Geometry and Energy of Substituted Phenyl Cations

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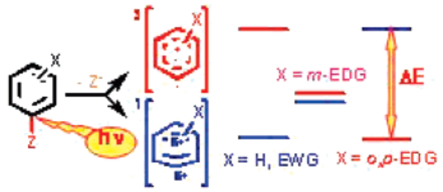

The geometry and the energy of a number of substituted phenyl cations have been calculated for both spin states at the UB3LYP/6-31G(d) level (*o*-, *m*-, *p*-Me, OMe, NH_2, CN, NO_2) or at the UB3LYP/6-311++G(2d,p) level (*o*-, *m*-, *p*-$SiMe_3$, SMe). The geometric differences were assessed by means of a self-organizing neural network. The triplets maintain a regular hexagonal structure that is minimally affected by substituents, while in the singlets C_1 puckers inward and, when an electron-donating group is present, shifts out of the plane. The triplets have the character of aromatic radical ions and are strongly stabilized by electron-donating substituents, independently of the position of the latter. In the case of singlets, the effect of substituents on the energy is weaker and depends on the position (the largest effect is exerted when the group is in meta). A two-parameter correlation of all of the triplet energies shows the predominant mesomeric effect of the substituents. In the case of singlets, linear correlations are obtained only when each position is treated separately and when the predominant effect is inductive for the ortho and, less markedly, the para position, whereas at the meta position, mesomeric and inductive effects are comparable. The ground state is determined to be the singlet for the parent cation and for electron-withdrawing substituted ions. With electron-donating substituents, the triplet is the ground state for ortho and para derivatives, while the two spin states are roughly isoenergetic when the donating group is in the meta position. These data allow predicting the reactivity of each cation.

Introduction

Although the role of trivalent (alkyl) carbocations has long been established and extensively studied, their divalent analogues, viz., vinyl and phenyl cations, have received less attention. This applies in particular to the latter intermediates,[1a] about which little has been reported. Until a few years ago, the literature included some spectroscopic studies in the gas phase[1b] or in a matrix at a low temperature[1c,d] and only a handful of studies in solution.[1e,f] Even the work in solution was mechanistically oriented and concerned only a few reactions of limited synthetic interest. Thus, the phenyl cation was an intermediate in the solvolysis of phenyldiazonium salts (under controlled conditions to avoid radical paths in the dediazoniation) as well as of a few phenyl triflates where the cation was stabilized by multiple silyl substitution (eq 1). Alternative precursors were tritiated benzenes, which were investigated by Speranza and shown to decay to the phenyl cation and to undergo various arylation reactions;[1g] however, this could be hardly considered a method suited for preparative purposes.

$$\mathrm{Ph{-}X} \rightarrow \mathrm{Ph}^{+}\ (\mathrm{X} = \mathrm{N_2}^{+}, \mathrm{OTs}, \mathrm{T});\qquad \mathrm{Ph}^{+} + \mathrm{Solv} \rightarrow \mathrm{Ph{-}Solv}^{+} \quad (1)$$

In parallel with experiments, theoretical studies were carried out. The most interesting point was evidenced already 30 years ago and had to do with the multiplicity of the cation. Thus, the two spin states of this intermediate have a quite different

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structure, with $\pi^6\sigma^0$ orbital occupation for the singlet that is a localized carbocation and $\pi^5\sigma^1$ for the triplet that has a diradicalic character.[2] It was also shown that in the parent phenyl cation the singlet is the ground state and the triplet lies 20−24 kcal/mol above it, but substituents shift the energy of the intermediates considerably and may reverse the order. The two structures are in a way reminiscent of those of singlet and triplet carbenes, and one may have expected that these cations could become, just as carbenes, synthetically useful intermediates. However, this has not been the case, and very little has been reported in the following years on the synthetic exploitation of these cations, let alone spin selectivity, although a pioneering paper by Schuster[3] did evidence that with some diazonium salts direct photolysis led to solvolysis via the singlet cation, while photosensitization led to reduction via the triplet. Clearly, the limited access to phenyl cations and the limited scope of the chemistry occurring discouraged planning synthetic applications of these intermediates.

However, the situation has recently changed, and these stumbling blocks have been removed. In fact, it has been found that phenyl cations are conveniently generated by photolysis in a polar medium not only of phenyl diazonium salts but also of phenyl chlorides, fluorides, phosphates, mesylates, and related compounds, at least when an electron-donating group is present (for many of the cases studied, the substituent was in the para position, but equally satisfactory cases have been found also for the other positions).[4] Furthermore, while confirming that the singlets are quite unselective electrophiles and that solvolysis is the normal result in this case, it was found that triplet phenyl cations add selectively to π, not to n, nucleophiles.[4] A lucky circumstance was that with the above-mentioned electron-donating substituted phenyl halides and esters intersystem crossing generally preceded fragmentation and thus photolysis led to the triplet cation, the synthetically most useful state. Actually, in this way, a large scope method for C−C bond forming arylation reactions was found, and several good yield synthetic procedures were developed that parallel transition-metal-catalyzed coupling reactions such as Suzuki, Heck, and Sonogashira reactions, while being considerably simpler from the experimental point of view.[4d]

Thus, interest in such intermediates may grow and lead to new synthetic procedures. We felt that at this juncture a new computational investigation was appropriate and may help the rationalization of the results obtained in the meantime as well as, possibly, foster further development. As a contribution toward understanding the mechanism and the scope of arylation reactions via phenyl cations, we report below a study of the structure and energy of a series of phenyl cations, both singlet and triplet.

Results and Discussion

The work was carried out by the DFT method, which appears to be well suited for charged intermediates and in particular for phenyl cations.[2c−e,4a,c] The merits of DFT for obtaining a quantitative estimate of the singlet−triplet gap for hypovalent species such as nitrenium ions[5a,b] and carbenes,[5c−i] as well as phenyl cations,[5j] have been evidenced. Of the ions considered, the parent phenyl cation as well as the *o*-, *m*-, *p*-amino, -methoxy, -methyl, -cyano, and -nitro derivatives were calculated at the UB3LYP/6-31G(d) level, whereas the *o*-, *m*-, *p*-trimethylsilyl (TMS) and -thiomethoxy derivatives (and again the parent ion for the sake of comparison) were calculated at the UB3LYP/6-311++ G(2d,p) level (see Experimental). All optimized geometries were found to have zero imaginary frequencies. The solvation energy in acetonitrile was evaluated accordingly to the CPCM method.[6]

As will appear in the following, substituent-dependent trends were recognized both in the geometry and in the energy of the cations investigated, and relations with experimental results could be established.

Geometry. To better understand the geometry of the cations studied, we made recourse to the method of self-organizing neural networks, a technique for processing data that has been applied recently in chemistry,[7] e.g., for the quantification of aromaticity.[7g] This method is well suited for comparing and classifying a large amount of data giving (semi)quantitative parameters as the output. A pattern classification with neural networks is expected to assess in an *objective* way the effect of substituents on the structure of phenyl cations.

We used self-organizing maps, as developed by Kohonen.[8] This is an unsupervised neural network that is used for creating a projection from a higher dimensional space onto a two-dimensional space, while preserving topological relations as faithfully as possible. We introduced geometrical parameters of the carbon skeleton of the benzene ring (bond lengths, angles, and dihedral angles but not the aryl−substituent distance to

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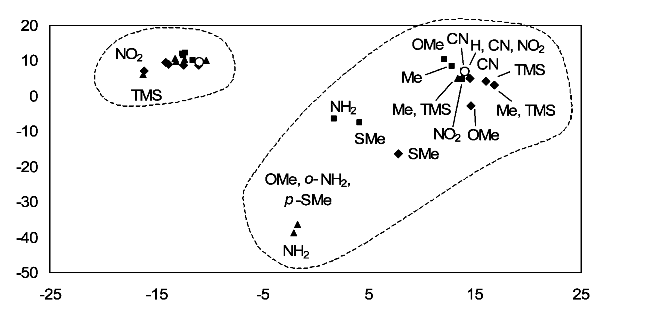
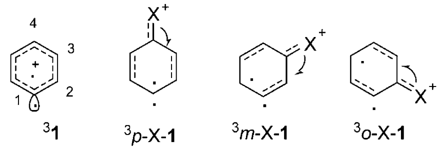


FIGURE 1. Sammon map obtained from the trained data set of phenyl cation geometric parameters (calculated bond lengths, angles, and dihedral angles). The larger set represents phenyl cations in the singlet state, and the smaller one represents the triplets. The parent cations in the two series (empty circles) and ortho- (diamond), meta- (squares), and para- (triangles) substituted derivatives are indicated.

CHART 1. Structure of Parent (^{3}1) and Substituted (^{3}X-1) Triplet Phenyl Cations



^{3}**1** ^3p-X-**1** ^3m-X-**1** ^3o-X-**1**

X = NH_2, SMe, OMe, Me, $SiMe_3$, CN, NO_2

avoid that this factor overcomes the other ones, see Supporting Information) as obtained from the optimization of all of the above phenyl cations. An 8 × 8 output grid with rectangular boundaries was chosen as the output as this is the best choice for identifying structure similarities. A visually effective way for presenting the results of this analysis is a Sammon map[8] (see Figure 1), a nonlinear projection generated through an iterative procedure. In this map, the input vectors are reduced to two-dimensional points on a plane. The closer two structures are in the map, the more similar they are, thus allowing the unbiased recognition of the similarity and difference.

The map shows the large difference between singlet (^{1}**1**) and triplet (^{3}**1**) phenyl cations. The triplets are confined within a small cluster with a small effect by the substituents. Actually, the corresponding points lie on a short horizontal segment with parent ^{3}**1** close to an extreme. ^3o-NO_2-**1** and ^3p-TMS-**1** are found at the other extreme, and the geometrical change is due to the interaction of the cationic site and the NO_2 oxygen in the first case and to the hyperconjugation with the methyl groups in the latter. Also in these cases the displacement is small.

The character of an aromatic radical cation and the presence of the half-filled sp^2 orbital in the molecular plane ($\pi^5\sigma^1$ electronic structure) have little effect on the geometry of the triplet cation (^{3}**1**, see Chart 1), and the regular hexagon geometry is conserved. Also in substituted triplets the angles remain close to 120° and the planarity is maintained (as an example, see ^1o-NH_2-**1** in Figure 2). The only significant change involves bond lengths. In these ions, the C−X bond is slightly shortened with respect to the corresponding neutral molecule (including the case of X═Me, where apparently hyperconjugation contributes) and so are the bonds in the 2,3 and 4,5 positions with respect to the substituent. This leads to some cross-conjugated character that may be envisaged as the 1-(C═X$^+$)-cyclohexa-2,5-diene structure contributing to some degree. Notice that the deformation is determined by the position of the substituent, *not* by that of the divalent carbon and thus of the formal charge, as visualized in formulas ^{3}X-**1** in Chart 1. As a matter of fact, if any group of isomeric cations ^3o-, *m*-, and *p*-X-**1** is piled up with the substituent on the same side, the ring carbons of the three ions superimpose exactly disregarding where the formal charge is.

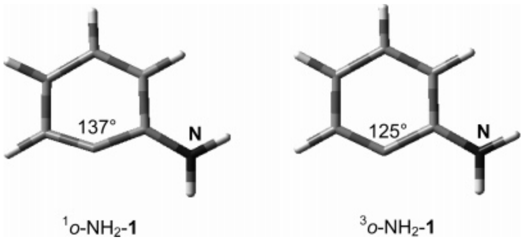
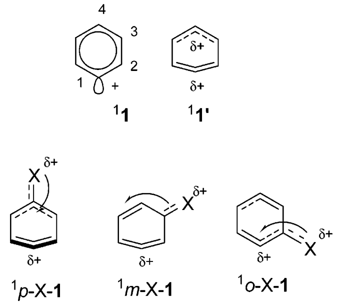


FIGURE 2. Optimized structure of phenyl cations ^1o-NH_2-**1** and ^3o-NH_2-**1**. In the singlet, C_1 is tilted 9° out of the plane, while the triplet is perfectly planar.

CHART 2. Structure of Parent (^{1}1) and Electron-Donating Substituted (^{1}X-1) Singlet Phenyl Cations



^{1}**1** ^{1}**1'**

^1p-X-**1** ^1m-X-**1** ^1o-X-**1**

X = electron-donating group

As for the singlets, these occupy a larger portion of the map in Figure 1, with no superimposition with the triplet zone, and are rather scattered in an area diagonal with respect to the axes, indicating that several geometric parameters are affected; in particular, dihedral angles are quite variable.

In fact, the different electronic structure of the singlet ($\pi^6\sigma^0$ orbital occupation, see formula ^{1}**1** in Chart 2) is accompanied by a large deviation from the regular hexagonal geometry due to puckering inward of C_1 (the C_2−C_1−C_6 angle opens up to 147° in ^{1}**1**). At the same time, the C_2−C_1 and C_1−C_6 bonds become shorter, giving some cumulene character to this moiety, while the C_2−C_3 and C_5−C_6 bonds are lengthened so that formula ^{1}**1′** may be taken to represent the structure of the parent singlet phenyl cation (Chart 2). The planarity of the ring is conserved, but a low-frequency vibration (457.3 cm^{-1}) has been located, which corresponds to the twisting of the "allene" moiety. The (Mulliken) charge is located in part at C_1 and in part at C_4.

As for substituted derivatives, those bearing a group that has electron-withdrawing action or a small donating effect are found in Figure 1 in an area close to the parent cation, indicating no major modification of the geometry. Cations bearing an *electron-donating* group, on the other hand, maintain the above features, but with further deformations that depend on the position. These groups participate in the delocalization, as indicated by a slight shortening of the C−X bond (by 2−3% with respect to the corresponding neutral derivative Ph−X). Furthermore, the carbon in 4 with respect to such substituents tilts out of the molecular plane "seeking" the heteroatom lone pair. This is most apparent when the substituent is in para (^1p-X-**1**) where the displacement out of plane of C_1 reduces puckering of the ring

TABLE 1. Substituent Effect on the Energy of Phenyl Cations 1: Δ*E* (kcal/mol) in MeCN of the Isodesmic Reaction in Equation 2

			singlet			triplet		
substituent	*F*	*R*	ortho	meta	para	ortho	meta	para
NH_2	0.037	−0.681	1.09	10.46	4.20	34.60	33.80	36.50
SMe	0.332	−0.186	−3.68	0.33	−4.28	23.86	22.42	24.15
OMe	0.413	−0.5	−8.69	0.16	−4.00	16.71	15.60	17.60
Me	−0.052	−0.141	2.07	1.30	−0.22	4.80	4.16	6.01
TMS	−0.047	−0.044	12.34	5.14	1.46	5.00	2.73	3.00
H	0	0	0.00	0.00	0.00	0.00	0.00	0.00
CN	0.847	0.184	−18.33	−13.11	−11.74	−13.60	−13.05	−11.00
NO_2	1.109	0.155	[a]	−15.65	−14.91	−19.09	−17.66	−17.40

[a] Attempted optimization of ^1o-NO_2-**1** failed because this ion collapsed toward a further intermediate with an oxygen bonded to C-1. Compare ref 2e.

at that position (as an example, the angle and the dihedral angle at C_1 are 134° and 13° for ^1p-NH_2-**1** and 141° and 10° for the *p*-OMe analogue, to be compared with 147° and 0° in ^{1}**1**). A (lower) tilt and a more complex deformation are observed also for C_5 in ortho derivatives (compare ^1o-NH_2-**1** in Figure 1). In meta derivatives, C_6 tilts out of plane, but because this atom is a part of the stiff “cumulene” function the latter moiety is slightly rotated. Furthermore $C_3{-}C_4$ and $C_4{-}C_5$ bonds acquire some single and double bond character, respectively, forming a conjugate $C{=}C{-}C{=}X^+$ moiety where the strong donation by the substituent is apparent (see formula ^1m-X-**1**, typical examples are ^1m-NH_2-**1** and ^1m-SMe-**1**).

Thus, geometric changes in the cation structure can be traced back to the multiplicity of the state (and thus to the electronic structure) and (for singlets) to the nature and position of the substituents, and the plot in Figure 1 can be used to predict the geometry of additional phenyl cations.

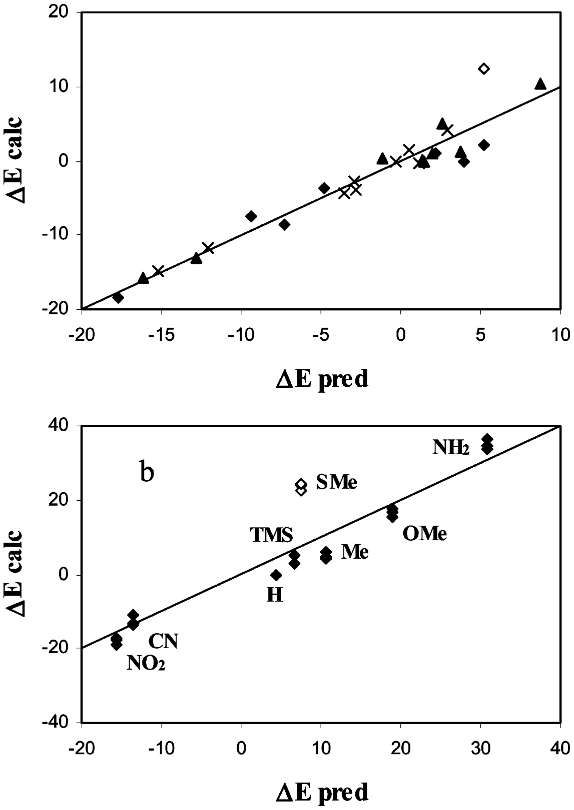


FIGURE 3. Stabilization by the substituent of the (a) singlet (diamonds, ortho-substituted; triangles, meta; crosses, para) and (b) triplet phenyl cations: comparison between the calculated value (Table 1) and that predicted according to the equations in Table 2. Empty symbols correspond to values not taken into account for establishing the correlations in Table 2. The substituent present is indicated for the triplet (*o*-, *m*-, *p*-isomers almost superimposed).

Energy. As mentioned in the Introduction, the singlet is the ground state of cation **1** by a large span (ΔE_{ST} 21.3 kcal/mol). Substituents, however, may cause a large effect on the energy of the cations. Thus, the energy of the above series of phenyl cations was calculated, and the substituent effect was assessed by comparing the energy of the cation and that of the corresponding benzene (calculated at the same level) for the substituted and the parent compound. The Δ*E* in MeCN of the isodesmic reactions in eq 2 gives a quantitative measure of the stabilization.

$$X{-}C_6H_4^+ + H{-}C_6H_5 \rightarrow X{-}C_6H_5 + H{-}C_6H_4^+ \qquad (2)$$

The values obtained are reported in Table 1, where it is apparent that electron-withdrawing substituents destabilize both singlet and triplet cations, while the electron-donating ones strongly stabilize the triplets but have a variable, and at any rate smaller, effect on the singlets.

To rationalize the results, a linear correlation of the above Δ*E* values by using substituent parameters from the literature was explored. No satisfactory correlation was found by using a single parameter treatment, such as $\sigma_{m,p}$ or $\sigma^{(+)}_{m,p}$. A two-parameter treatment by using the field ($\mathscr{F}$) and resonance ($\mathscr{R}$) indexes developed by Swain[9a,b] was next tested (see eq 3 and Figure 3).

$$\Delta E = f\mathscr{F} + r\mathscr{R} + \mathrm{i} \qquad (3)$$

This fitting was successful,[9c] and the stabilization by electron-donating substituents resulted in a negative value for both coefficients *f* and *r*, as expected for a cation. A value close to 0 was obtained for the intercept i, which attested a good agreement with the theoretical model. More precisely, the *m*- and *p*-substituted singlets gave a satisfactory correlation, whereas among the o-substituted cations the trimethylsilyl derivative was more stable than expected (see Figure 3a, empty symbol) and was excluded from the correlation (the parameters obtained are

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TABLE 2. Two-Parameters Linear Correlation for the Substituent-Induced Stabilization of Phenyl Cations According to Equation 3

	f	r	i	R^2
^{3}X-C$_6$H$_4$$^+$[a]	−11	−41	1.5	0.96
^{1}o-X-C$_6$H$_4$$^+$[b]	−21	−2.3	0.62	0.97
^{1}m-X-C$_6$H$_4$$^+$	−14	−12	1.4	0.96
^{1}p-X-C$_6$H$_4$$^+$	−13	−5.5	−0.3	0.98

[a] The values for the thiomethyl-substituted derivatives ^{3}*o*-, *m*-, and *p*-SMe were excluded. [b] The value for silylated ^{1}*o*-TMS was not taken into account.

reported in Table 2). As for the triplets, a *single* correlation was satisfactory for the *three* positions, provided that the three thiomethyl derivatives were excluded (see Figure 3b, empty symbols), since these were again more stable than expected.

The data in Table 2 evidence that for triplets the large substituent effect is mainly due to the resonance factor ($r = -41$). The high ratio $r/f \cong 4$ is unusual among aromatic molecules and reflects the radical cation nature of triplet ^{3}**1** resulting from the above evidenced $\pi^5\sigma^1$ orbital population in this state (see formula ^{3}**1**). Thus, substituents capable of mesomeric electron donation are highly effective in stabilizing the cation by delocalizing the electron vacancy in the π orbital (see formulas ^{3}X-**1** in Chart 2). Consistently with this representation, the stabilization is *independent of the substituent position* relative to the formal charge at C$_1$. The stabilization is larger than predicted by eq 2 with the thiomethyl group, possibly due to enhanced donation from the sulfur d orbitals. Correspondingly, mesomeric electron-withdrawing substituents cause the expected large destabilization.

As for the singlet states, the overall stabilization is smaller and characterized by a modest contribution of the resonance term. This is in accord with the $\pi^6\sigma^0$ population in this state and thus with the smaller electron withdrawal from the substituent to the ring. With the singlets, separate correlations have to be drawn for each position. For the *m*- and *p*-position, the r and f values are comparable (r/f ratio ca. 1 and 0.4, respectively), i.e., within the range observed for many reactions of aromatics,[9] again supporting that the full occupation of the bonding π orbitals in these states maintains the aromatic character much more than triplets. In particular, the largest r values are those of the meta isomers, and these cations are consistently more stable than the corresponding *o*-derivatives, with a difference that increases with mesomerically donating groups. This is a quantitative expression of the stabilization due to the conjugation shown in formula ^{1}*m*-X-**1** (Chart 2).

The contribution of the field effect follows, as expected, the order o > m ≈ p. In particular, with ortho substituents stabilization arises almost exclusively from a large contribution by the field effect ($f = -21$), while r is small, with an r/f value (0.1) again unusual for aromatics, in a way contrary to that evidenced above for triplets. This is consistent with the fact that the substituents lie side by side with the empty orbital at C$_1$. On top of this, the *o*-trimethylsilyl derivative enjoys an extra stabilization by ca. 8 kcal/mol with respect to the expected value (see Figure 3a) that appears to be an example of the well-known "β-stabilization" effect of silicon-bonded groups.[10] For the m- and *p*-derivatives, where the substituent is away from the divalent carbon, the f value is close to that (−11) found with the triplets.

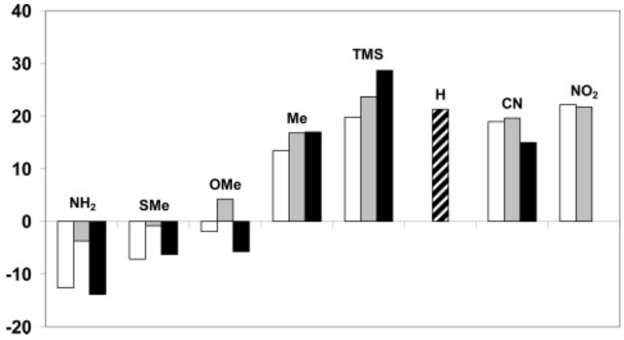

FIGURE 4. S/T energy gap for parent (slashed), *o*- (black), *m*- (gray), and *p*- (colorless) substituted phenyl cations.

An important consequence of the different effect on the two spin states (ΔE varies by almost 50 kcal/mol with the substituents considered for the triplets (see Table 1) while with singlets the span is 25 kcal/mol for substituents in meta and 20 kcal/mol in the other positions, excluding *o*-TMS) is that their energetic order changes, as can be appreciated by looking at the ΔE_{ST} values reported in Figure 4. As appears in Table 1, both electron-withdrawing groups and substituents with a small $\mathscr{R}$ value such as methyl and trimethylsilyl have a not too dissimilar effect on the singlet and triplet cations, so that ΔE_{ST} is little varied (notice that the *o*-TMS group tilts the balance further toward the singlet). With mesomeric electron-donating groups, however, the stabilization of the triplets is large. Whether this overcomes that enjoyed by the singlets by more than the 21.3 kcal/mol of the parent cation, thus reversing the order, depends on the position of the substituent. In fact, in the meta position the resonance term contribution is large also for the singlets. The two opposite effects make the two spin states roughly isoenergetic for *meta*-amino, methoxy, and thiomethoxy (and hydroxy, not reported) substituted cations. In the ortho and para positions, however, resonance is more important, and the triplet is the ground state.

Effect on the Chemical Reactivity. As mentioned in the Introduction, phenyl cations are conveniently generated by photochemical reactions. The chemistry of phenyl cations has been experimentally found to depend on the multiplicity of the reacting state, the triplet reacting preferentially with π nucleophiles and thus giving valuable C−C bond forming arylations, the singlet reacting unselectively and thus most often with the solvent. Which one of these behaviors is followed depends on the precursor used and the conditions. Electron-donating substituted phenyl halides and esters undergo photocleavage from the triplet and form the triplet phenyl cation (see Scheme 1). As it appears in Scheme 1 and Figure 4, in this case, this is the ground state, and thus under these conditions, arylation is the predominant process, at least with *o*- and *p*-substituted compounds. With the meta derivatives, however, the singlet is isoenergetic or even more stable, and thus in the absence of a good π trap, ISC to the singlet may occur and the reaction shifts to solvolysis. Indeed, we recently found that this peculiar "meta" effect is actually operating with chloroanisoles.[11]

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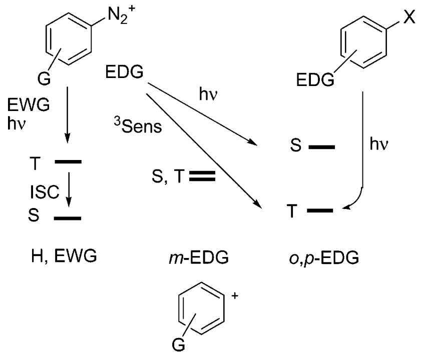
[10] Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677−2689. Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183−190.

[11] (a) Dichiarante, V.; Dondi, D.; Protti, S.; Fagnoni, M.; Albini, A. *J. Am. Chem. Soc.* **2007**, *129*, 5605. (b) The effect of the *m*-methoxy group on the (thermal) decomposition of diazonium salts has been early observed: Taft, R. W. *J. Am. Chem. Soc.* **1961**, *83*, 3350.

SCHEME 1. Generation of Singlet and Triplet Phenyl Cations from Phenyldiazonium Salts and from Phenyl Halides and Esters by Direct Irradiation (h*ν*) and Triplet Sensitization (^{3}Sens) and Effect of Electron-Withdrawing (EWG) and Electron-Donating (EDG) Substituents on the Energy Order



Another strong stabilization of the singlet is caused by an *o*-trimethylsilyl group. In the monosubstituted cation, this simply confirms its singlet nature. An interesting situation is expected to arise with polysubstituted phenyl cations when both triplet-stabilizing (e.g., amino, methoxy) and singlet-stabilizing (e.g., *o*-SiMe$_3$) groups were present.

When on the other hand the phenyl cation is photogenerated from phenyldiazonium salts, the situation is varied because the competition between ISC and fragmentation in the excited diazonium depends on the substituent (Scheme 1).[12] With electron-withdrawing substituents, direct irradiation gives the triplet phenyl cation. This is not the ground state in this case (see Figure 3), but it may arylate a good π trap before intersystem crossing to the singlet ground state. In the absence of such a trap, solvolysis via the cation is the result, as actually observed.[12] With electron-donating substituents, dediazoniation precedes ISC and direct irradiation leads to the singlet. Although this is the high-energy state with such substituents, solvolysis is too fast to allow competition by ISC. However, triplet sensitization gives the triplet diazonium and the triplet phenyl cation from it, and in this way, arylations can be obtained also from these derivatives.

Conclusions

The geometry and the energy of the singlet ($\pi^6\sigma^0$ structure, puckered) and triplet state ($\pi^5\sigma^1$ structure, planar) of a series of substituted phenyl cations have been investigated by DFT methods. The pattern of the effects with reference to the nature of the substituent and to its position has been recognized. The regular hexagon geometry of ring carbons in the triplet state is minimally affected by substituents. The singlet cation is more heavily deformed (cumulene character at the $C_2-C_1-C_6$ moiety) and is affected to a large extent both by the position and by the nature of the substituent in particular with electron-donating substituents that cause a ring carbon to shift out of plane. Besides preventing loss of planarity, the radical cation structure of the aromatic ring in the triplets maximizes the effect of substituents on the energy, whereas π^6 singlets are more easily deformed and their energy is less affected by substituents. This results in a change of the multiplicity of the ground state cations. In summary, electron-donating groups stabilize the singlets when in meta and the triplets in any position (and by a larger amount). As a result, the triplet is the ground state with *o*- or *p*-electron-donating substituted phenyl cations. Due to the different chemistry exhibited by the two spin states, these effects are of primary importance for predicting the reaction occurring when the phenyl cation is generated. Some of the predictions based on these calculations, in particular the “meta” effect on singlets, have been recently confirmed experimentally.[11] It is hoped that interplay between calculation and experiment will open the path toward a larger application in synthesis of these fascinating intermediates.

Experimental

Optimizations were carried out at the UB3LYP/6-31G(d) level (*o*-, *m*-, *p*-Me, OMe, NH$_2$, CN) or at the UB3LYP/6-311++G-(2d,p) level (*o*-, *m*-, *p*-NO$_2$, SiMe$_3$, SMe) by using the Gaussian 2003 package.[13] Frequency calculations were evaluated at the same level of theory to certify structures as minima. Energies of the solvated cation were evaluated with the CPCM method on the (in vacuo) optimized geometries by using acetonitrile as solvent.[6]

The structure optimization of some of the phenyl cations[1,3] **1** considered had been previously reported, and our results were perfectly compatible (these were the parent ions, the three methoxy, and all of the para derivatives).[2,4c] Energies and coordinates are reported as Supporting Information.

All calculations on the Self-Organizing Neural Network were evaluated with the SOM PAK program.[8b] The input table used for network training is reported as Supporting Information.

A rectangular topology and bubble function was used as a neighborhood kernel for generating a lattice of 8 × 8 neurons. Training was done in two phases: an ordering phase with 1000 steps and a self-organizing phase with 10000 steps. During the first cycle, the learning rate and initial neighborhood were set to 0.05 and 10, respectively. The parameter values for the second cycle were 0.02 and 3, respectively.

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Supporting Information Available: Cartesian coordinates and energies for phenyl cations **1** and training input and output of self-organizing neural network. This material is available free of charge via the Internet at http://pubs.acs.org.

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