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Substituent Effects on Singlet−Triplet Gaps and Mechanisms of 1,2-Rearrangements of 1,3-Oxazol-2-ylidenes to 1,3-Oxazoles

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Electronic structures, partial atomic charges, singlet−triplet gaps (ΔE_{ST}), substituent effects, and mechanisms of 1,2-rearrangements of 1,3-oxazol-2-ylidene (**5**) and 4,5-dimethyl- (**6**), 4,5-difluoro- (**7**), 4,5-dichloro- (**8**), 4,5-dibromo- (**9**), and 3-methyl-1,3-oxazol-2-ylidene (**10**) to the corresponding 1,3-oxazoles have been studied using complete-basis-set methods (CBS-QB3, CBS-Q, CBS-4M), second-order Møller−Plesset perturbation method (MP2), hybrid density functionals (B3LYP, B3PW91), coupled-cluster theory with single and double excitations (CCSD) and CCSD plus perturbative triple excitations [CCSD(T)], and the quadratic configuration interaction method including single and double excitations (QCISD) and QCISD plus perturbative triple excitations [QCISD(T)]. The 6-311G(d,p), 6-31+G(d,p), 6-311+G(d,p), and correlation-consistent polarized valence double-ξ (cc-pVDZ) basis sets were employed. The carbenes have singlet ground states, and the CBS-QB3 and CBS-Q methods predict ΔE_{ST} values for **5**−**8** and **10** of 79.9, 79.8, 74.7, 77.0, and 82.0 kcal/mol, respectively. CCSD(T), QCISD(T), B3LYP, and B3PW91 predict smaller ΔE_{ST} values than CBS-QB3 and CBS-Q, with the hybrid density functionals predicting the smallest values. The concerted unimolecular exothermic out-of-plane 1,2-rearrangements of singlet 1,3-oxazol-2-ylidenes to their respective 1,3-oxazoles proceed via cyclic three-center transition states. The CBS-predicted barriers to the 1,2-rearrangements of singlet carbenes **5**−**9** to their respective 1,3-oxazoles are 41.4, 40.4, 37.8, 40.4, and 40.5 kcal/mol, respectively. During the 1,2-rearrangements of singlet 1,3-oxazol-2-ylidenes **5**−**9**, there is a decrease in electron density at oxygen, N3 (the migration origin), and C5 and an increase in electron density at C2 (the migration terminus), C4, and the partially positive migrating hydrogen.

Introduction

Carbenes are neutral divalent carbon compounds with short lifetimes that are especially important in organic synthesis and polymer chemistry,[1−6] in organometallic chemistry including ligands for homogeneous catalysis and homogeneous activation of small molecules,[7] in computational chemistry, and in theoretical chemistry. Carbenes can exist in singlet and triplet states. In the singlet state, there is an empty p_π orbital on the carbene carbon, and the nonbonding electrons occupy an sp^2 orbital in the plane of the molecule. In the triplet state, the nonbonding electrons have parallel spins and occupy an sp^2 orbital as well as an orbital with substantial p character. Singlet carbenes are expected to show electrophilic and nucleophilic behavior because of the lone pair and the vacant orbital, whereas triplet carbenes are expected to exhibit diradical reactivity. Singlet carbenes undergo a variety of reactions including dimerizations, intramolecular rearrangements, intramolecular and intermolecular insertions, and cycloadditions to alkenes, alkynes, and other unsaturated functional groups. The relative stability, reactivity, singlet−triplet gap (ΔE_{ST}), lifetime, and philicity of carbenes are dependent on π-electron delocalization and the substituents bonded to the electron-deficient carbene carbon atom (spectator substituents), neighboring substituents (bystander substituents), and remote substituents.

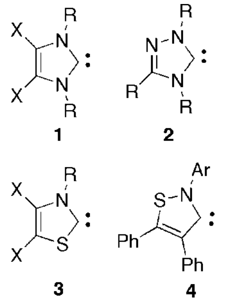

Figure 1. Examples of stable heterocyclic carbenes.

As short-lived reactive intermediates, carbenes are generally trapped or isolated in a matrix at low temperatures. However, following the report of the first isolated crystalline five-membered ring carbene [R = 1,3-di(1-adamantyl)imidazol-2-ylidene, **1**] by Arduengo and co-workers,[8] other stable heterocyclic carbenes have been synthesized. These include 1,2,4-triazol-5-ylidenes (**2**, R = alkyl, aryl),[9] 1,3-thiazol-2-ylidenes (**3**, R = alkyl, aryl),[10,11] and 1,2-thiazol-3-ylidenes (isothiazol-3-ylidenes, **4**, Figure 1).[12] The singlet carbene [**1**, X = H, R = 1,3-di(1-adamantyl)] is thermodynamically stabilized by resonance and kinetically stabilized by the bulky 1-adamantyl groups adjacent to the carbene carbon. The synthesis of derivatives of **1** with less bulky substituents than adamantyl (e.g., **1**, X = R = Me) showed that it was not only kinetic factors but also electronic effects [mesomeric (+M), inductive] that contribute to the stability of 1,3-imidazol-2-ylidenes.

1,3-Di(2,4,6-trimethylphenyl)-4,5-dichloroimidazol-2-ylidene (**1**, X = Cl)[13,14] and 1,3-di(2,4,6-trimethylphenyl)-4,5-dibromoimidazol-2-ylidene (**1**, X = Br)[14] are two examples of air-stable carbenes. The remarkable stability of these 4,5-dihalo carbenes might be due, in part, to the electronegativities of the

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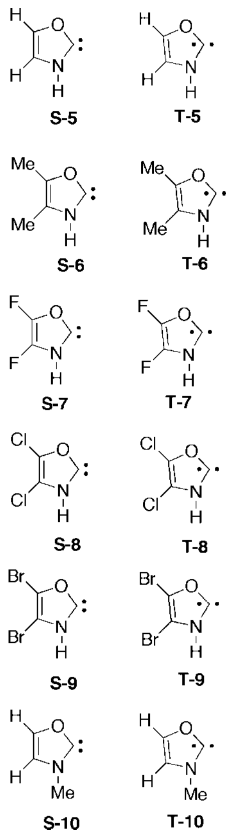

Figure 2. Singlet and triplet 1,3-oxazol-2-ylidenes.

halogens as well as to their larger covalent radii compared to that of hydrogen.[14] The π-electron-releasing abilities of the amino groups and the halogens as well as their σ-electron-withdrawing capabilities also contribute to the extraordinary stability of 4,5-dihalo carbenes **1**.[13] Experimental, computational, and theoretical studies suggest that large singlet−triplet gaps, π conjugation, and steric factors also contribute to the exceptional stability of 6π heterocyclic carbenes.[15,16] However, the isolation of a stable 1,3-imidazolin-2-ylidene[10] and a stable acyclic diaminocarbene[17] shows that the C═C double bond is not essential for the extraordinary stability observed in heterocyclic carbenes. In addition, the isolation of a stable 1,3-thiazol-2-ylidene (**3**) demonstrated that substituents other than nitrogen can be tolerated on the carbene center.[10,11]

The electronic structures of carbenes make them difficult to study computationally and theoretically. The computation of reliable singlet−triplet gaps for carbenes is a long-standing problem in quantum chemistry and previous theoretical studies have given different explanations for why 1,3-imidazol-2-ylidenes can be isolated as stable compounds. Although a few computational and theoretical studies on derivatives of 1,3-imidazol-2-ylidenes (**1**) have been published, there do not appear to be any systematic theoretical reports concerning 1,3-oxazol-2-ylidenes, which might have stabilizing properties similar to those of 1,3-imidazol-2-ylidenes. Because of the absence of studies on 1,3-oxazol-2-ylidene (**5**) and its derivatives and because of our desire to better understand the properties that contribute to the extraordinary stability of heterocyclic carbenes, we have investigated the singlet−triplet gaps, electronic structures, geometric features, partial atomic charges, and 1,2-rearrangements of **5** and 4,5-dimethyl- (**6**), 4,5-difluoro- (**7**), 4,5-dichloro- (**8**), 4,5-dibromo- (**9**), and 3-methyl-1,3-oxazol-2-ylidene (**10**) (Figure 2) to their respective 1,3-oxazoles using high-level contemporary methods of electronic structure theory. A better understanding of the factors that contribute to the stability of heterocyclic carbenes will enable more efficacious planning and synthesis of additional isolable examples including oxo and thia analogs. In addition, although a number of reports have been published concerning the properties of heterocyclic carbenes, relatively little attention has been paid to their reactivity.

Calculational and Theoretical Methods

All calculations were carried out with the Gaussian 03[18] and Spartan'02[19,20] computational programs.[21] No constraints were imposed on the structures in the equilibrium-geometry calculations or in the transition-state optimizations. Molecular geometries were optimized at the restricted level (closed-shell) for singlets and the unrestricted level (open-shell) for triplets. The equilibrium-geometry calculations were carried out using hybrid density functionals (B3LYP, B3PW91)[22−27] and the second-order Møller−Plesset perturbation method (MP2)[28] with the 6-31+G(d,p), 6-311+G(d,p), and 6-311G(d,p) basis sets.[29−31] Basis sets with diffuse functions are recommended for molecules with lone pairs, for anions, and for systems with significant negative charge. Energy calculations were performed with complete-basis-set methods (CBS-QB3, CBS-Q, CBS-4M)[32,33] and on the geometry-optimized structures using Bartlett's coupled-cluster theory with single and double excitations (CCSD) and CCSD plus perturbative triple excitations [CCSD(T)][34,35] and quadratic configuration interaction including single and double excitations (QCISD) and QCISD plus perturbative triple excitations [QCISD(T)][36,37] in conjunction with the Dunning[38] correlation-consistent polarized valence double-ξ basis set (cc-pVDZ). CBS-QB3 and CBS-Q are similar methods, and their accuracies are usually similar. CCSD and QCISD also are similar methods, with the latter requiring less disk space. CCSD and QCISD are excellent for estimating electron correlation energies and are two of the most satisfactory methods for the calculation of energy differences.

Vibrational frequency analyses were carried out in order to assess the nature of the stationary points and obtain the zero-point vibrational energies (ZPVEs). Each transition state has one imaginary frequency. Intrinsic reaction path calculations (IRCs) were used to connect the transition state to its respective minima.[39] The relative energy between two structures (ΔE) is the difference in the sum of the calculated electronic energy (E_{elect}) plus ZPVE for each at 0 K. The ZPVE is scaled by the factor defined in the model.[17,18,32,33,40] The enthalpy ($H°$) is the total electronic energy (without ZPVE) plus H_{corr}, and the free energy ($G°$) is the total electronic energy (without ZPVE) plus G_{corr}. These sums were used for calculating the enthalpies of reactions ($\Delta_r H°$) and the Gibbs free energies of reaction ($\Delta_r G°$)

$$\Delta_r H°(298.15) = \sum (E_{\mathrm{elect}} + H_{\mathrm{corr}})_{\mathrm{products}} - \sum (E_{\mathrm{elect}} + H_{\mathrm{corr}})_{\mathrm{reactants}}$$

$$\Delta_r G°(298.15) = \sum (E_{\mathrm{elect}} + G_{\mathrm{corr}})_{\mathrm{products}} - \sum (E_{\mathrm{elect}} + G_{\mathrm{corr}})_{\mathrm{reactants}}$$

The bond angles and torsion angles are given in degrees, bond lengths in angstroms (Å), total energies in atomic units (au), and ZPVE and ΔE in kilocalories per mole (kcal/mol). Dipole moments (μ) are given in debye (D), and entropies are given in entropy units [eu, or calories per mole per Kelvin (cal/mol·K)].

SCHEME 1

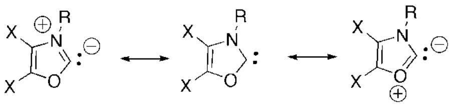

TABLE 1: Singlet−Triplet Gaps (ΔE_{ST}[a]) for 1,3-Oxazol-2-ylidenes 5−10

level of theory	H 5	Me 6	F 7	Cl 8	Br 9	NMe 10
CBS-QB3	79.9	79.8	74.7			82.0
CBS-Q	80.3	79.4	75.1	77.0		
CBS-4M	78.5		75.2	75.7	75.4	81.0
B3LYP[b]	76.4	76.1	70.3	72.7	73.5	77.6
B3LYP[c]	75.8	75.7	69.8	72.5	72.5	77.8
B3PW91[b]	74.1	74.6	68.5	70.7	71.4	75.6
B3PW91[c]	73.5	73.9	69.8	71.6	74.8	75.3
CCSD[d,e]	75.5	76.6	71.0	72.8	73.0	77.3
CCSD(T)[c,d]	77.7	78.5	72.8	74.8	75.1	79.5
QCISD[d,e]	75.6	76.6	70.8	72.7	73.0	77.3
QCISD(T)[d,e]	77.7	78.5	72.7	74.5	75.0	79.4

[a] $\Delta E_{ST} = E_{triplet} - E_{singlet}$. [b] 6-31+G(d,p) basis set. [c] 6-311+G(d,p) basis set. [d] cc-pVDZ basis set. [e] B3LYP/6-31+G(d,p)-optimized structure.

Results and Discussion

We used a wide range of high levels of electronic theory in this study owing to the difficulties inherent in calculations on carbenes, to assess the accuracy of different levels of theory and to compare results in this investigation with those of previous reports. The CBS methods are among the most accurate compound quantum mechanical methods, including the G-series developed by Pople and co-workers[41,42] and the W-series developed by Martin and co-workers,[43,44] which are capable of producing highly accurate (±1 kcal/mol) thermochemical data.

Singlet−Triplet Gaps. According to Hund's rule, the triplet state of a carbene should be more stable than the singlet state. However, the singlet−triplet gap (ΔE_{ST}) is dependent on the energy separation between the two nonbonding orbitals. If that gap is small, Hund's rule is operative, and the triplet state is favored. As the separation between the two orbitals increases, it eventually outweighs the greater Coulombic repulsion between the two electrons in the singlet state, and the singlet form becomes the ground state.[1−3,45−48] Although other factors also are operative, substituents with unshared electron pairs (π-electron-donating groups) might stabilize singlet structures more strongly than triplet structures. The less electronegative nitrogen is a better electron donor than oxygen and both hetero atoms influence the resonance contributors (ylides) for the 1,3-oxazol-2-ylidenes (Scheme 1).

Because the reactivity of a carbene is dependent on whether it is in the singlet or triplet state, the magnitude of the singlet−triplet gap is of great importance. A positive value of ΔE_{ST} implies that the singlet lies lower in energy than the triplet. Table 1 shows that all levels of theory predict the singlet states of 1,3-oxazol-2-ylidenes **S-5**−**S-10** to be lower in energy than their respective triplet states **T-5**−**T-10**. The CBS methods predict **S-5**−**S-10** to be lower in energy than their triplets by 79.9, 79.8, 74.7, 77.0, 75.4, and 82.0 kcal/mol, respectively. CBS-4M generally, but not always, predicts smaller values for ΔE_{ST} than either CBS-QB3 or CBS-Q. It can be seen in Table 1 that CCSD(T) and QCISD(T) predict smaller values for ΔE_{ST} than the CBS methods, whereas B3LYP and B3PW91 predict lower values than CCSD(T) and QCISD(T). It can also be seen in Table 1 that the calculational results from the hybrid density functionals B3LYP and B3PW91 are not very basis-set-dependent.[49]

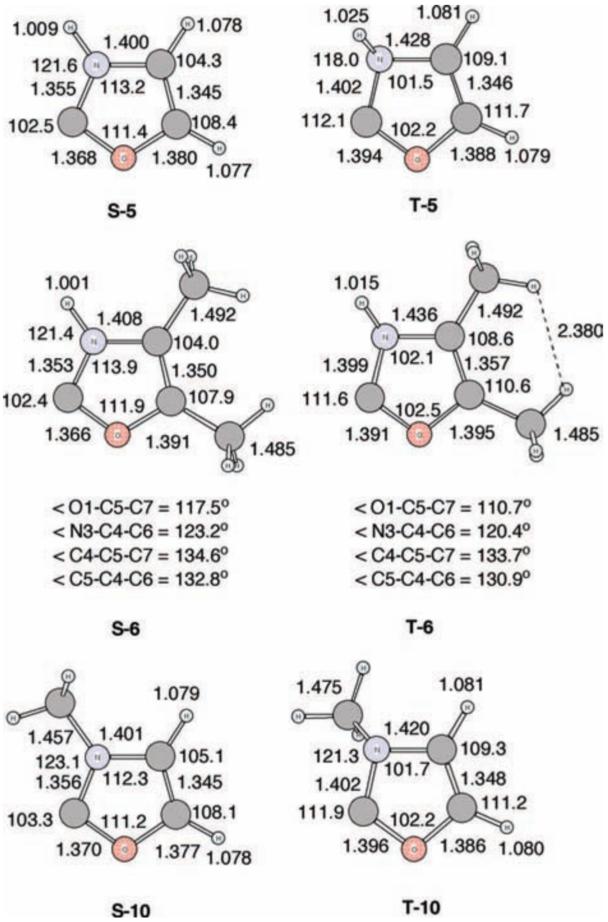

Figure 3. B3LYP/6-311+G(d,p)- (**5**) and B3LYP/6-31+G(d,p)- (**6**, **10**)-optimized structures for 1,3-oxazol-2-ylidenes.

The greater stability of the singlet carbenes stems from π conjugation, resonance contributors (Scheme 1), and the π-donor and σ-acceptor nature of the substituents, including the amino group that withdraws excess σ-electron density from the carbene carbon and diminishes the π-electron deficiency through $p_\pi - p_\pi$ back-donation from the nitrogen lone pair. Although the ΔE_{ST} value for **5** is large, it is about 5 kcal/mol smaller than that for 1,3-imidazol-2-ylidene (84.5 kcal/mol).[8e,15b,e,g] A large singlet−triplet gap is one of the properties that contribute to the stability of heterocyclic carbenes and is a factor in the subsequent reactivity of nascent carbenes.

Replacing the hydrogen on the nitrogen atom (N3−H) in **5** with a methyl group (N3−CH_3, **10**) leads to an increase in ΔE_{ST}. However, replacing the two hydrogens at positions 4 and 5 in **5** with inductive electron-releasing methyl groups (**6**, $\sigma_m = -0.07$, $\sigma_p = -0.17$)[50] does not appear to have a significant effect on ΔE_{ST} relative to that of the parent carbene, **5**. In contrast to **6**, replacing the hydrogens at positions 4 and 5 of **5** with electron-attracting fluoro (**7**, $\sigma_m = +0.34$, $\sigma_p = +0.06$), chloro (**8**, $\sigma_m = +0.37$, $\sigma_p = +0.23$), or bromo (**9**, $\sigma_m = +0.39$, $\sigma_p = +0.23$) substituents lowers the predicted values for ΔE_{ST}, with the most electronegative fluoro substituents having the largest effect. The σ_I values for the electron-withdrawing 1,3-oxazol-2-yl and 4,5-dimethyl-1,3-oxazol-2-yl systems are +0.38 and +0.35, respectively.[50]

It is well-known that the parent carbene (methylene, :CH_2) has a triplet ground state and that the singlet is more strongly

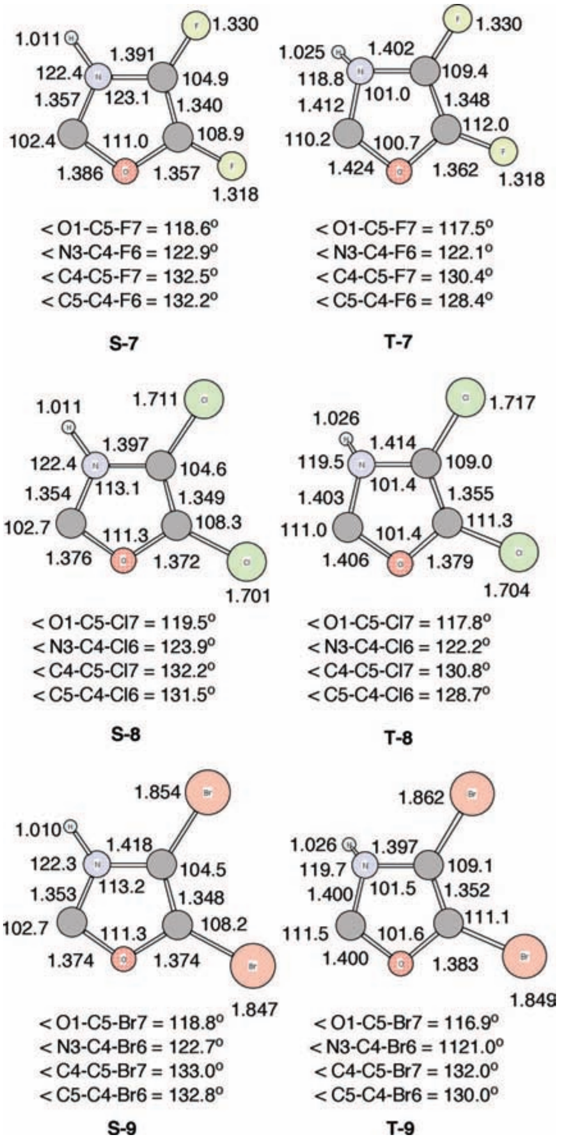

Figure 4. B3LYP/6-31+G(d,p)-optimized singlet and triplet structures of 4,5-dihalo-1,3-oxazol-2-ylidenes.

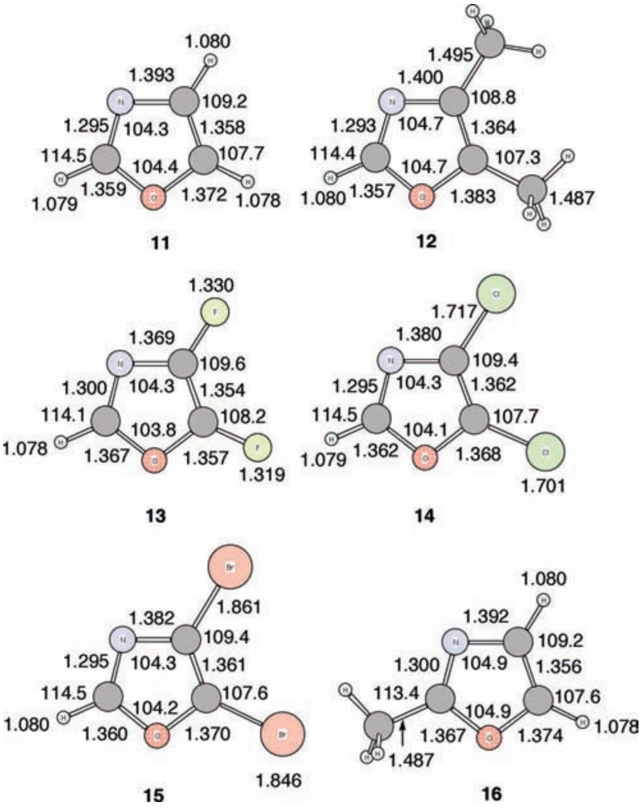

Figure 5. B3LYP/6-31+G(d,p)-optimized structures of 1,3-oxazoles.

stabilized by fluoro and chloro substitution than is the triplet. Consequently, halogenated methylenes have singlet ground states. This is reasonable given that simple singlet carbenes are π-electron deficient and σ-electron rich and are stabilized by π-electron donor and σ-electron substituents such as amino, chloro, and fluoro. Although groups at the 4 and 5 positions of **5** might be considered as remote substituents relative to the carbene carbon, it has been suggested that the introduction of chlorines in the 4 and 5 positions of the 1,3-imidazol-2-ylidene ring stabilizes the carbene through the σ-electronegativity effect of the chlorine atoms.[13] In contrast, other studies suggest that 4,5-dichoro substituents on the 1,3-imidazol-2-ylidene ring lower the stability of the carbene.[15e] It has also been suggested that the electron-withdrawing chlorines diminish the aromatic character of 1,3-imidazol-2-ylidene.[15d] Similarly, the decrease in ΔE_{ST} might imply that the 4,5-dichloro substituents (**8**) diminish the aromatic character of 1,3-oxazol-2-lidene (**5**, Table 1). However, it is of interest to note that 1,3-di(2,4,6-trimethylphenyl)-4,5-dichloro-imidazol-2-ylidene (**1**)[13,14] and 1,3-di(2,4,6-trimethylphenyl)-4,5-dibromoimidazol-2-ylidene (**1**)[14] have been isolated.

Electronic Structures of 1,3-Oxazol-2-ylidenes. Singlet 1,3-oxazol-2-ylidenes generally have larger dipole moments that the corresponding triplet carbenes. The nitrogen atoms in the singlet states are planar, whereas those in the triplet states are pyramidal or nearly pyramidal. The five-membered rings of singlet carbenes **S-5** and **S-10** are planar, and the substituents lie in the respective planes. In contrast, the triplet carbenes have structures similar to the envelope conformation of cyclopentane, in which four ring atoms are nearly coplanar (**T-5**, O1—C5—C4—N3 = 2°; **T-10**, O1—C5—C4—N3 = 1°) with the carbene carbons (C2) slightly above the planes (**T-5**, O1—C2—N3—C4 = −18°; **T-10**, O1—C2—N3—C4 = −19°) and the hydrogen of the N3—H bond and the methyl group of the N3—CH_3 bond below the planes. These trends also are observed in the singlet and triplet states of 1,3-oxazol-2-ylidenes **6**−**9**: **T-6**, O1—C2—N3—C4 = −20°; O1—C5—C4—N3 = 2°, C6—C5—C4—C7 = 2°. **T-7**, O1—C2—N3—C4 = −25°; O1—C5—C4—N3 = −2°, F6—C5—C4—F7 = 1°. **T-8**, O1—C2—N3—C4 = −23°; O1—C5—C4—N3 = 2°, Cl6—C5—C4—Cl7 = 2°. **T-9**, O1—C2—N3—C4 = 0.9°; O1—C5—C4—N3 = 29°, Br6—C5—C4—Br7 = 1°. Figures 3−5 provide comparisons of the geometrical parameters of singlet (**S-5**−**S-10**) and triplet (**T-5**−**T-10**) 1,3-oxazol-2-ylidenes and their respective planar aromatic 1,3-oxazoles (**11**−**16**).

It might not be readily obvious from examining the structural properties of a singlet heterocyclic carbene that it has aromatic character. However, π-bond delocalization can be observed by a comparison of the structural features of the respective singlet and triplet states. The bond lengths in the singlets are shorter than those in the triplets owing to delocalization of the electrons (aromaticity) in the five-membered rings (Figures 3−5). The shorter O1—C2 and C2—N3 bonds in the singlets reflect the delocalization of the unshared electrons on oxygen and nitrogen into the vacant p_π orbital of the singlet state that gives some double-bond character to these bonds. The largest differences between singlet and triplet O1—C2 bonds are seen with the

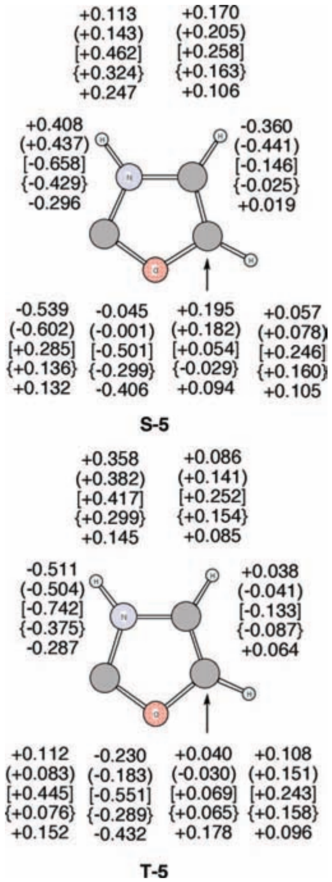

Figure 6. B3LYP/6-31+G(d,p) partial atomic charges for 1,3-oxazol-2-ylidene. From top to bottom: CHELPG, MKS (in parentheses), NBO (in brackets), MPA (in braces), and APT.

difluoro (**7**) and dichloro (**8**) substituents (Figure 4). With the exception of the halogen-substituted 1,3-oxazol-2-ylidenes (**S-7**−**S-9**), the O1−C5 bonds in the singlets are longer than the O1−C2 bonds. In all of the singlets, the C2−N3 bonds are shorter than the N3−C4 bonds. The O1−C2, O1−C5, C2−N3, and N3−C4 bonds in the singlet carbenes are longer than those in the respective 1,3-oxazoles. The O1−C2 and C2−N3 bonds in singlet 1,3-oxazol-2-ylidenes are shorter than would be expected for C_{sp^3}−N_{sp^3} and C_{sp^3}−O_{sp^3} bonds where there is no π overlap and are longer than a typical C=N or C=O bond, including the C2=N3 bonds but not the N3−C4 bonds in the corresponding 1,3-oxazoles (Figure 5). Thus, the bond lengths in the singlet 1,3-oxazol-2-ylidenes are consistent with aromatic character and are in agreement with other theoretical calculations on singlet 6π-electron heterocyclic carbenes that indicate some aromatic stabilization (cyclic π delocalization).[15,16] In contrast to earlier reports, more recent studies have concluded that significant π delocalization is a dominant factor for the enhanced stability of heterocyclic carbenes.

The bond length of the substituent at C4 is longer than that at C5 in the carbenes and in the 1,3-oxazoles, and the N−CH_3 bond in singlet **S-10** is longer than that in triplet **T-10** (Figures 3−5). In addition, the bond lengths of the substituents at C4 and C5 are essentially the same in the carbenes as those in the respective 1,3-oxazoles. The shortest O1−C5 and N3−C4 bonds among the 1,3-oxazoles are in the difluoro structure (**13**). A nonbonded repulsive interaction can be seen in triplet **T-6**, where the distance between the adjacent hydrogens on the two methyl groups is 2.380 Å, which is shorter than twice the van der Waals radius for hydrogen (Figure 3).

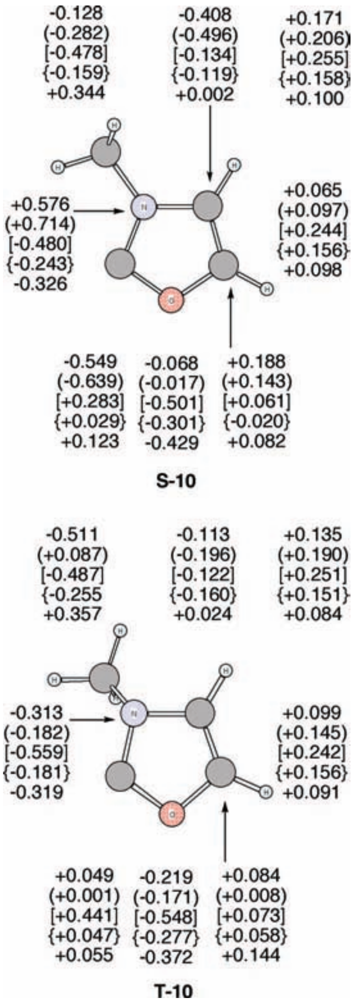

Figure 7. B3LYP/6-31+G(d,p) partial atomic charges for 3-methyl-1,3-oxazol-2-ylidene. From top to bottom: CHELPG, MKS (in parentheses), NBO (in brackets), MPA (in braces), and APT.

The O1−C2−N3 bond angles in the six singlet carbenes are virtually the same and are smaller than those in the respective triplet carbenes, as is generally the case among carbenes. The O1−C5−C4 and N3−C4−C5 bond angles in the singlet states are smaller than those in the triplet states. In contrast, the C2−O1−C5 and C2−N3−C4 bond angles in the singlets are larger than those in the triplets. It can also be seen that the bond angles in the singlet carbenes are generally larger than those in the corresponding 1,3-oxazoles whereas these angles in the triplet carbenes are smaller than those in the respective 1,3-oxazoles. It can also be seen in Figure 5 that the bond angles in the different 1,3-oxazoles are essentially the same.

Partial Atomic Charges. The distribution of partial charges on atoms is of particular interest in reaction mechanisms and transition-state structures. Because atomic charge is not a quantum mechanical observable, all methods for computing it are necessarily arbitrary,[51−56] and caution should be exercised in the application of population analysis approaches to heterocyclic carbenes. Several population analysis methods are generally used to calculate partial atomic charges in a wide range of chemical systems. In this study, partial atomic charges were computed using the Mulliken population analysis (MPA),[51] natural bond order population analysis (NBO, NPA),[52] the Merz−Kollman−Singh (MKS)[53] and CHELPG[54] electrostatic-potential-derived charges, and an approach that makes use of atomic polar tensors (APT).[55] Because the calculated atomic

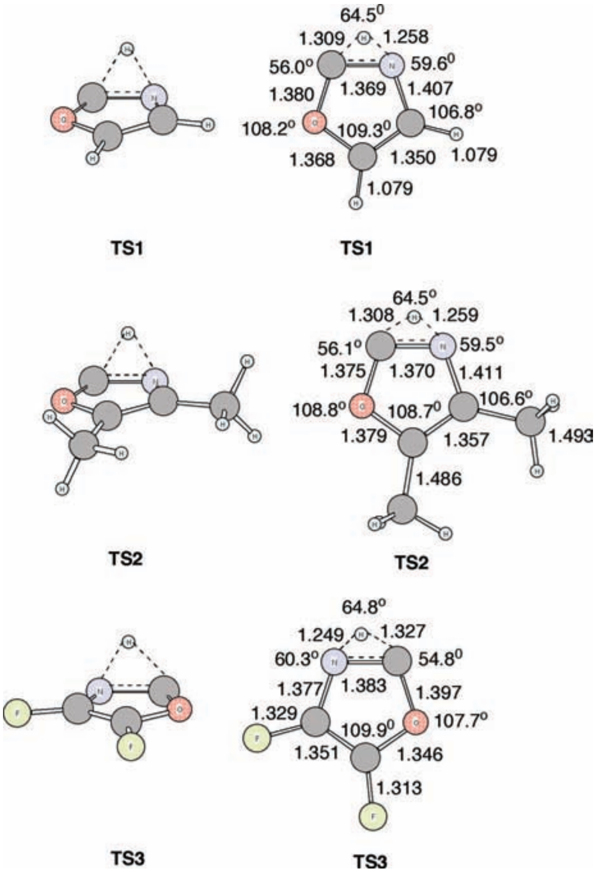

Figure 8. Two views of the B3LYP/6-31+G(d,p)-optimized transition states for the 1,2-rearrangements of singlet 1,3-oxazol-2-ylidenes **S-5**, **S-6**, and **S-7** to 1,3-oxazoles.

charges are dependent on the level of theory used and DFT methods can have difficulty with diffuse functions, no one approach is best for all systems. A general description of the results from the five approaches is given below, and the NBO method is used for the more detailed analyses of the relative charges.

Figures 6 and 7 and Table SI 1 (Supporting Information) show the partial atomic charges for the singlet and triplet states of 1,3-oxazol-2-ylidenes **5**−**10**. The difficulties in evaluating the effects of electronegativity, π-electron donation, σ-electron withdrawal, π-electron delocalization, and partial atomic charges are seen with the atoms in the 1,3-oxazol-2-ylidenes and especially with the atoms associated with the singlet carbene center (C2). An example is evaluating the influence of the halogens on the carbene center (C2), which can include both a π-releasing component and a σ-electron withdrawal component that might or might not act in concert.

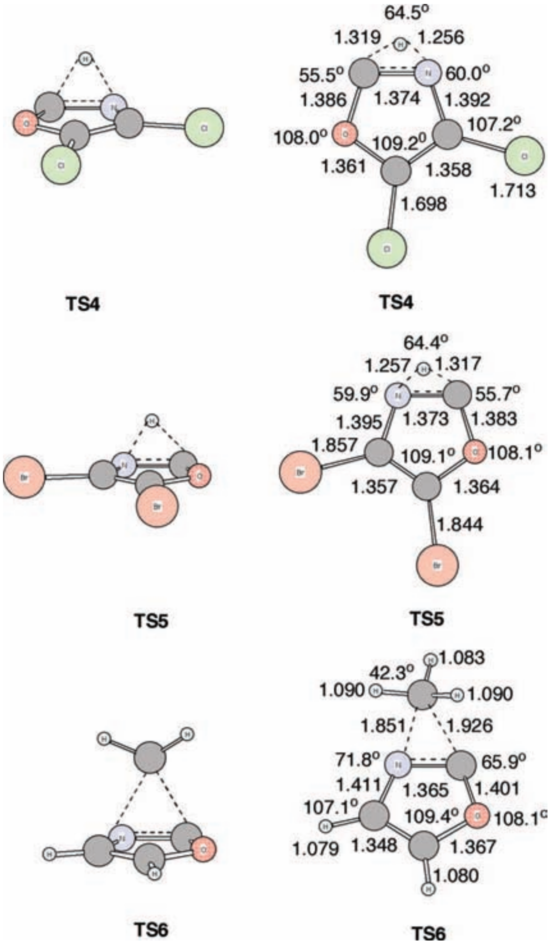

Figure 9. Two views of the B3LYP/6-31+G(d,p)-optimized transition states in the 1,2-rearrangements of singlet 1,3-oxazol-2-ylidenes **S-8**, **S-9**, and **S-10** to 1,3-oxazoles.

It can be seen in Figures 6 and 7 and in Table SI 1 (Supporting Information) that all population analysis methods predict a negative charge at oxygen in the singlet and triplet states of 1,3-oxazol-2-ylidenes **5**−**10**, with the charge being smaller in the singlets. The smaller charge on oxygen in the singlet and the shorter O1−C2 bond are consistent with delocalization of the oxygen lone pair into the vacant p_π orbital of the carbene carbon (C2). Although the resonance structures in Scheme 1 suggest a buildup of negative charge (electron density) at the carbene carbon and a decrease in electron density at the heteroatoms, the NBO, APT, and MPA approaches predict a positive charge at the singlet carbene carbon (C2), whereas the CHELPG and MKS methods predict a negative charge. The reverse trend is observed at N3. All approaches, except APT (in **7**−**9**), predict a positive charge at C2 in the triplets, and all methods predict a negative charge at N3 in the triplets. The population analysis approaches predict both negative and positive charges at C4 and C5 for the singlet and triplet 1,3-oxazol-2-ylidenes (**5**−**10**).

1,2-Rearrangements of 1,3-Oxazol-2-ylidenes. The 1,2-rearrangements of 1,3-oxazol-2-ylidenes afford aromatic 1,3-oxazole (**11**) and its derivatives. 1,3-Oxazole (**11**) and its derivatives are of great interest because they show biological activities, are synthetic intermediates, and are found in biologically active natural products.[57]

It is generally accepted that the intramolecular 1,2-rearrangement of a singlet carbene involves a unimolecular concerted mechanism that transforms the divalent carbon atom into a double-bonded carbon atom. 1,2-Migrations of alkyl groups and hydrogens in singlet carbenes are sometimes viewed as being analogous to carbocation rearrangements (migration into an empty orbital of the carbene carbon) and are often described as an intramolecular insertion of the divalent carbon into an adjacent C−X or X−H bond. Computational, experimental, and theoretical studies have shown that carbene−alkene π complexes are probably not involved in the 1,2-rearrangements of carbenes.[58] An intermolecular hydrogen-transfer mechanism between two molecules of singlet carbene is a possible alternative mechanism for the rearrangement.[15b,59,60] Correlation diagrams show that the 1,2-rearrangement is unlikely to proceed via an intramolecular process in the plane of the ring, as this would involve the crossing of two orbitals with the same symmetry,

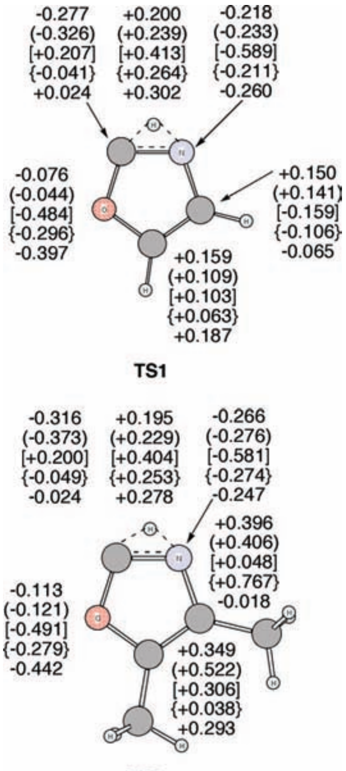

Figure 10. B3LYP/6-31+G(d,p) charges for transition states **TS1** and **TS2**. From top to bottom: CHELPG, MKS (in parentheses), NBO (in brackets), MPA (in braces), and APT.

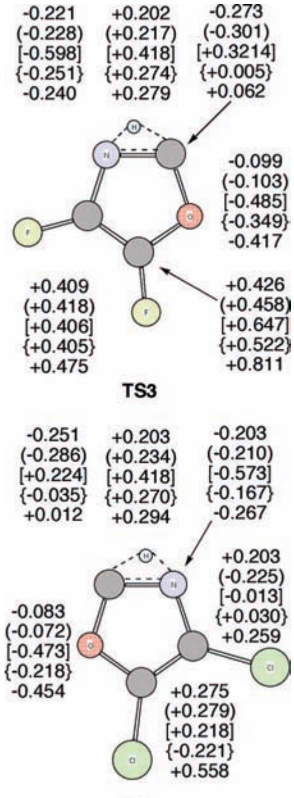

Figure 11. B3LYP/6-31+G(d,p) charges for transition states **TS3** and **TS4**. From top to bottom: CHELPG, MKS (in parentheses), NBO (in brackets), MPA (in braces), and APT.

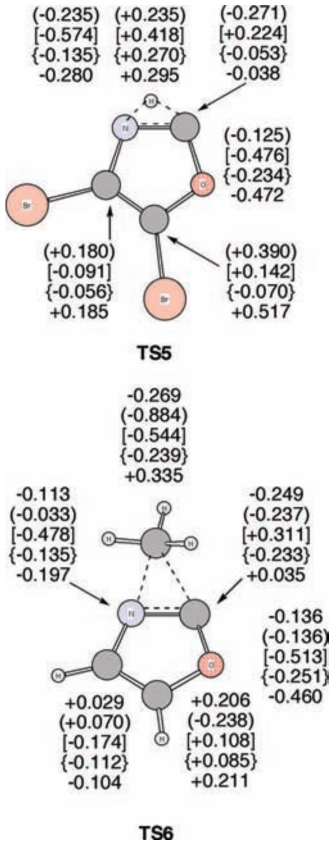

Figure 12. B3LYP/6-31+G(d,p) charges for transition states **TS5** and **TS6**. From top to bottom: CHELPG, MKS (in parentheses), NBO (in brackets), MPA (in braces), and APT.

TABLE 2: Energy Barriers ($\Delta E^{\ddagger\,a}$) to the 1,2-Rearrangements of Singlet 1,3-Oxazol-2-ylidenes S-5−S-10 to Their Respective 1,3-Oxazoles 11−16 through Transition States TS1−TS6

level of theory	H **TS1**	Me **TS2**	F **TS3**	Cl **TS4**	Br **TS5**	NMe **TS6**
CBS-QB3	41.4	40.4	37.8	40.4		
CBS-4M	41.5	40.5	37.9	40.3	40.54	
B3LYP^b	41.2	40.1	37.8	40.4	40.71	53.0
CCSD^{c,d}	41.6	41.0	38.7	45.0	41.41	55.6
CCSD(T)^{c,d}	39.5	38.9	36.7	42.9	39.32	53.1
QCISD^{c,d}	41.5	40.8	38.5	44.7	41.25	55.4
QCISD(T)^{c,d}	39.4	38.8	36.6	42.6	39.23	53.0

[a] $\Delta E^{\ddagger} = E_{TS} - E_{singlet}$. [b] 6-31+G(d,p) basis set. [c] cc-pVDZ basis set. [d] B3LYP/6-31+G(d,p)-optimized structure.

TABLE 3: Enthalpies ($\Delta_r H^{\circ\,a}$) of Reaction for the Rearrangements of Singlet 1,3-Oxazol-2-ylidenes S-5−S-10 to Their Respective 1,3-Oxazoles 11−16)

level of theory	H **11**	Me **12**	F **13**	Cl **14**	Br **15**	NMe **16**
CBS-QB3	−33.2	−30.0	−34.7	−32.2		−39.0
CBS-Q	−29.9	−29.6	−34.5	−31.8		−39.0
CBS-4M	−30.5	−30.3	−35.1	−32.5	−31.8	−39.5
B3LYP^b	−29.6	−29.3	−37.7	−31.6	−30.8	−38.7

[a] $\Delta_r H^{\circ}(298.15\ \mathrm{K}) = H_{oxazole} - H_{singlet}$. [b] 6-31+G(d,p) basis set.

which is a forbidden path. A reasonable 1,2-rearrangement mechanism involves the interaction of the N—H bond with the out-of-plane p_π orbital of the carbene carbon that leads to distortion of the ring, loss of delocalization of the nitrogen lone pair, and formation of a cyclic three-center transition state that lies above the plane of the ring (Figures 8 and 9).[15b,59] The hydrogen-shift plane N—H—C is almost perpendicular to the plane of the ring.

It can be seen in Figures 8 and 9 that the N3—H distances in the five transition states involving hydrogen migration are nearly the same, being close to 1.255 Å, and that there are variations in the C2—H distances from 1.308 to 1.327 Å. The C2—N3 bonds range from 1.369 Å in **TS1** to 1.383 Å in **TS3**, and the O1—C2—N3 bond angles range from 54.8° in **TS3** to 60.0° in **TS4**. The O1—C4—C5 bond angles in the six transition states are close to 109°.

Another important question is the charge distribution on the atoms and the changes in the partial atomic charges on going from reactant to transition state (Figures 10−12). The dipole moment (μ) of a singlet 1,3-oxazol-2-ylidene generally decreases in going from the ground state to the transition state. All population analysis approaches predict negative charges at oxygen and at N3 in each of the six transition states. For singlet **S-5**, in going from reactant to transition state **TS1**, the electron density decreases at oxygen, N3, and C5 and increases at C2, C4, and the partially positive migrating hydrogen. The NBO charge on the carbene carbon (C2) in singlet **S-5** is initially +0.285 but changes to +0.207 at the saddle point and to +0.319 in the 1,3-oxazole product (**11**). The NBO charge on the hydrogen at the migration origin in singlet **S-5** is +0.462 and decreases to +0.413 in transition state **TS1**. The positive charge on the migrating hydrogen argues against it having hydridic character. Among the five transition states with hydrogen migrations, the CHELPG and MKS methods generally predict a negative charge at the carbene carbon (C2), and NBO consistently predicts a positive charge at C2. The trends seen in the 1,2-rearrangement of singlet **S-5** also are observed with singlet carbenes **S-6**−**S-9** and their respective transition states **TS2**−**TS5**. These hydrogen migrations from nitrogen to carbon[61] are consistent with the partial atomic charges observed in 1,2-rearrangements involving hydrogen migrations from carbon to carbon.[45c,62−65]

NBO analysis predicts negatives charges for the fluoro substituents in singlet and triplet 4,5-difluoro-1,3-oxazoly-2-ylidene (**S-7** and **T-7**, respectively), in transition state **TS3**, and in 4,5-difluoro-1,3-oxazole (**13**), but it predicts positive charges for the halogens in the 4,5-dichloro- (**8**) and 4,5-dibromo-1,3-oxazol-2-ylidene (**9**), in their respective transitions states (**TS4** and **TS5**) for rearrangement, and in their respective 1,3-oxazoles (**14** and **15**).

During the rearrangement of 3-methyl-1,3-oxazol-2-ylidene (**10**) to 2-methyl-1,3-oxazole (**16**), **TS6** shows increases in electron density at O1, C4, and C6; decreases at C2 and C5; and essentially no change at N3. As with the partial-positive migrating hydrogen with increasing electron density, the migration of the N3 methyl group during the 1,2-rearrangement of singlet **(S-10)** via **TS6** to 2-methyl-1,3-oxazole (**16**) is predicted to have increasing negative charge (except for APT) on the migrating methyl carbon. As with the singlet 1,3-oxazol-2-ylidenes involving hydrogen migration, both negative and positive charges are predicted for the carbene carbon in **TS6** (Figure 12).

In contrast to the variations among the different levels of theory in the computed values of ΔE_{ST}, all levels give excellent agreement in the calculations of the barriers to the exothermic 1,2-rearrangements of the 1,3-oxazol-2-ylidenes to the corresponding 1,3-oxazoles (Tables 2 and 3). Although the CCSD(T)- and QCISD(T)-predicted values for ΔE_{ST} are in closer agreement with the CBS methods, CCSD and QCISD are in better agreement with the CBS methods in the calculations of the activation barriers ($\Delta E^{\ddagger}$) for the 1,2-rearrangements of the 1,3-oxazol-2-ylidenes (Table 2). The CBS-predicted barriers to the 1,2-rearrangements of singlet carbenes **5**−**9** to their respective 1,3-oxazoles are 41.4, 40.4, 37.9, 40.4, and 40.5 kcal/mol (Table 2). The CCSD- and CCSD(T)-predicted barriers for the 1,2-rearrangement of singlet 3-methyl-1,3-oxazol-2-ylidene (**S-10**) to 2-methyl-1,3-oxazole (**16**) are 55.6 and 53.1 kcal/mol, respectively. The stabilization of the transition states for the 1,2-rearrangements correlates with the ΔE_{ST} value of the reactant carbene; i.e., a smaller ΔE_{ST} results in a lower energy of activation. It can be seen that the electronegative halogens lower the barriers and substitution of a methyl group at N3 increases the activation barrier with respect to the unsubstituted carbene (**S-5**). 1,3-Oxazol-3-ylidenes should be kinetically stable toward 1,2-rearrangements because of the large activation energies, although the overall reactions are exothermic. The predicted barrier for the 1,2-rearrangement of 1,3-imidazol-2-ylidene (46.8 kcal/mol)[15b,f] is about 5 kcal/mol higher than that for 1,3-oxazol-2-ylidene (**5**), whereas the value for 1,3-thiazol-2-ylidene (42.3 kcal/mol)[11] is similar to that for **5**. The CBS-QB3 predicted enthalpies of reaction ($\Delta_r H°$) for the 1,2-rearrangements of singlet 1,3-oxazol-2-ylidenes (**S-5**, **S-6**, **S-7**, **S-8**, **S-10**) to 1,3-oxazoles range from –30 to –39 kcal/mol (Table 3) with **S-6** having the smallest value and **S-10** having the largest value. The enthalpy of reaction (kcal/mol) for the 1,2-rearrangement of **5** (–33.2) is larger than that for 1,3-imidazol-2-ylidene **1** (–30.1) and 1,3-thiazol-2-ylidene **3** (–32.7), but smaller than that for 2,3-rearrangement of 1,2-isothiol-3-ylidene **4** (–41.0).[12]

Conclusions

Large singlet−triplet gaps (ΔE_{ST}) and π-electron delocalization are strong contributors to the extraordinary stability of heterocyclic carbenes. By analogy with 1,3-imidazol-2-ylidenes and 1,3-thiazol-2-ylidenes, 1,3-oxazol-2-ylidenes should also be relatively stable. CBS-QB3, CBS-Q, CCSD, and QCISD are reliable methods for calculating singlet−triplet gaps, enthalpies of reaction ($\Delta_r H°$), Gibbs free energies of reaction ($\Delta_r G°$), and barriers to 1,2-rearrangements of the 1,3-oxazol-2-ylidenes to their respective 1,3-oxazoles. B3LYP and B3PW91 predict lower ΔE_{ST} values than the other methods. Electron-withdrawing substituents at C4 and C5 on the 1,3-oxazol-2-ylidene ring decrease ΔE_{ST}, whereas the electron-releasing 4,5-dimethyl substituents have little effect. However, a methyl group at N3 increases ΔE_{ST}. The predicted large singlet−triplet energy gaps of these 1,3-oxazol-2-ylidenes can be attributed in part to conjugative delocalization of electron density from the heteroatom substituents in the singlets.

The substituents on the ring influence the signs of the charges on atoms, including the migrating groups. The five population analysis methods predict positive and negative partial atomic charges at the carbene carbon in the singlet states, which reflects some of the complexicities and difficulties involved in evaluating the effects of electronegativity, π-electron donation, σ-electron withdrawal, and π-electron delocalization on charges. During the 1,2-rearrangements involving hydrogen migration, electron density decreases at oxygen, C5, and N3 (migration origin) and increases at C2 (migration terminus), C4, and the partially positive migrating hydrogen. Electron-withdrawing groups at C4 and C5 lower the activation barriers to the 1,2-rearrangements of the singlet 1,3-oxazol-2-ylidenes to 1,3-oxazoles.

Supporting Information Available: Tables of partial atomic charges and geometrical parameters. This information is available free of charge via the Internet at http://pubs.acs.org.

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