Molecular Orbital Theory of the Electronic Structure of Molecules. 30. Structure and Energy of the Phenyl Cation

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Abstract: Ab initio molecular orbital calculations are reported on the phenyl cation, $C_6H_5^+$, in singlet ($^1A_1$) and triplet ($^3B_1$, $^3A_2$) states. Geometries are optimized at the STO-3G level, energies calculated at 4-31G. The singlet cation is highly distorted, with a CC^+C angle of 145°, while the triplet geometries are close to that of benzene. Upon empirical correction of 4-31G results, the singlet is found to lie 20 kcal mol^{-1} below the lower triplet ($^3B_1$), and to be nearly equal in stability to the vinyl cation. Electrons in the π system of the singlet are strongly polarized toward C^+. Triplet charge distributions are different from those implied by previously published resonance forms.

The phenyl cation (I) was proposed in 1942 as an intermediate in the decomposition of benzenediazonium ion,[2] and its existence has been a matter of debate ever since.[3] In the gas phase, the phenyl cation is presumed to have been observed mass spectrometrically, although appearance potentials and reported heats of formation have varied widely[4-7] and acyclic $C_6H_5^+$ isomers cannot be ruled out.[8] In solution, kinetic and other data have been interpreted both for[9] and against[10] the involvement of phenyl cations, and to date there is no indication that they are generated in any reaction other than dediazoniation.[11,12] This reaction, however, has been thoroughly studied by Swain et al., whose work is summarized in a recent series of papers;[9a-c] these demonstrate clearly and convincingly that the phenyl cation has indeed been generated in solution. Additional evidence has been provided by Zollinger et al.[9d]

A few semiempirical molecular orbital studies have dealt with the electronic structure of the phenyl cation.[13-17] The geometrical structure has been determined theoretically,[9b] but with a method of limited accuracy in this regard (INDO). Although most of these studies agree that the ground electronic state of the phenyl cation is a singlet,[18] estimates of the energy difference between singlet and lowest triplet states vary from 30 to 150 kcal mol^{-1}. Finally, despite considerable experimental interest in substituent effects,[21-24] only one substituted phenyl cation has been calculated by SCF methods,[15] apart from our own studies.[25,26]

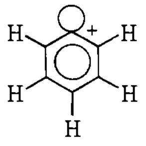
It was our feeling that much remained to be investigated, and that a thorough, systematic study would be useful if performed with accurate and well-documented ab initio methods. The present contribution comprises only a part of this study. In it, we obtain geometrical structures for both singlet ($^1A_1$) and triplet ($^3B_1$, $^3A_2$) phenyl cations and predict their relative stabilities and charge distributions. Stabilization energies comparing the ground state (singlet) with other small cations are determined using both theoretical and experimental energies, and phenyl is seen to be roughly equal in stability to the vinyl cation. Despite this fact, methods of cation generation which have yielded derivatives of the vinyl cation (e.g., solvolysis of alkenyl triflates) have to date been unsuccessful in producing phenyl cations.[12] Thus another phase of our theoretical study is the investigation of substituent effects, in search of modes of phenyl cation stabilization. In a previous contribution,[25] we assessed the stabilizing effects and positional and conformational preferences of a single amino substituent on the $^1A_1$ phenyl cation; in a following broader study,[26] we shall examine a series of substituents on both singlet and triplet systems.

Methods

Total energies were calculated as described elsewhere[27] using unrestricted Hartree–Fock (UHF) theory, employing both minimal STO-3G and split-valence 4-31G Gaussian basis sets. For geometry optimizations, the STO-3G basis was used together with a gradient minimization algorithm based on the method developed by Fletcher and Powell.[28] Planarity (C_{2v} symmetry) was assumed throughout the optimizations; this assumption was later tested, and found to be justified, by calculation of selected nonplanar geometries. All geometrical parameters except C–H bond lengths (held fixed at 1.08 Å) were varied through two cycles of the optimization procedure. Single 4-31G calculations were then carried out at the optimized geometries. Geometries are specified by the labels shown in Figure 1, and are given along with the calculated energies of both singlet and triplet states in Table I.

Geometries

Removal of a hydride ion from benzene without further electronic reorganization would lead to a singlet ($^1A_1$) state of the phenyl cation (I), in which the vacant orbital and aromatic π system are orthogonal and unable to interact directly. The situation is similar to removal of a hydride from ethylene, yielding the classical vinyl cation. In both cases, the vacant orbital is initially an sp^2 hybrid which then prefers to distort in such a way as to reduce its s character, i.e., the bond angle at C^+ tends toward 180°. The $C-C^+-H$ angle in the classical vinyl cation is calculated[29] to be 180°; the same value is obtained by INDO calculation for the $C-C^+-C$ angle (α) of the singlet phenyl cation.[9b] STO-3G (Table I) gives the smaller value of α = 145°, which still shows considerable flattening.



I $^1A_1$

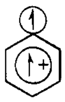
Table I. Ab Initio Energies and Geometries of Singlet and Triplet Phenyl Cation

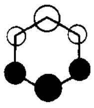
	Singlet ($^1A_1$)	Triplet ($^3B_1$)	Triplet ($^3A_2$)
Geometry^{a,b}			
r_1	1.347	1.481	1.375
r_2	1.403	1.391	1.463
r_3	1.394	1.409	1.392
$r_{CH}{}^c$	1.080	1.080	1.080
α	144.9	124.0	122.7
β	103.6	114.5	118.5
γ	125.6	123.4	120.1
δ	116.8	120.3	120.0
θ_1	128.2	125.0	119.0
θ_2	118.6	118.7	121.2
Energy^d			
E(STO-3G)	−226.98388	−227.01290	−226.99996
E(4-31G)	−229.42158	−229.43357	−229.42925

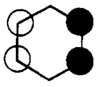
[a] Geometry determined at STO-3G level. Refer to Figure 1 for definitions of geometrical parameters. [b] Bond lengths in ångströms, angles in degrees. C_{2v} symmetry. [c] Assumed. [d] Hartrees.

At the same time, the C-C$^+$ bond lengths are reduced from the benzene value of 1.39 Å[30] to 1.35 Å, partly due to hybridization changes and partly because of σ-type hyperconjugation between the formally vacant orbital at C$^+$ (the p(C$^+$) orbital) and neighboring C-C and C-H bonds. Angular distortions occur elsewhere in the ring, especially at C_2 and C_6, in order to accommodate the large perturbation at C_1 (C_1 = C$^+$; see Figure 1). In short, the singlet is strongly distorted from an ideal D_{6h} benzene geometry. The optimized structure is calculated to be more favorable than the standard benzene geometry by 25 kcal mol^{-1} at STO-3G.

The singlet cation evidently undergoes such distortion in order to maximize charge delocalization into the p(C$^+$) orbital from the σ framework of the ring. A more direct method of supplying electron density to this vacant orbital is simply transfer of an electron into it from the π system, thus sacrificing some degree of aromatic stabilization. If this transfer is done with spin inversion, the result is a triplet state (II). Two low-lying triplet states are available: $^3B_1$, obtained by transfer of an electron out of the 2b$_1$ MO (III) or $^3A_2$, by transfer out of 1a$_2$ (IV). Optimized structures were obtained for both of these states at the STO-3G level (Table I). For $^3A_2$, satisfactory convergence was only achieved by the use of a direct minimization self-consistent procedure which avoids changes in electron configuration during the iterations.[31] These calculations indicate that $^3B_1$ is the lower of these two triplet states by 2.7 kcal mol^{-1} (4-31G). The same energy ordering had been found previously by several semiempirical methods.[16,17]


II


III b$_1$


IV a$_2$

The optimized triplet geometries (Table I) show some significant features. The in-plane orbital at C_1 is no longer vacant and its electronic demands are therefore reduced. Consequently, both triplet states show less flattening at C_1. For the $^3B_1$ state, there is a sharp increase in the length of the C_1-C_2 bond to 1.48 Å, presumably due to decreased hyperconjugation and reduced C_1-C_2 π bonding. For the $^3A_2$ state, the bonds C_2-C_3 and C_5-C_6 are lengthened to 1.46 Å. This is consistent with the removal of an electron from the a$_2$-type π-bonding molecular orbital IV. Apart from these changes, the structures are not far from those of benzene but distorted in the direction of the singlet. Both singlet and triplet structures are in reasonable agreement with those determined in unpublished MINDO/3 studies in Basel,[17] these being superior to MINDO/2[17] and INDO[9b] structures.

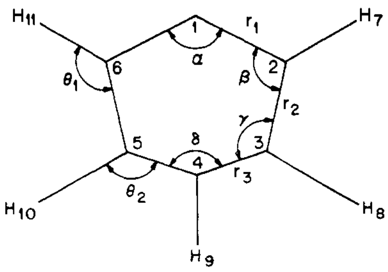
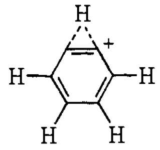


Figure 1. Geometrical parameters.

A few alternate $C_6H_5{}^+$ structures were calculated at the STO-3G level. As mentioned, nonplanar geometries were considered for both singlet and triplet, in each case by moving C_1 or C_4-H or both a small distance out of the plane; all such distortions led to energy increases. A protonated singlet benzyne structure (V) of C_{2v} symmetry was calculated with geometry optimization at STO-3G and found to lie 77 kcal mol^{-1} above I, although at MINDO/3 this difference is reduced to 44 kcal.[17] Finally, an open-chain isomer, $H_2C{=}C^+{-}CH{=}CH{-}C{\equiv}CH$, was considered at the 4-31G level (using a partially optimized STO-3G structure from $C_4H_5{}^+$ plus a standard ethynyl group);[32] this acyclic form was 17 kcal mol^{-1} above the singlet phenyl cation. There are, of course, many other $C_6H_5{}^+$ isomers and we have by no means shown phenyl to be the most stable one. This conclusion does appear to have been reached, however, by Bally and Haselbach,[17] who have to date studied at MINDO/3 more than 40 isomers of $C_6H_5{}^+$, each with complete geometry optimization. They find many close in energy to the phenyl cation, but essentially none below it.



V

Charge Distributions

The electronic structures of singlet and triplet may be partly interpreted by means of Mulliken population analysis, selected quantities from which (STO-3G) are given in Table II. We discuss these in turn.

π charges, populations of the p orbitals perpendicular to the ring, should be compared with the π charge of 1.00 at each site in benzene. In the singlet phenyl cation, although the total number of π electrons remains six, there is clearly a strong polarization of these electrons toward C_1, where a considerable excess (0.200 electron) accumulates. Evidently, despite the fact that π electrons cannot interact *directly* with the p(C$^+$) orbital in plane, positive charge is dispersed by moving them into the *vicinity* of C_1. This is an example of indirect "communication" between σ and π systems; a strong perturbation in the σ framework (formal removal of H$^-$) causes considerable reorganization in the π system even though the overlap between σ and π orbitals is strictly zero.[33]

In the triplet $^3B_1$, the number of π electrons is five and it is apparent from which positions the odd electron has been removed, namely C_1 (where 44% of an electron has been removed), C_4 (17%), and C_2, C_6 (12% each). This pattern is entirely reasonable, since the electron was removed from a b$_1$ π orbital polarized in the direction of C_1. For the $^3A_2$ state, π electrons are removed primarily from atoms C_2, C_3, C_5, and

Table II. STO-3G Population Data for Optimized Phenyl Cation Singlet and Triplet[a]

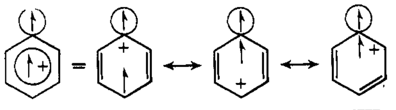
	Singlet ($^1A_1$)	Triplet ($^3B_1$)	Triplet ($^3A_2$)
π charge[b]			
C_1	1.200	0.561	1.008
C_2	0.988	0.876	0.681
C_3	0.943	0.929	0.821
C_4	0.937	0.828	0.987
π spin density[c]			
C_1		+0.497	+0.075
C_2		+0.360	+0.163
C_3		−0.388	+0.538
C_4		+0.561	−0.478
Total atomic charge			
C_1	+0.309	+0.272	+0.071
C_2	−0.048	−0.005	+0.069
C_3	−0.010	−0.023	+0.034
C_4	−0.020	+0.022	−0.046
H_7	+0.194	+0.161	+0.169
H_8	+0.146	+0.137	+0.149
H_9	+0.147	+0.147	+0.136

[a] From Mulliken population analysis. All values in electrons. [b] Population of p orbital perpendicular to ring (pπ orbital). [c] Excess of α spin (positive) or β (negative) in pπ orbital, see text.

C_6 which is consistent with the removal of an electron from the a_2 molecular orbital.

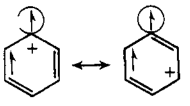
π spin densities further aid in understanding the triplet states. Positive spin densities for $^3B_1$ indicate an excess of α spin at C_4, C_1, and C_2, meaning that the odd electron in the π system spends most of its time at those positions. Again, this is understandable in terms of the half-vacated b_1 orbital. For the $^3A_2$ states, a negative spin density is found at C_4, this being on the node of the a_2 molecular orbital.

The structure of the lowest triplet ($^3B_1$) which emerges may be summarized in terms of the major resonance forms VI–VIII.



VI VII VIII

Note that these confirm our earlier suggestion that C_1–C_2 π bonding is reduced, leading to a large C_1–C_2 distance. Furthermore, they suggest that π-donor substituents will be most effective at C_2 or C_4, ortho or para to the p(C^+) orbital. This is in direct contradiction with Taft's argument[19] that meta substituents stabilize a triplet cation, which was represented in his paper by the resonance forms IX–X. While form X bears some relation to the π charge distribution in Table II of the alternate triplet state ($^3A_2$), resonance form IX does not, since in the $^3A_2$ π system positive charge is localized at C_2 and C_3 but not at C_1. Thus, the resonance forms proposed by Taft describe neither $^3B_1$ nor $^3A_2$ states accurately. Different forms might have been proposed had ortho substituent effects been considered in addition to meta and para. Further discussion of this situation is given elsewhere.[26]



IX X

Total charges show how the positive charge is distributed throughout the phenyl system. In the singlet, hyperconjugation and inductive effects are operative; all hydrogens act as σ donors, especially at ortho positions. As a result, almost 70% of the positive charge is away from C_1.

In the triplet $^3B_1$, despite the fact that the p(C^+) orbital has been populated directly, positive charge still resides largely at C_1 and is delocalized only slightly more effectively than in the singlet. Net positive charge at C_1, C_4, and C_2 mainly reflects electron deficiency in the π system, leading us to conclude that σ effects are less important in the triplet than in the singlet. The consequences of this with regard to substituent stabilization will be discussed.[26] In the $^3A_2$ state, more of the positive charge is located on the ortho and para carbon atoms.

Stabilities

In Table I, 4-31G energies give the $^3B_1$ state 7.5 kcal mol^{-1} below the singlet. However, it is well known that Hartree–Fock theory generally gives relatively lower energies for triplets, which have smaller correlation energies. In fact, the same level of theory (4-31G at STO-3G geometries) predicts the triplet state of CH_2 to lie 37.3 kcal mol^{-1} below the corresponding singlet,[29] whereas a careful estimate of the difference[34] is 9.7 kcal mol^{-1}. Thus, to a first approximation, we may correct singlet–triplet separations by lowering the singlet 27.6 kcal mol^{-1} relative to the triplet. This is equivalent to the hypothesis that the energy of the formal "spin-flip" reaction is given correctly by UHF/4-31G theory.

$$C_6H_5^+(\text{singlet}) + CH_2(\text{triplet}) \rightarrow C_6H_5^+(\text{triplet}) + CH_2(\text{singlet})$$

Accordingly we predict that the singlet state of I is *more* stable than the triplet by 20.1 kcal mol^{-1}. In at least qualitative agreement are several semiempirical studies, which give $^1A_1$ − $^3B_1$ separations of 20 (CNDO/S + CI),[16] 27.6 (MINDO/3),[17] 34 (MINDO/2),[17] 41 (EHT),[13] 80 (INDO),[15] and 146 kcal mol^{-1} (INDO optimized).[9b] In addition, a variety of experimental evidence points to a singlet ground state in solution.[9a]

The many gas-phase experimental heats of formation reported for $C_6H_5^+$ presumably refer to the singlet state.[4-8,35,36] Of these, the best value appears to be $\Delta H_f°_{298} = 270 \pm 4$ kcal mol^{-1}, recently determined by ion cyclotron resonance studies of fluorine transfer reactions.[6,36] This value agrees well with other recent determinations,[7] but is considerably lower than the selected value of 285 kcal mol^{-1} given in the extensive NBS compilation (1969).[4]

A theoretical determination of the singlet heat of formation is possible by obtaining calculated energies of the formal isodesmic stabilization reactions 1 and combining them with experimental values for R^+, RH, and benzene.

$$R^+ + C_6H_6 \rightarrow C_6H_5^+(^1A_1) + R\text{–}H \qquad (1)$$

Reaction 1 compares the stability of the phenyl cation with that of another cation, R^+, such that a positive reaction energy indicates R^+ to be the more stable. Values for five small cations are given in Table III. 4-31G results demonstrate the instability of the phenyl cation: it is only 8.9 kcal mol^{-1} more stable than CH_3^+, according to reaction 1, and is 6.3 kcal mol^{-1} less stable than $H_2C{=}CH^+$. However, if we instead evaluate reaction 1 using experimental heats of formation, we find the phenyl cation to be 3.3 kcal mol^{-1} *more* stable than vinyl. Either way, we may consider phenyl and vinyl cations to be roughly equal in stability. Evidently the energetic cost of restraining the C–C^+–C angle to less than 180° in the phenyl ring is just offset by the stabilizing effect of a larger, more polarizable π system.

Any of the stabilization energies in Table III may be used together with known data to estimate $\Delta H_f°(C_6H_5^+)$. This procedure does not provide any new information, but we mention the results nevertheless. 4-31G estimated heats of formation for the singlet phenyl cation (in kcal mol^{-1} at 298 °C) are as follows, together with the appropriate R^+ from eq

Table III. Singlet Phenyl Cation Stabilization Energies[a,b]

R^+	Stabilization energy, kcal mol^{-1} STO-3G	4-31G	Exptl
CH_3^+	−25.9	−8.9	−28.7
$H_2C{=}CH^+$	−1.5	+6.3	−3.3
$H_3C{-}CH_2^+$	+5.1	+21.0	+10.9
$H_3C{-}C^+{=}CH_2$	+24.4	+31.5	
Allyl$^+$	+34.8	+47.0	+29.1

[a] Energies of the reactions $R^+ + C_6H_6 \rightarrow C_6H_5^+(^1A_1) + RH$. [b] Experimental heats of formation (kcal mol^{-1}, 298 °C): $CH_4 = -17.889$, $C_2H_4 = 12.496$, $C_2H_6 = -20.236$, $C_3H_6 = 4.879$, $C_6H_6 = 19.820$ (ref 38); $CH_3^+ = 261$, $C_2H_5^+ = 219$ (ref 39); $C_2H_3^+ = 266$, allyl$^+ = 226$ (ref 40); $C_6H_5^+ = 270$ (ref 36). Calculated energies, STO-3G optimized and 4-31G (STO-3G geometries) taken from ref 41 (C_6H_6), 42 ($C_3H_5^+$), 43 (C_3H_6), 44 (all others).

1: 290 (CH_3^+), 280 ($C_2H_3^+$), 280 ($C_2H_5^+$), 288 (allyl$^+$). The most accurate of these is likely to be that involving the R^+ most similar in its bonding structure to the singlet phenyl cation. The best choice would be 2-propenyl cation, but its heat of formation is not known experimentally. We choose instead R = vinyl,[37] giving a theoretical estimate of 280 kcal mol^{-1} for the phenyl cation heat of formation. This appears to be in fair agreement with experiment.

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