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Molecular Orbital Theory of the Electronic Structure of Molecules. 31. Substituent Stabilization of the Phenyl Cation

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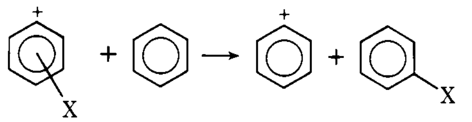
Abstract: Ab initio (STO-3G standard geometry) calculations are reported for singlet and π-type triplet series of substituted phenyl cations $X\text{-}C_6H_4^+$, where X = (ortho, meta, and para) Li, HBe, H_2B, H_3C, H_2N, HO, and F. The singlet is best stabilized by σ donors, o > m > p, but π donors are also effective (p > o > m). Triplet states are stabilized by π donors (p ~ o > m) to such an extent that triplet ground states are predicted for X = NH_2 and OH. σ donors also stabilize the triplet. These patterns reflect charge distributions in the parent phenyl cations and in the corresponding substituted benzenes.

Several methods are used to generate carbocations in solution.[2] Of these, only one (dediazoniation) has succeeded in producing phenyl cations.[3,4] The effects of substituents on this reaction have been studied[5-7] and found to be relatively small, but due to the nature of kinetic studies it cannot necessarily be concluded that substituents are incapable of significantly stabilizing the phenyl cation. In order to investigate this situation more directly, we have undertaken an ab initio study of a series of substituted phenyl cations.

In a previous paper[8] the unsubstituted phenyl cation was examined in detail. The singlet ground state and two ($^3B_1$, $^3A_2$) low-lying triplet excited states were found to have different geometric and electronic structures; the positive charge in the singlet residues in the σ system but is delocalized throughout the π system in both triplets. Substituents should thus influence the various states differently. Some information concerning stabilization of the singlet by NH_2 has already been published.[9] In this paper, we present a more extensive study of singlet and π-type triplet phenyl cations $X\text{-}C_6H_4^+$, where substituents X (Li, BeH, BH_2, CH_3, NH_2, OH, F) are considered in ortho, meta, and para positions and in various conformations. Of particular interest are the rotational isomers of $H_2N\text{-}C_6H_4^+$ and $H_2B\text{-}C_6H_4^+$, which permit a distinction to be made between σ and π effects.[9,10]

Although theoretical equilibrium geometries of the singlet and triplet phenyl cations are quite different,[8] we considered it adequate to employ benzene geometries for the present study of substituent effects. Since charge distributions are relatively insensitive to geometrical variations, perturbations of electronic structure due to substitution should yield meaningful information regardless of geometry. Singlet-triplet differences are not given well by singlet-determinant molecular orbital theory even with accurate geometries. Correction of errors due to variations in geometry would therefore not be sufficient to provide realistic singlet-triplet differences; instead, an attempt is made to circumvent this difficulty by calibrating the results against known singlet-triplet separations. Finally, geometrical errors roughly cancel in the assessment of substituent stabilizations, for which we employ the isodesmic[11] formal reaction 1. The following assumptions are implicit: (1) all phenyl units



(1)

are of benzene geometry; (2) electronic states of $X\text{-}C_6H_4^+$ and $C_6H_5^+$ are identical, so that singlet $X\text{-}C_6H_4^+$ is compared with singlet ($^1A_1$) $C_6H_5^+$, and triplet ($^3B_1$) $C_6H_5^+$ is compared with the corresponding π-type triplet of $X\text{-}C_6H_4^+$; and (3) conformations of the substituent groups are identical in $X\text{-}C_6H_4^+$ and $C_6H_5\text{-}X$. Thus, a positive energy for reaction 1 (positive stabilization energy) indicates stabilization of the phenyl cation by X relative to its effect on benzene.

Methods

The calculations were performed with the Gaussian 70 series of programs[12,13] using the STO-3G minimal basis set and standard valence-shell scaling factors.[14] Open shell species were calculated with the unrestricted Hartree-Fock procedure.[15] It was found necessary in some cases to alter the standard initial guess in order to obtain wave functions of the desired symmetry, and slow convergence (up to 80 cycles) of the SCF procedure was experienced for several of the triplet species.

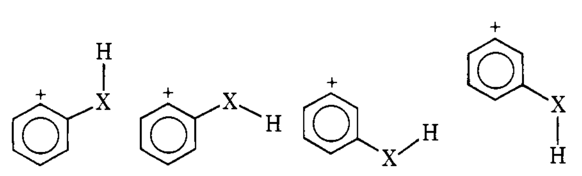
Standard bond lengths were assumed throughout.[10,16] Bond angles A-X-B were taken to be 180° for X = Be, 109.471 22°

Table I. Calculated (STO-3G) Energies of Substituted Phenyl Cations X-$C_6H_4^+$

			Singlet state[c]		Triplet state[d]	
X	CCXH conformation	Position	Total energy[a]	Rel energy[b]	Total energy[a]	Rel energy[b]
H			−226.943 99		−227.004 96	
Li		Ortho	−233.745 22	0	−233.793 08	0
		Meta	−233.715 12	18.9	−233.776 72	10.3
		Para	−233.704 46	25.6	−233.789 70	2.1
HBe		Ortho	−241.396 21	0	−241.449 03	0
		Meta	−241.388 64	4.8	−241.447 38	1.0
		Para	−241.383 60	7.9	−241.443 51	3.5
H_2B	Coplanar	Ortho	−251.899 26	0.1	−241.955 48	6.9
		Meta	−251.899 42	0	−251.961 59	3.0
		Para	−251.892 94	4.1	−251.949 54	10.6
H_2B	Orthogonal	Ortho	−251.892 49	4.3	−251.964 63	1.1
		Meta	−251.890 41	5.7	−251.959 41	4.4
		Para	−251.891 08	5.2	−251.966 42	0
H_3C	Coplanar, syn[e]	Ortho	−265.533 38	0.7		
		Meta	−265.534 10	0.2	−265.603 82	3.8
		Para	−265.534 42	0	−265.609 81	0
H_3C	Coplanar, anti[e]	Ortho	−265.533 93	0.3	−265.596 69	8.2
		Meta	−265.533 86	0.4		
		Para	−265.534 42	0	−265.609 81	0
H_2N	Coplanar	Ortho	−281.266 04	6.5	−281.409 05	0.0
		Meta	−281.266 26	6.4	−281.377 22	20.0
		Para	−281.276 47	0	−281.409 12	0
H_2N	Orthogonal	Ortho	−281.247 22	18.4	−281.314 16[f]	59.6
		Meta	−281.252 09	15.3	−281.314 74	59.2
		Para	−281.246 56	18.8	−281.310 93	61.6
HO	Coplanar, syn[e]	Ortho	−300.770 89	10.0	−300.891 06	0.6
		Meta	−300.780 53	3.9	−300.867 61	15.3
		Para	−300.786 78	0	−300.892 00	0
HO	Coplanar, anti[e]	Ortho	−300.781 95	3.0	−300.890 29	1.1
		Meta	−300.778 99	4.9	−300.864 61	17.2
		Para	−300.786 78	0	−300.892 00	0
F		Ortho	−324.389 60	5.1	−324.476 27	2.3
		Meta	−324.393 59	2.6	−324.468 89	6.9
		Para	−324.397 74	0	−324.479 95	0

[a] Hartrees. [b] Energy (kcal mol^{-1}) relative to lowest energy isomer. [c] Corresponding to $^1A_1$ of $C_6H_5^+$. [d] Corresponding to $^3B_1$ of $C_6H_5^+$. See text. $^3A_2$ at standard geometry = −226.990 72. [e] Syn indicates in-plane H on X is oriented toward C^+, anti indicates away from C^+. [f] $^3A'$ (ionized N lone pair) lies lower, at −281.328 40.

for $C(sp^3)$ and O, and 120° for B, $C(sp^2)$, and N. The latter represents a departure from the standard pyramidal configuration at nitrogen. The amino group was found[9,17] to prefer planarity in singlet aminophenyl cations, in contrast with its pyramidal conformation in aniline,[18,19] and we assumed that triplet aminophenyl cations would also be planar. Dihedral angles CCXH were taken as 0° as found to be favored in the corresponding monosubstituted benzenes.[18] For X = C and X = O there are then two rotamers designated "syn" and "anti", in which in-plane substituent hydrogens are oriented respectively toward or away from the disubstituted carbon (I-IV). Both rotamers were calculated in all cases except for triplet methyl-substituted phenyl cations X = C, where only those forms found to be favored for the singlet state (ortho, anti and meta, syn) were considered. The other two were disregarded due to the negligible syn-anti energy differences observed for the singlets and the expense of these calculations, which converged very slowly in the SCF routine. In addition to planar forms, orthogonal conformations were calculated for NH_2- and BH_2-substituted species.



I ortho, syn II ortho, anti III meta, syn IV meta, anti

Results and Discussion

Calculated total and relative (isomerization) energies of all species are presented in Table I. Various quantities from the Mulliken population analyses of the STO-3G wave functions are given in Table II, in which the notations q_σ and q_π represent transfer of electrons from the ring to the substituent group in the σ system (symmetric with respect to reflection in the ring plane) and π system (antisymmetric with respect to such reflection). The sum of these, q_{tot}, is the total number of electrons transferred. Positive values indicate transfer in the direction Ph → X.

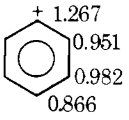
Singlet Phenyl Cation. Information concerning stabilization of the phenyl cation may be obtained by examining its electronic structure apart from substituents. Although the electronic structure of the optimized form has been analyzed elsewhere,[8] it is useful to repeat the arguments with substituent effects in mind. Furthermore, the population values reported here are slightly different due to the assumption of unmodified benzene geometries.

In the standard-geometry phenyl cation, the p populations (π charges) vary as shown in V. π electrons are polarized toward C^+ (C_1) where there is an excess of 0.267 relative to

Table II. Charge Transfer in Substituted Phenyl Cations X-$C_6H_4^+$ [a]

X	CCXH conformation[b]	Position	Singlet state q_σ	Singlet state q_π	Singlet state q_{tot}	Triplet state q_σ	Triplet state q_π	Triplet state q_{tot}
H			−0.153	0	−0.153	−0.151	0	−0.151
Li		Ortho	−0.512	0.052	−0.460	−0.523	0.014	−0.509
		Meta	−0.502	0.051	−0.451	−0.486	0.028	−0.458
		Para	−0.446	0.042	−0.404	−0.524	0.014	−0.510
HBe		Ortho	−0.364	0.057	−0.307	−0.344	0.048	−0.296
		Meta	−0.349	0.059	−0.290	−0.321	0.060	−0.261
		Para	−0.326	0.049	−0.277	−0.348	0.032	−0.315
H_2B	Coplanar	Ortho	−0.292	0.066	−0.226	−0.282	0.046	−0.237
		Meta	−0.280	0.069	−0.211	−0.261	0.070	−0.191
		Para	−0.260	0.056	−0.204	−0.283	0.035	−0.247
H_2B	Orthogonal	Ortho	−0.273	−0.010	−0.283	−0.271	−0.048	−0.319
		Meta	−0.256	−0.007	−0.263	−0.251	−0.026	−0.277
		Para	−0.246	−0.013	−0.259	−0.269	−0.048	−0.317
H_3C	Anti	Ortho	−0.131	−0.018	−0.149	−0.104	−0.019	−0.123
	Syn	Meta	−0.115	−0.017	−0.132	−0.118	−0.034	−0.151
		Para	−0.099	−0.023	−0.122	−0.137	−0.052	−0.189
H_2N	Coplanar	Ortho	0.080	−0.177	−0.097	0.281	−0.731	−0.450
		Meta	0.087	−0.166	−0.079	0.269	−0.694	−0.425
		Para	0.109	−0.196	−0.088	0.276	−0.712	−0.437
H_2N	Orthogonal	Ortho	−0.012	−0.018	−0.030	0.003	−0.039	−0.036
		Meta	−0.015	−0.015	−0.030	0.008	−0.031	−0.023
		Para	0.023	−0.022	0.001	0.013	−0.032	−0.019
HO	Anti	Ortho	0.098	−0.136	−0.038	0.292	−0.581	−0.289
	Syn	Meta	0.104	−0.125	−0.021	0.162	−0.255	−0.093
		Para	0.134	−0.153	−0.019	0.272	−0.529	−0.257
F		Ortho	0.143	−0.095	0.048	0.218	−0.245	−0.027
		Meta	0.147	−0.089	0.058	0.181	−0.151	0.030
		Para	0.170	−0.108	0.062	0.214	−0.232	−0.018

[a] Electrons transferred from substituent to ring in σ system (q_σ), π system (q_π), and total (q_{tot}). Negative values imply X → Ph direction.
[b] Refer to text and Table I.

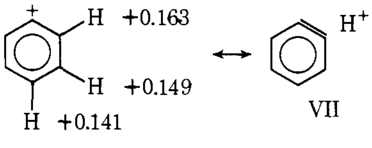


V

π charges

the π charge in benzene. These π electrons cannot be donated directly into the in-plane vacant orbital at C_1, but positive charge can be delocalized by polarization of the π electrons toward C_1. Stabilization should therefore result from an increase of electron density in the π system of the ring; hence a π donor should be favorable.

Stabilization may also result from σ interactions, as inferred from the total charges on hydrogens (VI) compared to that on



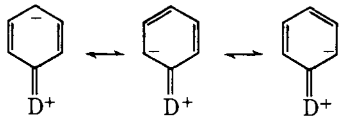
VI

VII

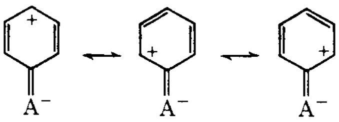
each hydrogen in benzene (+0.063).[18] The high positive charge on ortho hydrogens indicates contributions from hyperconjugative resonance structures such as VII, in agreement with experimental conclusions based on ortho deuterium isotope effects.[3b] Previous studies of stabilization of cationic centers[20] suggest that hyperconjugation will be most favorable if a σ donor substituent is introduced at the ortho position.

The meta and para hydrogens are also highly charged (VI), suggesting that σ donors will be of benefit at these positions as well. Since electrons are being withdrawn from the hydrogens in order to spread the positive charge, the substituents with readily available σ electrons (σ donors) will delocalize charge and lead to stabilization. Conversely, as experimental results have shown,[5-7,21] σ-withdrawing substituents destabilize due to unfavorable inductive effects. Hoffmann et al.[22] have pointed out that this inductive effect varies with distance between the substituent and C^+. Thus σ-withdrawing substituents are most destabilizing at the ortho position, least at para. It follows that σ donors should show an opposite order, being most stabilizing at ortho and least at para.

Substituted Benzenes. Studies of monosubstituted benzenes[18,23] indicate that π charges follow the pattern suggested by the resonance forms VIII (for a π donor D) and IX (for a π acceptor A). Thus, π charges are maximal ortho and para to a π donor but meta to a π acceptor. These positions are expected to be most favorable for removal of a hydride, since the resulting vacant σ orbital will then be nearest the maximum π charge.



VIII



IX

Substituted Singlet Phenyl Cations. Stabilization energies of singlet phenyl cations are given in Table III. These and the conformational and positional preferences in Table I may be explained in terms of σ, π, and steric effects.

σ Effects. Under the general designation "σ effects" are lumped together all interactions which all imply a movement

Table III. Singlet Stabilization Energies[a]

X	Stabilization energy, kcal mol^{-1}		
	Ortho	Meta	Para
Li	56.7	37.8	31.1
HBe	11.6	6.8	3.7
H_2B (coplanar)	2.0	2.1	−2.0
(orthogonal)[b]	4.9	3.6	4.0
H_3C (syn)	3.5	4.0	4.2
(anti)	3.9	3.8	4.2
H_2N (coplanar)	4.8	4.9	11.3
(orthogonal)[b]	3.7	6.7	3.2
HO (syn)	−7.4	−1.3	2.7
(anti)	−0.4	−2.3	2.7
F	−8.6	−6.1	−3.5

[a] Energies of $X\text{-}C_6H_4^+$ (singlet) + C_6H_6 = $C_6H_5^+$ ($^1A_1$) + $X\text{-}C_6H_5$, with identical geometries for PhX systems. [b] Stabilization energy relative to orthogonal $X\text{-}C_6H_5$.

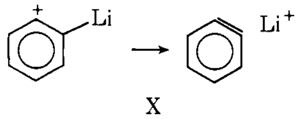
of electrons symmetric with respect to the ring plane. These interactions include inductive effects as well as in-plane hyperconjugation illustrated by VI and VII. (The latter, characterized by overlap of parallel p orbitals, is considered a π-type interaction in many contexts.[20] Here, however, it is less ambiguous to restrict π effects to those with a node in the ring plane.)

Based on electron withdrawal from the ring protons in the singlet phenyl cations (cf. VI), electronic demands in the σ system are expected to be severe. Stabilization energies in Table III clearly demonstrate that those substituents best able to meet these demands, the σ donors Li and HBe, provide much stabilization while σ-withdrawing substituents, e.g., OH and F, fare poorly. Fluorine, in fact, is the one substituent which is destabilizing at every position around the ring. These trends result from inductive effects.

That inductive effects are operative can be seen from the population analysis (Table II). Substituents Li to CH_3 have negative q_σ values and are thus σ donors, while NH_2 to F are σ acceptors. The total number of electrons transferred from substituent to ring (q_{tot}, Table II) roughly parallels the stabilization afforded by that substituent (stabilization energy, Table III). Thus in the case of lithium or beryllium substitution, where the vast majority of the transferred electrons are in the σ rather than the π system, the stabilization must be largely due to inductive effects. In contrast, NH_2 transfers mostly π electrons and confers stabilization due to π effects rather than σ.

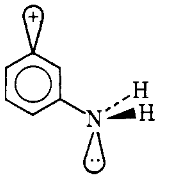
Those substituents exhibiting inductive effects most strongly, Li and F, clearly show the distance dependence suggested by Hoffmann et al.[22] Lithium is most stabilizing when closest (ortho) to C^+; ortho F is most destabilizing. These influences diminish ortho > meta > para. The distance-dependent inductive effect is also observed for BeH, which is most stabilizing at ortho, and OH, destabilizing except at the para position.

Part of this distance effect may be ascribed to in-plane hyperconjugation, a short-range interaction which can occur only with ortho substituents. Consider lithium, for example. A smoothly varying inductive effect should show a regular stability increase in going from para to meta to ortho. Instead, there is a jump at ortho, to a huge (56.7 kcal mol^{-1}!) stabilization. Strong hyperconjugation is evidently occurring, leading to a "lithiated benzyne" (X). For beryllium there is a more regular stability increase from para to ortho, and it is difficult to ascertain in this case whether in-plane hyperconjugation plays a role.

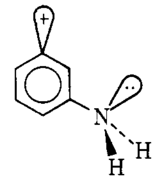


X

"Through-bond stabilization" was proposed by Hoffmann et al.[22] as an important mode of phenyl cation stabilization. This effect involves interaction between the p(C^+) orbital and a coplanar lone pair and is thus sensitive to conformation. However, studies of rotational barriers in aminophenyl cations led us to conclude that through-bond effects were of minor importance in the stabilization of phenyl cations.[9] No through-bond stabilization is possible when the lone pair is orthogonal to the ring plane, yet it is precisely in this arrangement that an amino substituent is most stabilizing. The energy difference between in-plane lone pair conformations XI and XII is small (1.0 kcal mol^{-1} favoring XI)[9] despite the fact that XI should be ideally oriented for through-bond stabilization[22] while XII is not. The stabilization energies in Table III appear to be explicable without invoking such through-bond effects.

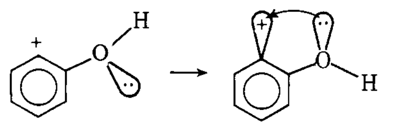


XI

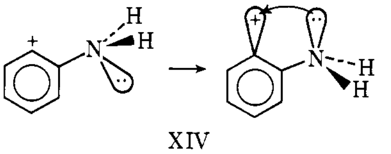


XII

One final type of σ effect deserves mention. In appropriately oriented systems, it is possible for a substituent to donate lone pair electrons directly into the p(C^+) orbital. Such an effect accounts partly for the 7.0 and 5.5 kcal mol^{-1} syn-anti differences, respectively, in ortho hydroxy (XIII) and amino (XIV) systems. These values are taken from Table I (OH) and ref 9 (NH_2).



XIII



XIV

π Effects. In this paper, "π effects" designate electron transfer which occurs in orbitals antisymmetric with respect to the plane of the ring. The population data in Table II serve to classify substituents in this regard: those with positive q_π values (π acceptors) tend to attract part of the six-electron π cloud of the ring into their vacant p orbitals; π donors supplement the ring π cloud with their lone pair or by hyperconjugation. π acceptors increase in effectiveness Li < BeH < BH_2 while π donors vary as F < OH < NH_2. These orderings are opposite those governing σ effects.

It is appropriate to comment on the general nature of "first-row sweep" substituent studies, which we have fond to be illuminating in a number of investigations.[10,23] In examining the series Li to F, a complete range of effects is scanned. At the electropositive end is lithium, a powerful σ donor but relatively weak π acceptor despite its two vacant p orbitals. Proceeding to BeH and BH_2, σ effects decrease in importance while vacant p orbitals become lower in energy and more effective as acceptors. CH_3 is intermediate, being weakly π donating due to hyperconjugation and at the same time weakly σ withdrawing (relative to hydrogen). The groups NH_2 to F are "mirror images" of BH_2 to Li, going from strongly π donating, weakly σ accepting (NH_2) to weakly π donating, strongly σ accepting (F). Thus, although there is a gradation of σ and π effects along the series, σ effects dominate with Li and F while BH_2 and NH_2 (in planar but not perpendicular conformations) show predominant π effects. The "first-row sweep" is thus an effective tool for understanding the electronic demands of a system of interest.

Returning to singlet phenyl cations, we now consider stabilization energies for π interacting BH_2 and NH_2 substituents (Table III). In the para position, NH_2 affords 11.3 kcal mol^{-1} of stabilization while BH_2 is weakly destabilizing. As anticipated from the dominant resonance structures of substituted benzenes, BH_2 is best at the meta position in the singlet cation, while NH_2 is best para. These are the positions where π density is highest in $C_6H_5BH_2$ and $C_6H_5NH_2$. σ effects operate in addition to π effects, so that at the ortho position BH_2 is slightly inductively stabilizing while NH_2 is destabilizing.

Now consider 90° rotation of these groups. In the case of (nonpyramidal) NH_2, such rotation prevents donation of lone-pair electrons to the ring, while rotation of BH_2 prevents interaction between ring π electrons and the vacant orbital on boron. Thus, both $H_2NC_6H_4^+$ and $H_2BC_6H_4^+$ prefer planar rather than orthogonal conformations. Rotation barriers (from Table I) are 11.9 kcal mol^{-1} (ortho NH_2), 8.9 (meta NH_2), 18.8 (para NH_2), and 4.2 (ortho BH_2), 5.7 (meta BH_2), and 1.1 (para BH_2).

Rotation does not destroy *all* π-type interaction between ring and substituent. In orthogonal conformations, NH_2 and BH_2 groups still provide some π electron density to the ring by hyperconjugation. This may be seen in the population analysis in Table II. Para NH_2, for example, provides $q_\pi = -0.196$ lone-pair electrons when coplanar with the ring. Upon rotation the electron donation is reduced to $q_\pi = -0.022$, this value being due to hyperconjugation. Similarly, 90° rotation converts a (para) BH_2 substituent from a π acceptor ($q_\pi = +0.056$) to a hyperconjgative π donor (orthogonal $q_\pi = 0.013$). The energetic consequences of such interaction are best seen in the stabilization energies (Table III), which compare coplanar $H_2X\text{-}C_6H_4^+$ (X = B, N) with coplanar $H_2X\text{-}C_6H_5$ and orthogonal $H_2X\text{-}C_6H_4^+$ with orthogonal $H_2X\text{-}C_6H_5$. Thus whereas a planar BH_2 is weakly stabilizing at ortho and meta and is destabilizing at para, orthogonal BH_2 is significantly stabilizing at all positions. NH_2, on the other hand, becomes a less potent π donor upon rotation and is thus less stabilizing in the orthogonal conformation (except in the meta position, where π donation is least important).

Steric Effects. In $X\text{-}C_6H_5$, the substituent X is flanked by two hydrogens, as it is in meta or para but not in ortho $X\text{-}C_6H_4^+$. If X is bulky there is a possibility that the ortho isomer may be stabilized relative to meta and para. The data in Tables I and III do not show this effect for the X groups considered. Planar ortho NH_2 and BH_2 substituents are bulkiest, but σ and π effects already discussed seem to explain their stabilizations relative to meta and para isomers adequately and no good case can be made for steric influences. In addition, neither CH_3 nor OH substituents at ortho positions prefer syn to anti conformations as the steric argument would imply. Steric effects will not be considered further in this paper.

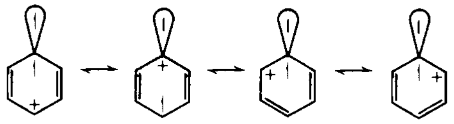
Triplet Phenyl Cation. In the unsubstituted C_{2v} phenyl cation, the two low-lying triplet states are designated $^3B_1$ and $^3A_2$. Both are π-type triplets but are easily distinguished by the presence of a nodel plane which in $^3A_2$ passes through C_1 and C_4. In substituted systems with symmetry lower than C_{2v}, distinction between the two π-type triplet states, both now designated ^3A,[11] becomes more difficult. As long as the substituent is weakly interacting the highest occupied π orbitals still retain b_1 and a_2 character; that is, the former has large p coefficients at C_1 and C_4, the latter small. In such a case, "$^3B_1$-like" and "$^3A_2$-like" states can be distinguished. With more strongly interacting substituents the distinction becomes less clear.

Table IV. Triplet Stabilization Energies[a]

X	Stabilization energy, kcal mol^{-1}		
	Ortho	Meta	Para
Li	48.4	38.2	46.3
HBe	6.5	5.4	3.0
H_2B (coplanar)	−1.0	2.9	−4.7
(orthogonal)[b]	11.9	8.6	13.0
H_3C	5.0[c]	9.5[d]	13.2
H_2N (coplanar)	56.2	36.3	56.3
(orthogonal)[b]	7.4	7.8	5.4
HO (syn)	29.8	15.1	30.4
(anti)	29.3	13.2	30.4
F	7.5	2.9	9.8

[a] Energies of $X\text{-}C_6H_4^+$ (triplet) + $C_6H_6 \rightarrow C_6H_5^+$ ($^3B_1$) + $X\text{-}C_6H_5$ with identical geometries for PhX systems. [b] Stabilization relative to orthogonal $X\text{-}C_6H_5$. See text. [c] Anti. [d] Syn.

In the parent system, 4-31G calculations at STO-3G optimized geometries[8] indicate $^3B_1$ to lie 2.7 kcal mol^{-1} below $^3A_2$. At STO-3G and at standard geometries, this energy difference is larger, 8.9 kcal mol^{-1}. In substituted systems, insofar as it is possible to distinguish "$^3B_1$-like" states from "$^3A_2$-like", the former have been obtained in this study. Since both states were not studied explicitly, we have no guarantee that the state selected corresponds to the lowest energy. It is possible to understand the results in terms of the charge distribution in the $^3B_1$ parent species. π chrges in this system are distributed according to resonance forms XV which suggest that a π donor substituent should be most stabilizing at ortho and para positions. A π acceptor is not expected to be stabilizing since the π system of the ring is already electron deficient relative to benzene; nevertheless, such a substituent will be least unfavorable at the meta position, where π density is highest.



XV

Substituted Triplet Phenyl Cations. σ Effects. Stabilization energies of triplets are given in Table IV. Since there is no vacant orbital in the σ system of the triplet, σ effects are not expected to be as important as in the singlets. Population analyses (Table II) do not bear this out but show that triplet σ transfer values are unchanged relative to singlets with electropositive substituents and are considerably increased with electronegative substituents. The latter is due to an increase in π donation which enhances σ withdrawal by a "push-pull" mechanism. However, energies are apparently less sensitive to electron transfer in triplets than in singlets. For example, lithium does not stabilize the triplet as strongly as the singlet, nor does the stability order o > m > p apply as inductive effects would dictate. Para lithium is as effective as ortho. Also, fluorine stabilizes the triplet; if inductive effects were dominant, it should destabilize. This evidence suggests that inductive effects are less important than π effects in triplet states.

π Effects. The triplet states under consideration have five π electrons and desire to obtain a sixth to increase aromaticity. π donors should therefore be strongly stabilizing, while π acceptors will be of little if any benefit. Triplet stabilization energies (Table IV) bear this out and follow the positional preferences expected on the basis of $^3B_1$ resonance forms (XV).

Table V. Calculated Singlet-Triplet Separations in X-$C_6H_4^+$ Systems[a]

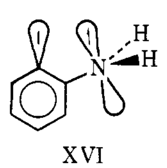
	Favored isomer		E(singlet) − E(triplet)[b]	
X	Singlet	Triplet	Calcd[c]	Corrected[d]
H			+38.3	−20.1
Li	Ortho	Ortho	+30.0	−28.4
HBe	Ortho	Ortho	+33.1	−25.3
H_2B	Meta, Copl[e]	Para, Orth[e]	+42.0	−16.4
H_3C	Para	Para	+47.3	−11.1
H_2N	Para, Copl[e]	Para, Copl[e]	+83.2	+24.8
HO	Para	Para	+66.0	+7.6
F	Para	Para	+51.6	−6.8

[a] Energy difference between most stable singlet and most stable π-type triplet. [b] kcal mol^{-1}. Negative value indicates singlet ground state. [c] Direct difference between STO-3G energies from Table I. [d] Corrected for geometrical and theoretical errors based on calculated vs. experimental values for CH_2. See text. [e] Copl = CCXH coplanar; Orth = CCXH orthogonal.

While σ effects complicate the picture for lithium and beryllium substituents, BH_2 is straightforward. It is destabilizing except at the meta position, where π density of the $^3B_1$ state of $C_6H_5^+$ is highest. Upon rotation by 90°, the BH_2 group becomes π donating (see populations in Table II) and is therefore more favorable in this conformation. As Table I shows, orthogonal BH_2 is most favorable at ortho and para positions, as is true for other π donors, and is substantially stabilizing. Stabilization energies comparing orthogonal triplet H_2B-$C_6H_4^+$ with orthogonal H_2B-C_6H_5 are 11.9 kcal mol^{-1} at ortho, 8.6 at meta, and 13.0 at para.

The major π donating substituents NH_2, OH, and to a lesser extent F, show precisely the trends implied by XV. All are stabilizing, especially NH_2, in order of effectiveness ortho ~ para > meta. As before, charge transfer values (q_{tot}) correlate roughly with stabilization energies; in this case π donation strongly dominates and the maximum stabilization of the series (56.3 kcal mol^{-1}) is found for NH_2.

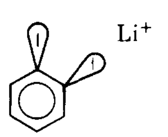
Rotation of the amino group reduces π donation into the ring and is thus costly energetically. Rotation barriers are 59.5 kcal mol^{-1} (ortho), 39.2 (meta), and 61.6 (para). The orthogonal amino group is still somewhat stabilizing, by 7.4 kcal mol^{-1} in the ortho position, 7.8 meta, and 5.4 para, due to its ability to donate π electrons by hyperconjugation (as shown by the population values). The initial calculation of the ortho orthogonal system led to a σ-type triplet XVI which was lower in energy by 8.9 kcal mol^{-1} than the π-type triplet given in Table I. We have not investigated similar σ-type triplets of meta or para isomers.



XVI

Syn-anti differences in hydroxy-substituted triplets are lower than those in the corresponding singlets. The differences are 0.5 kcal mol^{-1} (ortho) and 1.9 (meta), compared to singlet values of −7.0 and 1.0, where positive values indicate syn to be favored. The large variation at ortho demonstrates the decreased electronic demands of the in-plane σ orbital at C_1; when half-filled, in the triplet, it does not benefit from direct donation of oxygen lone pair electrons as it did in the singlet (see XIII).

In o-Li-$C_6H_4^+$, a low-lying σ-type triplet state (XVII) lies 7.1 kcal mol^{-1} above the π-type triplet given in Table I. Like the ground state of ortho, orthogonal H_2N-$C_6H_4^+$ (XVI), the low energy of XVII is easily rationalized; ionization of a readily available electron on Li (or NH_2) is comparable in energy to the reduction of ring aromaticity, which must occur in forming a π-type triplet. Further investigations of similar σ triplets were not pursued.



XVII

Singlet-Triplet Separations. In Table V, singlet-triplet differences are given between the most favorable conformation in each electronic state. Triplets are calculated to lie below singlets in all cases. However, it is well known that single-determinant theory gives artificially low energies for triplet states, and this error is compounded by the fact that the standard-geometry singlet is farther from its equilibrium geometry than is the triplet from optimized $^3B_1$. The singlet-triplet ($^3B_1$) separation for standard-geometry phenyl cations, 38.3 kcal mol^{-1}, is reduced to 7.5 kcal mol^{-1} upon STO-3G geometry optimization and calculation with the split-valence 4-31G basis.[8] The latter value was corrected[8] to −20.1 kcal mol^{-1} by using corresponding data for CH_2. If this number is accurate, then the standard geometry STO-3G singlet-triplet difference in Table V (38.3) is in error by 58.4 kcal. Thus, subtracting this amount from each number in the first column of the table should eliminate gross geometrical and theoretical errors in singlet-triplet separations. The resulting corrected values are given in the second column.

According to these values, the phenyl cation and derivatives with π acceptor ubstituents have singlet ground states. Triplets become increasingly favorable as substituents become π donating, so that the ground state of the aminophenyl cation is probably a triplet, in agreement with previous conclusions based on INDO calculations.[24] Hydroxy- and fluorophenyl cations are also predicted to have low-lying triplet states, although the ground states cannot be identified with certainty on the basis of present calculations. Experimental results do not appear to be conclusive on this point, though it has been suggested[21,25] that triplets might be involved in suitably substituted systems.

Experimental Evidence

Both gas-phase and solution data are available concerning phenyl cations. In the gas phase, the majority of studies deal with unsubstituted $C_6H_5^+$ and are discussed elsewhere.[8] In addition, the complete series of fluorinated phenyl cations $C_6H_nF_{5-n}^+$ (n = 0 to 5) has been studied,[26] giving the following appearance potentials: 16.9 eV ($C_6F_5^+$), 16.5 ($C_6HF_4^+$), 15.9 ($C_6H_2F_3^+$), 15.2 ($C_6H_3F_2^+$), 15.1 ($C_6H_4F^+$), and 14.5 ($C_6H_5^+$). These indicate fluorine to be destabilizing, in agreement with the calculations (Table III). In other gas-phase studies,[27] the species $C_7H_7^+$, $C_6NH_6^+$, and $C_6OH_5^+$ have been observed but the structures of these ions have not definitely been established to be substituted phenyl cations; other possibly more stable isomers (e.g., tropylium ion or Ph–X^+) may be involved.

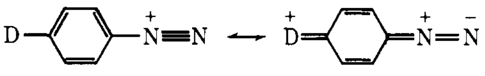
Rates of decomposition of a variety of substituted diazonium ions X–C_6H_4–N_2^+ have been determined in solution.[3,5–7,28,29] Such studies provide only indirect information concerning stabilization of the phenyl cation, since the quantity measured reflects an energy difference between transition state ($XC_6H_4^+$) and starting material ($XC_6H_4N_2^+$). Thus an increase in dediazoniation rate with substitution may be due to substituent stabilization of the phenyl cation or destabilization of the benzenediazonium ion, or both.

The rate data are summarized by Swain et al.[3a] Rate decreases are observed with σ-withdrawing substituents (Cl, Br, NO_2) at meta and para positions and with π-donating substituents (CH_3, C_2H_5, $C(CH_3)_3$, C_6H_5, OH, OCH_3) at para. π donors at the meta position lead to rate increases. It is concluded[3] that σ-withdrawing substituents destabilize the phenyl cation, while π donors at the meta position stabilize. π donors at the para position, however, preferentially sta-

Table VI. Estimated Heats of Formation of Singlet Phenyl Cations $X\text{-}C_6H_4^+$ [a]

X	$\Delta H_f°{}_{298}(C_6H_5X)$,[b] kcal mol^{-1}	$\Delta H_f°{}_{298}(X\text{-}C_6H_4^+)$, kcal mol^{-1}		
		Ortho	Meta	Para
H	19.82	270[c]		
Li	62.2[d]	255	274	281
HBe	54.6[d]	293	298	301
H_2B	45.0[d]	293[e]	293[e]	297[e]
H_3C	11.9	258[f]	258[g]	257
H_2N	20.8[h]	268[i]	268[i]	262[i]
HO	−23.1	227[f]	228[g]	224
F	−27.9[j]	230	228	225

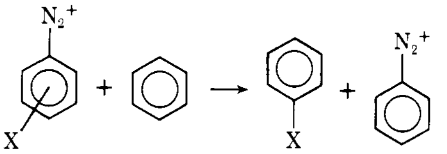
[a] Estimated from calculated energies of reaction 1. [b] Experimental (ref 32) unless noted otherwise. [c] Experimental (ref 34). [d] Calculated from methyl stabilization energies. See ref 33. [e] CCBH coplanar. [f] Anti. [g] Syn. [h] Pyramidal at N. [i] CCNH coplanar, but calculated with reference to pyramidal aniline (ref 18); thus stabilization energies used were 2.1 (o), 2.2 (m), 8.6 kcal mol^{-1} (p). [j] Experimental value from ref 35.



XVIII

bilize the benzenediazonium ion. This is due to resonance (XVIII), which not only stabilizes but also has the effect of strengthening the CN bond and decreasing the rate of its rupture.[30]

Given this situation, it is not possible to correlate the observed rate changes with te calculated phenyl cation substituent effects in Table III. Such a correlation is justified only if stabilities of the corresponding arenediazonium ions are invariant with substitution, and a variety of evidence suggests that this is not the case. In the first place, the charge distribution of $C_6H_5N_2^+$ (STO-3G, standard geometry)[31] is entirely analogous to that in singlet $C_6H_5^+$, in π and σ systems of the ring. This suggests that substituents should have similar effects on both species, at least qualitatively. In addition, energies of the "benzenediazonium stabilization reaction" 2 have been calculated[23,31]



(2)

at STO-3G for a typical substituent, X = (planar) NH_2; stabilization energies are 5.4 kcal mol^{-1} (ortho), 3.5 (meta), and 10.7 (para).[31] Thus an amino group stabilizes the benzenediazonium ion in the same way it stabilizes the phenyl cation. Phenyl cation stabilization energies for an amino substituent are, from Table III, 4.8 (ortho), 4.9 (meta), and 11.3 (para). This suggests that the rather small rate changes observed in dediazoniation reactions reflect detailed variations in substituent influences, and rate studies may be thus misleading with regard to phenyl cation stabilization. Further discussion is reserved for a future publication dealing with arenediazonium ions.[23]

Heats of Formation. Theoretical energies may be used to obtain estimates of the heats of formation of substituted singlet phenyl cations. For this purpose, the stabilization reaction 1 is employed, together with known or estimated heats of formation of C_6H_6, $C_6H_5^+$, and the appropriate XC_6H_5.[32,33] Results are given in Table VI. The aim in providing these values is to establish guidelines for future thermochemical studies.

σ donors (a) stabilize the singlet phenyl cation strongly by providing charge to the vacant orbital, and favor o > m > p; (b) stabilize the triplet phenyl cation less strongly by neutralizing the positive charge in the π system, favoring o, p > m; and (c) lead to singlet ground states.

π acceptors (a) provide little stabilization of either singlet or triplet; (b) favor meta substitution; (c) interact more strongly if rotated to become a hyperconjugative π donor (this refers to BH_2); and (d) lead to singlet ground states.

π donors (a) stabilize the singlet by helping to delocalize the positive charge in the σ system; (b) strongly stabilize the triplet by relieving electron deficiency in the π system of the ring; (c) favor o, p > m substitution; (d) appear to stabilize the benzenediazonium ion strongly at para, weakly at ortho, and not at meta; (e) lead therefore to increased dediazoniation rates at meta, but decreased at ortho and para; and (f) favor triplet ground states.

σ acceptors (a) destabilize the singlet, favoring p > m > o; (b) interact less strongly with the triplet, in which π rather than σ effects determine stabiliation energies and positional preferences; and (c) give singlet–triplet separations near zero.

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Conjugative Interaction between Π and Cyclobutane Orbitals. The Synthesis and Electronic Structure of Bicyclo[4.1.1]octa-2,4-diene

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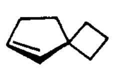
Abstract: The photoelectron (pe) spectra of bicyclo[4.1.1]octa-2,4-diene (**4**), bicyclo[4.1.1]oct-3-ene (**5**), and bicyclo-[4.1.1]octane (**6**) have been recorded. Based upon assignment of the first bands in the pe spectrum of **4**, it is concluded that the interaction between the Walsh orbitals of the cyclobutane ring and the olefinic moiety can be described by a resonance integral $\beta = -1.9$ eV. This analysis is based on a simple ZDO model and substantiated by semiempirical calculations. The theoretical results are in reasonable agreement with experiment. Synthetic access to **4–6** was gained in several steps from diethyl *cis*-1,3-cyclobutanediacetate (**8**).

The study of conjugative interactions between a cyclobutane ring and an adjacent vinyl group or sp^2-hybridized center has attracted increasing interest in recent years.[3-9] A method very well suited to the investigation of such interactions is provided by photoelectron (pe) spectroscopy. The experimentally observed band positions in various pe spectra were shown to be satisfactorily reproduced within the framework of a ZDO model by adopting a resonance integral for the interaction between a 2p atomic orbital on the double bond (p_π) and a 2p atomic orbital on the cyclobutane ring (p_w) separated by one carbon–carbon single bond.

$$\beta = \langle p_\pi | H | p_w \rangle = -1.9 \text{ eV} \tag{1}$$

Recently we reported[7,8] pe spectroscopic evidence concerning the direct conjugation of the Walsh orbitals in a cyclobutane ring with the π orbitals of adjacent double bonds. The systems studied so far have been rigid 1,1- and 1,3-disubstituted cyclobutanes such as spiro[3.4]oct-5-ene (**1**), spiro[3.4]octa-5,7-diene (**2**),[7] and tricyclo[3.3.0.0^{2,6}]octene (**3**).[8] In the case of **1** and **2**, analysis of the interaction between the π and Walsh orbitals was complicated because two Walsh orbitals (ϕ_1 and ϕ_3, see below) had to be considered. Furthermore, in the region below 10 eV, interpretation of the pe spectra was difficult due to strongly overlapping bands. As regards **3**, a simpler pattern was seen,[8] but only the interaction between π and one Walsh orbital (ϕ_1) could be studied. These uncertainties and difficulties gave rise to different assignments[7,9] and as a result different interaction parameters were obtained.



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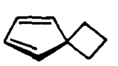

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Given these shortcomings, bicyclo[4.1.1]octa-2,4-diene (**4**) deserves special interest. For reasons of symmetry, we considered that it should be possible to study separately the interaction between ψ_1 and ϕ_1 (defined below) and between ψ_2 and ϕ_3 and thus to check our previous assignments.[7,8] In this paper, we also provide details of the synthesis of **4**, bicyclo-[4.1.1]oct-3-ene (**5**), and bicyclo[4.1.1]octane (**6**).

4

5

6

Synthetic Considerations

1,3-Cyclobutanedicarboxylic anhydride (**7**), which can readily be prepared from pentaerythritol in several steps,[10] was bishomologated to dimethyl *cis*-1,3-cyclobutanediacetate (**8**) according to the published procedure.[11] Cyclization of **8** under acyloin conditions in the presence of trimethylsilyl chloride[11,12] led in high yield to 3,4-bis(trimethylsiloxy)bicyclo[4.1.1]-oct-3-ene (**9a**, Scheme I). This key intermediate was in turn hydrolyzed[12] to provide α-hydroxy ketone **10** and reduced directly with sodium borohydride in ethanol to deliver the crystalline cis diol **11a**. Stereochemical assignment to **11** followed principally from its ^{13}C NMR spectrum which exhibits the five signals required by a plane of symmetry (point group C_s); its trans counterpart which possesses axial symmetry (point group C_2) should display only four peaks.

In our development of a convenient route to **5**, several methods were examined for their efficiency. The reductive elimination of dimesylate **11b** with sodium anthracenide in