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Selectivity in the Reaction of Triplet Phenyl Cations

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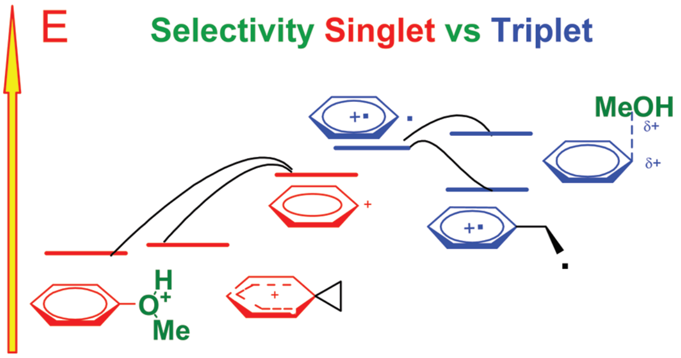

A DFT study of the reaction of phenyl cation and some 4-substituted derivatives (cyano, methyl, methoxy, amino) with a π nucleophile (ethylene) as well as with representative n nucleophiles (NH_3, MeOH, and MeCN) reveals a multiform behavior depending on both the cation multiplicity and the trap used. A straightforward addition takes place with the singlet ($\pi^6\sigma^0$ structure) both with ethylene, where a spiro[2,5]octa-4,7-dienyl (phenonium) cation is formed, and with n nucleophiles, where the corresponding onium cations result. On the contrary, with the triplet ($\pi^5\sigma^1$ structure) the reaction depends on the nature of the nucleophile, as indicated by MO correlation diagrams. Thus, with ethylene a bonding interaction occurs between the singly occupied $\sigma(sp^2)$ orbital of the cation and the alkene π orbital and leads to a planar distonic diradical cation. On the contrary, no addition takes place with n nucleophiles, which interact only with the phenyl cations π MO, leading to weakly bonded, face-to-face complexes. An electron-withdrawing substituent such as CN allows the formation of a stabilized adduct cation also from the triplet, but only with a good nucleophile, such as ammonia. The spin-dependent dichotomy in the chemical behavior rationalizes recent experimental findings and fits with the prediction formulated by Taft 45 years ago. The unusual combination of a carbocation nature and of triplet multiplicity originates the peculiar chemistry of phenyl cations that appear to be promising intermediates in synthesis.

Introduction

In contrast to aliphatic chemistry, substitution via a S_N1 mechanism is a rare occurrence among aromatic compounds.[1,2a,b] This is indeed a textbook example of a mechanistic difference, since this reaction would involve the unassisted detachment of the nucleofugal group and the formation of an aryl cation. This intermediate is expected to be planar, just as aliphatic cations. However, whereas in the latter ones the stable sp^2 orbitals are filled and a p orbital

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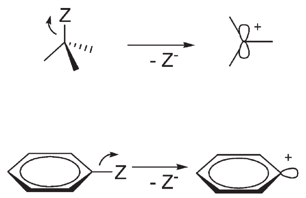
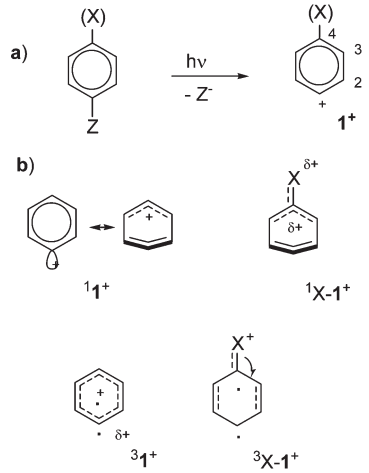
SCHEME 1. **Alkyl and Phenyl Cations**



SCHEME 2. **(a) Photochemical Generation of Phenyl Cations; (b) Structure of Singlet (^{1}1$^+$) and Triplet (^{3}1$^+$) Phenyl Cations**



is vacant, phenyl cations would be in the uncommon situation where the p orbital is filled (it is a part of the aromatic π system) and the sp^2 orbital is vacant.[2a,c,d] (see Scheme 1).

Experimental evidence for the role of this cation is limited to cases where such a good leaving group as the neutral nitrogen molecule is involved, as in the decomposition of phenyl diazonium salts[3a−c] (or similarly in the release of phenyl iodide from iodonium salts).[3d] However, the view has been presented that even in the dediazoniation reaction a very loose S_N2Ar rather than a S_N1Ar mechanism actually gives the most appropriate description of the reaction.[3e]

Mechanistic studies are thus limited in scope, and this is not compensated for by a synthetic interest. Indeed, the most useful reactions from diazonium salts involve the phenyl radical, not the cation,[4] and the few other methods for arriving at this intermediate, such as the decay of tritiated benzene, are not suitable for synthetic application.[5] Furthermore, there might be little point in preparing a high-energy intermediate that would react unselectively, typically with the solvent, as indeed suggested by early studies. However, it was observed early that some of the reactions attributed to this intermediate were ill-reconciled with a $\pi^6\sigma(\mathrm{sp}^2)^0$ structure, and in 1961 this led Taft[6a] (and later Abramovitch)[6b] to consider the possibility of an alternative diradical (triplet) structure ($\pi^5\sigma^1$) and to expect a "versatility of reactions" (ionic/radicalic) for the phenyl cation. Early computational studies evidenced that triplet states were high in energy and not accessible in the decomposition of diazonium salts.[6c] Further theoretical work well documented the different electronic character of the two spin states and showed that although the singlet is by far the most stable state in the parent cation, substituents may revert the order.[6d−h] However, in the four decades following Taft's proposal very little beyond solvolysis has emerged in the chemistry *via* phenyl cation and one may sum up the situation by stating that the thermal generation of this intermediate has elicited a limited interest in theory and spectroscopy and none at all in synthesis.

Things are different in photochemistry, not only because irradiation in matrix is a convenient method for spectroscopic studies on this cations[7] but also for preparative purposes. In fact, photolysis is the best method for the clean cleavage of phenyldiazonium salts ($Z = N_2^+$, see Scheme 2a) and the generation of phenyl cation (**1**$^+$) in the singlet or triplet multiplicity according to the substituents present.[8] Furthermore, the photolysis of various phenyl halides (Z = Cl, F) and esters ($Z = OSO_2CF_3$, $OPO(OR)_2$, etc.) has been found to generate smoothly *triplet* phenyl cations.[9] These intermediates have thus become accessible, and their spin-dependent chemistry has been revealed. The singlet acts as an indiscriminate electrophile (most often adding to the solvent), while the triplet behaves as a selective intermediate attacking preferentially π nucleophiles (and then, with some differentiation of the rate) and anions, but not (or much less) neutral n nucleophiles[9,10] Several synthetic protocols for arylation reactions have been developed that appear to parallel (in some cases with advantage from the environmental point of view) modern transition-metal-catalyzed arylations.[9c] This fostered a new computational investigation. An analysis of energy and geometry of (substituted) phenyl cations was recently carried out.[11] The key question of the (spin-dependent) reactivity of these intermediates is discussed here.

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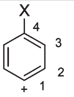
TABLE 1. Representative Data about the Calculated Geometry of Phenyl Cations $^{1,3}\mathbf{1}^{+}$ and Adduct Cations Arising from the Reaction with Ethylene, $^{1}\mathbf{2}^{+}$ and $^{3}\mathbf{3}^{+a}$

X	**a)** Phenyl cations						
	^{1}**X-1**$^{+}$				^{3}**X-1**$^{+}$		
	C_4-C_3	C_3-C_2	C_2-C_1		C_4-C_3	C_3-C_2	C_2-C_1
CN	1.407	1.429	1.328		1.442	1.377	1.405
H	1.395	1.435	1.327		1.434	1.378	1.412
Me	1.403	1.433	1.327		1.444	1.376	1.406
MeO	1.415	1.415	1.341		1.444	1.378	1.397
NH_2	1.430	1.400	1.360		1.440	1.378	1.397

	b) Adducts with ethylene									
	$^{1}\mathbf{2}^{+}$					$^{3}\mathbf{3}^{+}$				
	C_4-C_3	C_3-C_2	C_2-C_1	C_1-C_a	C_a-C_b	C_4-C_3	C_3-C_2	C_2-C_1	C_1-C_a	C_a-C_b
CN	1.414	1.378	1.429	1.632	1.432	1.435	1.371	1.429	1.500	1.490
H	1.405	1.381	1.430	1.627	1.433	1.428	1.373	1.432	1.497	1.489
Me	1.416	1.375	1.433	1.614	1.439	1.429	1.369	1.439	1.503	1.490
MeO	1.425	1.368	1.440	1.594	1.448	1.436	1.367	1.428	1.511	1.491
NH_2	1.434	1.359	1.448	1.582	1.455	1.433	1.372	1.420	1.515	1.492

[a] Distances in angstroms.

Results and Discussion

To rationalize and generalize the dramatically different chemistry of singlet and triplet phenyl cations found in the experiment, it was decided to explore computationally the reactions of both spin states of these cations with different traps. These were n nucleophiles, viz., methanol, acetonitrile (both often used as the solvent in the studies involving these intermediates), and ammonia, as well as a representative π nucleophile, ethylene. The experiments suggest that, as one may expect, substituents have a large effect on the reactivity of these ions, and thus the 4-cyano, methyl, methoxy, and amino derivatives were considered in addition to the parent cation. The study was carried out by using a DFT method at the UB3LYP/6-31G(d) level. This is easily implemented even with substituted derivatives and has proven to offer a good quantitative estimate of the singlet/triplet energy gap in phenyl cations[3e,6h] and other ionic intermediates[12] and a reliable description of geometry and electronic structure of triplet phenyl cations, in good accord with CASSCF/6-31G(d) data.[9b,10d,11] When weak complexes were involved, this was supplemented by using the M05-2x method, which is optimized for such a case and was combined with a triple-ζ basis set.[13] Since the heterolytic cleavage of the phenyl cations precursors is effective only in polar solvents, all of the calculations are referred to an acetonitrile solution by using the diffuse polarizable continuous solvent model (CPCM) method (see Experimental Section).

Phenyl Cations: Characteristics. Geometry, energy, spin, and charge distribution were calculated for phenyl cations and the corresponding adduct cations. The geometric parameters for the first intermediates have been previously determined[11] and are reported in Table 1, part a for facilitating the comparison (see below). As summarily indicated through mesomeric formulas $^{1}\mathbf{1}^{+}$ (see Scheme 2b), C_1 is puckered inside in the singlet phenyl cation and the C_2/C_1/C_6 moiety has some cumulene character, lessened to a degree in electron-donating substituted derivatives, where C_1 lies above the molecular plane. In contrast, the triplet is planar with a pronounced bond alternance (formula $^{3}\mathbf{1}^{+}$).

The calculated energies and solvation free energies of the cations are reported in Supporting Information. To assess the effect by substituents, we used the isodesmic reaction in eq 1. This compares the substituent effect on 4-substituted phenyl cations (X-$C_6H_4^{+}$ = **X-1**$^{+}$) with respect to the stabilization of the corresponding hydrocarbon (X-C_6H_5). In other words, this measures the substituent effect on the free energy change for the reaction of the phenyl cation with the hydride anion, and thus the electrophilicity of cations **X-1**$^{+}$, actually the target of the study.

The resulting free energy data (referred to the ground state - the singlet - of the parent cation) gave a linear fit by using

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TABLE 2. Two-Parameters Linear Correlations for Substituent-Induced Stabilization of Phenyl and Adduct Cations and for the Charge at C_1 in Phenyl Cations

	singlet				triplet			
cation	*f*	*r*	*i*	R^2	*f*	*r*	*i*	R^2
				Stabilization				
$X\text{-}C_6H_4^+$	−13.3	−7.58	−0.17	0.99	−5.92	−45.9	0.65	0.98
$X\text{-}C_6H_4\text{-}C_2H_4^+$	−5.81	18.1	−0.96	0.97	−1.21	−5.49	0.00	0.98
$X\text{-}C_6H_4NH_3^+$	−8.18	−2.29	−0.23	0.97	−10.1	−26.9	1.02	0.98
$X\text{-}C_6H_4OMe^+$	−7.84	−1.88	−0.16	0.97	−0.63	−9.72	0.09	0.99
$X\text{-}C_6H_4N{=}C^+Me$	−8.05	2.16	−0.04	0.99	−0.39	−2.54	0.28	0.95
				Charge at C_1				
$X\text{-}C_6H_4^+$	0.007	0.201	0.558	0.997	−0.016	0.164	0.399	0.999

the two parameters field ($\mathscr{F}$) and resonance ($\mathscr{R}$) indexes equation developed by Swain[14] (eq 2).

$$X\text{-}\mathbf{1}^+ + C_6H_5\text{-}H \rightarrow X\text{-}C_6H_4\text{-}H + \mathbf{1}^+ \tag{1}$$

$$\Delta G(1) = f\mathscr{F} + r\mathscr{R} + i \tag{2}$$

The resulting coefficients are reported in Table 2, first line. In the case of the triplet the resonance term dominates with *r* large and negative (−45.9), in accord with the $\pi^5\sigma^1$ structure that gives to these states the character of aromatic radical cations. The quite unusual *r*/*f* ratio of almost 9 leads one to expect a major effect of the mesomeric electron-donating substituents (and polar solvents) on properties linked to the stability of such intermediate. The large stabilization by mesomeric electron-donating groups explains the effective photogeneration of phenyl cation from the corresponding substituted phenyl chlorides by cleavage in the triplet state. The coefficients are both negative also with the singlets, but *r* is small (here π orbitals are filled). Notice that in the thermal decomposition of diazonium salts, a reaction involving the singlet cation as the intermediate, a positive *r* has been measured.[15] This is due to the different solvation of the two cations, the starting diazonium and the intermediate phenylium, whereas the present calculation refers to the latter species per se.

The charge distribution was then explored by using the NBO method,[16] considered the best suited for this assessment.[17] As it is shown in Table 3, the charge is to a large extent localized at C_1 in the singlet cation $^1\mathbf{1}^+$ (+0.4 to +0.6, the lower values refer to electron-donating substituents) and to a somewhat lesser degree in the triplet cation $^3\mathbf{1}^+$ (+0.3 to +0.4). With donating substituents the charge at C_4 is large, in particular with the methoxy derivative.

Thus, the charge distribution, in particular at C_1, changes moderately with the solvent, and indeed even with the multiplicity, even if it is consistently lower in the triplet. An attempted double parametrical correlation of the charge at C_1 (ΔC) by using the Swain indexes (eq 3) did not give a satisfactory correlation (see the proportionally large i value, indicating the impossible separation of resonance contributions, see Table 2b).

TABLE 3. NBO Charge and Spin Density on Phenyl Cation X-1⁺

	singlet, ^{1}X-**1**$^+$		triplet, ^{3}X-**1**$^+$				
	charge		charge		spin density		
	C_1	C_4	C_1	C_4	C_1	C_4	X^a
CN-**1**$^+$	0.584	−0.174	0.409	0.023	1.31	0.39	0.17
1$^+$	0.553	−0.244	0.402	0.023	1.38	0.49	
Me-**1**$^+$	0.550	−0.036	0.378	0.196	1.37	0.41	0.05
MeO-**1**$^+$	0.502	0.355	0.324	0.455	1.35	0.17	0.24
NH_2-**1**$^+$	0.383	0.215	0.274	0.222	1.33	0.05	0.35

[a] Sum of the spin densities over the substituent atoms.

$$\Delta C = f\mathscr{F} + r\mathscr{R} + i \tag{3}$$

This supports that all phenyl cations are electrophiles at C_1 and the difference in reactivity is not due to this characteristic.

Finally, the spin distribution was analyzed in triplet cations (see Table 3). The spin density in triplet $^3\mathbf{1}^+$ is mainly at C_1 (1.3−1.4) in accordance with the $\pi^5\sigma^1$ structure of this intermediate, a biradical with an electron in the σ orbital and the latter one delocalized in the π system, with the highest value at C_4 (0.4). Here again, the spin at C_1 is little affected by the substituent, but an electron-donating substituent at 4 displaces the spin at that carbon toward itself.

Adduct Cations. Singlets. The reaction of phenyl cations with the above-mentioned nucleophiles was next explored. Minima were located with the structures sketched in Scheme 3; the free energy change values for the corresponding processes are reported in Table 4.

With singlets, addition of ethylene to C_1 occurs with the alkene orthogonal to the benzene ring and forms the strongly stabilized spiro[2,5]octa-4,7-dienyl (phenonium) cation $^1\mathbf{2}^+$ (57.9 kcal/mol for the parent cation; the energies of the substituted cations are reported in Table 4, and schematic formulas are indicated in Scheme 3). Adduct $^1\mathbf{2}^+$ is characterized by a slightly longer $C_1{-}C_{a(b)}$ bond with respect to a non-spiro cyclopropane ring[18] (1.628 Å, shortened however in the presence of donating substituents) and by a pronounced bond-alternance in the cyclohexadienyl moiety that is increased by substituents. Similar conclusions on the structure of phenonium ions and its formation from singlet

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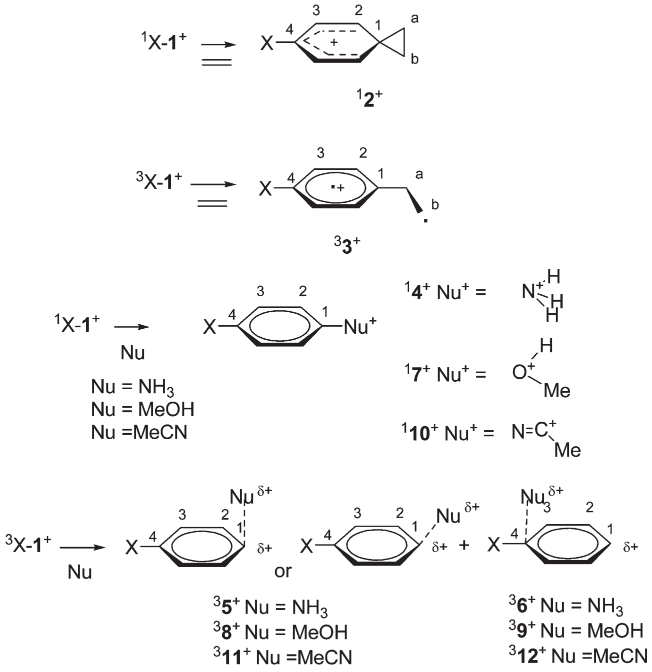
TABLE 4. Free Energy Change for the Addition of Phenyl Cations ^{1,3}**X-1**$^+$ to Various Nucleophiles (kcal/mol)

	singlet				triplet						
X	^{1}**2**$^+$ C_2H_4	^{1}**4**$^+$ NH_3	^{1}**7**$^+$ MeOH	^{1}**10**$^+$ MeCN	^{3}**3**$^+$ C_2H_4	^{3}**5**$^+$ NH_3	^{3}**6**$^+$ NH_3	^{3}**8**$^+$ MeOH	^{3}**9**$^+$ MeOH	^{3}**11**$^+$ MeCN	^{3}**12**$^+$ MeCN
CN	−60.9	−84.9	−57.0	−66.5	−35.3	−28.3	−9.5	−1.6	2.2	4.0	4.5
H	−57.9	−77.5	−50.1	−60.1	−33.4	−15.2	−10.8	0.7	1.4	4.5	7.8
Me	−61.9	−77.5	−50.0	−60.2	−32.7	−8.1	−3.4	2.4	4.5	5.5	5.4
MeO	−69.4	−80.6	−53.3	−64.8	−31.5	−3.3	1.8	5.7	5.2	5.9	4.8
NH_2	−72.1	−75.9	−48.6	−61.7	−29.4	2.1	4.8	7.2	0.3	6.4	4.2

SCHEME 3. **Adducts Formed by Singlet and Triplet Phenyl Cations with Ethylene, Ammonia, Methanol, and Acetonitrile**



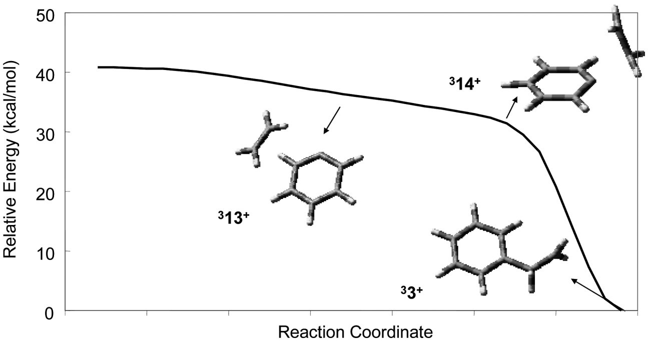


FIGURE 1. Energy profile (PES) for the addition of cation ^{3}**1**$^+$ to ethylene.

TABLE 5. Spin Density in Triplet Adducts

	^{3}X-**1**$^+$		^{3}**3**$^+$			^{3}**5**$^+$		^{3}**8**$^+$		^{3}**11**$^+$	
	C_1	C_4	C_1	C_4	C_b	C_1	C_4	C_1	C_4	C_1	C_4
CN	1.31	0.39	0.37	0.40	1.08	0.73	0.62	1.15	0.37	1.23	0.40
H	1.38	0.49	0.43	0.46	1.08	0.96	0.62	1.20	0.41	1.28	0.45
Me	1.37	0.41	0.44	0.40	1.08	1.09	0.39	1.22	0.38	1.30	0.41
OMe	1.35	0.17	0.45	0.20	1.08	1.15	0.22	1.26	0.20	1.32	0.19
NH_2	1.33	0.05	0.44	0.09	1.08	1.17	0.12	1.26	0.08	1.31	0.08

phenyl cation had been previously reached,[19] and this point will not be commented further.

As for n nucleophiles, strongly stabilized (by 50 to > 80 kcal/mol) planar adducts with ammonia, methanol, and acetonitrile (^{1}**4**$^+$, ^{1}**7**$^+$, and ^{1}**10**$^+$) are formed. In the adducts the aromaticity of the ring is conserved and the distance between the nucleophile heteroatom and C_1 is 1.50, 1.48, and 1.38 Å, respectively, evidencing the fully formed σ bond (see Table 6). In fact, these are the anilinium cation (in which the C−N distance is in fact 1.50 Å),[20] protonated anisole, and *N*-phenylisocyanide cation, respectively. The bent geometry of the iminium moiety in the acetonitrile adducts ^{1}**10**$^+$ is well suited for the ensuing addition of water leading to *N*-phenylacetamides (Ritter reaction; the C_1-heteroatom distances are listed in Table 6, and the ring bond lengths are reported as Supporting Information).

Adduct Cations: Triplets. Quite a different behavior is found with triplets. With ethylene, no low-lying spiro-cyclopropane adduct analogous to ^{1}**2**$^+$ is found and the lowest-lying adduct cation has a planar, singly bonded structure (^{3}**3**$^+$) with the $C_1-C_a-C_b$ angle close to the sp^2 angle of 120° (120 ± 1°). Examination of the spin distribution (see Table 5) shows that this species has to be considered a distonic diradical, with one of the unpaired electrons at the outer carbon C_b (consistent value 1.08) and the other one delocalized over the aromatic ring, mainly at C_1 and C_4 in parent ^{3}**3**$^+$ (in part delocalized on the heteroatom in the amino and methoxy derivatives, not shown; see below for a discussion of the electronic structure).

These adducts are again strongly stabilized (> 30 kcal/mol, though not as much as the singlet phenonium, see Table 4). A convenient representation in terms of Lewis structures was obtained through the natural resonance theory (NRT).[21] With this approach the structure of triplet cations ^{3}X-**1**$^+$ is well represented by the formula in Scheme 2, with five electrons in almost degenerate π orbitals and one in the C_1 sp^2 orbital.

The unpaired spin makes the phenonium structure characteristic of singlets unattainable for the triplets, and an in-plane approach is followed instead. The cation singly occupied sp^2 orbital interacts with the ethylene π forming a

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TABLE 6. Heteroatom−C_1 (or C_4) Distance (Å) in the Adduct Cations with Ammonia, Methanol, and Acetonitrile

	adducts with NH_3			adducts with MeOH			adducts with MeCN		
	^{1}**4**$^+$ C_1−N	^{3}**5**$^+$ C_1−N	^{3}**6**$^+$ C_4−N	^{1}**7**$^+$ C_1−O	^{3}**8**$^+$ C_1−O	^{3}**9**$^+$ C_4−O	^{1}**10**$^+$ C_1−N	^{3}**11**$^+$ C_1−N	^{3}**12**$^+$ C_4−N
CN	1.497	1.484	2.512	1.473	2.252	2.676	1.389	2.316	2.512
H	1.499	1.581	2.206	1.479	2.268	2.409	1.389	2.319	2.206
Me	1.498	2.170	2.416	1.479	2.305	2.546	1.385	2.430	2.416
OMe	1.494	2.279	2.775	1.475	2.390	3.182	1.378	2.597	2.775
NH_2	1.493	2.342	2.971	1.474	2.462	3.514	1.372	2.665	2.971

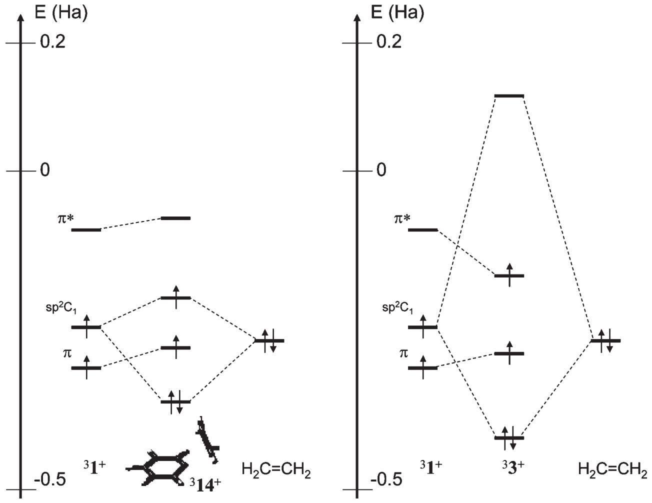


FIGURE 2. MO correlation diagram for the addition of cation ^{3}**1**$^+$ to ethylene: intermediate ^{3}**14**$^+$ and final adduct ^{3}**3**$^+$.

σ bonding orbital and a singly occupied p orbital, while the other cation SOMO (π) remains essentially unperturbed in the adduct. This is shown for the parent cation ^{3}**1**$^+$ in Figure 1 and has been found to hold true also for ^{3}CN-**1**$^+$ and $^3NH_2$ -**1**$^+$, although the MOs energies change are in the latter case significantly higher. The formula drawn in Scheme 3 is thus a reasonable representation of the electronic structure of adduct ^{3}**3**$^+$ and the energy and the structure of the open-chain adducts change little by changing the substituent.

The course of the reaction was examined by stretching the σ bond by 0.05 Å intervals and optimizing the structure at every step. Initially (structure ^{3}**13**$^+$, Figure 1) the ethylene is superimposed to the cation, and the first interaction involves the ethylene π orbitals and an *ortho* hydrogen atom, then interaction with the sp^2 orbital increases with the ethylene forming a 74° angle with the ring (^{3}**14**$^+$, see Figure 2 for MO correlation diagram) . At this point the energy rapidly decreases while the ethylene moiety rotates allowing the formation of a σ bond. As a consequence of the rotation, the C_b (p) orbital becomes lower in energy than the σ* orbital and one of the unpaired electrons ends up in it (final structure ^{3}**3**$^+$, MO description in Figure 2).

With n nucleophiles, the difference is even more dramatic and triplets do not undergo the straightforward addition typical of singlets. The reaction with ammonia leads to the moderately stabilized (15 kcal/mol) adduct cation ^{3}**5**$^+$, exhibiting a loose C_1−N bond (1.58 Å), a pronounced bond alternation in the ring, and a large deviation from planarity (70°). With ^{3}CN-**1**$^+$ the adduct with ammonia is more stable (28 kcal/mol) and more similar to the singlet adducts ^{1}X-**4**$^+$, with a short C_1−N distance (1.48 Å, see Table 6) and only a small (15°) out of plane deviation of that bond. On the other hand, inserting electron-donating groups on the ring, from methyl to amino, further reduces the limited stabilization available, so that the C_1−N bond is lengthened and the stabilization decreases, so that with the last substituent the addition is slightly endoergonic. In these cases different modes of attack become competitive and lead to adducts where the C_1−N bond forms a 90° angle with the aromatic ring plane. As a matter of fact, two complexes of this type were individuated, respectively, with the nucleophile sitting above C_1 or above C_4 (see structures ^{3}**5**$^+$ and ^{3}**6**$^+$). The former ones are more stable (by 3−5 kcal/mol) and somewhat more strongly bonded to the ring (C_1−C_4, 2.17 to 2.24 Å) than the latter ones.

In Figure 4a,b the correlation diagram for the addition to ammonia is reported for two cases, parent **1**$^+$ and ^{3}CN-**1**$^+$. The latter cation yields adduct ^{3}CN-**5**$^+$, where a σ bond is formed and the two unpaired electrons sit in a π and a π* orbital respectively. The species actually corresponds to the triplet state (ππ*) of cation ^{1}CN-**4**$^+$, viz., the one formed from ^{1}CN-**1**$^+$ and ammonia. This well explains the large energy difference between the two adducts despite the geometric similarity. With the parent cation, on the other hand, it is the π orbital of the cation that combines with the n_N orbital to form an essentially non-bonding orbital.

Also in this case, a more detailed picture was obtained by stretching the σ bond. Two spin-parallel electrons cannot be placed in a orbital, and thus the in-plane approach of singlets is prohibited. With ^{3}**1**$^+$ a weak complex is initially formed prior to the interaction with the $(\pi)^1$ orbital (structure ^{3}**17**$^+$, Figure 3a; for the coordinates, see Supporting Information). Development of a σ bond leads to structure ^{3}**5**$^+$, but reaching this requires an orbital rearrangement (developed after transition state), so that a π* orbital shifts below the σ* orbital, and configuration ^{3}**5**$^+$ is reached, (see Figure 4a1,a2 for the MO description of the structures discussed).

Different is the reaction course for the addition of ammonia onto ^{3}CN-**1**$^+$ (Figure 3b), in which a weak intermediate ^{3}CN-**16**$^+$ is observed along the reaction path, followed (similarly to parent cation) by an orbital rearrangement giving structure ^{3}CN-**17**$^+$ (Figure 4b1). This undergo a further rearrangement in which the bond C−N is ultimately formed by interaction of the sp^2 SOMO on C_1 leaving the π SOMO unchanged (Figure 4b2). This interaction brings the ammonia molecule almost coplanar with the aromatic ring.

In the reactions of the triplet cations with methanol, no planar adduct is formed. Only "orthogonal" associations could be located, slightly endo- or exoergonic (ΔG = −1.6 to +5.2 kcal/mol; see Table 4). This caused minimal changes in the ring geometric parameters and in spin distribution with respect to the starting phenyl cation. Again, two different structures with the heteroatom close to C_1 or to C_4 were

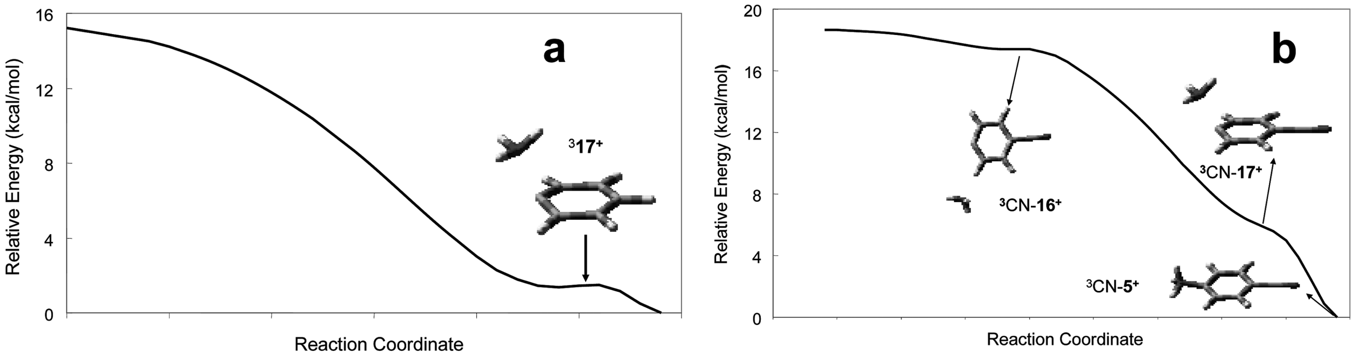


FIGURE 3. PES for the attack onto ammonia by cations (a) ^{3}**1**$^+$ and (b) ^{3}CN-**1**$^+$.

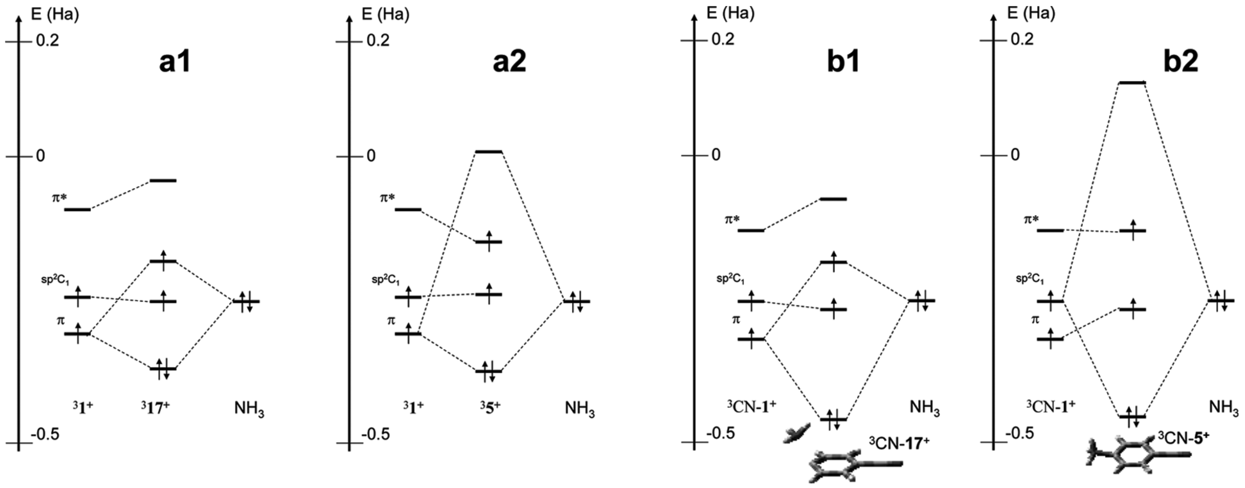


FIGURE 4. Orbital correlation diagram for the attack onto ammonia by cations (a) ^{3}**1**$^+$ (a1, transition state ^{3}**17**^{1}, a2, final adduct ^{3}**5**$^+$) and (b) ^{3}CN-**1**$^+$ (b1, intermediate ^{3}CN-**17**$^+$, b2, final adduct ^{3}CN-**5**$^+$).

located. Among the complexes with methanol, the former structure is somewhat stabilized with X = CN, H, Me, while the latter is more stable with X = NH_2, probably because the charge in the starting cation is displaced toward the amino group in 4 in that case (see Table 3). Finally, in the case of acetonitrile there is no interaction at all and formation of "complexes" ^{3}**11**$^+$ and ^{3}**12**$^+$ is endoergonic (ΔG ca. +5 kcal/mol) and involves no change with respect to the starting cations ^{3}X-**1**$^+$ either in geometry (see Supporting Information) or in charge and spin distribution (see Table 5), as one may expect since there is practically no interaction. This characteristic fostered further analysis by different computational methods, in order to check the authenticity of the result. The M05-2x method, which is optimized for weak interactions, was adopted and was combined with a triple-ζ basis set. The results reported in Table 7 for three complexes with MeCN show limited (and not systematic) differences in the C−N distance between the different approaches and superimposition of the optimized structure evidenced the close similarity (see as an example the figure in Supporting Information for the case of ^{3}CN-**11**$^+$). This lent credibility to the conclusions drawn above on structure and role of such intermediates.

Summing up, except for in the case of ^{3}CN-**1**$^+$, phenyl cations behave as π, not σ, acceptors with n donors, forming weak adducts of formula ^{3}**5**$^+$ for ammonia. It is easily understood that when using donors weaker than ammonia this mode of interactions is the only one available. The different mode of interaction is also reflected in the calculated[21] resonance structures for the adduct cations that are summarily depicted in Scheme 4, ordered from the most to the least important.

The parameters obtained (see Table 2) from the Swain−Lupton correlation of the adducts energy (eqs 4 and 5) gave further evidence for the structure of such cations.

$$\text{X-C}_6\text{H}_4^+ + \text{C}_6\text{H}_5\text{-Nu}^+ \rightarrow \text{X-C}_6\text{H}_4\text{-Nu}^+ + \text{C}_6\text{H}_5^+ \qquad (4)$$

$$\Delta G(4) = f\mathscr{F} + r\mathscr{R} + i \qquad (5)$$

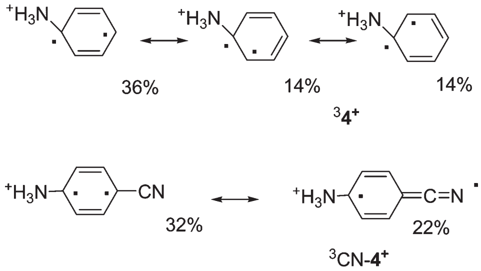
Key points are the positive *r* value (18) with phenonium ions ^{1}**2**$^+$, a delocalized π (Wheland) cation, in contrast with σ cation ^{1}**1**$^+$; and the almost identical *f* and *r* values (ca. −8 and −2) for the three singlet adduct with n donors, smaller than those of singlet phenyl cations since the charge lays roughly in the same region as in ^{1}**1**$^+$ but farther from the aromatic moiety. As for the triplets, the most interesting point is the much smaller resonance effect in the distonic adduct cations ^{3}**3**$^+$ with respect to phenyl cations ^{3}X-**1**$^+$, indicating that the two unpaired electrons interact significantly and lessen the character of aromatic radical cation.

Selective Arylation. Phenyl cations are obviously strong electrophiles.[11] The usefulness of these intermediates is linked to the selective reaction with π, not n, nucleophiles in the *triplet manifold*, in contrast to the unselective reaction

TABLE 7. Comparing C_1-N Distances in Weak Complexes of Triplet Phenyl Cations with Acetonitrile

^{3}CN-**1**$^+$ + CH_3CN				
program	Gaussian	Gaussian	gamess	gamess
functional	B3LYP	B3LYP	B3LYP	M05-X2
basis set	6-31G(d)	6-311++G(2d,p)	6-311G(2d,p)	6-311G(2d,p)
$d(C_1-N)$	2.316	2.356	2.3241	2.2583
^{3}1$^+$ + CH_3CN				
program	Gaussian			gamess
functional	B3LYP			M05-X2
basis set	6-31G(d)			6-311G(2d,p)
$d(C_1-N)$	2.31948			2.3762
^{3}MeO-**1**$^+$ + CH_3CN				
program	Gaussian			gamess
functional	B3LYP			M05-X2
basis set	6-31G(d)			6-311G(2d,p)
$d(C_1-N)$	2.59735			2.646

SCHEME 4. Most Important Calculated NRT Resonance Structures for Adduct Cations ^{3}5$^+$, ^{3}CN-5$^+$ with Percent Weight[a]



[a] In the case of the first intermediate, notice the nonplanar structure and the fact that the C_1 sp^2 orbital, though distorted, is still populated. This is orthogonal to the π system, as indicated by the dot outside the ring.

TABLE 8. Free Energy Changes $\Delta G(6)$ for the Reaction of Solvent-Complexed Triplet Phenyl Cations with an Added Nucleophile (see eq 6)

	C_2H_4 vs MeOH	C_2H_4 vs MeCN	NH_3 vs MeOH	NH_3 vs MeCN
^{3}CN-**1**$^+$	−33.7	−39.3	−26.7	−32.3
^{3}**1**$^+$	−34.1	−37.9	−15.9	−19.7
$^3NH_2$ -**1**$^+$	−29.7	−33.6	+1.8	−2.1

of the singlets. This is an important issue; because phenyl cations are conveniently generated in polar (and nucleophilic) solvents such as MeOH and MeCN that are the media of choice for generating these intermediates by photoheterolysis. We were unable to locate transition states in the addition to ethylene, which similarly to other strongly exothermic reactions appears to occur over a slippery surface leading to the adduct cations. Thus, the activation energy is < 1 kcal/mol, and the available data are not sufficient for a kinetic prediction. However, the different free energy change involved in the addition to ethylene versus to the solvent [$\Delta G(6)$] is apparent when considering the isodesmic reaction in eq 6, which refers to the trapping of the solvent-bonded phenyl cation by an added nucleophile (see Table 8).

$$X\text{-}C_6H_4\text{-}Solv^+ + Nu \rightarrow X\text{-}C_6H_4\text{-}Nu^+ + Solv \qquad (6)$$

$$(Solv = MeOH, MeCN) \quad (Nu = C_2H_4, NH_3)$$

The adducts with ethylene are consistently stabilized with respect to those with MeOH and MeCN by 30−40 kcal/mol and also those with ammonia (for some of which a slight barrier has been located; see Figure 4b) are more stabilized than those with MeOH and MeCN, except for the case of the aminophenyl cation. It appears reasonable to think that such large thermodynamic differences translate into a preferential reaction path. Thus, the reaction with ethylene is always preferred to that with the solvents, and so is the reaction with ammonia except for electron-donating substituted derivatives.

Conclusions

In this work the different reactivity of singlet/triplet ions with π/n nucleophiles has been documented through a computational analysis. Interaction with the π system distributes part of the charge on the ring (particularly with electron-donating substituents), so that the simplified representation with an empty sp^2 orbital orthogonal and not influenced by the π orbitals is misleading even for the singlet state and insignificant for the triplet. The peculiar structure and the all-important fact the triplet state, too high in energy to have a role with aliphatic cations, is here accessible characterize these intermediates. In particular, the triplet has a biradical structure with the charge essentially on the ring. The initial approach with nucleophiles thus occurs in every case toward the ring (see the initial relative position in Figures 2 and 4). In a later phase, however, alkenes interact with the sp^2 orbital and a strongly σ bonded, distonic biradical is generated, whereas this is *not* the case with n-donors, where the cation continues to behave as π electrophile and form weak complexes (except for the reaction of ^{3}CN-**1**$^+$ with a good nucleophile such as ammonia). The changing approach in the former case is reminiscent of the non-least-path mechanism of the addition of (singlet) carbenes to alkenes,[22] altough the similarity is rather formal.

Summing up, the above computation supports that the chemistry of the phenyl cation spin states is even more divergent than that of carbenes,[23] further taking into account

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that both the presence of the charge and the thermodynamic drive toward re-establishing aromaticity introduce important differences in the chemistry.

The accessibility of triplet cations by photoheterolysis of simple aromatic derivatives, such as phenyl halides, lends interest to the computational predictions. Literature results support that the rate of reactions of triplet phenyl cations is very high,[24] so that, if formed in the photofragmentation step, they may react in that multiplicity before intersystem crossing to the singlet occurs and one has access to the synthetically valuable (selective) triplet chemistry. Which state will be formed first upon irradiation has thus a determining role and is fortunately predictable according to the rules that were previously reported;[11] at any rate the triplet can be alternatively obtained by energy transfer sensitization.

Importantly, the different course of the initial addition of the phenyl cation is not the only partition point. Thus, the addition of the triplet to alkenes leads to distonic biradical cation $^{3}\mathbf{3}^{+}$ that requires some time before losing the triplet identity and attaining the structure of an electron-paired (cationic) intermediate, open-chain or cyclic (phenonium). This complex course of the reaction has been followed by laser flash photolysis,[24] and the competition between the cationic steps, involving either inter- or intramolecular nucleophile trapping or cationic rearrangement, can be in turn directed by the appropriate choice of the structure of the starting material and the experimental parameters.[25]

Thus, with phenyl cations not only may one have either a ionic (singlet) or a carbene/radical (triplet) chemistry, as predicted by Taft, but in the latter case one combines radical/carbene chemistry in the first step and cationic chemistry in the last ones, which offers a large potential for directing the reaction. These results suggest that triplet phenyl cations are powerful synthetic intermediates that are expected to become as versatile and rewarding as carbenes, besides being one of the best examples of the smooth generation of a highly reactive intermediate by photochemical means.

Experimental Section

Optimizations were carried out at the UB3LYP/6-31G(d) level (*p*-Me, OMe, NH_2, CN and parent) by using the Gaussian 03 package.[26] Frequency calculations were evaluated at the same level of theory, and in this way the structures reported were certified as minima. Energies of the solvated cation were evaluated with the CPCM method on the (in vacuo) optimized geometries by using acetonitrile as solvent.[27] The calculations with the M05-X2 functional were performed by using the US-GAMESS package version 12 Jan 2009 (R3).[28] For the calculation of Gibbs free energies in Table 4 and in the isodesmic reactions in eqs 1, 4, and 6 entropic corrections at 25 °C have been included. Energies and coordinates are reported as Supporting Information.

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Supporting Information Available: Cartesian coordinates and energies for phenyl cations **1** and of the adduct cations **2**−**12**, **17** (with comparison of the different structures calculated by different methods for the case of CN-**11**). This material is available free of charge via the Internet at http://pubs.acs.org.

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