

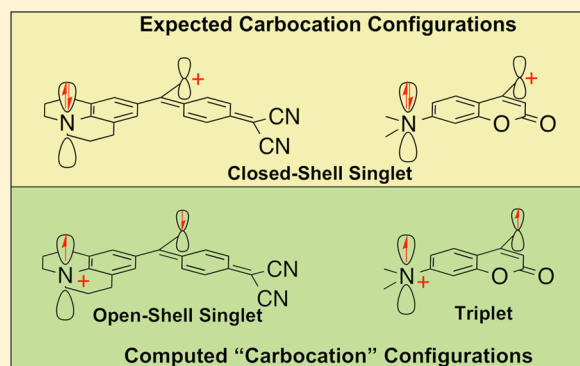
# A Fine Line Separates Carbocations from Diradical Ions in Donor-Unconjugated Cations

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**S** Supporting Information

**ABSTRACT:** Carbocations are traditionally thought to be closed-shell electrophiles featuring an empty orbital rich in p character. Here, density functional theory computations indicate that when strong  $\pi$  donors are not placed in direct conjugation with benzylic-type cations, alternative diradical configurations that resemble non-Kekulé diradicals are possible. For certain donor–acceptor frameworks, an open-shell singlet configuration is the computed ground state for the cation, whereas for coumarin and xanthenyl cations substituted with strong donors, a triplet diradical configuration is the computed ground state. Changing the substituent nature and attachment location substantially alters the energy gaps between the different electronic configurations and can manipulate the computed ground-state electronic configuration. There are few known examples of ground-state triplet carbocations, and, to our knowledge, no other examples of open-shell singlet carbocations. The open-shell singlet and triplet “carbocations” described here may have reactivity distinct from that of typical closed-shell singlet carbocations and, if appropriately stabilized, lead to organic materials with interesting electronic and magnetic properties.



## INTRODUCTION

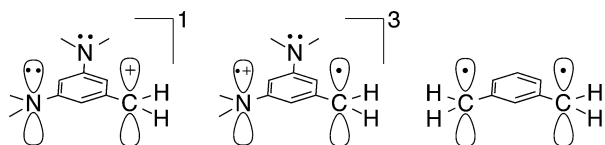
Carbocations are generally thought to be closed-shell singlet species, and consequently, there has been little investigation into the possibility that they have alternative energetically accessible electronic states.<sup>1</sup> The generic electronic picture of simple carbocations is that of a roughly  $sp^2$ -hybridized carbon with an empty p orbital. In contrast, other atom-centered reactive intermediates such as nitrenes,<sup>2–6</sup> carbenes,<sup>7–10</sup> nitrenium ions,<sup>11–14</sup> and oxenium ions<sup>15–19</sup> have one or more lone pairs that can be distributed in two orbitals, leading to different energetically accessible electronic configurations that can be adopted. These configurations can include two distinct closed-shell singlet configurations, an open-shell singlet configuration, and a triplet configuration. A rich history of research spanning many decades has been dedicated to understanding the effect of substituents on the energetic orderings of these electronic states and how differences in these electronic configurations adopted by the reactive intermediate change the reactivity and properties of these important species.<sup>20</sup> Carbocations lack a lone pair, so envisioning alternative electronic states for these intermediates is less immediately obvious for simple systems. Additionally, early computational investigations<sup>21</sup> suggesting very large energetic gaps to higher electronic states in simple carbocations may have discouraged subsequent investigations into the possibility that carbocations can adopt alternative electronic configurations.

Some exceptions exist, however. Certain antiaromatic carbocations have low-energy diradical states<sup>22</sup> and in a few

cases adopt high-spin triplet ground states with observable EPR spectra (e.g., cyclopentadienyl cation<sup>23</sup>). Certain substituted dicoordinated carbocations (aryl/vinyl cations) are also known to have triplet ground states, with electronic structures resembling triplet carbenes.<sup>24–26</sup> More recent computational and experimental investigations have suggested that meta-donor-substituted benzylic cations can have a triplet configuration that is near in energy to the closed-shell singlet state.<sup>27</sup> For example, the 3,5-bis(dimethylamino)benzyl cation is computed to have essentially degenerate singlet and triplet energies, and experimental investigations of this species indicate the formation of products consistent with a diradical-like species.<sup>27,28</sup> The triplet configuration for this meta-donor-substituted cation can be obtained conceptually by promoting one of the lone pairs on the meta-donor substituent to the empty p orbital at the formal carbenium center, leading to a triplet  $\pi, \pi^*$  diradical state reminiscent of the electronic state of the *m*-xylylene diradical (see Figure 1).<sup>29–31</sup> Although the triplet state involves a formal promotion of an electron from a bonding orbital to an antibonding orbital, it gains back the exchange energy that arises from electrons with parallel spin. For singly occupied molecular orbitals (SOMOs) that are non-disjoint (i.e., share wave function amplitude on some of the same atoms), it is possible for the exchange energy to match or exceed the energetic cost of the electron promotion.

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**Figure 1.** Schematic illustration of singlet and triplet 3,5-bis(dimethylamino)benzyl cation and *m*-xylylene diradical.

Here we demonstrate that this meta-substituted carbocation is just a single member of a class of carbocations possessing  $\pi$  donors that are not in direct conjugation with the carbenium center and featuring low-energy or ground-state diradical states. With multiple strong donors substituted at appropriate ring positions, the triplet state is the computed ground state and the singlet state has significant diradical character. Extensive benchmarking on systems derived from coumarin, xanthene, and donor–acceptor cations demonstrate the often-subtle effects of the nature and placement of substituents on the relative energetic orderings of closed-shell singlet, open-shell singlet, and triplet states of carbocations. Depending on the substitution, it is possible for each of these configurations (closed-shell singlet, open-shell singlet, triplet) to be the computed ground-state configuration.

## COMPUTATIONAL METHODS

All density functional theory (DFT) computations were performed using the Gaussian 09 software suite<sup>32</sup> employing the B3LYP functional, which consists of Becke's three-parameter gradient-corrected exchange functional<sup>33</sup> and the Lee–Yang–Parr correlation functional,<sup>34,35</sup> along with the 6-31G(d,p) polarized double- $\zeta$  basis set. Energies, geometries, and analytical frequencies were calculated at this level of theory. In all cases, optimized geometries were found to have zero imaginary frequencies, and corrections for the zero-point vibrational energy were added unscaled. All single-reference computations (CBS-QB3, G3, G3B3, and CCSD(T)) were computed using Gaussian 09. CASSCF and MRMP2 calculations were performed using the GAMESS software package<sup>36</sup> with the 6-31G(d) basis set. Ions **10** and **11** were investigated using a (12,12)  $\pi$  active space, and **19** was investigated with a (14,13)  $\pi$  active space (more details, including visualization of the active orbitals chosen, can be found in the Supporting Information).

In order to investigate the electronic states of the benzylic cations, we computed the singlet–triplet energy gaps ( $\Delta E_{ST}$ ) using DFT (B3LYP). Here  $\Delta E_{ST}$  refers to the gas-phase adiabatic energy difference between the lowest-energy singlet state and the lowest-energy triplet state (including unscaled zero-point vibrational energies). A positive value of  $\Delta E_{ST}$  indicates a triplet ground state, whereas a negative value indicates a singlet ground state.

Numerous benchmarking studies have indicated that B3LYP performs well compared to experimental values or multireference computational methods such as CASPT2 for computing singlet–triplet energy gaps of hypovalent species.<sup>27</sup> For example, the 3,5-bis(dimethylamino)benzyl cation is computed to have  $\Delta E_{ST} = +1.9$  kcal/mol by B3LYP/6-31G(d,p) and essentially degenerate energies at the CASPT2 level of theory. Furthermore, B3LYP has been shown to perform well for quantitative predictions of singlet–triplet energy gaps of hypovalent species such as nitrenium ions and carbenes,<sup>37–41</sup> although it is important to note that such DFT computations frequently underestimate the singlet energies by 2–4 kcal/mol compared with experimental values or converged quantum-chemical calculations because correlation is more important for the singlet state than the triplet state.

In order to calibrate the usefulness of our DFT calculations for looking at the closed-shell singlet–triplet gaps described in this study, benchmarking studies of 3-aminobenzyl cation and 3,5-diaminobenzyl cation were carried out using higher-level computations, including

CBS-QB3, G3, G3B3, and CCSD(T). CBS-QB3, G3, and G3B3 calculations attempt to capture correlation and basis set incompleteness errors via an extrapolation scheme. Compared with these methods, the B3LYP computations of  $\Delta E_{ST}$  for the 3,5-aminobenzyl cation underestimate the closed-shell singlet–triplet gap by 4.0–6.6 kcal/mol (B3LYP = –2.3 kcal/mol, CBS-QB3 = –8.5 kcal/mol, G3 = –8.1 kcal/mol, G3B3 = –8.9 kcal/mol, CCSD(T)/aug-cc-pVDZ = –7.0 kcal/mol, MRMP2/6-31G(d) = –6.3 kcal/mol). This underestimation of the singlet energy was also true for the computed  $\Delta E_{ST}$  of the 3-aminobenzyl cation (B3LYP = –10.7 kcal/mol) but with a smaller magnitude of 2.5–5.4 kcal/mol (CBS-QB3 = –13.8 kcal/mol, G3 = –15.1 kcal/mol, G3B3 = –16.1 kcal/mol, MRMP2 = –13.2 kcal/mol), although in this case the CCSD(T)/aug-cc-pVDZ value (–9.7 kcal/mol) is nearly the same as the B3LYP value. From these benchmark calculations, it seems likely that, similar to the computations of  $\Delta E_{ST}$  for carbenes, the DFT values for these cations underestimate the closed-shell singlet energy relative to the triplet by ~3–6 kcal/mol.

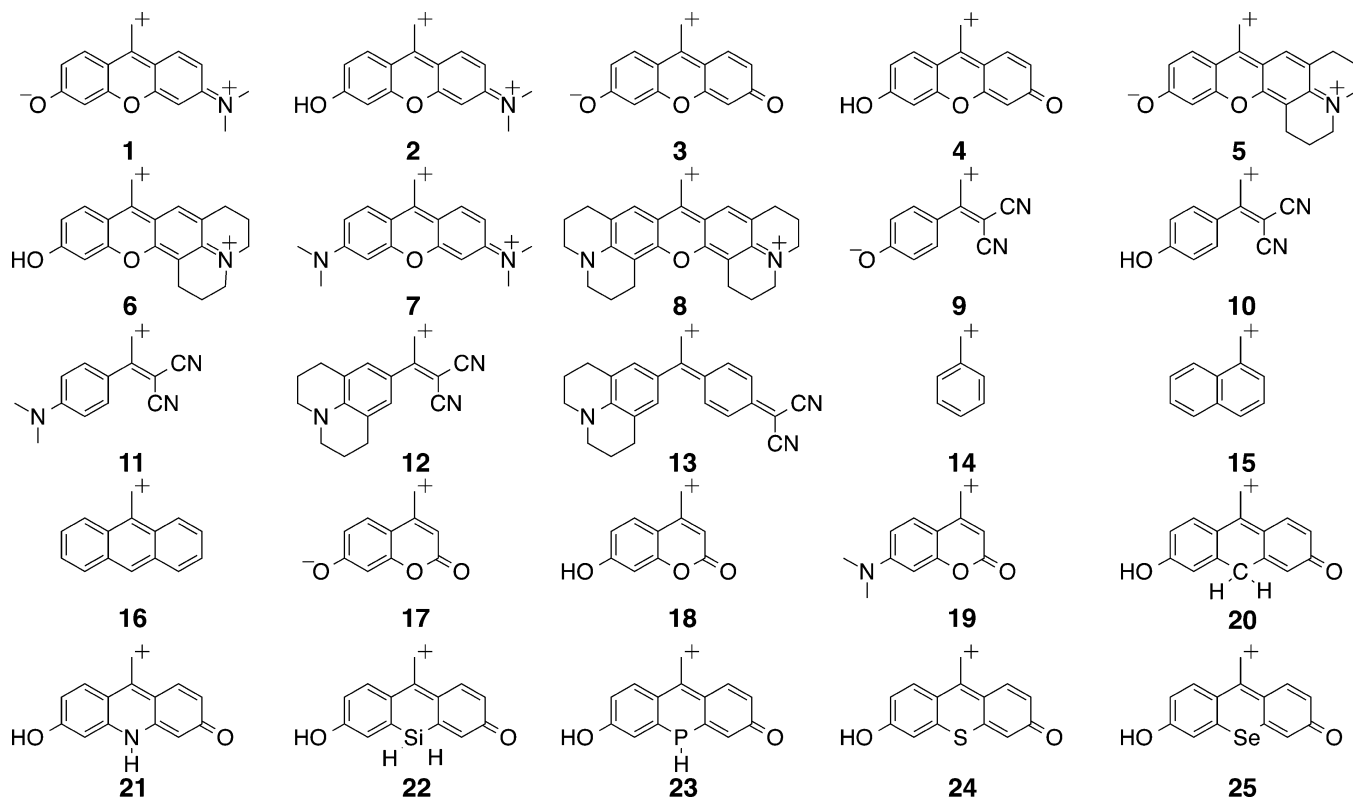
One limitation of the B3LYP, CBS-QB3, G3, G3B3, and CCSD(T) methods occurs when two configurations of the singlet state have nearly equal weight in a multireference expansion. In these cases (e.g., singlet aryl nitrenes and the trimethylenemethane diradical), such single-reference methods are inadequate. Such problems can be identified by stability calculations on singlet states that indicate a restricted  $\rightarrow$  unrestricted (R  $\rightarrow$  U) instability. Because the electronic structures of some of the carbocations described in this study resemble classic open-shell non-Kekulé diradicals, this problem needs to be addressed explicitly.

Indeed, many of the singlet species computed here possess such R  $\rightarrow$  U instabilities. Thus, we used an unrestricted broken-symmetry approach to compute the singlet state in these cases. In this approach,  $\alpha$  and  $\beta$  electrons are optimized independently of each other (UB3LYP). Unfortunately, such broken-symmetry singlet calculations using DFT very often suffer from considerable spin contamination when there is also a low-energy triplet state, as indicated by  $\langle S^2 \rangle$  values greater than zero. Therefore, in cases where broken-symmetry calculations were performed, the energy of the singlet state was corrected using eq 1, which attempts to titrate out contamination from a low-energy triplet state:<sup>42–45</sup>

$$E_{\text{singlet}} = \frac{2E_{(S_z)=0} - \langle S^2 \rangle E_{(S_z)=1}}{2 - \langle S^2 \rangle} \quad (1)$$

where  $E_{\text{singlet}}$  is the corrected singlet energy,  $E_{(S_z)=0}$  is the broken-symmetry energy,  $\langle S^2 \rangle$  is the expectation value of the total-spin operator for the broken-symmetry calculation (anywhere from about 0 to 1), and  $E_{(S_z)=1}$  is the energy of the triplet state at the singlet geometry. Ion **17** was found to have the largest effect of R  $\rightarrow$  U instability, with the projected broken-symmetry singlet energy being 15.4 kcal/mol lower than that for the restricted singlet. The largest effect of R/U switching for compounds without a neutral charge was found for **13**, with a 14.2 kcal/mol difference between the projected broken-symmetry and restricted singlets relative to the triplet. Very large energy differences between restricted and corrected unrestricted singlet energies give some indication that the singlet is a diradical or possesses considerable diradical character.

In order to validate our use of this unrestricted broken-symmetry approach, we computed the singlet–triplet energy gaps using a multireference MRMP2//CASSCF approach for compounds **10**, **11**, and **19**, using a  $\pi$  active space. Details can be found in the Supporting Information. All of the energy gaps were found to be in general agreement with the DFT results indicating low-energy diradical configurations for the cations, although there was imperfect quantitative agreement with the DFT-computed values. For example, **10** was computed to have  $\Delta E_{ST} = -1.4$  kcal/mol at the DFT level of theory and +6.6 kcal/mol at the MRMP2 level of theory; **11** was computed to have  $\Delta E_{ST} = +3.5$  kcal/mol at the DFT level and –1.4 kcal/mol at the MRMP2 level; and **19** was computed to have  $\Delta E_{ST} = +8.9$  kcal/mol by DFT and +5.2 kcal/mol by MRMP2. The larger

Chart 1. Cations Included in This Computational Study<sup>a</sup>

<sup>a</sup>Note that drawing these ions as closed-shell carbocations was done for clarity and is not an indication of the preferred electronic configurations of these ions.

quantitative discrepancy between the two methods for **10** may be explained by the large torsion from planarity in both the singlet and triplet states for **10**, possibly making the (12,12)  $\pi$  active space we used in our MRMP2 computation insufficiently large (unfortunately, much-expanded active spaces that include  $\sigma$  orbitals become computationally intractable). As has been appreciated in modeling of related species such as non-Kekule diradicals (e.g., trimethylene-methane or oxallyl diradical),<sup>46</sup> open-shell singlet diradicals are pathologically challenging to model because of the importance of electron correlation for these species. Thus, the uncertainties in the  $\Delta E_{ST}$  values for the cations described in this paper are very likely to be higher than for modeling of related reactive intermediates such as typical carbenes.

In cases where different rotamers are possible (e.g., **4a–h**), we computed the energies of the different rotamers using semiempirical AM1 calculations. The lower-energy rotamer was then used in the higher-level computations. The rotamers for **32e** and **32f** were found to have less than a 3.5 kcal/mol difference when our unrestricted broken-symmetry approach was used. While all of the computations reported herein are gas-phase computations, ion **19** was selected as a representative compound and investigated using a PCM-water model. Solvation of water was found to have a negligible effect on  $\Delta E_{ST}$ , with only a 0.5 kcal/mol difference between the  $\Delta E_{ST}$  values from the gas-phase and the water model computations. Thus, all of the reported values are gas-phase-computed values.

## ■ COMPUTATIONAL RESULTS

The carbocations investigated in this study can be seen in Chart 1. Four types of structures were included in this study: xanthene-based cations (fluorescein/rhodamine derivatives) **1–8**, coumarinyl-based ions **17–19**, conjugated donor–acceptor cations **9–13**, and structures representing typical benzylic

carbocations **14–16** as reference standards for “normal” closed-shell singlet benzylic carbocations.

**Nonconjugated Donor Substituents Favor Open-Shell Singlet and Triplet Configurations.** As might be expected, normal benzylic cations **14–16** all have large singlet–triplet gaps in favor of the closed-shell singlet state ( $\Delta E_{ST} < 0$  and  $|\Delta E_{ST}| > 27$  kcal/mol; Table 1). Additionally, these carbocations have stable singlet wave functions, indicating that the closed-shell singlet state is the lowest-energy state. Thus, these computations are likely to be quite robust. One would expect that placement of electron donors in direct conjugation with the carbenium ion center would raise the energy of the LUMO and lead to a larger HOMO–LUMO gap, which would disfavor open-shell states (open-shell singlet, triplet). However, for carbocations substituted with nonconjugated  $\pi$  donors, the  $\pi$  donors may act only to raise the HOMO without significantly perturbing the LUMO. Indeed, for all cases where  $\pi$  donors are not in direct conjugation with the carbenium ion center, a dramatic swing in  $\Delta E_{ST}$  in favor of the triplet state occurs. In virtually all cases seen with  $\pi$  donors not directly conjugated to the carbocation center, the  $\Delta E_{ST}$  values diminish to less than 7 kcal/mol in favor of the singlet, and in many cases the triplet state is computed to be the overall ground state. With moderately strong  $\pi$  donors (e.g., OH), the singlet and triplet states are computed to be roughly degenerate, with the singlet states having some open-shell character (**4**, **6**, **10**, and **18**). With one or more very strong donors (e.g., NMe<sub>2</sub>, O<sup>−</sup>), the triplet state is the computed ground state, in some cases by a substantial margin (e.g., **3**, **5**, **7**, **8**, **9**, **11**, **12**, **17**, and **19**). For these species, the singlet states are also likely to be diradicals (or have considerable diradical



**Table 1. DFT-Computed Singlet–Triplet Energy Gaps ( $\Delta E_{ST}$ , kcal/mol) and Singlet Spin Contamination (A Positive Value of  $\Delta E_{ST}$  Indicates a Triplet Ground State)**

compound	$\Delta E_{ST}$			$\langle S^2 \rangle$
	restricted singlet	unrestricted singlet	spin-purified singlet	unrestricted singlet
1	8.4	2.2	1.7	0.8
2	8.8	2.6	3.4	0.8
3	22.9	4.5	8.2	1.1
4	4.2	0.2	−1.7	0.7
5	13.6	4.3	6.2	0.9
6	9.6	2.3	2.5	0.9
7	14.3	3.5	5.9	1.0
8	15.1	3.2	5.6	1.0
9	16.9	4.8	5.5	1.0
10	3.8	0.0	−1.4	0.6
11	12.3	2.8	3.5	0.9
12	14.6	2.8	3.8	1.0
13	8.9	1.1	−5.2	0.9
14	−39.7	−39.7	−39.7	0.0
15	−30.8	−30.8	−30.8	0.0
16	−27.9	−27.9	−27.9	0.0
17	25.8	6.1	10.4	1.0
18	7.9	3.1	2.4	0.6
19	16.1	5.9	8.9	0.9
20	−1.7	−3.4	−5.9	0.5
21	9.8	3.8	3.9	0.8
22	−3.6	−4.4	−6.4	0.3
23	1.2	−0.5	−2.5	0.5
24	4.9	2.0	0.5	0.6
25	4.9	2.1	0.8	0.6

character), as evidenced by substantial differences between the spin-purified unrestricted singlet energies and the restricted singlet energies. Indeed, the unrestricted singlet energies for these latter species suffer from essentially complete spin contamination ( $\langle S^2 \rangle \approx 1$ ), which is often the case for species having a triplet ground state. Thus, the results arising from these computations need to be interpreted with an appropriate degree of caution, as the errors are likely to be higher than for the computation of “normal” closed-shell species.

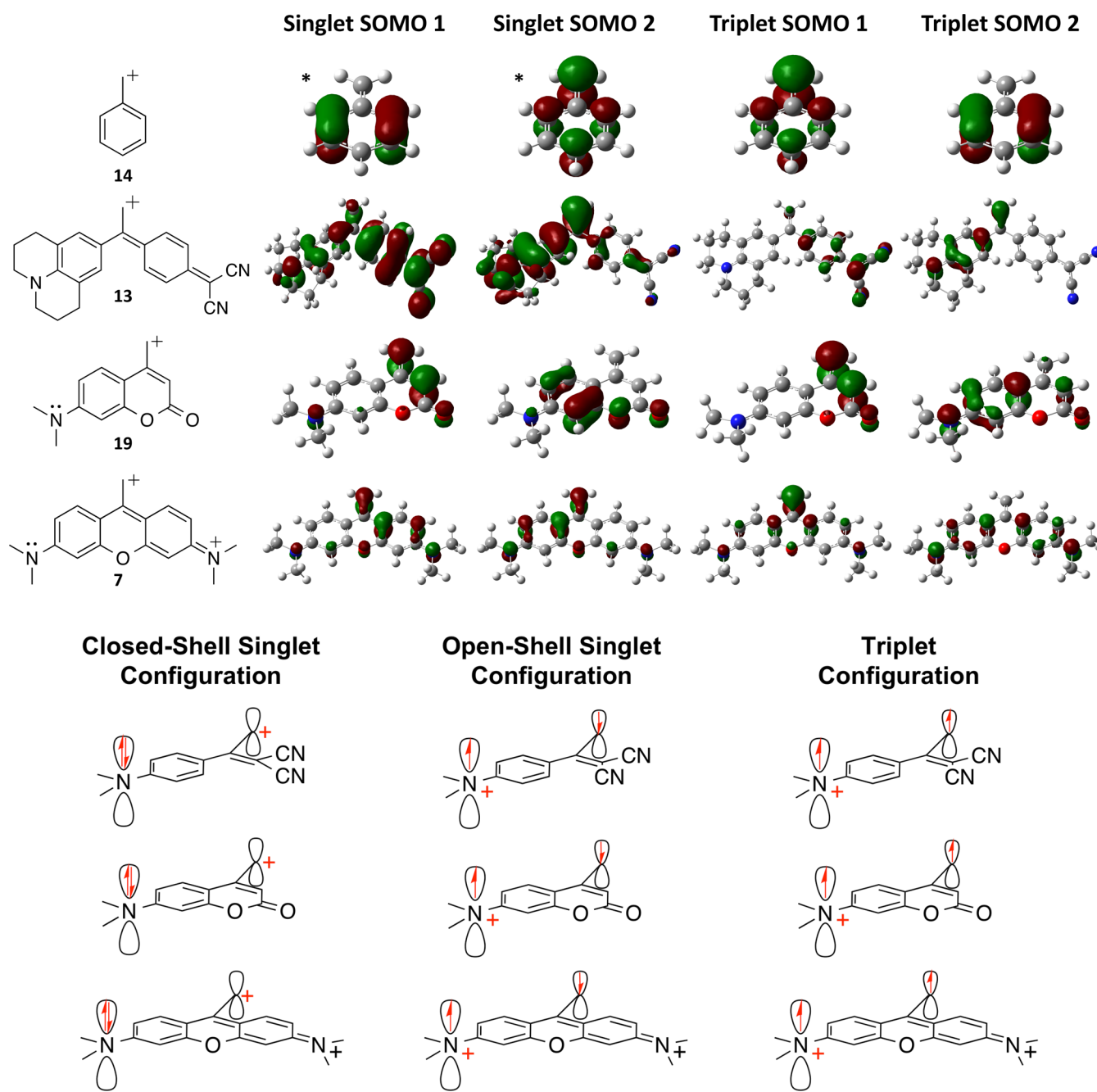
**Donor–Acceptor Cations May Have Open-Shell Singlet Diradical Ground States.** The donor–acceptor cations 9–13 are an intriguing class of carbocations. While ions 9, 11, and 12 are computed to be ground-state triplet ions, 10 and 13 are computed to have singlet ground states. Both 10 and 13 have singlet ground states with considerable diradical character, as evidenced by substantial energy differences between the restricted singlet values and the corrected unrestricted singlet values. For example, the difference between the corrected unrestricted singlet energy and the restricted singlet energy for 13 is  $\sim 14$  kcal/mol, suggesting that the ground state is an open-shell singlet diradical. It is unusual for a singlet diradical configuration to be the ground-state configuration for a molecule because triplet configurations occupying the same orbitals have the added favorable exchange energy between electrons with parallel spin. Inspection of the triplet SOMOs (Figure 2) reveals why it is possible to have a singlet diradical ground state for this ion. The two SOMOs appear to be essentially disjoint, with one electron compartmentalized to the ring and the donor substituent attached to the ring and the other electron localized to the exocyclic acceptor unit. Because

the SOMOs do not have significant wave function amplitudes on the same atoms, the exchange integral between these two unpaired electrons would be expected to be vanishingly small. Houk has observed a similar effect for polyacenes, some of which are computed by DFT to have open-shell singlet ground states as a result of the disjoint nature of the triplet SOMOs (that study also employed the broken-symmetry method for the singlet states).<sup>47</sup> The disjoint nature of the triplet SOMOs for this ion 13 contrasts with the xanthenyl ions (1–8) and coumarinyl ions (17–19), which share SOMO wave function amplitude on some of the same atoms (Figure 2). Thus, for these latter species the triplet configuration would be expected to have a non-negligible exchange energy and is computed to be lower in energy than the open-shell singlet configuration.

**Detailed Linear Free Energy Relationships (LFERs) as a Function of Substitution Location on the  $\Delta E_{ST}$  of Xanthenyl Cations.** How does the location and nature of the substituent on the carbocation affect the singlet–triplet gap? We chose to investigate in detail the effect of changing the donor/acceptor nature of the substituent and its subsequent position around the xanthenyl backbone 4. A range of electron-withdrawing and electron-donating groups were examined (see Figure 3 and Table 2). The Hammett plots shown in Figure 3 give a summary of the effect of the donating/withdrawing nature of the substituent on  $\Delta E_{ST}$  at various positions. Before detailing the trends, we add the cautionary note that such broken-symmetry DFT computations are likely to have higher errors associated with the relative energy values of the electronic states than for typical closed-shell species such as 14–16. Thus, it is likely best to focus on overall trends in the LFERs rather than the exact numerical values. As expected, electron donors in conjugation with the carbocation (e.g., 4g–h and 26g–h) favor a closed-shell singlet ground state, whereas electron donors not in conjugation with the carbocation (e.g., 29g–h, 30g–h, and 31g–h) favor an open-shell singlet or triplet. We elected to use the Hammett  $\sigma_{para}^+$  parameter to quantify the donating/withdrawing abilities of the substituents, but other Hammett parameters give qualitatively similar plots (see the Supporting Information for plots vs other parameters).

Several trends are worth noting. First, substitution ortho to the carbenium ion center (27 and 28) has essentially no effect on  $\Delta E_{ST}$ , except in two exceptional cases for 28 (with NMe<sub>2</sub> and NO<sub>2</sub> groups), where a through-space bond is formed between the substituent and the carbenium center, stabilizing the closed-shell singlet.

As might be expected, substitution of ion 4 with electron-donating groups that are in direct conjugation with the carbenium ion center leads to a species with closed-shell singlet character typical of a “normal” closed-shell singlet carbocation (4, 26, and 32). In contrast, electron-withdrawing groups substituted in those same positions lead to ions that favor the diradical states. From the plots in Figure 3A,G,H, for ions in which substituents are in direct conjugation with the carbenium center, it can be seen that donor groups favor the singlet states and withdrawing groups favor the diradical configurations in a fairly linear fashion up to a threshold at which increasing the substituent electron-withdrawing character no longer increases  $\Delta E_{ST}$  in favor of the triplet. This threshold occurs when the open-shell singlet becomes the lowest-energy singlet state, as evidenced by substantial differences between the restricted singlet energy and the corrected unrestricted singlet energies. This result suggests that the open-shell singlet and triplet surfaces parallel each other. At this threshold point,

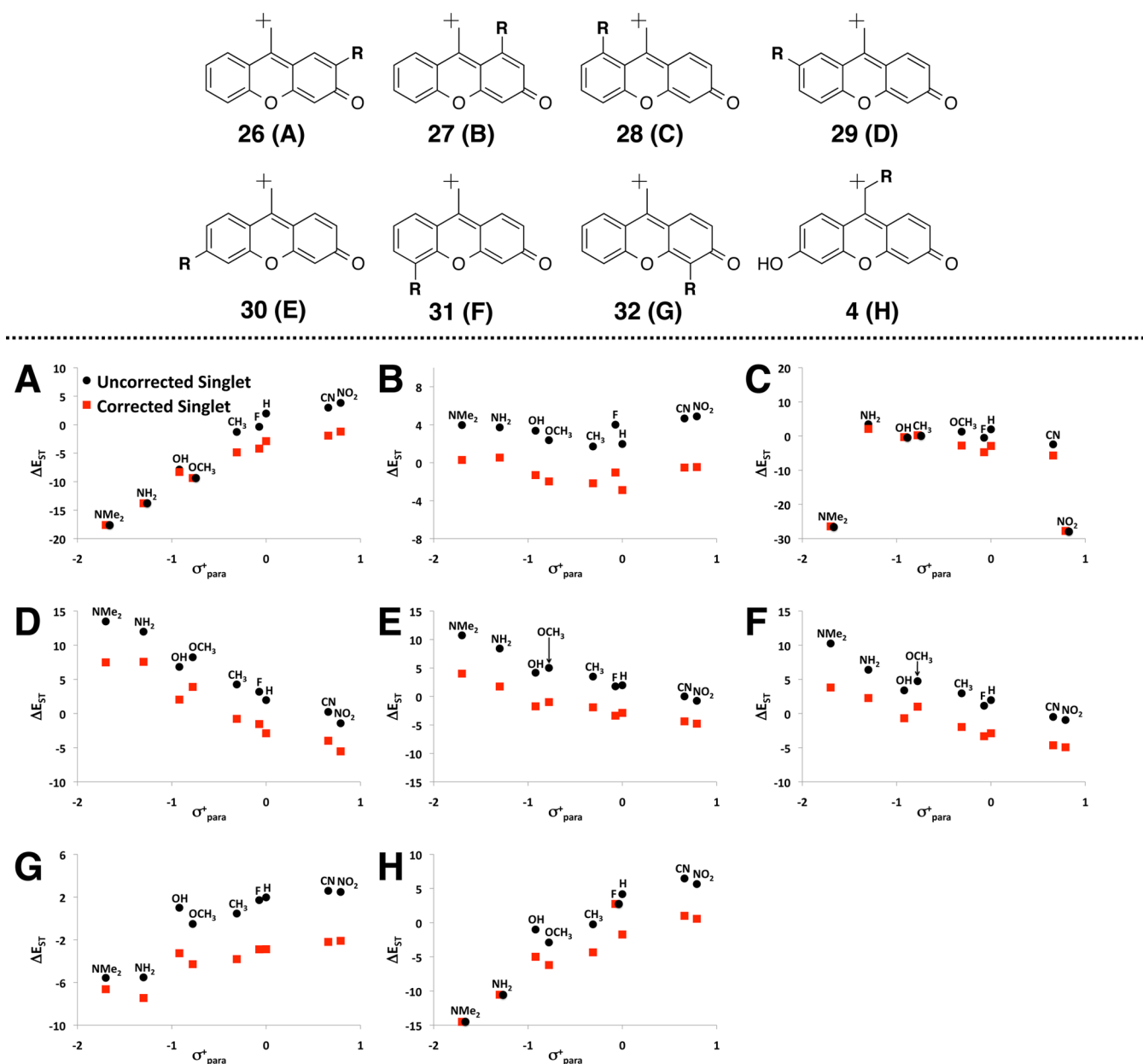


**Figure 2.** (top) UB3LYP Kohn–Sham SOMOs for singlet and triplet states of ions 14, 13, 19, and 7. For singlet benzyl cation 14, the first and second orbitals depicted (labeled with \*) are the HOMO and LUMO, respectively. (bottom) Approximate schematic representations of the closed-shell singlet, open-shell singlet, and triplet states of ions 11, 19, and 17.

the lowest-energy singlet state switches from being the closed-shell configuration to being the open-shell configuration, and increasing the electron-withdrawing character of the substituent ceases to have a major effect on  $\Delta E_{ST}$ . For ions 4, 26, and 32, it appears that this inflection point is reached when the substituent is hydrogen.

In contrast, the opposite trend holds true when substituents are *not* in direct conjugation with the carbocation (ions 29–31). In these cases, strong donors favor the diradical configurations. Indeed, the LFERs between the donor strength (as measured by the  $\sigma_{para}^+$  parameter) and  $\Delta E_{ST}$  increase roughly linearly as a function of donor strength.

**The Bridging Heteroatom Has a Substantial Effect on  $\Delta E_{ST}$  for Xanthenyl Cations.** Ions 20–25 were included to look at the effect of altering the bridging atom in the xanthenyl ion. If the bridging atom contains a lone pair, this lone pair is *not* in direct conjugation with the carbenium ion center, so on the basis of the results described above one might expect that increasing the donor strength of this bridging atom should favor the diradical configuration. This is indeed the case. With carbon or silicon bridging atoms, which lack donor lone pairs, the singlet is the computed ground state by ca. 6 kcal/mol. With weak donor bridging atoms (oxygen in 4, phosphorus in 23, sulfur in 24, and selenium in 25) the singlet is still the computed ground state but has a reduced energy gap (<2.5



**Figure 3.** Hammett plots for compounds 4 and 26–32. A positive value of  $\Delta E_{ST}$  indicates a triplet ground state. A large difference between corrected and uncorrected  $\Delta E_{ST}$  values suggests that the singlet state possesses diradical character. Hammett plots with linear fits can be found in the Supporting Information.

kcal/mol), and with a strong donor bridging atom (nitrogen in 21) the triplet is the computed ground state by 3.9 kcal/mol. Thus, switching the bridging atom from carbon to nitrogen causes a swing in  $\Delta E_{ST}$  by  $\sim 10$  kcal/mol in favor of the triplet and switches the computed ground-state configuration from singlet to triplet.

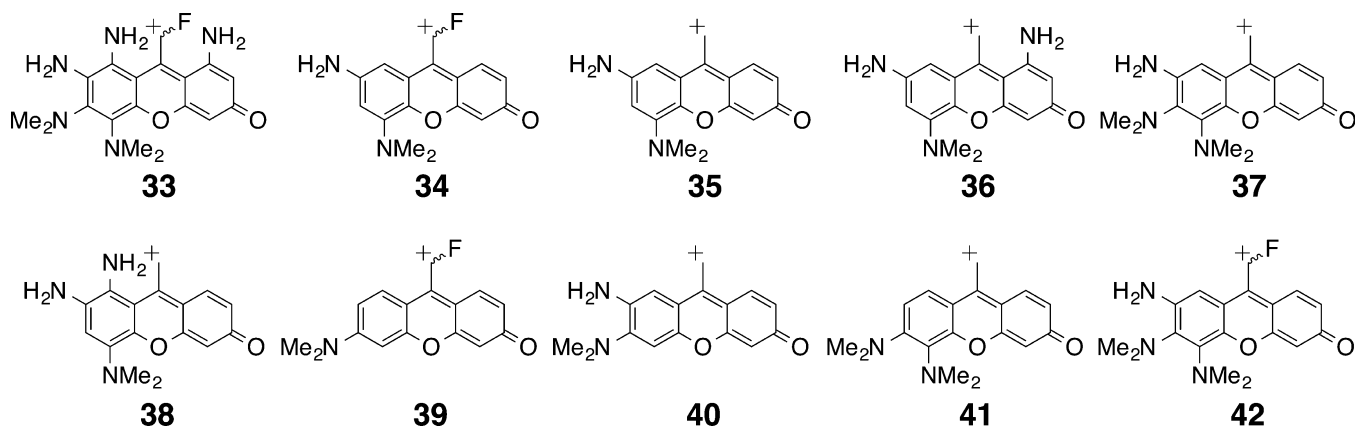
**Substituent Effects on  $\Delta E_{ST}$  Are Not Additive.** We wondered whether these substituent effects are additive. That is, would adding multiple substituents that favor the triplet configuration lead to an even larger gap in favor of the triplet state in a polysubstituted ion? Could  $\Delta E_{ST}$  be predicted from the sum of the effects for monosubstitution? To answer this question, we computed the singlet–triplet gaps for polysubstituted ions 33–42 (Chart 2). We found that the singlet–triplet gaps for these polysubstituted species do not increase, but all have  $\Delta E_{ST}$  values of approximately +5 kcal/mol in favor

of the triplet state (Table 3). This compares similarly to the monosubstituted xanthenone ion 29g, which is computed to have a  $\Delta E_{ST}$  of 7.6 kcal/mol in favor of the triplet. Thus, adding additional substituents has very little effect on the overall  $\Delta E_{ST}$ . However, a closer examination shows that the difference in energy between the restricted singlet energy and the unrestricted spin-purified singlet energy increases for these polysubstituted systems. Thus, a plausible explanation is that the inflection point where the singlet state becomes open-shell has been reached, and additional donors affect the energies of both the open-shell singlet and the triplet configuration similarly without perturbing the closed-shell singlet state as much. Thus, the singlet–triplet gap remains the same upon the inclusion of additional substituents beyond the point at which the open-shell singlet state becomes the lowest-energy singlet

Table 2. Computed Singlet–Triplet Energy Gaps ( $\Delta E_{ST}$ , kcal/mol) and Singlet Spin Contamination for Substituted Xanthylium Cation Analogues

compound	R	$\Delta E_{ST}$			$\langle S^2 \rangle$	compound	R	$\Delta E_{ST}$			$\langle S^2 \rangle$
		restricted singlet	unrestricted singlet	spin-purified singlet	unrestricted singlet			restricted singlet	unrestricted singlet	spin-purified singlet	unrestricted singlet
4a	NO <sub>2</sub>	5.7	2.0	0.6	0.7	29a	NO <sub>2</sub>	-1.4	-3.0	-5.5	0.5
4b	CN	6.5	2.4	1.0	0.7	29b	CN	0.2	-1.7	-4.0	0.5
4c	F	2.7	-0.1	2.7	0.6	29c	F	3.2	0.3	-1.5	0.6
4d	CH <sub>3</sub>	-0.2	-1.9	-4.3	0.5	29d	CH <sub>3</sub>	4.3	1.0	-0.8	0.6
4e	OCH <sub>3</sub>	-2.9	-3.9	-6.2	0.4	29e	OCH <sub>3</sub>	8.2	4.2	3.9	0.7
4f	OH	-1.0	-2.6	-5.0	0.5	29f	OH	6.8	2.8	2.0	0.7
4g	NH <sub>2</sub>	-10.5	-10.5	-10.5	0.0	29g	NH <sub>2</sub>	12.0	5.9	7.6	0.8
4h	NMe <sub>2</sub>	-14.5	-14.5	-14.5	0.0	29h	NMe <sub>2</sub>	13.5	5.3	7.5	1.0
26a	NO <sub>2</sub>	3.8	0.7	-1.2	0.6	30a	NO <sub>2</sub>	-0.8	-2.4	-4.8	0.5
26b	CN	3.0	0.0	-1.9	0.6	30b	CN	0.0	-2.0	-4.4	0.5
26c	F	-0.4	-1.9	-4.2	0.5	30c	H	2.0	-0.7	-2.9	0.6
26d	CH <sub>3</sub>	-1.3	-2.6	-4.9	0.4	30d	F	1.8	-1.0	-3.4	0.6
26e	OCH <sub>3</sub>	-9.4	-9.4	-9.4	0.0	30e	CH <sub>3</sub>	3.5	0.1	-1.9	0.7
26f	OH	-7.9	-7.9	-8.3	0.1	30f	OCH <sub>3</sub>	5.0	0.7	-1.0	0.7
26g	NH <sub>2</sub>	-13.8	-13.8	-13.8	0.0	30g	NH <sub>2</sub>	8.4	2.2	1.7	0.8
26h	NMe <sub>2</sub>	-17.6	-17.6	-17.6	0.0	30h	NMe <sub>2</sub>	10.7	3.4	4.0	0.9
27a	NO <sub>2</sub>	4.9	1.2	-0.5	0.7	31a	NO <sub>2</sub>	-0.9	-2.5	-4.9	0.5
27b	CN	4.7	1.2	-0.5	0.7	31b	CN	-0.5	-2.3	-4.6	0.5
27c	F	4.0	0.8	-1.0	0.6	31c	F	1.1	-1.1	-3.3	0.5
27d	CH <sub>3</sub>	1.7	-0.2	-2.2	0.5	31d	CH <sub>3</sub>	3.0	0.1	-2.0	0.6
27e	OCH <sub>3</sub>	2.4	0.1	-2.0	0.6	31e	OCH <sub>3</sub>	4.7	2.1	1.0	0.6
27f	OH	3.4	0.6	-1.3	0.6	31f	OH	3.4	0.9	-0.7	0.6
27g	NH <sub>2</sub>	3.7	2.1	0.5	0.5	31g	NH <sub>2</sub>	6.4	2.8	2.3	0.7
27h	NMe <sub>2</sub>	4.0	2.6	0.3	0.5	31h	NMe <sub>2</sub>	10.3	3.6	3.8	0.9
28a	NO <sub>2</sub>	-27.8	-27.8	-27.8	0.0	32a	NO <sub>2</sub>	2.5	-0.2	-2.1	0.6
28b	CN	-2.4	-3.4	-5.7	0.4	32b	CN	2.6	-0.3	-2.2	0.6
28c	F	-0.5	-2.3	-4.7	0.5	32c	F	1.7	-0.8	-2.9	0.6
28d	CH <sub>3</sub>	1.3	-0.6	-2.8	0.5	32d	CH <sub>3</sub>	0.5	-1.7	-3.8	0.5
28e	OCH <sub>3</sub>	0.2	0.2	0.2	0.0	32e	OCH <sub>3</sub>	-0.5	-2.1	-4.3	0.5
28f	OH	-0.3	-0.3	-0.3	0.0	32f	OH	1.0	-1.2	-3.3	0.5
28g	NH <sub>2</sub>	3.5	3.1	2.1	0.2	32g	NH <sub>2</sub>	-5.5	-5.8	-7.5	0.2
28h	NMe <sub>2</sub>	-26.4	-26.4	-26.4	0.0	32h	NMe <sub>2</sub>	-5.6	-5.7	-6.6	0.1

Chart 2. Polysubstituted Xanthylium Cation Analogues



state, but the difference in energy between the open-shell singlet and the restricted singlet energy increases.

## CONCLUSIONS

This computational investigation has identified carbocations that are computed to have open-shell ground-state configurations

and how the nature and location of substituents impact the electronic configuration of the ion. Carbocations have historically been considered to be special among reactive intermediates because they almost always adopt closed-shell singlet ground-state configurations. This single-configuration paradigm contrasts with other common reactive intermediates



**Table 3. Computed Singlet–Triplet Energy Gaps ( $\Delta E_{ST}$ , kcal/mol) and Singlet Spin Contamination for Polysubstituted Xanthenyl Cation Analogues**

compound	$\Delta E_{ST}$			$\langle S^2 \rangle$
	restricted singlet	unrestricted singlet	spin-purified singlet	unrestricted singlet
33	17.1	4.7	5.1	1.0
34	16.4	4.8	6.3	1.0
35	16.9	3.1	4.7	1.1
36	17.6	4.6	6.1	1.1
37	15.7	6.0	7.6	1.0
38	16.8	1.3	1.4	1.1
39	9.0	3.0	2.8	0.8
40	15.9	5.1	7.7	1.0
41	15.0	3.5	4.1	1.0
42	15.1	6.6	7.7	0.9

such as carbenes, nitrenes, nitrenium ions, and oxenium ions, which all have various electronic configurations that must be considered depending on the substituent structure. This and prior investigations<sup>27–31</sup> increasingly show that carbocations are less special in this regard than previously thought and suggest that these ions may have alternative low-energy electronic configurations that may need to be considered.

It should be noted that a part of the motivation for this study came from a recent computational investigation from our lab suggesting that photoheterolysis reactions of carbon–leaving group bonds may be governed by conical intersection control.<sup>48</sup> A conical intersection provides a facile channel for the photochemical reaction to proceed from the excited state to the ground-state product. Although speculative, carbocations that have low-energy singlet diradical states may be good candidates for photocaging structures. A low-energy singlet diradical configuration may suggest a nearby conical intersection between the closed-shell singlet and open-shell singlet configurations. In contrast, a carbocation with a very large energy gap between the closed-shell singlet and open-shell singlet configurations may not have an energetically accessible conical intersection. We note that some of the structures described in this study are likely to be good chromophores with low-energy singlet diradical configurations.

Indeed, carbocation **19** is the cation generated from one of the most popular photocages derived from the coumarin structure.<sup>49–51</sup> Photoheterolysis reactions to provide this cation have been used in numerous studies to release bioactive leaving groups such as neurotransmitters in cells.<sup>52–58</sup> It is interesting to note that the possibility that this carbocation may possess a ground-state triplet diradical structure has never been considered. This is likely the case because the reported product from this carbocation is its water adduct, the typical product expected from a closed-shell singlet carbocation. Our DFT computations give a singlet–triplet gap of +9 kcal/mol for this ion in favor of the triplet, and the MRMP2 calculations agree with this computed triplet ground state. These calculations provide a mystery of why one observes typical closed-shell singlet carbocation products for an ion that almost certainly has a triplet ground state. One possibility is that the singlet carbocation is too short lived to undergo intersystem crossing (ISC). Once the cation is born in the singlet state, it is trapped rapidly by solvent water prior to ISC. Intersystem crossing for this ion may be slow because it is anticipated to be spin–orbit coupling forbidden ( $^1\pi, \pi^* \rightarrow ^3\pi, \pi^*$ ), where there is no change

in orbital angular momentum to compensate for the change in spin angular momentum. However, the prediction from these computations is that matrix isolation of this carbocation should give an observable EPR spectrum characteristic of a triplet diradical.

Additionally, we are excited to see whether we can directly detect some of these species because there is little information on how ion diradicals behave. For example, how does the reactivity of an open-shell singlet diradical ion (such as **19**) differ, if at all, from the reactivity of a typical closed-shell singlet carbocation? What are the reactivity patterns for a triplet carbocation, and does the thermodynamic ground-state configuration of an ion matter if ISC rate constants are small in solution relative to trapping rate constants? We hope to answer these stimulating basic science questions in future work.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Computational coordinates, absolute energies, raw figure data, and additional Hammett plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### 📝 Notes

The authors declare no competing financial interest.

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