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

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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 the phenyloxenium ions 13 are ground-state singlets but S0–T1 gaps are smaller than those of the corresponding nitrenium ions. The S0 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 carbene 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-phenyl- 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 singulet à l’état fondamental, toutefois les écarts S0–T1 sont plus faibles que ceux des ions nitrénium correspondants. Dans les deux classes d’ions, les états S0 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-hydroxy cyclohexa-2,5-diène (17) et les fréquences d’étirement 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’étirement des ions phényloxénium ne sont respectivement que faiblement plus courtes et plus longues que celles de leur produit d’hydratation, la 4-hydroxy cyclohexa-2,5-diène (16). La meilleure façon de décrire les ions oxénium correspondent aux structures de résonance du carbène 4-oxocyclohexa-2,5-diène. En conséquence, un groupe 4-phényle stabilise plus un ion phényloxénium que l’ion phénylnitrénium conduisant à une géométrie plane et beaucoup plus de charge dans le noyau distal, ce qui expliquerait les régiosélectivités des réactions avec l’ion azote. 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 nitrenium 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.
**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, in certain cases, can 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 behavior. The lifetimes of 4-biphenylnitrenium ion (300 ns at 30 °C) and its bridged counterpart, 2-fluorenlnitrenium 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) and as upon oxygen (30, 33) have been ascribed to the electrophilic behavior of these species, but the regiochemistry of these 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-biphenylyl)ethyl and 4-phenylcyclopropyl 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-fluoroquinoline 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'-regiosomer signals significantly greater delocalization of positive charge on 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 (lifetimes of 0.8 ns in aqueous acetone 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-methylquinolin 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...

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

4-Biphenyloxynium 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 cal = 4.184 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 phenyloxenonium 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 phenyloxenonium 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 Sₒ-Tₐ energies of phenyloxenonium 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 biphenyloxenonium 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-methylphenyloxenonium ion 13b and 4-biphenyloxenonium ion 13c relative to the parent phenyloxenonium 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 phenyloxenonium ion 13a and phenylnitrenium ion 14a, 4-methylphenyloxenonium ion 13b and 4-methylphenylnitrenium ion 14b, and 4-biphenyloxenonium 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 °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 Sₒ-Tₐ splittings at the HF/6-31G*, pBP/DN*/HF/6-31G*, and pBP/DN* levels are presented in Table 1. Sₒ-Tₐ 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 (Sₒ-Tₐ = −21.9 and −21.3 kcal mol⁻¹, respectively) lower the singlet state marginally relative to the triplet state when compared to phenylnitrenium ion (Sₒ-Tₐ = −18.8 kcal mol⁻¹) (44). The pBP/DN* level performed
<table>
<thead>
<tr>
<th>Method</th>
<th>Type</th>
<th>13a</th>
<th>13b</th>
<th>13c</th>
<th>14a</th>
<th>14b</th>
<th>14c</th>
<th>14d</th>
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<td>$T_1$</td>
<td>-304.67688</td>
<td>-3443.72152</td>
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<td>0.5</td>
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<td>0.3</td>
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<td>$S_0$</td>
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<td>72.54, 51.7</td>
<td>105.86, 83.1</td>
<td>63.83, 44.83</td>
<td>80.35, 60.21</td>
<td>(113.45, 91.89)</td>
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<td>-345.92421</td>
<td>-21.6</td>
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<td>-21.6</td>
<td>-22.5</td>
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<tr>
<td></td>
<td>$S_0-T_1$</td>
<td>(ZPE)</td>
<td>(52.95, 69.36)</td>
<td>(62.54, 51.7)</td>
<td>(105.86, 83.1)</td>
<td>(63.83, 44.83)</td>
<td>(80.35, 60.21)</td>
<td>(113.45, 91.89)</td>
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<tr>
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<td>(S_0-T_1)_{ZPE}</td>
<td>-11.4</td>
<td>-16.4</td>
<td>-19.0</td>
<td>-22.6</td>
<td>-24.6</td>
<td>-21.3</td>
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*Difference in energy between the orthogonal and geometry-optimized biphenyl geometries in kcal mol$^{-1}$.  
*Zero-point energies and free energies (kcal mol$^{-1}$) from frequency calculations at the pBP/DN*/HF/6-31G* level.  
*Geometry optimized at the pBP/DN* level.  
*Calculation failed because of SCF convergence difficulties.  
*BPW91/cc-pVDZ value from ref. 44.
similarly for the unsubstituted and 4-methylphenylnitrenium ion \((S_0 - T_1 = -19.0 \text{ and } -22.6 \text{ kcal mol}^{-1})\) and the splitting for the 4-chlorinated analogue was marginally higher \((-24.5 \text{ kcal mol}^{-1})\). 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 \(S_0 - T_1\) 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 \(S_0 - T_1\) energies for 13a and 13b \((-11.4 \text{ and } -16.4 \text{ kcal mol}^{-1}\), respectively) indicate that, like phenylnitrenium ions, the donor methyl substituent stabilized the singlet state relative to hydrogen. While the \(S_0 - T_1\) differences are negative, the magnitude of the splitting is smaller than that found for the corresponding phenylnitrenium ions \((-19.0 \text{ and } -22.6 \text{ kcal mol}^{-1}\) 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 \((-8.6 \text{ kcal mol}^{-1}\) relative to 13a) is significantly greater than that computed for the corresponding nitrenium ion \((-3.2 \text{ kcal mol}^{-1}\) ).

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 \(p_z\) orbital on the heteroatom and one more electron in the \(\pi\) system than the \(S_0\) 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
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 \( \pi \) 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 phenyloxyen 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 phenyloxyen, phenylnitreniun, 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 phenyloxyen ion 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 \( S_0 \) phenyloxen 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 phenyloxen 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 CH—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-biphenylyl (13c) cases and this was better reflected in both the C=O and the symmetric and antisymmetric \( C_2=\) C_3 (C_5=C_6) 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 C_2=C_3=C_5=C_6 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

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\(^3\) Dipole 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 \(-0.516 \) 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.

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<th>Bond</th>
<th>13a</th>
<th>16a</th>
<th>Δν</th>
<th>13b</th>
<th>16b</th>
<th>Δν</th>
<th>13c</th>
<th>16c</th>
<th>Δν</th>
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<tr>
<td>C=O</td>
<td>1799.6</td>
<td>1790.6</td>
<td>9.0</td>
<td>1807.6</td>
<td>1789.7</td>
<td>17.9</td>
<td>1812.1</td>
<td>1788.8</td>
<td>23.3</td>
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<td>C=C(s)</td>
<td>1604.4</td>
<td>1681.4</td>
<td>−77.0</td>
<td>1623.2</td>
<td>1682.3</td>
<td>−59.1</td>
<td>1643.8</td>
<td>1678.7</td>
<td>−34.9</td>
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<td>C=C(as)</td>
<td>1541.7</td>
<td>1649.1</td>
<td>−107.4</td>
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<td>1647.4</td>
<td>−105.6</td>
<td>1586.5</td>
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<td>1735.1</td>
<td>−107.4</td>
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<td>1736.0</td>
<td>−87.7</td>
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<td>−76.1</td>
<td>1598.1</td>
<td>1660.8</td>
<td>−62.7</td>
<td>1614.2</td>
<td>1652.7</td>
<td>−38.5</td>
</tr>
<tr>
<td>C=C(as)</td>
<td>1535.4</td>
<td>1654.5</td>
<td>−119.1</td>
<td>1518.4</td>
<td>1654.5</td>
<td>−136.1</td>
<td>1542.6</td>
<td>1648.2</td>
<td>−105.6</td>
</tr>
</tbody>
</table>

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 biphenylly 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].

<table>
<thead>
<tr>
<th>Isodesmic reaction</th>
<th>R</th>
<th>$\Delta E_{\text{react}}$ HF/6-31G*</th>
<th>$\Delta E_{\text{react}}$ pBP/DN*//HF/6-31G*+ZPE</th>
<th>$\Delta E_{\text{react}}$ pBP/DN*//HF/6-31G*+ZPE+G</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]$^a$</td>
<td>Me</td>
<td>18.9</td>
<td>-19.2</td>
<td>-18.4</td>
</tr>
<tr>
<td>[1]$^a$</td>
<td>Ph</td>
<td>12.2</td>
<td>-12.3</td>
<td>-11.0</td>
</tr>
<tr>
<td>[2]$^b$</td>
<td>Me</td>
<td>10.6</td>
<td>9.5</td>
<td>10.3</td>
</tr>
<tr>
<td>[2]$^b$</td>
<td>Ph</td>
<td>25.9</td>
<td>28.2</td>
<td>29.0</td>
</tr>
<tr>
<td>[3]$^c$</td>
<td>Me</td>
<td>8.2</td>
<td>9.0</td>
<td>9.4</td>
</tr>
<tr>
<td>[3]$^c$</td>
<td>Ph</td>
<td>16.7</td>
<td>20.8</td>
<td>20.6</td>
</tr>
</tbody>
</table>

$^a$ Stability of phenyloxonium ions 13a–13c relative to the nitrenium ions 14a–14c.

$^b$ Stability of 13b and 13c relative to 13a.

$^c$ Stability of 14b and 14c relative to 14a.

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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-substituted group results in similar stabilization of the ions 13a and 14a, a 4-phenyl substituent stabilizes phenyloxonium 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-phenyloxonium 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 phenyloxonium 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 $a'$ 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 position vary inversely (Fig. 4) and similar variations in LUMO contributions were found for the corresponding phenyl- and 4-methylphenylbenzenium ions. Accordingly, in aqueous conditions, attack of water at the 4 position is the major process with biphenyloxonium ion (37, 38), while phenylnitrenium 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 to twisted 15c to planar 13c (Fig. 4). Solvolysis studies on biphenyloxonium ion indicate that water ($k_w = 8.4 \times 10^7$ s$^{-1}$) and, to a degree, acetate ($k_{OAc} = 2.8 \times 10^6$ mol$^{-1}$ L$^{-1}$ s$^{-1}$) are more selective nucleophiles than Br$^-$ ($k_{Br^-} = 3.9 \times 10^9$ (mol/L)$^{-1}$ s$^{-1}$) and azide ($k_{NaN} = 6.5 \times 10^8$ (mol/L)$^{-1}$ s$^{-1}$) (38). Our experimental studies have detected addition of water and acetate to the 4 position in 4-biphenyloxonium 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'-azidobiphenyl (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-biphenyl (37).

### Conclusion

Phenyloxonium ions 13 are predicted to have a $S_0$ ground state that is lowered, relative to the $T_1$ state, by electron donor substituents. Analysis of computed ground-state geometries and IR vibrational frequencies shows that phenyloxonium 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-biphenylininium ion 14c, and (c) 4-biphenylycarbenium ion 15c.

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihedral (°)</td>
<td>0.0</td>
<td>21.9</td>
</tr>
<tr>
<td>C—C (Å)</td>
<td>1.421</td>
<td>1.437</td>
</tr>
<tr>
<td>Barrier (kcal mol⁻¹)</td>
<td>18.6</td>
<td>13.8</td>
</tr>
</tbody>
</table>

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

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References