasing distance between $p(C^+)$ and the lone pair.

The conclusions to be drawn from Table I, which differ somewhat from those which might be inferred from the work of Gleiter *et al.*,⁸ are as follows

1. The greatest stabilization of the phenyl cation (11.3 kcal/mole) is achieved with a para amino group in a planar conformation.
2. In all the planar conformations (o, m and p), stabilization is obtained, despite the fact that through-bond interaction between the lone-pair and the vacant orbital is conformationally prohibited. According to Gleiter *et al.*,⁸ only the destabilizing inductive effect should be operative in these cases
3. Generally, the phenyl cation is less stabilized by the amino group if the lone-pair axis lies in the phenyl plane. The only exception is the perpendicular arrangement in the meta position.
4. Among the possible conformations with lone-pair axes in-plane, those with the perpendicular arrangement (planar at nitrogen) are more effective in stabilizing the cation than the "cis" or "trans" pyramidal structures (see final column of Table I).
5. Among the lone-pair in-plane forms, the order of increasing stabilization is $p < o < m$ rather than $o < m < p$ as the distance argument⁸ would predict

Some remarks can be made on the interpretation of these results. In the first place, there is a reasonable correlation between the PCSE and the amount of charge dispersal of the cation as given by Mulliken population analysis. When the lone pair axis on nitrogen is orthogonal to the ring (planar isomers), there is a substantial degree of π -donation and σ -withdrawal, the net result of which is a high electron density in the ring. This dominant effect is clearly most effective in the planar conformations. The extent of such π -donation is reflected by relatively large C-N π -type overlap populations.

For the in-plane conformations, the perpendicular arrangement (planar at nitrogen) will lead to greatest availability of the lone-pair electrons so that their interaction with the σ -framework of the phenyl cation will be greatest, as illustrated by the stabilization energies. In the para position (perpendicular conformation), however, the symmetry of the lone pair orbital (b_2 for point group C_{2v}) will be different than that of the vacant orbital (a_1 for point group C_{2v}) and through-bond stabilization cannot occur. The stabilization found must be due to interaction with other b_2 orbitals

In conclusion, our data suggest that the stabilization of the phenyl cation by an amino substituent is most effective by a π -donation mechanism (greatest in the para position). Through-bond stabilization by an amino group with an in-plane lone-pair axis is less effective but is greatest in the meta-position. However, as mentioned above, the maximum stabilization afforded by any such substitutions may be too small to be of practical significance, at least as far as possible solvolytic generation of aryl cations is concerned.

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2. (a) C.G. Swain, J.E. Sheats, and K.G. Harbison, J. Amer. Chem. Soc , 97, 783, 796 (1975), (b) C.G. Swain, J.E. Sheats, D.G. Gorenstein, and K.G. Harbison, ibid , 97, 791 (1975), and (c) H. Zollinger, Accts. Chem. Res., 6, 335 (1973), and references cited therein
3. Experimental heats of formation for cations (kcal/mole): phenyl = 270 (T.B. McMahon, Ph.D. Thesis, California Institute of Technology, 1973), ethyl = 219, allyl = 226, isopropyl = 291 (F.P. Lossing and G.P. Semeluk, Can. J. Chem , 48, 955 (1970), 49, 357 (1971)).
4. (a) Cf. E.M. Evleth and P.M. Horowitz, J. Amer. Chem. Soc , 93, 5636 (1971) and ref. 8, and (b) We are currently pursuing further studies of singlet and triplet $X-C_6H_4^+$ species for $X = In, BeH, BH_2, CH_3, NH_2, OH,$ and F. J.D. Dill, P.v R. Schleyer, and J.A. Pople, to be submitted for publication.
5. $CC = 1.40A, C-H = 1.08, C-N = 1.40, N-H = 1.01$. All angles 120° except when tetrahedral at N in pyramidal forms. The assumption of benzene geometries here and in refs. 4 and 8 may be a poor one, Haselbach^{6a} has found at the MINDO/2 level, Bischof with MINDO/3^{6b} and we at STO-3G that the singlet phenyl cation is far from being a regular hexagon. Optimized geometries will be given in a forthcoming publication, these differ significantly from the unrealistic structure ($\angle C-C-C = 180^\circ$) found by the INDO method in ref. 2b.
6. (a) E. Haselbach, private communication, (b) P. Bischof, private communication.
7. Note that this is the reverse of the stabilization reaction of reference 8.
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