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Computational studies of the properties of phenyloxenium ions — A comparison with phenylnitrenium and phenylcarbenium ions¹

Stephen A. Glover and Michael Novak

Abstract: Properties of phenyloxenium ion **13a**, phenylnitrenium ion **14a**, and their 4-methyl and 4-phenyl analogues have been studied at the HF/6-31G* and pBP/DN*/HF/6-31G* levels to explain differences in their relative ease of formation and their stabilities. The phenyloxenium ions **13** are ground-state singlets but S_0-T_1 gaps are smaller than those of the corresponding nitrenium ions. The S_0 states are stabilized by donor methyl and phenyl substituents in both classes of ions, but phenyloxenium ion has much greater charge localization on the ring, primarily at the 4 position. Evidence for this difference stems from ground-state HF/6-31G* geometries, dipole moments, and vibrational frequencies. Nitrenium ions exhibit some quinoidal character, but the calculated C—N bond lengths are longer than those of their 4-hydroxy-2,5-cyclohexadienone imine hydration products **17** and the symmetric C—N stretching frequencies are ca. 60–100 cm^{-1} less than those of **17**. However, the C—O bond lengths and stretching frequencies of the phenyloxenium ions are slightly shorter and greater, respectively, than those of their 4-hydroxy-2,5-cyclohexadienone hydration products (**16**). The oxenium ions are best described by their 4-oxo-2,5-cyclohexadienyl carbenium resonance structures. Accordingly, a 4-phenyl group stabilizes the phenyloxenium ion more than the phenylnitrenium ion leading to a planar geometry and considerably more charge in the distal ring, thus accounting for regioselectivities of azide reactions. Isodesmic comparisons of the energy difference between phenyloxenium and phenylnitrenium ions and their neutral hydration products explains their relative stabilities under aqueous conditions; whereas 4-biphenyloxenium ion **13c** has a lifetime in water of 12 ns as opposed to the corresponding nitrenium ion **14c** (300 ns), the 4-methylphenyloxenium ion **13b** is less stable to hydration by 18.7 kcal mol^{-1} (1 cal = 4.184 J) and cannot be observed under the conditions used to generate **13c**.

Key words: oxenium ions, nitrenium ions, computational chemistry, nucleophilic addition, singlet state properties.

Résumé : Les propriétés de l'ion phényloxénium **13a**, de l'ion phénylnitrénium **14a** et de leurs analogues 4-méthyl- et 4-phényl- ont été étudiées aux niveaux HF/6-31G* et pBP/DN*/HF/6-31G* pour tenter d'expliquer les différences dans leurs facilités relatives de formation dans leurs stabilités. Les ions phényloxénium **13** sont des singulets à l'état fondamental, toutefois les écarts S_0-T_1 sont plus faibles que ceux des ions nitrénium correspondants. Dans les deux classes d'ions, les états S_0 sont stabilisés par les substituants donneurs méthyle et phényle; toutefois, la délocalisation de la charge sur le cycle est beaucoup plus grande avec l'ion phényloxénium, particulièrement vers la position 4. Les bases pour ces différences sont tirées des géométries HF/6-31G* de l'état fondamental, des moments dipolaires et des fréquences de vibration. Les ions nitrénium exhibent un caractère quinoidal, mais les longueurs calculées des liaisons C—N sont supérieures à celle de leur produit d'hydratation, l'imine de la 4-hydroxycyclohexa-2,5-diénone (**17**) et les fréquences d'élongation symétrique du C—N sont de 60 à 100 cm^{-1} inférieures à celle du composé **17**. Toutefois, les longueurs des liaisons C—O et les fréquences d'élongation des ions phényloxénium ne sont respectivement que faiblement plus courtes et plus longues que celles de leur produit d'hydratation, la 4-hydroxycyclohexa-2,5-diénone (**16**). La meilleure façon de décrire les ions oxénium correspond aux structures de résonance du carbénium 4-oxocyclohexa-2,5-diényl. En conséquence, un groupe 4-phényle stabilise plus un ion phényloxénium que l'ion phénylnitrénium conduisant à une géométrie planaire et beaucoup plus de charge dans le noyau distal, ce qui expliquerait les régiosélectivités des réactions avec l'ion azoture. Des comparaisons isodesmiques des différences d'énergie entre les ions phényloxénium et phénylnitrénium et leurs produits neutres d'hydratation explique leurs stabilités relatives dans des conditions aqueuses; alors que le temps de vie de l'ion 4-biphenyloxénium **13c** dans l'eau est de 12 ns par rapport à 300 ns pour celui de l'ion nitrénium correspondant **14c**, l'ion 4-méthylphényloxénium **13b** est moins stable à l'hydratation par 18,7 kcal mol^{-1} (1 cal = 4,184 J) et il ne peut pas être observé dans les conditions utilisées pour générer le composé **13c**.

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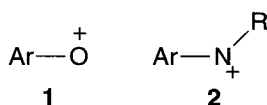
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Mots clés : ions oxénium, ions nitrenium, chimie théorique, addition nucléophile, propriétés de l'état singulet.

[Traduit par la Rédaction]

Introduction

Arylnitrenium ions **2**, which are widely accepted to be the intermediates derived from metabolites of carcinogenic aromatic amines, have been studied extensively. As a result, factors affecting their stability, their lifetimes under aqueous conditions and their reactivity with a range of inorganic and biological nucleophiles have been the subject of many investigations (1–15). Undoubtedly, these ions are strongly delocalized and they can best be regarded as 4-imino-2,5-cyclohexadienyl carbocations, although they do retain some electrophilic reactivity at nitrogen (4–7, 11, 15–25). Delocalization leads to predominant reaction on the aryl ring with attendant disruption of aromaticity. The intrinsic barrier resulting from this loss of aromaticity leads to long lifetimes in aqueous solution, which in certain instances accounts for elevated carcinogenic behaviour. The lifetimes of 4-biphenylnitrenium ion (300 ns at 30 °C) and its bridged counterpart, 2-fluorenylnitrenium ion (30 μs at 20 °C) derived from mutagenic and carcinogenic arylamines, are longer in aqueous solution than those of nitrenium ions derived from noncarcinogenic arylamines (4, 13, 16, 18, 26).

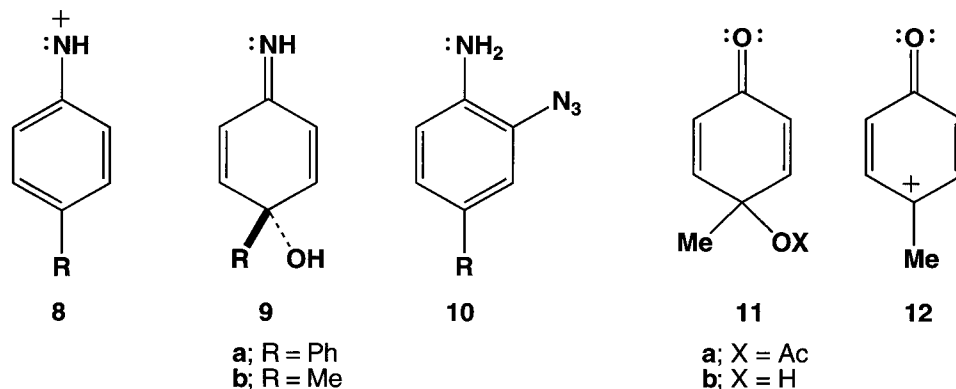


The oxygen counterparts of arylnitrenium ions (aryloxenium ions **1**), have, on the other hand, received relatively little attention. They have been proposed to explain the products of the synthetically useful electrochemical and chemical oxidations of phenols (27–33), and the copper-catalysed generation of commercially useful polymers such as poly(2,6-dimethyl-1,4-phenylene oxide) (34, 35). Reactions on both the aryl substituent (28, 29, 31, 32) as well as upon oxygen (30, 33) have been ascribed to the electrophilic behaviour of these species, but the regiochemistry of reactions of purported examples of **1** generated from different sources is confusing; surprisingly, little is known of the reactivity and selectivity of these species, or even whether they have actually been generated in the cases in which they have

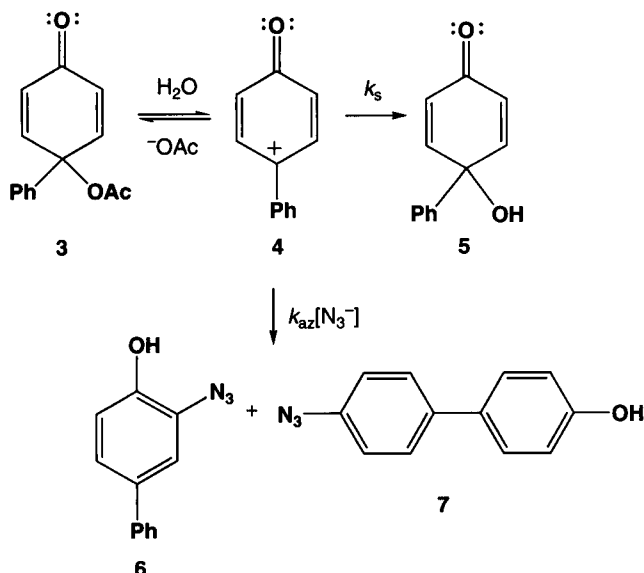
been invoked. The possible formation of **1** with electron-deficient aryl groups is particularly intriguing (29). Compounding this, there is the possible involvement of triplet ions. A recent report has described a relatively unreactive, hindered form of **1** but this long-lived (0.55 μs) species provides little insight into the reactions of more transient members of this class of ions (36).

We recently described the solvolysis of the 4-acetoxy-4-phenyl-2,5-cyclohexadienone (**3**) and showed that, in neutral, acidic, and basic aqueous media, it solvolyses to 4-biphenyloxenium ion **4** (37, 38). This ion has a lifetime in water at 30 °C of 12 ns, considerably longer than the analogous 1-(4-biphenyl)ethyl and 4-phenylcumyl carbenium ions (0.1 and 0.5 ns, respectively) (39, 40), but more than an order of magnitude shorter than that of 4-biphenylnitrenium ion **8a** (13). Water reacts at the 4 position giving the 4-phenylquinol **5**, but in the competition reactions with azide, from which its lifetime was determined, both the 2- and the 4'-azidobiphenols (**6** and **7**) were formed in a 4.7:1 ratio (Scheme 1) (37).

In similar competition reactions, 4-biphenylnitrenium ion **8a** afforded the 4-hydroxy-4-phenyl-2,5-cyclohexadienone imine (**9a**) and only the 2-azidobiphenylamine (**10a**) (4). Thus, apart from their differences in lifetimes, 4-biphenyloxenium and 4-biphenylnitrenium ions differ in the regiochemistry of azide addition. The isolation of appreciable quantities of the 4'-regioisomer signals significantly greater delocalization of positive charge in the oxenium ion (37). In addition, substituents influence the stabilities of nitrenium ions and oxenium ions to a different extent. While 4-methylnitrenium ion **8b** has been detected from solvolysis of *N*-(4-methylphenyl)-*O*-pivaloyl hydroxylamine (lifetime of 0.8 ns in aqueous acetonitrile at 20 °C) and reacts with water and azide giving **9b** and **10b** (16, 17), we were not able to observe 4-methylphenyloxenium ion **12** from solvolysis of **11a** under any conditions. While the 4-methylquinol **11b** is formed, it does so through normal ester hydrolysis; in aqueous conditions and with 10 atom% ¹⁸O water there is little or no incorporation of ¹⁸O into the 4-hydroxyl of the product **11b** that is formed upon solvolysis of **11a**. However, there is full incorporation into **5** upon solvolysis of **3** (38). Relative to the phenylnitrenium ion, either the phenyloxenium ion is



Scheme 1.



stabilized far more weakly by a 4-methyl substituent or, alternatively, a 4-phenyl group can provide extra stabilization.

4-Biphenyloxonium ion generated in this manner appears to react as a singlet species, but, as with nitrenium ions, oxenium ions can be both singlet and triplets. For the simplest form (HO^+), the triplet is lower in energy by 54 kcal mol^{-1} ($1 \text{ cal} = 4.184 \text{ J}$) (41), but electron-donating substituents are expected to stabilize the singlet state more than the triplet state. An earlier MNDO study indicated that singlet states of phenylnitrenium ion and *N*-formylphenylnitrenium ion were lower than the triplet states by about 20 kcal mol^{-1} (42). At the UHF/6-31G* level, singlet phenyloxonium ion is computed to be more stable than its triplet form by only 4 kcal mol^{-1} (34), but Li et al. (43) demonstrated that for both phenylnitrenium ion and phenyloxonium ion the computed energy difference was strongly dependent upon the size of the basis set and, particularly, on the inclusion of correlation energy. However, their calculations utilized HF/STO-3G optimized geometries. Using density functional theory, Cramer and co-workers (25, 44) have calculated singlet states of arylnitrenium ions to be significantly more stable than the triplets (by between 13 and 28 kcal mol^{-1}), and the gap is greatest with electron-donor groups at the 4 position.

In this study, we have compared the influence of 4-methyl and 4-phenyl substituents upon S_0 - T_1 energies of phenyloxonium and phenylnitrenium ions and singlet ground-state properties of these, and their carbenium analogues, with a view to understanding the differences in their lifetimes and reactivities.

Methods

Geometries were optimized up to the HF/6-31G* (closed shell) and UHF/6-31G* (triplets) levels and these were used to compute energies, including correlation energies, at the density functional level (pBP/DN*//HF/6-31G*) using the Spartan suite of programs (45, 46). Energies at the pBP/DN*//HF/6-31G* level were on average 1 to

2 kcal mol^{-1} higher than those obtained from full optimization at the pBP/DN* level. Energies of orthogonal conformations of biphenyl ions were obtained by constraining the inter-ring dihedral angles at 90° and fully optimizing the remaining structural parameters. HF/6-31G* geometries differed only marginally and systematically from those obtained by full DFT analysis and hence were used for comparative purposes. Gas-phase vibrational frequencies were determined using HF/6-31G* optimized geometries and corrected according to the HF/6-31G* scaling factor (0.8953) published by Scott and Radom (47). Trends in these were mirrored in vibrational frequencies of the pBP/DN* fully optimized structures where calculated. The pBP/DN* DFT method was benchmarked against higher level DFT methods by comparing singlet-triplet energies for unsubstituted, 4-chlorophenyl and 4-methylphenyl ions with previously published data. Singlet-triplet splittings were obtained at the pBP/DN*//HF/6-31G* level and, where practical, at the pBP/DN* level.

Isodesmic rxns. [1]-[3] were used to evaluate the relative hydration energies of 4-methylphenyloxonium ion **13b** and 4-biphenyloxonium ion **13c** relative to the parent phenyloxonium ion **13a** as well as the relative stabilities of 4-methylphenylnitrenium ion **14b** and 4-biphenylnitrenium ion **14c** relative to the parent phenylnitrenium ions **14a**. Relative hydration energies of phenyloxonium ion **13a** and phenylnitrenium ion **14a**, 4-methylphenyloxonium ion **13b** and 4-methylphenylnitrenium ion **14b**, and 4-biphenyloxonium ion **13c** and 4-biphenylnitrenium ion **14c** were determined likewise.

Isodesmic reactions were carried out using: (i) HF/6-31G* energies without electron correlation; (ii) pBP/DN*//HF/6-31G* with electron correlation and including ZPEs; (iii) pBP/DN*//HF/6-31G* with electron correlation, including ZPEs and free energies at $298.15 \text{ }^\circ\text{C}$. A comparison of isodesmic reaction energies confirms that, for the most part, the inclusion of electron correlation or thermodynamic quantities makes little difference to the results. Where all relevant species could be fully optimized at the pBP/DN* level, isodesmic energies were almost identical to those obtained by the pBP/DN*//HF/6-31G* method.

Energies are given in atomic units (au) or kcal mol^{-1} . Bond lengths are given in Å and vibrational frequencies are reported in cm^{-1} . Dipole moments are given in Debye (D). Energies for all ions and molecules in this study are presented in Tables 1 and 2.

Results and discussion

Singlet-triplet splittings

Energies of singlet and triplet states of **13a-13c** and **14a-14d** as well as S_0 - T_1 splittings at the HF/6-31G*, pBP/DN*//HF/6-31G*, and pBP/DN* levels are presented in Table 1.

S_0 - T_1 splittings for unsubstituted-, **14a**, 4-methyl-, **14b**, and 4-chlorophenylnitrenium ions, **14d**, have been determined previously at the BPW91/cc-pVDZ level and indicate that methyl and chloro (S_0 - $T_1 = -21.9$ and $-21.3 \text{ kcal mol}^{-1}$, respectively) lower the singlet state marginally relative to the triplet state when compared to phenylnitrenium ion (S_0 - $T_1 = -18.8 \text{ kcal mol}^{-1}$) (44). The pBP/DN* level performed

Table 1. HF/6-31G*, pBP/DN**/HF/6-31G*, and pBP/DN* total energies (au) and zero-point energies, free energies, and S_0-T_1 splittings (kcal mol⁻¹) for **13a-13c** and **14a-14d**.

Method	Type	13a	13b	13c	14a	14b	14c	14d
HF/6-31G*	T ₁	-304.67688	-3443.72152	-534.25228	-284.85064	-323.89344	-514.42163	
	T ₁ ⁹⁰ (ΔE) _T ^a			-534.23654 (9.8)				
	S ₀	-304.66543	-343.72070	-534.25212	-284.85012	-323.90167	-514.42703	
	S ₀ ⁹⁰ (ΔE) _S ^a			-534.22898 (14.5)			-514.41016 (10.5)	
	S ₀ -T ₁	7.2	0.5	0.1	0.3	-5.2	-3.4	
	T ₁	-306.58635	-345.92174	-537.73050	-286.70995	-326.04468	-517.85319	
pBP/DN**/HF/6-31G	T ₁ ⁹⁰ (ΔE) _T ^a			-537.72669 (2.4)				
	S ₀	-306.60706	-345.94925	-537.76495	-286.74054	-326.07909	-517.88898	
	(ZPE, G) ^b	(55.72, 36.5)	(72.54, 51.7)	(105.86, 83.1)	(63.83, 44.83)	(80.35, 60.21)	(113.45, 91.89)	
	S ₀ ⁹⁰ (ΔE) _S ^a			-537.73537 (18.6)			-517.86702 (13.8)	
	S ₀ -T ₁	-13.0	-17.3	-21.6	-19.2	-21.6	-22.5	
	T ₁	-306.58830	-345.92421	-	-286.70749	-326.04147	-746.37877	
pBP/DN**	(ZPE)	(52.95)	(69.36)		(59.87)	(76.72)	(54.38)	
	S ₀	-306.61024	-345.95367	-537.77092	-286.74344	-326.08333	-746.42314	
	(ZPE)	(55.43)	(71.48)		(63.34)	(79.47)	(57.59)	
	(S ₀ -T ₁) _{ZPE}	-11.4	-16.4	-	-19.0	-22.6	-24.6	
	(S ₀ -T ₁) _{ZPE} ^e				-18.8	-21.9	-21.3	

^aDifference in energy between the orthogonal and geometry-optimized biphenyl geometries in kcal mol⁻¹.^bZero-point energies and free energies (kcal mol⁻¹) from frequency calculations at the pBP/DN**/HF/6-31G* level.^cGeometry optimized at the pBP/DN* level.^dCalculation failed because of SCF convergence difficulties.^eBPW91/cc-pVDZ value from ref. 44.

Table 2. HF/6-31G*, pBP/DN*//HF/6-31G*, and pBP/DN* energies (au) and zero-point energies and free energies (kcal mol⁻¹) for 15a-15c, 16a-16c, and 17a-17c.

Method	Type	15a	15b	15c	16a	16b	16c	17a	17b	17c
HF/6-31G*	S ₀	-268.886732	-307.93433	-498.45358	-380.38881	-419.42716	-609.93427	-360.53951	-399.57797	-590.08976
	S ₀ ⁹⁰			-498.44300 (6.6)						
pBP/DN*// HF/6-31G	(ΔE) _S ^a									
	S ₀	-270.71771	-310.05274	-501.85666	-382.78554	-422.11152	-613.89610	-362.88591	-402.21018	-594.00042
pBP/DN* ^b	(ZPE, G)	(71.27, 52.61)	(87.90, 67.86)	(119.61, 116.37)	(65.83, 46.47)	(81.97, 61.77)	(114.47, 92.32)	(72.9, 53.3)	(89.5, 69.1)	(122.0, 99.7)
	S ₀ ⁹⁰			-501.84012 (10.4)						
	(ΔE) _S ^a									
	S ₀				-382.79152 (65.1)	-422.11753 (81.3)				
	(ZPE)									-402.21669 (88.7)

^aDifference in energy between the orthogonal and geometry-optimized biphenyl geometry in kcal mol⁻¹.

^bGeometry optimized at the pBP/DN* level.

similarly for the unsubstituted and 4-methylphenylnitrenium ion (S₀-T₁ = -19.0 and -22.6 kcal mol⁻¹) and the splitting for the 4-chlorinated analogue was marginally higher (-24.5 kcal mol⁻¹). While there are no experimental values with which to compare these computed splittings, the pBP/DN* method works at least as well as Cramer's density functional approach using the correlation consistent polarized Valence double zeta basis set (44).

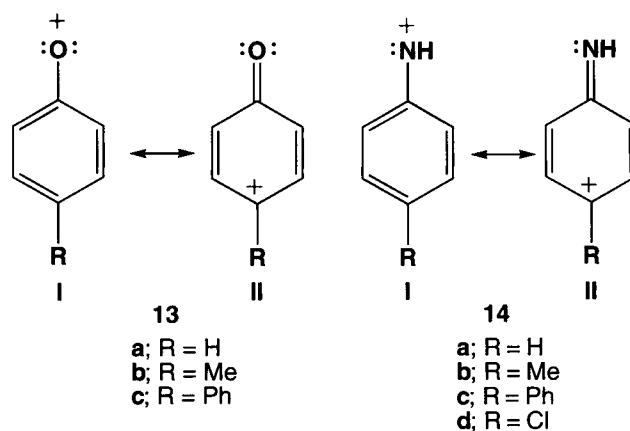
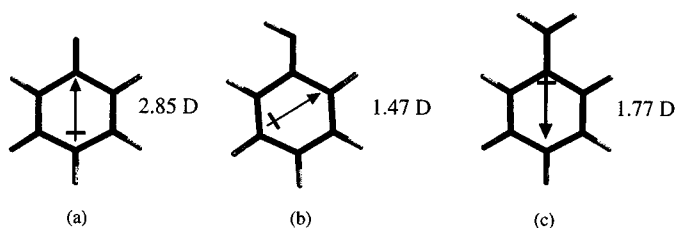


Table 1 gives the S₀-T₁ energy differences for phenyloxenium **13a** and its 4-methyl and 4-phenyl counterparts (**13b** and **13c**). HF/6-31G* predicts triplet states to be marginally lower than the singlet states. However, as expected, the inclusion of electron correlation at the pBP/DN* level radically alters the singlet state energy relative to the triplet state, at least in the cases studied. SCF convergence difficulties prevented calculation of the triplet state of **13c**, but the S₀-T₁ energies for **13a** and **13b** (-11.4 and -16.4 kcal mol⁻¹, respectively) indicate that, like phenylnitrenium ions, the donor methyl substituent stabilized the singlet state relative to the triplet state. While the S₀-T₁ differences are negative, the magnitude of the splitting is smaller than that found for the corresponding phenylnitrenium ions (-19.0 and -22.6 kcal mol⁻¹) although the impact of the donor methyl group appears greater in the oxenium ion case. The single point pBP/DN*//HF/6-31G* method, for which a value could also be obtained for **13c**, shows a similar trend for **13a** and **13b**, with comparable singlet-triplet splittings. However, the results indicate that a 4-phenyl group more strongly stabilizes the singlet state relative to the triplet state. This stabilization (-8.6 kcal mol⁻¹ relative to **13a**) is significantly greater than that computed for the corresponding nitrenium ion (-3.2 kcal mol⁻¹).

In these reduced valence cations, it is expected that electron-donating groups will stabilize singlet states more than the triplets in line with conventional molecular orbital arguments; cationic resonance stabilization results in lowering in energies of valence electrons (in the HOMO), but the triplet states are radical-like, having one electron localized in a p_y orbital on the heteroatom and one more electron in the π system than the S₀ state. However, when compared to phenylnitrenium ions **14**, the greater stabilization by methyl and phenyl relative to hydrogen in the phenyloxenium ion case suggests that there is greater localization of positive charge on the 4 position. In valence bond terminology, there

Fig. 1. Dipole moments in S_0 states of: (a) phenyloxenium **13a**, (b) phenylnitrenium **14a**, and (c) phenylcarbenium **15a** ions.



is a greater preponderance of (II) in the resonance hybrid of **13** than is the case in **14**. The HF/6-31G* S_0 and T_1 ground-state geometries of **13c** are planar, signifying extensive π delocalization into the distal ring in both species. However, this would be expected to be more important in the singlet state than in the triplet state; while localization of charge on the 4 position in phenyloxenium ion is a consequence of the electronegativity of oxygen, in the triplet state there is no similar driving force for spin localization onto that position. The barriers to rotation about the connecting bond for the S_0 and T_1 states, computed at the pBP/DN*//HF/6-31G* level from the orthogonal conformations, are 18.6 and 2.4 kcal mol⁻¹, respectively. In addition, the interconnecting bond in the singlet state (1.421 Å) is considerably shorter than that in the triplet state (1.431 Å).

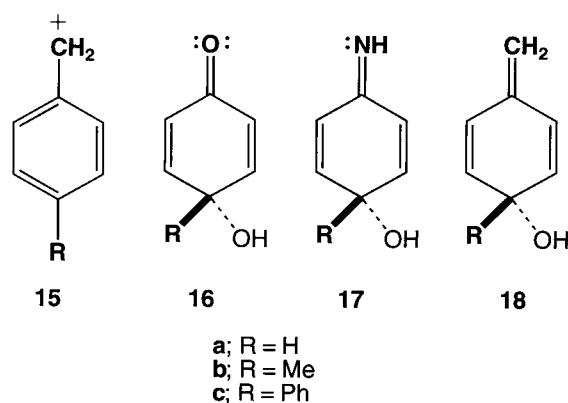
Properties of S_0 state phenyloxenium, phenylnitrenium, and phenylcarbenium ions

Evidence for a higher degree of localization of positive charge at the 4 position in **13** relative to **14** and **15** can be found in the properties of their respective S_0 states. Figure 1 illustrates the orientations and magnitudes of HF/6-31G* computed dipole moments in phenyloxenium **13a**, phenylnitrenium **14a**, and phenylcarbenium **15a** ions.

The electron deficiency in **15a** is clearly on the exocyclic carbon (Fig. 1c). In contrast, the magnitude and orientation of the dipole moment predicted for S_0 phenyloxenium ion **13a** clearly indicates a strong localization of positive charge at the 4 position in the ring. From the magnitude and orientation of the dipole moment in **14a**, appreciably less charge must reside on the ring. The contribution to the dipole in the direction of nitrogen and along the axis of the ring-to-nitrogen bond is estimated at 1.41 D, considerably less than for **13a**.³ While computed charges should be treated with caution, in support of this, HF/6-31G* electrostatic charges at O in **13a** and NH in **14a** are -0.36 and -0.16, respectively, and for each species, total electrostatic charges at the ortho carbons are respectively +0.06 and -0.09 while at the para carbon they are calculated to be +0.4 and +0.24.

Greater localization of charge at the 4 position in **13** is evident from the optimized ground-state geometries. HF/6-31G* optimized geometries for **13a**, **14a**, and **15a** are presented together with those of the respective 4-hydroxylated products **16a**, **17a**, and **18a** in Fig. 2. A comparison of the bond lengths of **13a** (Fig. 2a) with those for **16a** (Fig. 2d) clearly indicates that the phenyloxenium ion has a stronger carbonyl bond than the hydration product as evidenced by

the shorter C—O bond length. In addition, the degree of bond alternation around the ring in **13a** and **16a** is relatively similar. In contrast, the C—N bond in **14a** (Fig. 2b) is longer than that in the neutral imine (Fig. 2e). Although there is bond alternation around the ring, a comparison with that in **13a** (Fig. 2a) indicates a smaller degree of alternation in the nitrenium ion. In the carbenium ion case (Fig. 2c), the geometry accords with the exocyclic cationic form; the CH₂—C bond, in this case, is much longer than the cross-conjugated double bond in the hypothetical hydration product **18a** (Fig. 2f).



The short C=O bonds and high degree of alternation in the phenyl rings was reproduced in the 4-methyl (**13b**) and 4-biphenyl (**13c**) cases and this was better reflected in both the C=O and the symmetric and antisymmetric C₂=C₃ (C₅=C₆) vibrational frequencies determined from full frequency analyses on the S_0 states of **13a–13c** and **14a–14c**. These, together with the vibrational frequencies for the hydrated adducts **16a–16c** and **17a–17c**, are presented in Table 3.

Introduction of a 4-methyl and 4-phenyl substituent stabilizes positive charge at the 4 position or, in valence bond terms, the resonance hybrid II of **13**. This is evidenced by greater differences between the C=O vibrational frequencies in **13b** and **13c** relative to the corresponding hydrated adducts **16b** and **16c**. While the C₁=C₂/C₅=C₆ symmetric and asymmetric stretch frequencies are lower than those in the neutral hydrated adducts, these too increase with electron donor substitution reflecting strengthening of the C=C bonds (Table 3). The effect of the 4 substituents upon the corresponding nitrenium ions is, however, much more marked. While the C=N stretch frequencies in **14a–14c** are significantly lower than those in the hydrated adducts **17a–17c**, the difference reduces by 20 and 47 cm⁻¹, respectively, upon introduction of a 4-methyl and 4-phenyl substituent. This indicates that while the oxenium ion **13** is essentially in resonance form II, the nitrenium ion **14** has an appreciable contribution from I; upon substitution by an electron donor methyl or phenyl group, the proportion of II is increased more markedly leading to larger changes in C=NH vibrational frequencies. In other words, unlike **13a**, **14a**, on account of the reduced electronegativity of nitrogen, can still sustain some positive charge on the nitrogen. This picture

³Dipole moment = 1.468 D, $x = 1.16$, $y = 0.000$, $z = 0.890$, CNH angle = 114°; the component from the N—H bond in the z direction, which is along the C—N bond, is $-(1.16 \tan 24^\circ) = -0.516$ D.

Fig. 2. Optimized bond lengths for: (a) phenyloxenium ion **13a**, (b) phenylnitrenium ion **14a**, and (c) phenylcarbenium ion **15a** and their hydrated adducts (d) **16a**, (e) **17a**, and (f) **18a**.

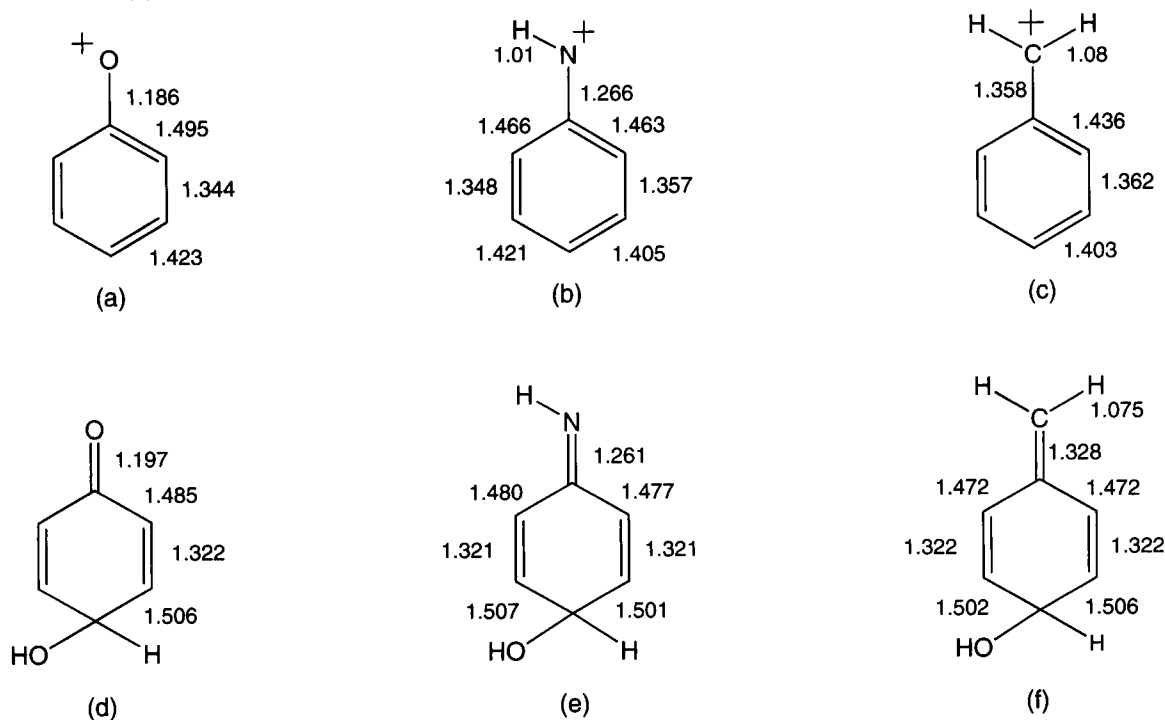


Table 3. HF/6-31G* vibrational frequencies (cm^{-1}) for phenyloxenium ions **13a–13c**, phenylnitrenium ions **14a–14c**, and their hydrated adducts **16a–16c** and **17a–17c**.

Bond	13a	16a	Δv	13b	16b	Δv	13c	16c	Δv
C=O	1799.6	1790.6	9.0	1807.6	1789.7	17.9	1812.1	1788.8	23.3
C=C(s)	1604.4	1681.4	-77.0	1623.2	1682.3	-59.1	1643.8	1678.7	-34.9
C=C(as)	1541.7	1649.1	-107.4	1541.7	1647.4	-105.6	1586.5	1643.8	-57.3
Bond	14a	17a	Δv	14b	17b	Δv	14c	17c	Δv
C=NH	1627.7	1735.1	-107.4	1648.2	1736.0	-87.7	1671.5	1731.5	-60.0
C=C(s)	1584.7	1660.8	-76.1	1598.1	1660.8	-62.7	1614.2	1652.7	-38.5
C=C(as)	1535.4	1654.5	-119.1	1518.4	1654.5	-136.1	1542.6	1648.2	-105.6

accords with reactivity patterns of arylnitrenium ions in that nucleophiles react on both the ring and at nitrogen (4–7, 12, 14, 48, 49).

Relative stabilities

Isodesmic rxn. [1] was used to estimate the hydration energies of phenyloxenium ions **13a–13c** relative to their corresponding nitrenium ions **14a–14c** and reflect relative stabilities of the correspondingly substituted ions.

From energies in Tables 1 and 2, the isodesmic energies from eq. [1] were calculated at the three levels indicated in

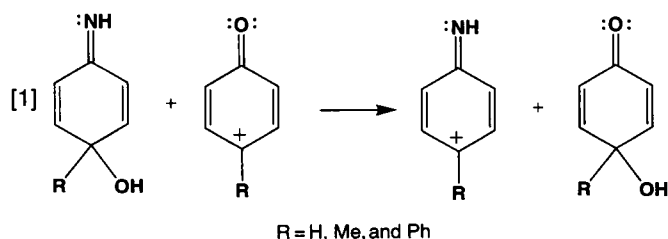
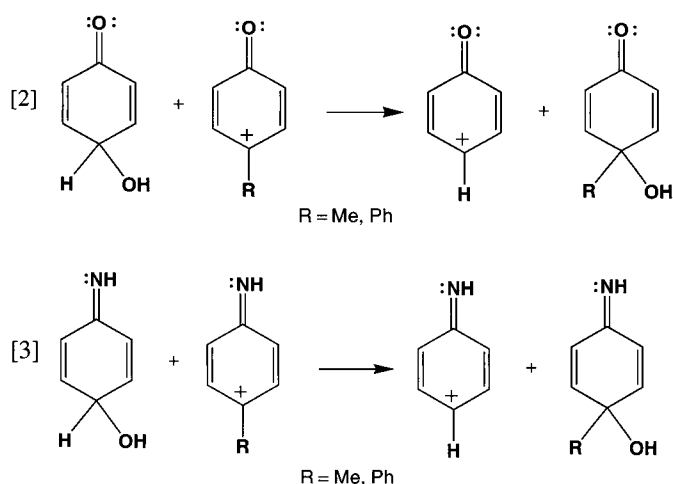


Table 4. The data show these energies to be largely independent of electron correlation as well as ZPEs and free energies in line with previous findings (50). The negative values indicate that, relative to their hydrated adducts **17** and **16**, phenylnitrenium ions are, in all three instances, more stable than the corresponding phenyloxenium ions, in line with their more delocalized positive charge. The difference between stabilities of **14c** and **13c** is in accord with the relative lifetimes of these ions in aqueous solution as determined from our competition reactions with azide (300 ns in the case of **14c** as opposed to 12 ns in the case of **13c** at 30 °C (37)). However, while a 4-methyl group exerts only a small influence upon the energies, the 4-phenyl group clearly provides greater relative stabilization to **13c** than to **14c** (the energy difference reduces in magnitude from 18 to 19 kcal mol⁻¹ in the case of unsubstituted and methylated ions to 11 kcal mol⁻¹ in the case of biphenyl ions).

A similar conclusion can be reached from isodesmic reactions comparing the relative hydration energies of 4-methyl- **13b** and 4-biphenyloxenium ions **13c** with the

Table 4. Isodesmic reaction energies from rxns. [1]–[3].

Isodesmic reaction	R	ΔE_{react} HF/6-31G*	ΔE_{react} pBP/DN*//HF/6-31G*+ZPE	ΔE_{react} pBP/DN*//HF/6-31G*+ZPE+G
[1] ^a	H	-21.3	-19.8	-19.3
[1] ^a	Me	-18.9	-19.2	-18.4
[1] ^a	Ph	-12.2	-12.3	-11.0
[2] ^b	Me	10.6	9.5	10.3
[2] ^b	Ph	25.9	28.2	29.0
[3] ^c	Me	8.2	9.0	9.4
[3] ^c	Ph	16.7	20.8	20.6

^aStability of phenyloxenium ions **13a**–**13c** relative to the nitrenium ions **14a**–**14c**.^bStability of **13b** and **13c** relative to **13a**.^cStability of **14b** and **14c** relative to **14a**.

unsubstituted ion **13a** (rxn. [2]) and rxn. [3] that gives corresponding estimates for the nitrenium ions **14b** and **14c** relative to **14a**.

Data for rxns. [2] and [3] in Table 4 clearly indicate that both methyl and phenyl stabilize both ions (positive values). However, whereas a 4-methyl group results in similar stabilization of the ions **13a** and **14a**, a 4-phenyl substituent stabilizes phenyloxenium ion by between 8 and 9 kcal mol⁻¹ relative to the phenylnitrenium ion. This is a critical difference. This stabilization accounts for the fact that it is possible to generate and trap **13c** in aqueous media in a similar manner to the generation and trapping of **14b** and **14c** (4, 13, 16, 17, 37, 50). However, **13b** could not be observed under any of the conditions used for the trapping of **13c** (37, 38). We estimate, using the differences in hydration energies from isodesmic rxn. [2] (Table 4), and previously published correlations of nitrenium ion lifetimes and hydration energies of rxn. [3] that the lifetime of the 4-methylphenyloxenium would be of the order of 3–5 ps, approaching that of a transition state rather than an intermediate (38, 50).

The increased stabilization of phenyloxenium ion by a 4-phenyl group relative to phenylnitrenium ion also manifests itself in the ground-state geometries of the two ions (Fig. 3). Whereas **15c** and **14c** are nonplanar with inter-ring dihedrals of 22° and 28°, respectively, **13c** is computed to be planar at the HF/6-31G* level. The extent to which there is overlap between the two rings is also evident from the length of the connecting bonds as well as the barriers to rotation around the rings. The twist angles in biphenyls are determined by a


balance between electronic and steric influences. In the case of **13c**, the resonance interaction is strong enough to overcome the strain imposed by the repulsion between *m* and *o'* hydrogens and the barrier to rotation about the C4–C4' bond is clearly significantly higher than that for **14c** and **15c**.

The degree of delocalization in **13c**, **14c**, and **15c** clearly manifests itself in the nature of the LUMOs of all three. Relative contributions to the LUMO at the exocyclic atom and the 4 positions vary inversely (Fig. 4) and similar variations in LUMO contributions were found for the corresponding phenyl- and 4-methylphenylnitrenium ions. Accordingly, in aqueous conditions, attack of water at the 4 position is the major process with biphenyloxenium ion (37, 38), while biphenylcarbenium ion reacts at the benzylic position. As alluded to previously, biphenylnitrenium reacts with water at the 4 position, but is also known to react at nitrogen (4–7, 12, 14, 48, 49). In this series, there is also a progressively greater contribution to the LUMO from the distal ring from twisted **15c** to planar **13c** (Fig. 4). Solvolysis studies on biphenyloxenium ion indicate that water ($k_s = 8.4 \times 10^7 \text{ s}^{-1}$) and, to a degree, acetate ($k_{\text{OAc}} = 2.8 \times 10^8 \text{ (mol/L)}^{-1} \text{ s}^{-1}$) are more selective nucleophiles than Br⁻ ($k_{\text{Br}^-} = 3.9 \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1}$) and azide ($k_{\text{Az}} = 6.5 \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1}$) (38). Our experimental studies have detected addition of water and acetate to the 4 position in 4-biphenyloxenium ion (37). With the more reactive azide, the major products were **6** and **7**. While reversible attack of azide at the 4 position cannot be discounted, the formation of these products reflects the lower selectivity of azide when compared to water. In addition, the formation of the 4'-azidobiphenol (**7**) from azide–water competition reactions with **3** (Scheme 1) and the failure to detect the attack of azide at the 4' position on the corresponding nitrenium ion, reflects the attendant planarity in this ion and the increased delocalization of the positive charge in **13c**. Bromide appeared to react on **13c** giving only 2-bromo-4-biphenol (37).

Conclusion

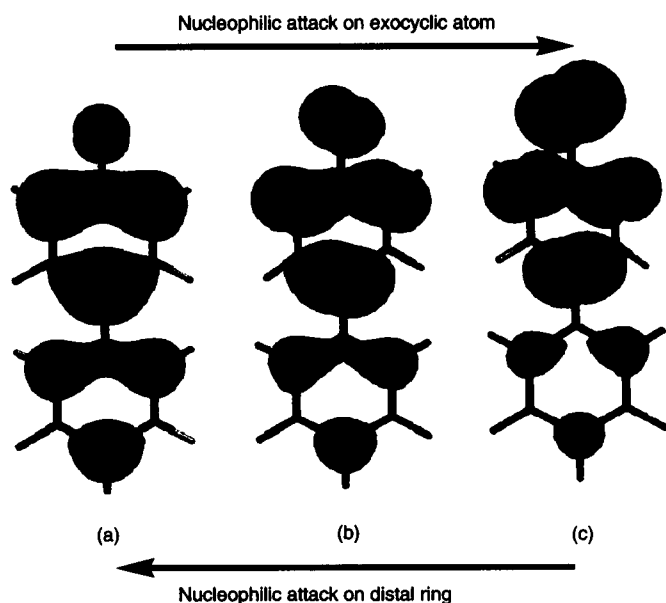
Phenyloxenium ions **13** are predicted to have a S₀ ground state that is lowered, relative to the T₁ state, by electron donor substituents. Analysis of computed ground-state geometries and IR vibrational frequencies shows that phenyloxenium ion is best described as a 4-oxo-2,5-cyclohexadienyl cation. Accordingly, it is stabilized effectively by a 4-phenyl substituent, which is coplanar to maximize charge delocalization. This results in products from attack of

Fig. 3. Ground-state HF/6-31G* geometries, twist angles, inter-ring bond lengths, and rotational barriers (pBP/DN*/HF/6-31G*) for: (a) 4-biphenyloxenium ion **13c**, (b) 4-biphenylnitrenium ion **14c**, and (c) 4-biphenylcarbenium ion **15c**.



	(a)	(b)	(c)
Dihedral (°)	0.0	21.9	28.3
C—C (Å)	1.421	1.437	1.457
Barrier (kcalmol ⁻¹)	18.6	13.8	10.4

Fig. 4. LUMO contributions to: (a) 4-biphenyloxenium ion **13c**, (b) 4-biphenylnitrenium ion **14c**, and (c) 4-biphenylcarbenium ion **15c**.



nonselective nucleophiles like azide on both rings. The 4-methyl analogue **13b** is predicted to be considerably less stable in support of the experimental finding that it cannot be observed under conditions in which **13c** is readily detected. Relative to their hydrated products, 4-biphenyloxenium ion is predicted to be less stable than 4-biphenylnitrenium ion in support of their respective lifetimes in aqueous conditions. The difference in properties between nitrenium and oxenium ions can be ascribed to differences in the electronegativity of oxygen and nitrogen. Whereas nitrogen can sustain partial positive charge, the more electronegative oxygen atom in the phenyloxenium ion causes a high degree of charge localization on the ring. The attendant destabilization of oxenium ions relative to nitrenium ions is reflected in the aqueous solution lifetimes of **13c** and **14c** and in the difference in the ability to detect **14b** and **13b**.

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