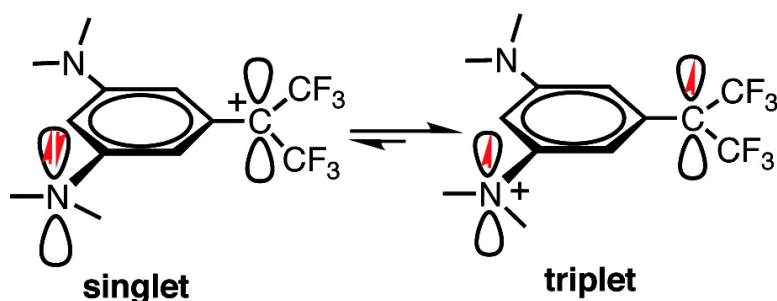


## Benzylic Cations with Triplet Ground States: Computational Studies of Aryl Carbenium Ions, Silylenium Ions, Nitrenium Ions, and Oxenium Ions Substituted with Meta $\pi$ Donors

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## Benzylic Cations with Triplet Ground States: Computational Studies of Aryl Carbenium Ions, Silylenium Ions, Nitrenium Ions, and Oxenium Ions Substituted with Meta $\pi$ Donors

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**Abstract:** Density functional theory (B3LYP/6-31G(d,p)) was used to predict the effect of meta substitution on aryl cationic (Ar-X<sup>+</sup>) species, including aryloxenium ions, arylsilylenium ions, arylnitrenium ions, and arylcarbenium ions. Multireference second-order perturbation theory (CASPT2) calculations were used to benchmark the quantitative accuracy of the DFT calculations for representative systems. Substituting the meta positions on these species with  $\pi$  donors stabilizes a  $\pi, \pi^*$  diradical state analogous to the well-known *m*-xylylene diradical. Notably, the 3,5-bis(*N,N*-dimethylamino)benzyl cation is predicted to have a triplet ground state by 1.9 kcal/mol by DFT and to have essentially degenerate singlet–triplet states at the CASPT2(10,9) level of theory. Adding electron-withdrawing CF<sub>3</sub> groups to the exocyclic carbon of this meta-disubstituted benzyl cation further increases the predicted singlet–triplet gap in favor of the triplet. Other aryl cationic species substituted with strong  $\pi$  electron-donating groups in the meta positions are predicted to have low-energy or ground-state triplet states. Systems analogous to the naphthaquinodimethane diradicals are also reported.

### Introduction

One long-standing interest of synthetic chemists has been in finding persistent high-spin organic molecules.<sup>1,2</sup> Such high-spin molecules could potentially be used as building blocks to construct ferromagnetic organic polymers with interesting magnetic and electronic properties. Searches for these high-spin building blocks have focused primarily on diradicals<sup>3</sup> with triplet ground state configurations. Examples include the classic triplet non-Kekulé diradicals discovered at the beginning of the 20th century such as trimethylenemethane<sup>4,5</sup> and *m*-xylylene,<sup>6,7</sup> and, more recently, atom-centered triplet diradicals such as nitrenes<sup>8,9</sup> and carbenes.<sup>10–12</sup> Many current efforts in this area have been directed toward stabilizing these paramagnetic entities by appropriate substitution;<sup>12–17</sup> others have focused on stitching

together known triplet diradical units to make oligomers with very high spin values.<sup>18–23</sup> Fewer recent efforts have been aimed at finding new paramagnetic building blocks.

Unfortunately, while there are several examples of triplet diradical building blocks that have been stitched together to make very high-spin oligomers, many are kinetically unstable. Therefore, we thought it worthwhile to search for a new class of triplet building blocks that could potentially be stabilized via appropriate substitution. Our search started with a density functional theory (DFT) investigation of arylnitrenium ions, Ar–N–H<sup>+</sup>.<sup>24</sup> Nitrenium ions are dicoordinate nitrogen intermediates with a lone pair and a positive charge on nitrogen, and they are

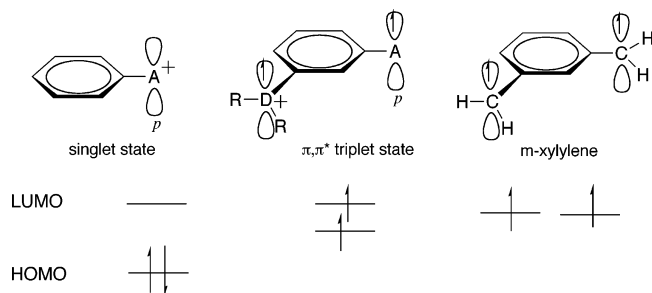
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**Figure 1.** General schematic representations of a typical singlet state and a  $\pi,\pi^*$  triplet state.

isoelectronic to the better known carbenes.<sup>25–27</sup> We were surprised to find that meta substitution of phenylnitrenium ions with  $\pi$  donors stabilizes a  $\pi,\pi^*$  triplet diradical state with an electronic configuration similar to *m*-xylylene. *m*-Xylylene is a well-known triplet diradical that has been the subject of extensive theoretical<sup>3,28</sup> and experimental studies.<sup>1,6,7,28–32</sup> This change in the electron configuration of phenylnitrenium ions to a *m*-xylylene-like triplet state upon meta donor substitution can be pictured by promoting an electron from the lone pair associated with the meta donor substituent (D, e.g., NMe<sub>2</sub>) into the LUMO formally associated with the nitrenium based *p* orbital (see Figure 1).

Thus, while the unsubstituted phenylnitrenium ion (PhNH<sup>+</sup>) is predicted to be a ground state singlet by 19 kcal/mol, adding sufficiently strong  $\pi$  electron donors (such as two *N,N*-dimethylamino substituents, NMe<sub>2</sub>) to the meta positions stabilizes the triplet state sufficiently to make the  $\pi,\pi^*$  triplet state the predicted ground state by DFT.

We considered that this same ‘meta effect’ might translate to other cationic species. In particular, we were interested if this triplet stabilization by meta  $\pi$  donors would occur with benzylic cations, since these intermediates hold a central place in the historical development of physical organic chemistry in general, and the understanding of electronic effects of substituents in particular. For example, historically the first experimental observation of cationic carbon has been accredited to Baeyer and others for the discovery of the triply benzylic triphenylmethyl cation using conductivity measurements at the beginning of the 20th century.<sup>33–35</sup> These types of benzylic cations were further characterized by NMR in the mid 1960s under stable ion conditions.<sup>36,37</sup> There are also several linear free energy relationships in use based on the quantitative effects of substituents on the reactivity of benzylic cations, including

the Hammett  $\sigma^+$  substituent parameters.<sup>38,39</sup> Despite this intense activity over many decades, there are to our knowledge no investigations of the effects of extremely strong meta- $\pi$ -donors (e.g., 3,5-bis(*N,N*-dimethylamino) substitution) on the behavior of benzylic cations.

The prospect that such an important species could have a stabilized triplet state caused us to turn our attention toward these intermediates. In fact, the DFT calculations described below predict low-energy or ground-state triplet states for benzylic cations substituted with strong  $\pi$  donors in the meta positions. Moreover, the current computational investigation suggests that the previously reported meta-substituted triplet arylnitrenium ions<sup>24</sup> are just one member of a broad class of ion diradicals exhibiting the connectivity of a  $\pi$  donor linked through non-disjoint  $\pi$  orbitals to a  $\pi$  acceptor.

The cationic species calculated in this study include aryloxenium ions (Ar–O<sup>+</sup>), arylnitrenium ions (Ar–NH<sup>+</sup>), arylsilylenium ions (Ar–SiH<sub>2</sub><sup>+</sup>), and benzyl cations (Ar–CH<sub>2</sub><sup>+</sup>). As with the previously reported phenylnitrenium ions,<sup>24</sup> all of these species show a stabilization of a  $\pi,\pi^*$  diradical state when substituted with meta  $\pi$  donors, as shown by a marked change in the singlet–triplet state energy gaps ( $\Delta E_{ST}$ ) with strong donors. Here the symbol  $\Delta E_{ST}$  is used to refer to the 0 K adiabatic energy differences (plus zero point vibrational energies) between the singlet and triplet states. In nearly all cases the triplet state is stabilized sufficiently to make it the predicted ground state when the cationic intermediates are substituted with the strongest meta  $\pi$  donors.

## Results/Discussion

**State-Energy Calculations.** In order to model the cations, we chose two different levels of electronic structure theory. The first, multireference second-order perturbation theory (CASPT2),<sup>40</sup> provides a rigorous method for constructing singlet and triplet states and comparing their relative energies. It is a particularly appropriate method for describing singlet states with small frontier orbital separations (which is typical for molecules having nearly degenerate singlet and triplet states) because it incorporates non-dynamical electron correlation directly into its multireference complete active space self-consistent field formulation.<sup>41</sup> Moreover, a recent level-shift modification to the CASPT2 model has corrected for a small bias in earlier formulations that favored high-spin states over low-spin analogs by 1–5 kcal/mol.<sup>42</sup>

While the CASPT2 model is rigorous, as a highly correlated wave function theory (WFT) model it imposes high demands on computational resources, in part because good convergence in relative energies typically requires reasonably complete one-electron basis sets, e.g., polarized valence-triple- $\zeta$  or better. Given the size of some of the molecules in which we are interested, we also explored the utility of density functional theory (DFT) calculations, noting that we can benchmark DFT against CASPT2 in smaller instances in order to gauge its

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effectiveness for the problem at hand. In prior studies, DFT models have been shown to predict singlet–triplet state energy gaps to within 2–4 kcal/mol of experiment (or converged quantum chemical calculations) at a fraction of the cost of high-level WFT methodologies for hypovalent species such as nitrenium ions and carbenes,<sup>43–47</sup> and somewhat more delocalized diradical species such as vinylidenes.<sup>48</sup> For example, DFT accurately predicts the singlet–triplet energy gap of the two nitrenium ions for which experimental values are available for comparison: the parent nitrenium ion,  $\text{NH}_2^+$ , for which the DFT (BLYP/cc-pVTZ) value of 30.6 kcal/mol agrees closely with the 30.1 kcal/mol gap found by photoelectron spectroscopy;<sup>49</sup> and the triazolium cation, a stable nitrenium ion for which the DFT value of  $-64.7$  kcal/mol (BPW91/cc-pVDZ) is within the experimental error of the value determined by traditional photophysical methods ( $-66 \pm 3$  kcal/mol).<sup>46</sup> However, in cases where two configurations for a singlet state have nearly equal weight in a multireference expansion, Kohn–Sham DFT has been shown to be less robust, e.g., for cases such as aryl-nitrenes<sup>50</sup> and trimethylenemethane (TMM).<sup>51,52</sup> Given the similarity of the  $\pi,\pi$  triplets considered here to, say, TMM, a careful calibration of DFT against CASPT2 seems particularly important.

Using unrestricted broken-symmetry formulations for the singlet state can improve the accuracy of Kohn–Sham DFT predictions in the event of narrow frontier orbital separations.<sup>41</sup> Thus, the restricted Kohn–Sham determinants for all singlets were tested for instability to breaking spin-state symmetry (i.e., a restricted  $\rightarrow$  unrestricted instability). For those singlets that were found to have such an instability, single-point broken symmetry calculations were performed at the restricted geometries. As expected, most singlet wavefunctions were stable, but instabilities were found in cases where the triplet state was either very close to or lower in energy than the singlet. In such cases, the energy of the singlet state was computed using eq 1:<sup>53–56</sup>

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

where  $E_{\text{singlet}}$  is the desired singlet energy,  $E_{\langle S_z \rangle=0}$  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 0.2 to 1.0), and  $E_{\langle S_z \rangle=1}$  is the energy of the triplet at the singlet geometry. The largest effect of R/U instability was

**Table 1.** Singlet–Triplet State Energy Gaps (kcal/mol) and Triplet Ar–X Bond Distances (Å)<sup>a</sup>

structure number	X	Y	$\Delta E_{\text{ST}}$			
			CASPT2/ pVTZ	CASPT2/ pVDZ	B3LYP/ 6-31G(d,p)	triplet Ar–X bond distance
<b>4</b>	$\text{CH}_2^+$	H	–44.6	–43.2	–39.7	1.403
<b>5</b>		F			–26.8	1.401
<b>7</b>		$\text{CH}=\text{CH}_2$	–27.7	–26.5	–17.4	1.403
<b>9</b>		$\text{NH}_2$	–10.1	–7.7	–4.4 <sup>b</sup>	1.402
<b>10</b>		$\text{NMe}_2$		–0.1	+1.9 <sup>b</sup>	1.403
					(+1.4)	
<b>11</b>	$\text{CHCF}_3^+$	$\text{NMe}_2$		+2.0	+5.1 <sup>b</sup>	1.410
<b>12</b>	$\text{C}(\text{CF}_3)_2^+$	H			–29.8	1.433
<b>13</b>		$\text{NMe}_2$		+8.7	+12.2 <sup>b</sup>	1.430
<b>14</b>	$\text{CF}_2^+$	$\text{NMe}_2$			–7.8 <sup>b</sup>	1.391
<b>15</b>	$\text{O}^+$	H			–13.5	1.263
<b>16</b>		$\text{NH}_2$	+4.5	+5.9	+11.4 <sup>b</sup>	1.250
					(+8.8)	
<b>17</b>		$\text{NMe}_2$			+15.4 <sup>b</sup>	1.252
					(+11.8)	
<b>18</b>	$\text{SiH}_2^+$	H			–47.7	1.880
<b>19</b>		$\text{NH}_2$	–19.1	–20.4	–9.7	1.875
<b>20</b>		$\text{NMe}_2$			–4.6	1.874
<b>21</b>	$\text{Si}(\text{CF}_3)_2^+$	$\text{NMe}_2$			+5.1 <sup>b</sup>	1.878

<sup>a</sup> All S–T splittings include differential zero-point vibrational energy computed at the B3LYP level. A negative value for  $\Delta E_{\text{ST}}$  indicates a singlet ground state. <sup>b</sup> Indicates a spin-projected broken symmetry calculation on the singlet state (energies in parentheses refer to a singlet geometry reoptimized using UB3LYP).

observed for aryloxonium ion **17** where the projected broken-symmetry singlet energy relative to the triplet was 3 kcal/mol lower than that for the restricted singlet.

**Molecular Geometries.** Although we expect the CASPT2 model to provide the most accurate description of the molecular energetics examined here, this level of theory is not particularly convenient for the determination of molecular structures because analytic gradients of the energy are not available for use in geometry optimization. DFT, on the other hand, is well established to provide excellent molecular geometries, particularly when hybrid functionals (incorporating exact Hartree–Fock (HF) exchange) are used; B3LYP is particularly accurate based on many benchmark studies.<sup>41</sup> Thus, we began by optimizing the molecular geometries for all of the molecules listed in Table 1 at the B3LYP/6-31G(d,p) level of theory, using the restricted and unrestricted Kohn–Sham formalism for the singlets and triplets, respectively. However, for the particular case of **9**, which was chosen because it falls roughly in the middle of the predicted spectrum of S–T splittings for the aryl-nitrenium ions, we examined the sensitivity of the geometries to choice of functional. Thus, we optimized the more difficult singlet state not only with the B3LYP functional, but also the BLYP, *mPWPW*,<sup>57–59</sup> *mPWP1PW*,<sup>57–59</sup> and TPSSH<sup>60,61</sup> functionals employing the 6-31G(d,p) basis set. We then assessed the variation in energy at the B3LYP/6-31G(d,p) level: over all five structures the total variation in energy was less than

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0.8 kcal/mol. On that basis, we elected to continue to use B3LYP geometries for all purposes, noting that any error introduced by this choice is likely to be no more than 1 kcal/mol.

A separate question, in cases where the singlet state is subject to breaking spin-symmetry, is whether one should ideally use the restricted singlet or unrestricted mixed-spin-state geometry. Restricted singlet geometries are sometimes found to be superior to broken-symmetry geometries after spin purification,<sup>62</sup> since the broken-symmetry formalism introduces spin contamination. In the case of **17**, which exhibits the largest value of  $\langle S^2 \rangle$  for the broken-symmetry Kohn–Sham determinant, allowing the broken-symmetry geometry to reoptimize at the unrestricted B3LYP level led to a change in the spin-projected singlet energy of 3.6 kcal/mol. As this value is reasonably small, and is moreover likely to be considerably reduced in the other molecules because of their smaller values of  $\langle S^2 \rangle$ , we adopted restricted singlet geometries throughout.

**Singlet–Triplet Splittings.** Meta disubstituted cations were chosen to enhance the meta effect described above and also to take computational advantage of the molecular symmetry of the disubstituted systems. Table 1 provides the computed singlet–triplet energy gaps ( $\Delta E_{ST}$ ) for these species and the Ar–X bond length predicted for the triplet state. Because of their smaller size, it proved possible to compute S–T splittings at the CASPT2/pVTZ level for **4**, **7**, **9**, **16**, and **19**. Repeating the calculation with a smaller pVDZ basis set led to a systematic stabilization of the triplet state relative to the singlet in all of these cases except for **19**, by 1.3 to 2.4 kcal/mol. This trend is in the expected direction, since electron correlation is more important for the singlet than the triplet (owing to its additional set of paired electrons) and reducing the size of the basis set degrades the CASPT2 model's ability to capture this correlation energy. However, the effect is small and systematic, suggesting that it should be transferrable to the remaining systems, where molecular size restricts the CASPT2 calculations to use of the pVDZ basis set. Such calculations were completed for **8**, **10**, **11**, and **13**.

Comparing the CASPT2 calculations to the B3LYP calculations, we see that the DFT model predicts the triplet state to be too stable relative to the singlet. Comparing to the CASPT2/pVTZ values, or to the value derived from adding  $-2$  kcal/mol to the CASPT2/pVDZ value (this being a conservative estimate of the transferrable basis set effect), we see that the B3LYP model's error is a fairly consistent 5–10 kcal/mol.

Turning to specific substitutions, as shown in Table 1, the unsubstituted benzyl cation **4** is predicted at this level of theory to be a ground-state singlet by 39.7 kcal/mol (a negative value for  $\Delta E_{ST}$  indicates a singlet ground state). Substituting the meta position with weak  $\pi$  donors (such as fluoro **5**) has a modest effect on the singlet–triplet energy gap. However, substituting with moderate to strong  $\pi$  donors significantly stabilizes the triplet state and dramatically increases the  $\Delta E_{ST}$ . In all cases, increasing the strength of the  $\pi$  donor (e.g., going from  $\text{NH}_2$  to  $\text{NMe}_2$ ) or making the cationic acceptor more electron deficient (such as by adding  $\text{CF}_3$  groups) favors the triplet state as a result of decreasing the gap between the frontier molecular orbitals. With the 3,5-bis(dimethylamino) benzyl cation **10** the meta substituents are sufficiently strong  $\pi$  donors to make the triplet

state the predicted ground state by 1.9 kcal/mol at the B3LYP level. However, the systematic error in the DFT model and the CASPT2/pVDZ prediction suggest that the correct ground state will still be the singlet for **10**, albeit by only a small margin. Adding one or two trifluoromethyl ( $\text{CF}_3$ ) substituents to make the cationic center even more electron-deficient (and thus a better electron receptor) enhances the importance of the meta effect, and cations **11** and **13** are predicted to have still more stable triplet states relative to their singlet states. In the case of **11**, uncertainty in the theory does not allow a firm prediction of the ground state: the singlet and triplet are likely to be nearly degenerate. In the case of **13**, on the other hand, the preference for a triplet ground state is sufficiently large that remaining quantitative uncertainty in the theory is unlikely to affect this prediction.

It is a significant finding from this study that the benzylic carbocation **13** has a triplet ground state, and triplet reactivity from carbocations **10** and **11** may be thermally accessible if intersystem crossing is facile. Virtually all previous studies on simple substituted carbenium ions have assumed that these species have singlet ground states. Moreover, the extant chemical and spectroscopic behavior of typical carbenium ions is consistent with strongly electrophilic singlet states. Exceptions to this are limited to the antiaromatic cyclopentadienyl cation<sup>63</sup> and some substituted phenyl cations ( $\text{X-Ph}^+$ ).<sup>64,65</sup> The current study is to our knowledge the first to identify a new class of carbocations with triplet ground states.

Similarly, phenylsilylenium cations and phenyloxenium cations show an increase in the  $\Delta E_{ST}$  by substituting the meta position with  $\pi$  donors.<sup>66</sup> Substituting the phenylsilylenium cation **18** with two bis(*N,N*-dimethylamino) groups, **20**, stabilizes the triplet state by approximately 41 kcal/mol relative to the singlet, but not sufficiently enough to overcome the 47 kcal/mol required to make the triplet the ground state; **20** is predicted to be a singlet by about 5 kcal/mol at the B3LYP level.<sup>67</sup> By making the silylenium center more electron-deficient (and thus a better acceptor) by substituting the silicon with two electron-withdrawing trifluoromethyl ( $\text{CF}_3$ ) substituents, **21**, the triplet is predicted to be the ground state by 5.1 kcal/mol at the B3LYP level. Given the magnitude of the systematic error in B3LYP, this suggests that the two spin states will be nearly degenerate, but with the singlet being more likely to be lower. With phenyloxenium ion **15**, which is predicted to be a singlet by approximately 14 kcal/mol at the B3LYP level, adding either two amino groups (**16**) or two bis(dimethylamino) groups (**17**) is enough to make the triplet the ground state by margins sufficiently large that they exceed likely uncertainty in the theory; we expect these species to be ground state triplets.

We close our discussion of the substituted phenyl systems with a brief assessment of the more general utility of DFT in this context. As B3LYP incorporates exact HF exchange, which

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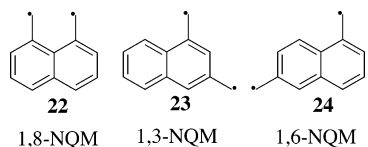
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(66) The changes in the singlet–triplet gap for the aryloxenium and arylitrenium ions upon substitution with  $\pi$  donors cannot be used as accurate quantitative measures of the perturbation in the  $\pi, \pi^*$  triplet state, as the unsubstituted analogs typically have  $n, \pi^*$  triplet states lower in energy than the  $\pi, \pi^*$  triplet states.

(67) The triplet silylenium ions appear to be approximately  $\text{sp}^3$  hybridized, in contrast to the singlet states which appear to be approximately  $\text{sp}^2$  hybridized.



**Figure 2.** Naphthaquinodimethanes.

**Table 2.** Singlet–Triplet State Energy Gaps (kcal/mol) from Various DFT Protocols for **9**

functional	restricted singlet	BS singlet	spin-purified BS singlet
BLYP	−6.0	−6.2	−7.2
B3LYP	−2.5	−3.0	−4.3
<i>m</i> PWPW	−4.7	−5.0	−6.1
<i>m</i> PW1PW	0.7	−0.2	−1.7
TPSSh	−0.7	−1.4	−2.8

stabilizes systems having a larger number of unpaired electrons, it is consistent that the model appears biased in favor of the triplet state in **4–21**. In Table 2, we compare a variety of functionals and broken-symmetry protocols with respect to their ability to predict  $\Delta E_{ST}$  for **9**. The CASPT2/pVTZ value of  $-10.1$  kcal/mol is likely to be reasonably converged and serves as a benchmark against which to judge the DFT models. The conclusions to be drawn from Table 3 are that spin-purified broken-symmetry singlet energies (i.e., computed using eq 1 above) are to be preferred over either raw broken-symmetry energies or restricted singlet energies, and that pure functionals (i.e., those not incorporating any HF exchange) are superior to hybrid functionals, but in the latter instance by a margin that is moderate in magnitude. Thus, comparing BLYP to B3LYP, the spin-projected broken-symmetry S–T splitting predicted by the former is  $-7.2$  kcal/mol, which represents a 2.9 kcal/mol improvement over the B3LYP result; the B3LYP functional incorporates 20% exact HF exchange. Similarly, the *m*PWPW prediction of  $-6.1$  kcal/mol improves on the hybrid *m*PW1PW prediction by 4.4 kcal/mol; the latter functional incorporates 25% HF exchange. We note that for **9** all functionals predict a singlet Kohn–Sham determinant that is unstable to symmetry breaking, although the pure functionals deliver smaller values of  $\langle S^2 \rangle$  for the converged unrestricted solution.

**Substituted Naphthalenes.** We also chose to explore if this same triplet-stabilizing effect would be found in systems that were analogous to non-Kekule diradicals other than *m*-xylylene. 1,8-naphthaquinodimethane (1,8-NQM), **22**, is a well-known non-Kekule triplet diradical with a recorded ESR spectrum. The 1,3- and 1,6-naphthaquinodimethane diradicals (**23** and **24**) are also thought to have low-energy triplet states as predicted by the Borden–Davidson method<sup>3</sup> (Figure 2). Therefore, we examined the effect of applying this electron-donor electron-acceptor motif to select naphthyl systems containing a positively charged center (nitrenium ion or oxenium ion) at the 1 position, and  $\pi$ -donating amino substituents at the 3, 6, and 8 positions. The B3LYP/6-31G(d,p) results are given in Table 3; the size of the naphthyl systems, with typically 16 electrons in 14 active  $\pi$  orbitals, just exceeds the current practical limit for CASPT2, so we do not present any results from this level of theory, but bear in mind that the B3LYP model is likely to retain a systematic bias in favor of the triplet state.

As the results in Table 3 show, both parent naphthyl nitrenium ion **25** and naphthyl oxenium ion **30** are ground state singlets with singlet–triplet energy gaps of ca.  $-23$  kcal/mol. In all

**Table 3.** Singlet–Triplet Energy Gaps ( $\Delta E_{ST}$ ) for Select Naphthyl Systems

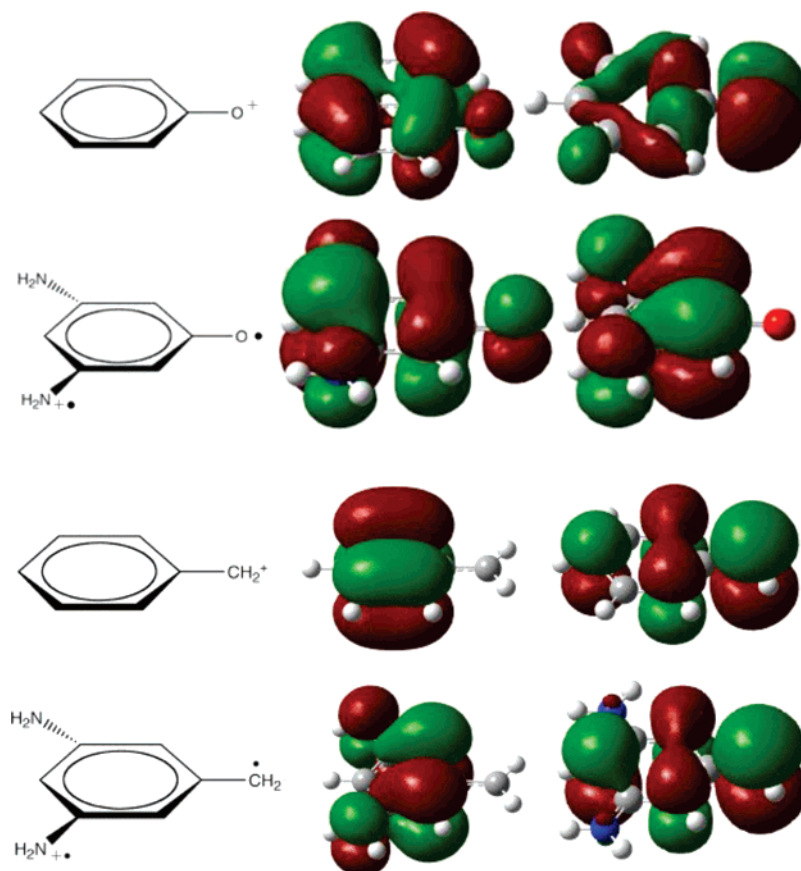
structure number	W	X	Y	Z	$\Delta E_{ST}$ (kcal/mol)	Ar–W bond length
<b>25</b>	NH <sup>+</sup>	H	H	H	−23.0	1.352
<b>26</b>		NH <sub>2</sub>	H	H	−8.5	1.333
<b>27</b>		H	NH <sub>2</sub>	H	−4.3	1.328
<b>28</b>		H	H	NH <sub>2</sub>	−4.8	1.337
<b>29</b>		NH <sub>2</sub>	NH <sub>2</sub>	NH <sub>2</sub>	+0.6 <sup>a</sup>	1.334
<b>30</b>	O <sup>+</sup>	H	H	H	−23.1	1.263
<b>31</b>		NH <sub>2</sub>	H	H	−6.8	1.242
<b>32</b>		H	NH <sub>2</sub>	H	−3.2	1.247
<b>33</b>		H	H	NH <sub>2</sub>	−7.5	1.257
<b>34</b>		NH <sub>2</sub>	NH <sub>2</sub>	NH <sub>2</sub>	−2.9 <sup>a</sup>	1.254

<sup>a</sup> Indicates a spin-projected broken-symmetry (UB3LYP) calculation on the singlet state.

cases, substituting the 3, 6, or 8 position with amino groups stabilizes the triplet state relative to the singlet, although only in the case of the trisubstituted naphthyl nitrenium ion **29** is the triplet stabilized sufficiently to make it the predicted ground state at the B3LYP level. Given the likely bias in this calculation, even **29** is probably a ground state singlet, although not by a very large margin. The lack of state switching in these cases may be due to the extended  $\pi$  system of the naphthyl system as compared to the phenyl system. Extended conjugated systems tend to favor the singlet state because of their  $\pi$ -donating ability, which acts to raise the energy of the p orbital on nitrogen. Indeed, the singlet–triplet energy splitting in phenyl nitrenium ion is predicted to be  $-19$  kcal/mol at this level of theory, 4 kcal/mol smaller than the naphthyl nitrenium ion ( $-23$  kcal/mol).

**Geometric Effects.** In the previous report on phenyl nitrenium ions,<sup>24</sup> geometrical changes were observed for the triplet states upon changing the character of the substituent attached to the meta position. These geometrical changes are consistent with the change in the nature of the triplet electronic state from  $n, \pi^*$  to  $\pi, \pi^*$ . For example, upon changing the character of the meta substituent from electron-withdrawing (or weakly donating) to strongly donating, a systematic increase in the Ar–N bond distances and a decrease in the Ar–N–H bond angles were observed. Moreover, while the N–H bond for the non-meta donor systems was found to be orthogonal to the aromatic ring, it was typically found to be coplanar to the aromatic ring for those systems substituted with  $\pi$  donors.

In agreement with the previous report,<sup>24</sup> the naphthyl nitrenium ions included in this study show a decrease in the bond angle for the triplets upon substitution with  $\pi$  donors. For example, the unsubstituted naphthyl nitrenium ion **25** has an Ar–N–H bond angle of  $120^\circ$ , whereas all the amino-substituted analogs have bond angles between  $110$  and  $111^\circ$ . Also consistent with the previous report, the NH bond is orthogonal to the ring in the unsubstituted naphthyl nitrenium ion **25**, but coplanar in all others substituted with  $\pi$  donors **26–29**. On the other hand, all meta donor-substituted naphthyl nitrenium ions show an increase in the Ar–N bond of between  $0.018$  Å and  $0.024$  Å for the triplets. For the aryl oxenium ions included in this study, a decrease in the triplet Ar–O bond length was observed upon appropriate substitution with  $\pi$  donors. Conversely, for the phenyl silylenium ions and benzyl carbenium ions, no major geometrical changes were observed between the non-meta- $\pi$ -



**Figure 3.** Kohn–Sham SOMOs for representative triplet phenyl oxenium ions and benzyl cations.

donor systems and those substituted with  $\pi$  donors (the aryl silylenium ions show a slight shortening of the Ar–Si bond).

This lack of systematic geometrical change in the triplet states upon meta-donor substitution of the benzyl carbenium ions and benzyl silylenium cations may be explained by observing the nature of the starting electronic states between the oxenium ions and nitrenium ions as compared to the silylenium ions and carbenium ions. That is, for the nitrenium ions and oxenium ions, the triplet electronic states for most of the non-meta donor systems adopt electron configurations that are  $n,\pi^*$  in nature, and change to  $\pi,\pi^*$  upon meta substitution with  $\pi$  donors. Observing the Kohn–Sham SOMOs for these molecules shown in Figure 3 demonstrates this change. The unsubstituted phenyloxenium ion **14** is taken as representative of the former case, and the diamino oxenium ion **16** is taken as representative of the latter. Conversely, because aryl silylenium ions and benzyl cations lack a lone pair on the positively charged atom, the triplet states begin as  $\pi,\pi^*$  in the unsubstituted system and do not change upon adding the meta-donating substituent. Figure 3 shows the Kohn–Sham orbitals of the unsubstituted benzyl cation **4** which is taken as representative of the former case as well as the diamino substituted benzyl cation **9** which is taken as representative of the latter. Thus, it appears that large systematic geometrical changes between the non-meta  $\pi$  donors and those substituted with meta  $\pi$  donors are observed primarily for those systems undergoing a change in the electron configuration of the triplet state.

One interesting exception to this trend is found with the unsubstituted naphthyloxenium ion **30**. In this case, the lowest energy triplet state is found to be  $\pi,\pi^*$  in nature rather than

$n,\pi^*$  such as the phenyloxenium ion **15**. Apparently, the additional conjugation of the naphthyl system relative to the phenyl system stabilizes the  $\pi,\pi^*$  triplet state sufficiently to make it lower in energy than the  $n,\pi^*$  triplet state. For all species, however, significant Mulliken spin density was found to be located on all  $\pi$ -donating substituents, but little or none was observed on weak donors (such as F) or electron-withdrawing groups (such as CN).

In conclusion, these calculations predict that substituting the meta position (or the 3, 6, and 8 positions for the naphthyl series) of aryl cationic species with  $\pi$  donors stabilizes a  $\pi,\pi^*$  triplet state analogous to non-Kekule diradicals. While we have only demonstrated this effect for phenyl and select naphthyl systems, in principle this  $\pi$ -donor– $\pi$ -acceptor connectivity should hold for alternative ionic species analogous to other non-Kekule diradicals conjugated with non-disjoint SOMOs, such as other variants of the naphthoquinodimethane system (e.g., those with the cationic center at the 3, 6, and 8 position), the biphenylquinodimethanes, and the trimethylenemethane diradical. Theoretically, any system with a strong  $\pi$  donor coupled to a strong electron acceptor with non-disjoint SOMOs could see a stabilization of a  $\pi,\pi^*$  triplet (or at least diradical) state similar to the ones described in this paper. Such benzylic cations can be generated and characterized using a variety of well-known methods, such as photolysis of meta-substituted esters or alcohols. In fact, preliminary experiments show that benzylic cations **10** and **12** can be generated photochemically in protic solvents from appropriate precursors. An initial product study shows that the corresponding toluene derivative is the minor product of **10** but is the major product for **12**. These results

suggest the intermediacy of a triplet cationic species but are by no means definitive evidence (the major product of **10** and the minor product of **12** are typical solvent alcohol addition products). Additionally, preliminary DFT investigations suggest that the reverse connectivity also stabilizes a  $\pi, \pi^*$  triplet state in analogous fashion (e.g., a  $\pi$  electron-donating group conjugated through non-disjoint  $\pi$  orbitals to  $\pi$ -withdrawing groups). Thus, the 3,5-dinitrobenzyl anion is predicted to have a  $\Delta E_{\text{ST}}$  of ca.  $-1$  kcal/mol at the B3LYP/6-31+G(d,p) level, in contrast to the unsubstituted benzyl anion which has a predicted  $\Delta E_{\text{ST}}$  of roughly  $-40$  kcal/mol. These further computational studies and experimental investigations aimed at characterizing these ion diradicals will be reported in due course.

### Computational Methods

All DFT calculations were performed using the Gaussian03 software suite<sup>68</sup> employing primarily the B3LYP functional that consists of Becke's three-parameter gradient-corrected exchange functional<sup>69</sup> and the LYP correlational functional of Lee, Yang, and Parr<sup>70,71</sup> along with the 6-31G(d,p) polarized double- $\zeta$  basis set. Spin contamination in the triplet state was found to be small, as shown by spin eigenvalues  $\langle\langle S \rangle\rangle$  very near the expected value

(2.0 for triplets). Geometries, energies, 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.

CASPT2 calculations were accomplished with the MOLCAS program.<sup>72,73</sup> Active spaces were composed of all  $\pi$  electrons (including the six aromatic ring electrons and any conjugated double bonds or lone pairs of the meta substituents) and all  $\pi$  orbitals. Polarized atomic natural orbital basis sets of double- $\zeta$ <sup>74</sup> and triple- $\zeta$ <sup>75</sup> quality were used.

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**Supporting Information Available:** Cartesian coordinates and absolute energies; complete refs 68 and 73; Table 1 reordered by magnitude of  $\Delta E_{\text{ST}}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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