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DFT Study of Substituted and Benzannelated Aryl Cations: Substituent Dependency of Singlet/Triplet Ratio[1a]

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By using density functional theory (DFT) method at the B3LYP/6-311+G* level, it has been shown that the preference for the singlet-state phenyl cation can be dramatically increased relative to the triplet state by introducing onium cationic substituents in the para position. At this level of theory, the singlet ground state for the parent phenyl cation was found to be lower than the triplet by 19.6 kcal/mol. Introduction of electron-donating substituent groups, namely $-NMe_2$, $-NH_2$, and −SMe in the para position, strongly favors the triplet state. The −OMe and −SH groups cause a similar but smaller effect, whereas −OH substitution results in an energetically identical system. Protonation of these substituent groups form onium−phenyl dications for which a complete reversal of the relative stabilities in favor of the singlet ground state are indicated with $-SH_2^+$, $-SMeH^+$, and $-NH_3^+$ showing the largest singlet/triplet energy difference. The $-N_2^+$ group in the para position has a similar effect. Benzannelation also increases the relative stability of triplet aryl cation. Whereas the 1-naphththyl and 2-naphthyl cations are energetically identical, in the 9-anthracenyl cation the triplet minimum lies 13.4 kcal/mol below the singlet minimum. Introduction of activating groups, i.e., OH and NMe_2 at the 4-position of the 1-naphthyl cation, greatly increases the relative stability of the triplet state. Upon heteroatom protonation, the singlet/triplet energy gap is substantially narrowed but the triplet state still remains lower in energy. Structural features in the resulting dications are discussed and compared with the corresponding monocations. The NBO charges at the cationic centers were also compared. We have also calculated the dediazoniation and decarbonylation energetics for mono- and bis-*o*-trimethylsilyl-substituted benzenediazonium and benzoyl cation to aryl cations in order to probe the effect of β-silyl stabilization of the positive charge.

Introduction

On a relative scale of carbocation stability, aryl cations appear to be alongside primary vinyl cations with regard to stability.[2] The parent phenyl cation (Ph^+) is 27 kcal/mol less stable (at the MP2/6-31G* level) than the solvolytically accessible 2-propenyl cation.[3] Although aryl cations are produced in abundance in the gas phase,[4] proof for their existence in solution has been difficult to obtain and quite challenging. The studies of Zollinger and associates on the mechanism of heterolytic dediazoniation (including demonstration of the reversibility of dediazoniation and exchange with external nitrogen) established Ph^+ as the implied intermediate.[5,6] Attempts to generate aryl cations, in low nucleophilicity, highly ionizing solvents including superacids, failed to give evidence for Ph^+.[2,7] Hyperconjugative stabilization of Ph^+ was subsequently achieved via ortho substitution with Me_3Si- or tBu− groups leading to solvolytic generation and trapping of such ions by Sonoda and associates.[8] Ab initio calculations by Apeloig and Arad predicted that the introduction of ortho $-SiH_3$ groups or ring fusion to a cyclopropane ring should bring about significant stabilization.[3]

The parent phenyl cation has been studied theoretically at various levels by several groups[9,10] showing that the singlet minimum lies 20−25 kcal/mol below the triplet minimum. The minimum energy crossover point between the two surfaces lies just above the higher energy minimum. Using a matrix isolation technique, Winkler and Sander[11] recently generated Ph^+ from PhCl and PhBr and via IR studies demonstrated that Ph^+ reacts with N_2 to form PhN_2^+. Their work reinforced that Ph^+ is a ground-state singlet. Previously, Speranza et al. had studied a series of $XC_6H_4^+$ cations formed via nuclear

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Table 1. Total Energies (−au), ZPE,[a] Relative Energies (kcal/mol),[b] and Proton Affinity (kcal/mol)[b] of Singlet and Triplet States of Monocations 1^+−8^+

no.	singlet/triplet	B3LYP/6-31G*// B3LYP/6-31G*	ZPE	B3LYP/6-311+G*// B3LYP/6-311+G*	rel energy (kcal/mol)	proton affinity (kcal/mol)
1^+	singlet	231.263 01	52.4	231.307 00	0.0	
2^+	triplet	231.234 12	53.0	231.276 72	19.6	
3^+	singlet	306.476 54	54.9	306.545 27	0.0	71.9
	triplet	306.480 65	56.6	306.547 67	0.2	
4^+	singlet	345.788 93	72.7	345.863 70	0.0	83.6
	triplet	345.796 46	74.0	345.869 99	−2.6	
5^+	singlet	629.444 27	51.9	629.514 92	0.0	85.6
	triplet	629.453 44	53.6	629.524 40	−4.3	
6^+	singlet	668.768 00	70.5	668.846 44	0.0	98.5
	triplet	668.78270	71.8	668.861 42	−8.1	
7^+	singlet	286.629 67	63.3	286.690 54	0.0	101.3
	triplet	286.647 06	64.6	286.707 01	−9.0	
8^+	singlet	365.254 29	98.6	365.327 70	0.0	115.4
	triplet	365.276 51	99.3	365.349 33	−12.9	

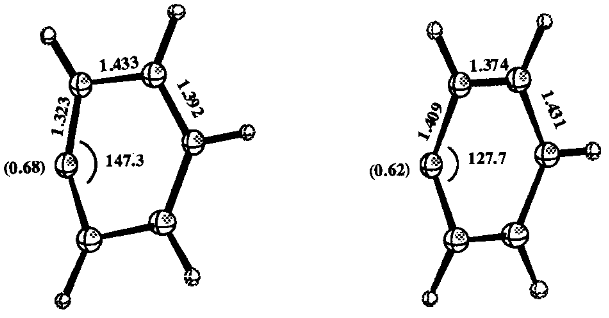
[a] Zero-point vibrational energies (ZPE) at B3LYP/6-31G*//B3LYP/6-31G* scaled by a factor of 0.98. [b] At B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level.

Table 2. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b] of Singlet and Triplet States of Dications $3H^{2+}$−$8H^{2+}$ and 9^{2+}

no.	singlet/triplet	B3LYP/6-31G*// B3LYP/6-31G*	ZPE	B3LYP/6-311+G*// B3LYP/6-311+G*	rel energy (kcal/mol)
$3H^{2+}$	singlet	306.600 27	61.9	306.66863	0.0
	triplet	306.560 20	61.6	306.627 49	26.1
$4H^{2+}$	singlet	345.932 20	79.5	346.005 38	0.0
	triplet	345.897 71	79.8	345.969 84	22.6
$5H^{2+}$	singlet	629.590 08	58.2	629.658 97	0.0
	triplet	629.546 89	57.9	629.614 83	28.0
$6H^{2+}$	singlet	668.934 30	76.3	669.010 31	0.0
	triplet	668.891 88	76.0	668.966 97	27.5
$7H^{2+}$	singlet	286.804 15	71.5	286.862 63	0.0
	triplet	286.762 25	71.1	286.819 47	27.5
$8H^{2+}$	singlet	365.450 76	106.4	365.521 67	0.0
	triplet	365.413 64	106.4	365.483 45	24.0
9^{2+}	singlet	339.658 23	51.3	339.729 24	0.0
	triplet	339.613 66	50.7	339.683 72	29.1

[a] Zero-point vibrational energies (ZPE) at B3LYP/6-31G*//B3LYP/6-31G* scaled by a factor of 0.98. [b] At B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level.

decay of tritiated precursors and performed ab initio calculations on several regioisomeric $O_2NC_6H_4^+$ and $HOC_6H_4^+$ cations.[12] Most recently, Aschi and Harvey used density functional theory (DFT) method at the B3LYP/6-31G* level to examine a series of *p*-X-substituted phenyl cations and calculated their relative energies.[13] STO-3G calculations of Schleyer and co-workers[9] on $XC_6H_4^+$ cations showed that σ-donors stabilize the singlet Ph^+ and π-donors are effective in stabilizing triplet Ph^+.



1^+ (C_{2v}) **2^+** (C_{2v})

Figure 1. B3LYP/6-311+G*-optimized structures (calculated NBO charges) of **1** and **2**.

In an effort to search for alternate methods for solvolytic generation and possibly direct observation of aryl cations, we have carried out a DFT study to examine the effect of protonation in *p*-$XC_6H_4^+$ ions (X = OH, OMe, SH, SMe, NH_2, and NMe_2) to generate $HX^+{-}C_6H_4^+$ dications. Because synthesis of the precursors of the type $XC_6H_4{-}Y$ (Y = N_2^+ or triflate) can be readily accomplished and since dications can be generated by protonation in superacidic solvents, these calculations also appeared attractive as an indication for future experimental studies. Laali and Olah previously showed that $MeO{-}PhN_2^+$ is O-protonated in superacids to give an oxonium−diazonium dication at low temperature.[14] Much less is known about Ar^+ derived from polycyclic aromatics despite the fact that suitable precursors are readily available. We therefore also examined the effect of benzannelation on the relative singlet/triplet stability in 1-naphthyl, 2-naphthyl, and 9-anthracenyl cations and probed the influence of onium substitution at C-4 in the 1-naphthyl cation. Further, the effect of β-silyl-stabilization on the energetics of dediazonation and decarbonylation in mono- and bis-TMS-substituted PhN_2^+ and $PhCO^+$ ions to the corresponding phenyl cations were also calculated.

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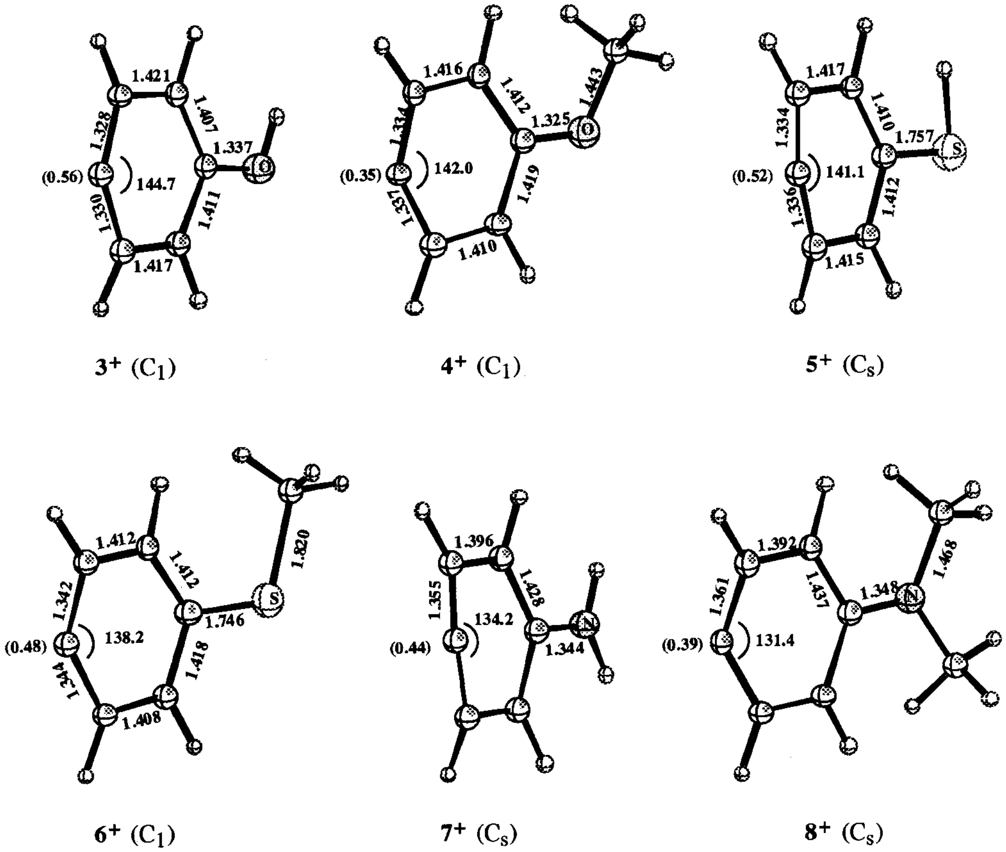
Table 3. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)[b] of Singlet and Triplet States of Monocations $\mathbf{10^+}$−$\mathbf{13^+}$ and Dications $\mathbf{12H^{2+}}$ and $\mathbf{13H^{2+}}$

no.	singlet/triplet	B3LYP/6-31G*// B3LYP/6-31G*	ZPE	B3LYP/6-311+G*// B3LYP/6-311+G*	rel energy (kcal/mol)
$\mathbf{10^+}$	singlet	384.919 99	79.8	384.993 71	0.0
	triplet	384.924 17	81.1	384.996 77	−0.6
$\mathbf{10a^+}$	singlet	384.918 32	80.1	384.992 06	0.0
	triplet	384.921 78	80.9	384.994 40	−1.6
$\mathbf{11^+}$	singlet	583.567 71	108.4	583.671 07	0.0
	triplet	583.592 23	109.7	583.694 55	−13.4
$\mathbf{12^+}$	singlet	460.138 20	82.9	460.236 71	0.0
	triplet	460.156 14	84.1	460.253 41	−9.3
$\mathbf{13^+}$	singlet	518.901 81	125.5	519.005 61	0.0
	triplet	518.926 85	126.3	519.029 68	−14.3
$\mathbf{12H^{2+}}$	singlet	460.277 57	89.1	460.375 10	0.0
	triplet	460.280 97	89.9	460.376 67	−0.2
$\mathbf{13H^{2+}}$	singlet	519.115 10	132.8	519.215 16	0.0
	triplet	519.120 72	133.6	519.219 64	−2.0

[a] Zero-point vibrational energies (ZPE) at B3LYP/6-31G*//B3LYP/6-31G* scaled by a factor of 0.98. [b] At B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level.



$\mathbf{3^+}$ (C_1) $\mathbf{4^+}$ (C_1) $\mathbf{5^+}$ (C_s)

$\mathbf{6^+}$ (C_1) $\mathbf{7^+}$ (C_s) $\mathbf{8^+}$ (C_s)

Figure 2. B3LYP/6-311+G*-optimized structures (calculated NBO charges) of singlet $\mathbf{3^+}$−$\mathbf{8^+}$.

Calculations

Calculations were performed by using the Gaussian 98 program.[15] The geometry optimizations were carried out using the DFT[16] method at the B3LYP[17]/6-31G* level.[18] Vibrational frequencies at the B3LYP/6-31G*//B3LYP/6-31G* level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.98. Further optimizations were carried out at the higher B3LYP/6-311+G* level. Final energies were calculated at the B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE level. Atomic charges were obtained using the natural bond orbital analysis (NBO) method[19] at the B3LYP/6-311+G* level. Calculated

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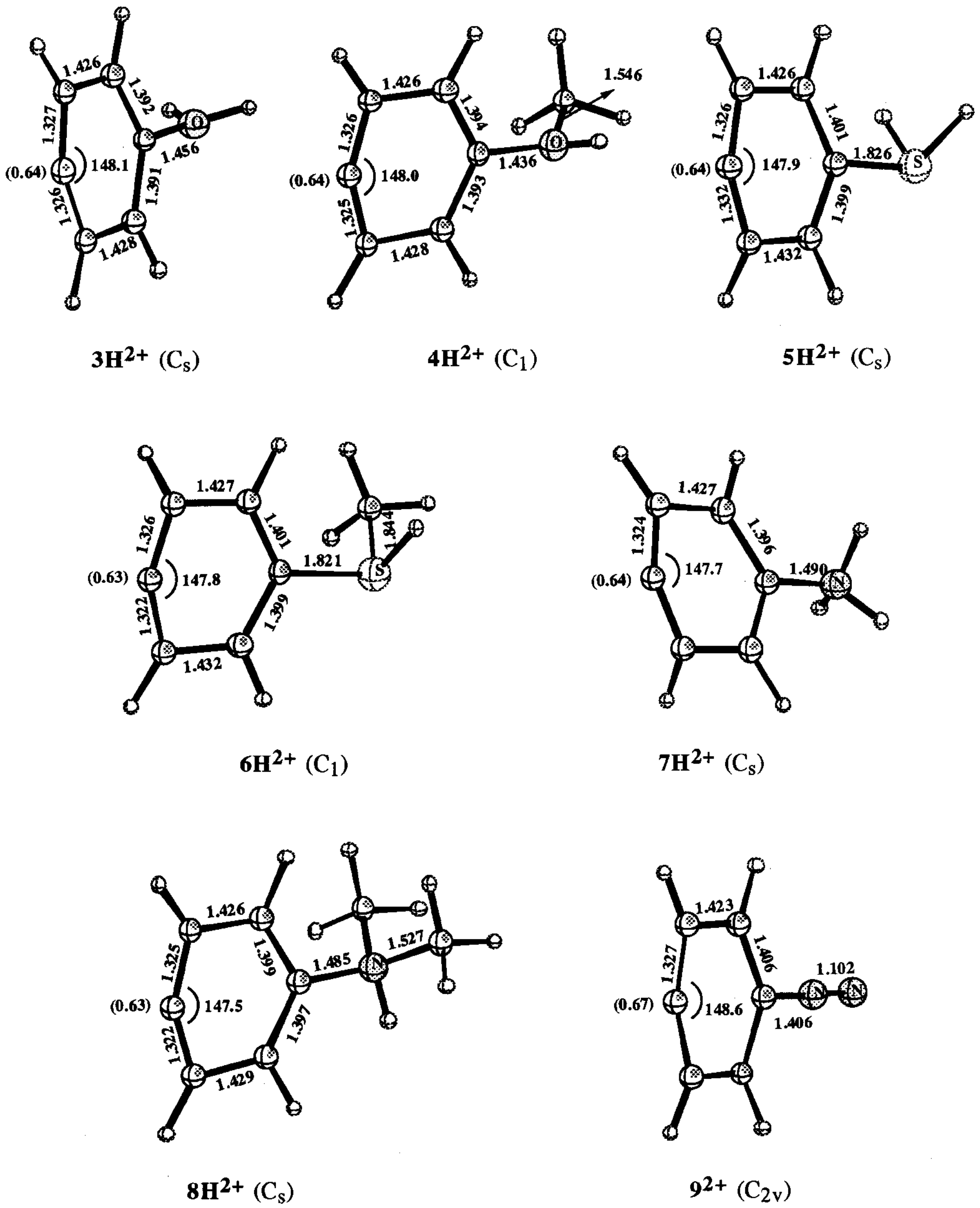


3H^{2+} (C_s) **4H^{2+}** (C_1) **5H^{2+}** (C_s)

6H^{2+} (C_1) **7H^{2+}** (C_s)

8H^{2+} (C_s) **9^{2+}** (C_{2v})

Figure 3. B3LYP/6-311+G*-optimized structures (calculated NBO charges) of singlet **3H^{2+}**−**8H^{2+}** and **9^{2+}**.

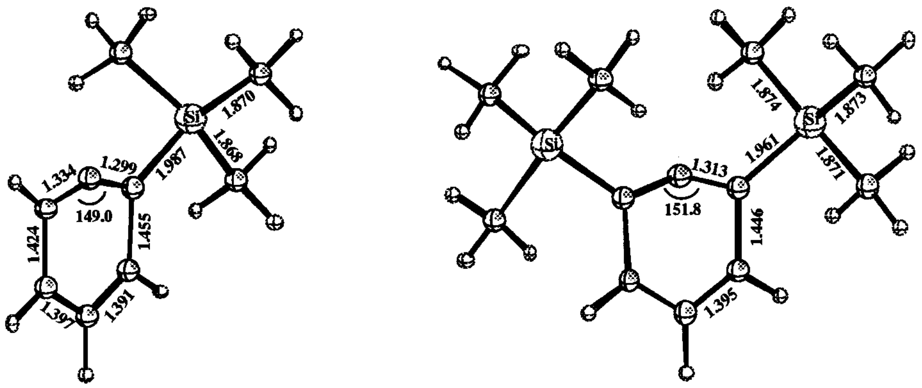
energies are given in Tables 1−3. B3LYP/6-311+G* geometrical parameters and final energies will be discussed throughout, unless stated otherwise.

Results and Discussion

Figure 1 shows the B3LYP/6-311+G*-calculated minimum energy singlet **1**$^+$ and triplet **2**$^+$ structures of the phenyl cation (Ph$^+$). The singlet **1**$^+$ has C_{2v} symmetry with a C−C$^+$−C angle of 147.3°, whereas the triplet **2**$^+$ (also has C_{2v} symmetry) is very much benzene-like with a C−C$^+$−C angle of 127.7°. It has been suggested previously[9] that the distortion is a driving force to maximize charge delocalization into the p(C$^+$) orbital from the σ framework of the ring. The C−C$^+$ bond in **1**$^+$ is noticeably shorter than **2**$^+$ (1.323 vs 1.408 Å). At our highest level. i.e., at B3LYP/6-311+G*//B3LYP/6-311+G* + ZPE, **1**$^+$ is 19.6 kcal/mol lower in energy relative to **2**$^+$. Overall, our DFT calculations are in very good agreement with the previously reported data on parent Ph$^+$.[9,10] Calculated NBO charge at the carbocation center in **1**$^+$ is +0.68.

Figure 2 summarizes the structural parameters and the NBO charges at the cation center for the singlet p-XC$_6$H$_4$$^+$ monocations. Substituents studied were −OH (**3**$^+$), −OMe (**4**$^+$), −SH (**5**$^+$), −SMe (**6**$^+$), −H$_2$N (**7**$^+$), and −NMe$_2$ (**8**$^+$). Among these, only **3**$^+$ and **7**$^+$ had previously been calculated.[10] The most significant changes that these activating electron-donating substituents bring about are that the magnitude of positive charge at C$^+$ diminishes and the C−C$^+$−C angle tightens, with **7**$^+$, **8**$^+$, and **5**$^+$ showing the largest changes.

Figure 3 illustrates the minimum energy structures, geometries, symmetries, and the NBO charges at the carbocationic center for the corresponding onium-substituted singlet phenyl dications **3H^{2+}**−**8H^{2+}**, as well as for the singlet p-N$_2$$^+$−Ph$^+$ dication **9^{2+}**. Upon heteroatom protonation, positive charge at the carbocation center increases and the C−X bond lengthens, consistent with diminishing of p−π overlap between the heteroatom and the arene. At the same time, the phenyl cation undergoes rather significant geometrical changes; most notable are



14^+ (C_s)

15^+ (C_2)

Figure 4. B3LYP/6-311+G*-optimized structures of 14^+–15^+.

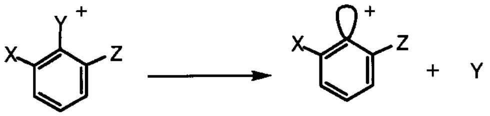
widening of the C–C$^+$–C angles and shortening of C–C$^+$ bond lengths. These changes are most pronounced for the ammonium- and sulfonium-substituted **8H**$^{2+}$, **7H**$^{2+}$, and **6H**$^{2+}$. Total energies, zero-point vibrational energies (ZPE), and proton affinities are summarized in Tables 1 and 2.

It can be seen that the p-X-$C_6H_4{}^+$ monocations gradually shift from singlet ground state to triplet ground state. Thus, whereas **3**$^+$ is energetically identical (as also shown previously[10]), introduction of –SMe, –NH$_2$, and –NMe$_2$ groups further lowers the energy of the triplet ground state. Calculated geometries for the singlet p-X-$C_6H_4{}^+$ monocations (Figure 1) show a trend of decreasing C–C$^+$–C bond angles and reduced positive charge at the carbocationic center in the singlet minima. Upon protonation, there is a significant reversal of singlet/triplet preference in favor of the singlet minimum, with the sulfonium and ammonium substituents showing larger ΔE (singlet–triplet) values. Judging from the relative proton affinities (Table 1), generation of these onium dications are more favored. Introduction of p-$N_2{}^+$ creates an even larger preference for the singlet-state aryl cation.

Effect of Benzannelation. Generation of aryl cations from polyaromatic hydrocarbons (PAHs) is also attractive because precursors to such intermediates are widely available, for example, amino-PAHs for diazotization and aryl triflates, which can be made from phenols. However, the search for aryl cations in solution has mostly focused on the parent phenyl cation.[2–8] In a search for other potential systems that could produce aryl cations, we have calculated the singlet and triplet 1-naphthyl (**10**$^+$), 2-naphthyl (**10a**$^+$), and 9-anthracenyl (**11**$^+$) monocations, as well as 4-OH (**12**$^+$), 4-NMe$_2$ (**13**$^+$), and the onium–aryl dications resulting from protonation of **12**$^+$ and **13**$^+$, i.e., **12H**$^{2+}$and **13H**$^{2+}$ (the relevant energies are listed in Table 3). Whereas in all cases both singlet and triplet states are minima, the preference for the triplet ground state increases as the system becomes more electron rich. The C–C$^+$–C angle in the singlet **10**$^+$ is 148.6° and remains very close to **1**$^+$. The C–C$^+$ bond in **10**$^+$ is shorter at the nonbenzylic position (1.308 Å) and longer at the benzylic position (1.340 Å).

Overall, the effect of benzannelation is similar to placing strongly activating substituents into the para position in parent Ph$^+$. Data in Table 3 show that whereas **10**$^+$ and **10a**$^+$ are potentially energetically identical, **11**$^+$ is a triplet ground state. Introduction of –OH or –NMe$_2$ substituents into **10**$^+$ (**12**$^+$ and **13**$^+$) lowers the triplet ground-state energy substantially. The reversal of the triplet to singlet preference is again seen in the case of **12H**$^{2+}$ and **13H**$^{2+}$; however, the effect is just sufficient to result in energetically identical dications rather than singlet ground states.

Scheme 1



	ΔH (kcal/mol)
X = H; Y = N$_2$; Z = H	+28.9
X = H; Y = N$_2$; Z = Si(CH$_3$)$_3$	+13.4
X = Si(CH$_3$)$_3$; Y = N$_2$; Z = Si(CH$_3$)$_3$	+1.8
X = H; Y = CO; Z = H	+65.7
X = H; Y = CO; Z = Si(CH$_3$)$_3$	+50.2
X = Si(CH$_3$)$_3$; Y = CO; Z = Si(CH$_3$)$_3$	+37.5

Effect of β-Silyl Stabilization in Dediazoniation and Decarbonylation. With the view to exploit the effect of β-silyl stabilization in dediazoniation as a means of generating the singlet Ph$^+$ under suitable conditions in solution, we have calculated the energetics of dissociation of $PhN_2{}^+$ into Ph$^+$ + N$_2$ and PhCO$^+$ into Ph$^+$ + CO. The outcome is shown in Scheme 1. Dediazoniation and decarbonylation of the parent systems are strongly endothermic with decarbonylation being less favorable than dediazoniation. By stepwise introduction of o-TMS groups, the endothermicity of dediazoniation is reduced to the point that the corresponding Ph$^+$ and $PhN_2{}^+$ become energetically almost comparable. o-Silyl substitution is less effective in decarbonylation to give mono-trimethylsilyl-substituted phenyl cation **14**, although it does reduce the endothermicity for decarbonylation. These trends suggest that 2,6-(TMS)$_2$PhN$_2{}^+$ could be expected to spontaneously lose N$_2$ in solution to give bis-o-trimethylsilyl-substituted phenyl cation **15** in the singlet state. Optimized structures of **14** and **15** are given in Figure 4. The corresponding triplet states were also calculated, but they were found to be significantly less stable than the singlets **14** and **15** by 26.7 and 34.5 kcal/mol, respectively.

Conclusion

We have carried out a theoretical study using the DFT method to examine the effect of protonation on *p*-$XC_6H_4^+$ cations (X = OH, OMe, SH, SMe, NH_2 and NMe_2) to form $HX^+{-}C_6H_4^+$ dications. We have also examined the effect of benzannelation on the relative singlet/triplet energy gap. It was shown that the singlet minimum is strongly preferred for $HX^+{-}C_6H_4^+$ dications, with the sulfonium and ammonium substituted Ph^+ showing the largest ΔEs. Benzanneled Ar^+ are either energetically identical or are triplet ground-state ions. Preference for the triplet ground state diminishes by onium substitution but not sufficiently to create singlet ground states (the systems are at best energetically identical).

Relative energetics of dediazoniation and decarbonyaltion in *o*-TMS-substituted PhN_2^+ and $PhCO^+$ suggest that in 2,6-$(TMS)_2PhN_2^+$ heterolytic N_2 loss should be quite facile.

Acknowledgment. Support of our work by the National Science Foundation at USC and the National Institutes of Health at Kent State University is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates and total energies (hartrees) of the optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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