Computational Study of the Electronic Structure of Substituted Phenylcarbene in the Gas Phase

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Gas-phase calculations for ortho-, meta-, and para-substituted phenylcarbenes demonstrate that aromatic ring substituents can have a large effect on the singlet−triplet splitting in these molecules. For example, *p*-aminophenylcarbene is predicted to have a singlet−triplet splitting (ΔE_{ST}) of 0.7 kcal/mol, which is 4.7 kcal/mol smaller than that of the parent phenylcarbene. However, when the mesomeric effect of π-donation is removed, as in the meta-substituted molecules, this affect is greatly attenuated. *m*-Amino substitution lowers the ΔE_{ST} to 5.2 kcal/mol, a change of only 0.2 kcal/mol from the parent phenylcarbene. The sensitivity of phenylcarbene to substitution is judged by the slope of the line correlating the singlet−triplet gaps to linear free energy (LFE) parameters. In this study, the best linear correlation for ΔE_{ST} in the para-substituted phenycarbenes is observed when plotted against σ_p^+. The resultant slope (ρ) is 5.0. The origin of this effect is preferential interaction of aryl substituents with the singlet rather than the triplet species as demonstrated by electron density analyses.

I. Introduction

The physical and chemical characterization of reactive intermediates has been of seminal importance to the development of our understanding of physical organic chemistry. Arguably the most intriguing reactive intermediate is the carbene.[1] Indeed, phenyl carbene has been well suited for the application of some of the favorite tools of analysis for transient divalent carbon species. From a practical standpoint, ground-state triplet arylalkylcarbenes (Ar−C−R) are readily detected by low-temperature EPR spectroscopy.[2,3] The lifetimes of singlet arylalkylcarbenes can be measured by laser flash photolysis as they form strongly absorbing ylides upon reaction with pyridine facilitating conclusive identification via their characteristic UV absorption.[4−8] The small energy difference between the lowest lying triplet electronic state and the lowest energy singlet state in phenylcarbene makes possible the study of intersystem crossing; however, experimental results have not been obtained for phenylcarbene. The singlet−triplet energy gap for phenylcarbene has been experimentally estimated to be less than 2 kcal/mol at ambient temperature in solution by indirect kinetic analyses.[9−12] It should be noted that the value measured in these phenylcarbene experiments refers to the relative energy of the equilibrated triplet ground state and the lowest point of intersection for rearrangement on the singlet surface. Thus, in the solvent systems used, the true ΔE_{ST} must be even lower in energy than the kinetically derived ΔE_{ST}. Several high level ab initio studies have predicted that the energy difference (ΔE_{ST}) is less than 4−5 kcal/mol in the gas phase.[13−16] (A positive value indicates that the triplet state is more stable.)

Density functional theory (DFT) studies have provided great success in modeling the chemistry of carbenes.[17] A recent DFT study at the B3LYP/6-31G* level predicted that ΔE_{ST} in phenylcarbene is 7.08 kcal/mol.[17a] Elegant

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theoretical studies by Bally, McMahon and co-workers,[13] Wong and Wentrup,[14] and Schreiner et al.[15] have elucidated the stability of the C_7H_6 isomers that are related to phenylcarbene through its rearrangements. The higher ΔE_{ST} calculated for phenylcarbene in the gas phase, as compared to condensed phase observations, is typical of arylcarbenes.[18] To understand the explicit role of solvent in these systems, there must first be a comprehensive understanding of the intrinsic factors that affect the stability and ultimately the reactivity of these molecules. This is where gas-phase calculations have and will continue to play an indispensable role.

Another molecule that has received considerable attention is the phenylnitrenium ion.[16,19−24] It has been shown that addition of a phenyl group to the divalent center lowers the ΔE_{ST} for the carbene by ~5 kcal/mol, whereas the substituent effect on the nitrenium species is much larger, ~40 kcal/mol. Conjugation to the π orbital of the nitrenium ion, allowing for delocalization of the positive charge, has been the explanation of this dramatic difference.[16,21]

It has even been explicitly noted that "...it is not clear that [conjugative interactions with an extended π-system] will play much of a role in [the preferential stabilization of substituted singlet] neutral carbenes."[21] If this were, in fact, the case, one would suspect the ΔE_{ST} of substituted phenylcarbene to be less sensitive to substituent effects than substituted phenylnitrenium ions.

The intent of this work is to use computational methods to explore the effect that substitution on the aromatic ring of phenylcarbene has on the electronic properties of these molecules, and specifically on the ΔE_{ST}. Moreover, Sullivan et al. has recently reported on electronic structure effects of para-substitution on the isoelectronic phenylnitrenium ion.[23] Specifically, linear free energy relationships[25] (LFE) of the ΔE_{ST} were correlated with several LFE scales.[26−30] To date, there have been no systematic studies that have explored the effect of substituents on ΔE_{ST} in substituted phenylcarbenes. DFT methods have been shown to predict the ΔE_{ST} of analogous systems accurately (within 2−3 kcal/mol),[13,16,17] and therefore are seen as an appropriate compromise of computational expense and accuracy for our current endeavor.

II. Computational Methods

All geometries were first optimized using one of two different DFT methods.[31] First, optimizations were carried out using the gradient-corrected functionals of Becke[32] for exchange and of Perdew and Wang[33] for correlation (BPW91) with the 6-31G* basis set.[34] Full geometry optimizations were also carried out on all species using the three-parameter hybrid functional B3LYP[35,36] with the 6-31G* basis set. Analytical second derivatives were computed to confirm each stationary point to be a minimum by yielding zero imaginary vibrational frequencies. These frequency analyses also provided zero-point vibrational energy (ZPE) corrections that were scaled by 0.9806.[37] Furthermore, single-point energy calculations were carried out at both BPW91 and B3LYP, on the geometries obtained by their respective optimizations, using a 6-311+G** basis set.[34b] All basis sets utilized six Cartesian d functions.

Single-point energies for phenylcarbene were evaluated at the QCISD(T)/6-31G* with the B3LYP/6-31G* geometries.[38] Some evaluations were carried out using the CBS-QB3,[39] G2(MP2)[40] and G2[41] methods. Further analysis was performed using natural population analysis[42] (NPA) and Bader's theory of atoms in molecules[43] (AIM) to evaluate the atomic charge on the carbene carbon for both the singlet and the triplet, as well as to determine the spin density for the triplet species. The NPA charges were qualitatively consistent with the AIM results within each series. That is, as the electron-withdrawing ability of the substituent increases, the charge on the carbene center also increases. However, NPA predicts that the carbene center in the singlet state will have a more negative charge than for the triplet state, while AIM predicts that the charge on the carbene center in the singlet state will be greater (more positive) than for the triplet state. Nevertheless, all results reported below correspond to the AIM values and the NPA results are provided in the Supporting Information. All calculations were carried out with the Gaussian 98[44] suite of programs.

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Table 1. Calculated ΔE_{ST} Values for Phenylcarbene at Various Theoretical Levels in the Gas Phase[a]

theoretical level	ΔE_{ST}
B3LYP/6-31G* [b]	7.3
BPW91/6-31G* [b]	9.4
B3LYP/6-311+G**//B3LYP/6-31G* [c]	5.4
BPW91/6-311+G**//BPW91/6-31G* [d]	7.7
QCISD(T)/6-31G*//B3LYP/6-31G* [c]	6.5
CBS-QB3	4.0
G2(MP2)	−0.5
G2	0.2

[a] Values are given in kcal/mol, and all energies include the scaled zero-point vibrational energy at the indicated level. [b] Fully optimized geometries at the indicated level. [c] Single-point energy using the B3LYP/6-31G*-optimized geometry. [d] Single-point energy using the BPW91/6-31G*-optimized geometry.

In this paper, ΔE_{ST} is defined as the energy difference, including the scaled ZPE correction, between the singlet and triplet states at their respective equilibrium geometries.

III. Results and Discussion

To assess the basis set and correlation effects on the calculated ΔE_{ST} of phenylcarbene, a series of geometry optimizations and single-point energy calculations were carried out at the BPW91 and B3LYP DFT levels with flexible basis sets and with the QCISD(T) theoretical level. Higher correlated methods were also used, including CBS-QB3,[39] G2(MP2),[40] and G2.[41] The results are summarized in Table 1. Of the DFT calculations performed, the B3LYP/6-311+G**//B3LYP/6-31G* level gives the smallest value for ΔE_{ST} (5.4 kcal/mol). This is consistent with the results obtained at the QCISD(T) level as well as with the CBS-QB3 method. The results of the G2(MP2) and G2 methods suggest a smaller value for ΔE_{ST} and predict ΔE_{ST} values of −0.5 and 0.2 kcal/mol, respectively. Indeed, they are also consistent with the results of extrapolation of previous CCSD(T)/cc-pVDZ calculations to a TZ basis set, which estimated a ΔE_{ST} of 2.5 kcal/mol.[13] However, our results suggest that the G2(MP2) and G2 calculations are plagued by a large amount of spin-contamination for the triplet (both have an $\langle S^2 \rangle$ value of 2.5 to 2.6, as compared to 2.04 for the B3LYP calculations).

A comparison of the MP2/6-31G* geometry (used in the G2 procedure) and the B3LYP/6-31G† (used in the CBS-QB3 procedure) geometry reveals significant differences for the triplet state of phenylcarbene (Figure 1), while the singlet's geometry is nearly identical. Given the small amount of spin contamination as well as the agreement of B3LYP/6-311+G**//B3LYP/6-31G* with other available ab initio calculations,[13−16] the values reported in the subsequent discussion will correspond to this level of theory. While the ΔE_{ST} values appear to be overestimated by ~1.5 kcal/mol with this method, the qualitative trends and relative values are expected to be reliable.

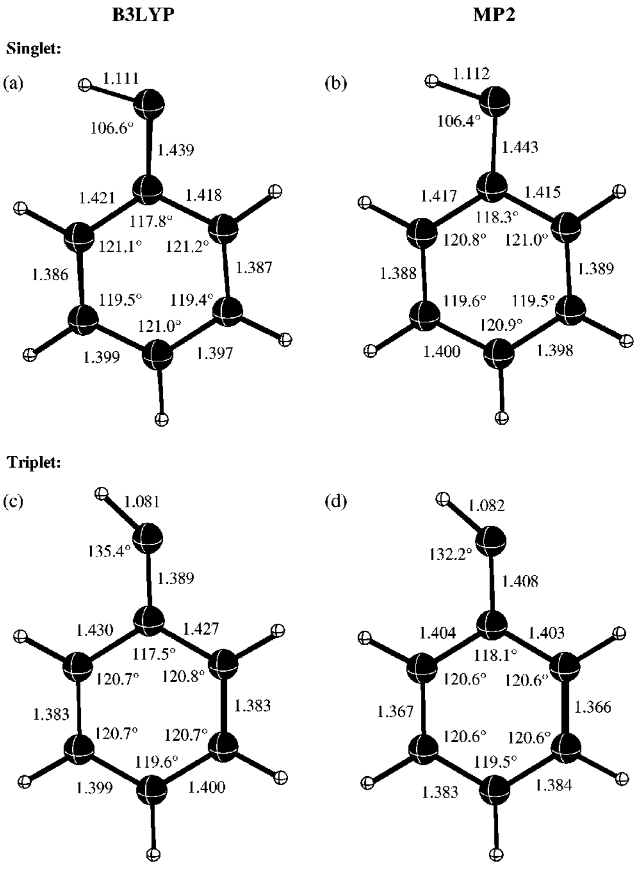

Figure 1. Comparison of the calculated geometrical data for the singlet (a, B3LYP; b, MP2) and triplet (c, B3LYP; d, MP2) states of phenylcarbene used in the CBS-QB3 (a and c) and the G2 (b and d) methods. Distances are in angstroms, and bond angles are in degrees.

A. Para-Substituted Phenylcarbenes. As previously stated, considering the change in ΔE_{ST} on going from methylene to phenylcarbene, it may be expected that substitution on the aromatic ring of phenylcarbene will have only a small effect on the ΔE_{ST}. However, our calculations show that substitution on the aromatic ring does have a pronounced effect on the preference for the singlet or triplet electronic state of the substituted phenylcarbene (Table 2). The change is qualitatively consistent with our understanding of phenylcarbene based upon valence orbital arguments. The empty π-orbital of the singlet phenylcarbene should have a stronger interaction with the aromatic π-system than the singly occupied π-orbital of the triplet state (we will return to this point later). It is therefore expected that strong π-donors (NH_2, OH, OCH_3) should preferentially stabilize the singlet state relative to the triplet state, while π-acceptors, such as CN and NO_2, will destabilize the singlet state. This trend is exactly what is observed. Upon alkyl substitution (CH_3) in the para position, the predicted singlet−triplet energy gap decreases to 4.1 kcal/mol. The strongest π-donors studied, NH_2, OH and OCH_3 have calculated ΔE_{ST} values less than 2 kcal/mol and may actually have singlet ground states if one considers the overestimation of ΔE_{ST} by our method of calculation. This is a very important result, as it illustrates that not only is conjugation to this extended π-system important for phenylcarbene, but it may even change the multiplicity of the electronic ground state. 4,4′-(*N*,*N*)-dimethyldiaminodiphenylcarbene has been

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Table 2. ΔE_{ST} for Para-Substituted Phenylcarbenes[a]

para substituent	σ_p^+	B3LYP/ 6-31G*[b]	BPW91/ 6-31G*[b]	B3LYP/6-311+G**// B3LYP/6-31G*[c]	BPW91/6-311+G**// BPW91/6-31G*[d]
NH_2	−1.111	1.5	3.2	0.7	1.3
OH	−0.853	3.7	5.5	1.7	3.8
OCH_3	−0.648	3.6	5.4	1.4	3.4
CH_3	−0.256	6.3	8.4	4.1	6.4
F	−0.247	5.8	7.8	4.1	6.3
H	0.000	7.3	9.4	5.4	7.7
Cl	0.035	7.5	9.3	5.3	7.3
NC	*e*	9.1	11.4	7.3	9.8
CF_3	0.582	9.6	11.8	8.1	10.6
CO_2CH_3	*e*	10.1	12.1	8.2	10.6
CN	0.674	10.8	12.6	9.0	11.1
CHO	*e*	11.1	12.9	9.3	11.6
NO_2	0.740	11.9	13.4	10.3	12.1

[a] Values are given in kcal/mol. [b] Fully optimized geometries. [c] Single-point energy using the B3LYP/6-31G*-optimized geometry. [d] Single-point energy using the BPW91/6-31G*-optimized geometry. [e] σ_p^+ value is not available.

shown experimentally to be a ground-state triplet.[45] It is noteworthy to consider, though, that steric hindrance imposed by the large phenyl rings in the substituted diphenylcarbene may equally alter its electronic properties to favor the triplet with the larger C−C−C angle around the carbene center,[46] thereby canceling any mesomeric stabilization provided by the amino substitution. Studies are underway to experimentally characterize 4-(*N*,*N*)-dimethylaminophenylcarbene, as our calculations at the B3LYP/6-311+G**//B3LYP/6-31G* level indicate this carbene has a triplet ground state, but with a ΔE_{ST} of only 0.7 kcal/mol.

Electron-withdrawing substituents raise the ΔE_{ST}. The extent of their effect is proportional to their propensity to act as a π-acceptor. The inductively electron-withdrawing CF_3 group raises the ΔE_{ST} by ~3 kcal/mol from unsubstituted phenylcarbene, whereas better π-acceptors, such as CHO and NO_2, do have a larger effect on the ΔE_{ST}, raising it by ~5 kcal/mol to 9.3 and 10.3 kcal/mol, respectively.

Despite the large electronic effect, the geometry for both the singlet and triplet states do not change significantly with substitution − tables of the geometric results are provided in the Supporting Information. For the singlet states, the angle around the carbene carbon (a1) ranges from 106.3° to 106.6°, and the bond length from the carbene carbon to the ipso-carbon (r1) ranges from 1.43 to 1.45 Å. This is similar to the geometrical changes observed in para-substituted phenylnitrenium ions,[23] where the range for r1 was observed to be 1.303 to 1.310 Å.

While the magnitude of the effect of para-substitution on the ΔE_{ST} for phenylcarbene is smaller than the effect observed by Sullivan et al.[23] for phenylnitrenium ion, the relative changes are very similar (the range for phenylcarbene spans 9.6 kcal/mol and phenylnitrenium ion spans 15.6 kcal/mol). An LFE analysis of these substituent effects better quantifies this similarity. When ΔE_{ST} is plotted versus σ_p^+, the slope (ρ) is 5.0 (Figure 2). This compares to a ρ value of 5.6 for the substituted phenylnitrenium ions.[23] This seems to indicate that while delocalization of the positive charge in the nitrenium ion is of some importance, the stabilization imparted by conjugation to the empty π orbital common to both phenylcarbene and phenylnitrenium ion is the dominant factor. This conclusion is supported by electron density analyses via Bader's theory of atoms in molecules (AIM) for the singlet and triplet states.[43,47]

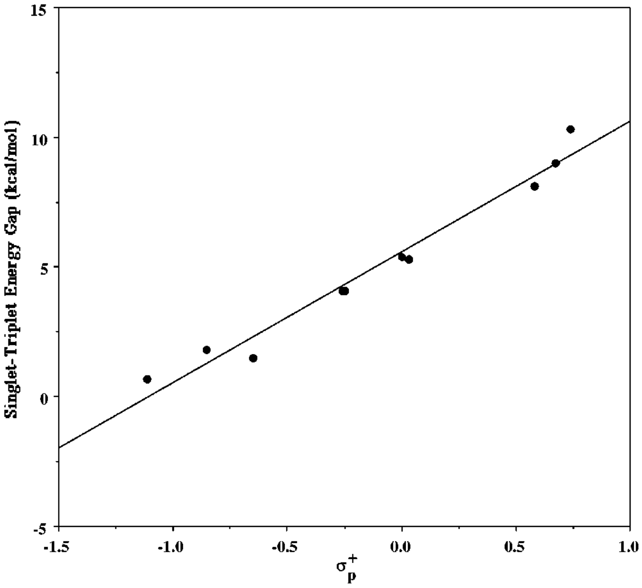

Figure 2. LFE relationship of ΔE_{ST} vs σ_p^+ in para-substituted phenylcarbenes at the B3LYP/6-311+G**//B3LYP/6-31G* level.

As can be seen in Figure 3, the charge on both the singlet and triplet carbenes gives a good linear correlation to σ_p^+. The data are given in Table 3. The slope for this correlation is 0.03 for the singlet and 0.02 for the triplet. While this difference is small, this effect would indicate that the singlet state displays slightly more charge separation due to substitution than the triplet state does. In addition, AIM calculations for methylene (CH_2) were performed at the B3LYP/6-311+G**//B3LYP/6-31G* level for the corresponding singlet and the triplet states. The calculated atomic charge on the C in methylene is −0.03 e^-, whereas for the triplet, it is −0.18 e^-. Thus, on phenyl substitution from methylene to phenylcarbene, the carbene center gains 0.07 e^- in the singlet state, while in the triplet state, the C loses 0.02 e^-. This is expected, as the singlet is conjugated to the π-system via an empty p

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(45) Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1979**, *57*, 2652.

(46) (a) Nazran, A. S.; Gabe, E. J.; LePage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Am. Chem. Soc.* **1983**, *105*, 2912. (b) Nazran, A. S.; Lee, F. L.; Gabe, E. J.; LePage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Phys. Chem.* **1984**, *88*, 5251. (c) Nazran, A. S.; Griller, D. *J. Chem. Soc., Chem. Commun.* **1983**, 850.

(47) For a comparison of different methods for analyzing charge density distributions, see: Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

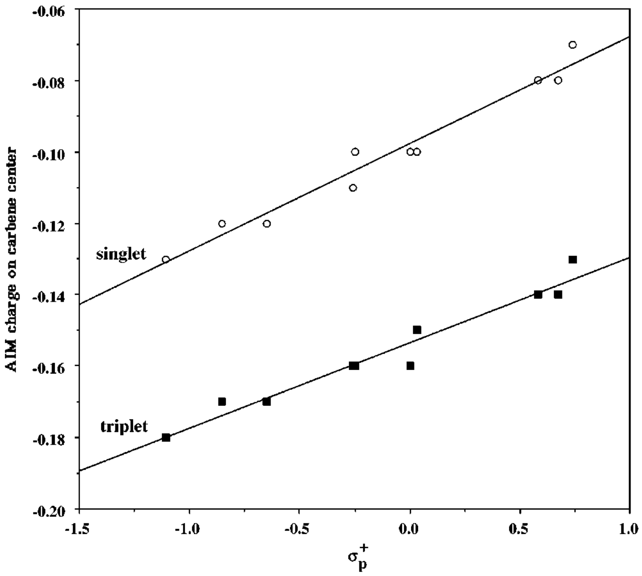


Figure 3. LFE relationship of the charge on the carbene carbon versus $\sigma_p{}^+$ in the singlet and triplet para-substituted phenylcarbenes at the B3LYP/6-311+G**//B3LYP/6-31G* level.

Table 3. AIM Results for the Carbene Carbon in the Singlet (Charge) and Triplet (Charge and Spin Density) States of Para-Substituted Phenylcarbenes[a]

para substituent	$\sigma_p{}^+$	triplet spin density	triplet atomic charge	singlet atomic charge
NH_2	−1.111	1.50	−0.18	−0.13
OH	−0.853	1.51	−0.17	−0.12
OCH_3	−0.648	1.51	−0.17	−0.12
CH_3	−0.256	1.52	−0.16	−0.11
F	−0.247	1.52	−0.16	−0.10
H	0.000	1.52	−0.16	−0.10
Cl	0.035	1.51	−0.15	−0.10
NC	*b*	1.50	−0.14	−0.09
CF_3	0.582	1.52	−0.14	−0.08
CO_2CH_3	*b*	1.50	−0.14	−0.09
CN	0.674	1.49	−0.14	−0.08
CHO	*b*	1.48	−0.14	−0.08
NO_2	0.740	1.49	−0.13	−0.07

[a] For the B3LYP/6-311+G**//B3LYP/6-31G* wave functions. [b] $\sigma_p{}^+$ value is not available.

Table 4. ΔE_{ST} for Meta-Substituted Phenylcarbenes[a]

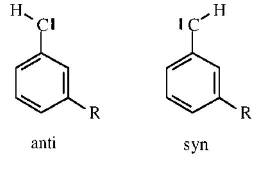
meta substituent	σ_m	B3LYP/ 6-31G* [b]	BPW91/ 6-31G* [b]	B3LYP/6-311+G**// B3LYP/6-31G* [c]
NH_2	−0.160	7.1	8.8	5.2
CH_3	−0.069	7.2	9.2	5.2
H	0.000	7.3	9.4	5.4
OCH_3	0.115	7.1	8.9	5.1
CO_2CH_3	*d*	7.7	10.1	5.7
OH	0.121	7.3	9.1	5.3
F	0.337	8.3	10.1	6.6
Cl	0.391	8.2	10.0	6.4
CF_3	0.430	8.5	10.8	6.9
CHO	*d*	8.1	11.7	6.1
NC	*d*	8.9	11.3	7.0
CN	0.560	9.0	11.6	7.2
NO_2	0.710	9.2	11.9	7.8

[a] Values are given in kcal/mol. [b] Fully optimized geometries. [c] Single-point energy using the B3LYP/6-31G*-optimized geometry. [d] σ_m value is not available.

orbital, whereas the triplet presents only a singly occupied p orbital to the π-system. However, for substituted phenylcarbenes, the degree of delocalization of the unpaired electron may have a stabilizing effect on the triplet carbene and therefore could be the source of the electronic effect of aryl substitution. However, as shown in Table 3, the spin density at the carbene center does not depend on substitution, and therefore does not appear to contribute to the observed differential singlet−triplet energy gap in these carbenes. Experimentally, the zero-field splitting parameter (*D*), which is a measure of the average distance between the unpaired electrons, indicates the amount of delocalization of the unpaired electrons in triplet carbenes. It is observed in para-substituted diphenylcarbenes that the *D* parameter—which is proportional to $1/r^3$ (where *r* is the average separation of the unpaired electrons)—only slightly decreases upon para substitution.[45,48] Based upon these observations, we conclude that the preferential stabilization of the singlet state is the dominant effect for altering the electronic state preference of these para-substituted phenylcarbenes.

B. Meta-Substituted Phenylcarbenes. The effect of meta substitution on ΔE_{ST} is much smaller than for the para case (Table 4). Here, mesomeric electron-donating substituents such as NH_2 and OCH_3 have very little effect on the ΔE_{ST}. *m*-Aminophenylcarbene has a ΔE_{ST} value that is only 0.2 kcal/mol less than the unsubstituted phenylcarbene. However, strong inductively electron-withdrawing groups do seem to destabilize the singlet species, raising the singlet−triplet energy gap to as high as 7.8 kcal/mol in meta-nitrophenylcarbene. *m*-Hydroxy substitution decreases the ΔE_{ST} relative to phenylcarbene. The decrease in ΔE_{ST} is smaller than is observed in the para case, and is exemplary of the importance of mesomeric stabilization. This effect can be mitigated in the methoxy case, in which polarization of the oxygen in the O−CH_3 bond can act to minimize the overall dipole associated with the meta substituent.

Again, as in the para-substituted species, the meta-substituted carbenes show very small variation in geometry with respect to substituent (see the Supporting Information). Here, the carbene carbon bond to the ipso-ring carbon only varies by 0.01 Å, from 1.44 to 1.45 Å for the singlet carbene. For the triplet states, the calculated bond distance does not change from 1.39 Å. The angle about the carbene carbon in the singlet states varies from 106.2° to 106.6°, which is a very small geometric variance. For the triplet states, this angle varies from 134.1° to 134.8°. It should also be noted that for all of the structures studied here, the lowest energy isomer of each multiplicity is reported. Of course, depending on the R substituent, the syn and anti rotational isomers could be considered and all of these possibilities were explored in this study.



An LFE analysis has been performed on the ΔE_{ST} for the meta-substituted phenylcarbenes (Figure 4). In this case, however, ΔE_{ST} was plotted against σ_m.[28] The range of values for ΔE_{ST} in the meta-substituted phenylcarbenes was only 5.1−7.8 kcal/mol, considerably less than

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(48) (a) Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1977**, *55*, 2286. (b) Arnold, D. R.; Humphreys, R. W. R. *J. Chem. Soc., Chem. Commun.* **1978**, 181.

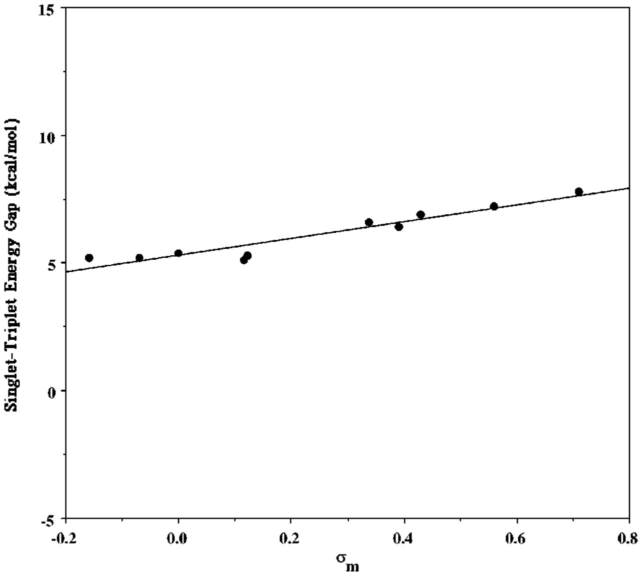

Figure 4. LFE relationship of ΔE_{ST} vs σ_m in meta-substituted phenylcarbenes at the B3LYP/6-311+G**//B3LYP/6-31G* level.

Table 5. AIM Results for the Carbene Carbon in the Singlet (Charge) and Triplet (Charge and Spin Density) States of Meta-Substituted Phenylcarbenes[a]

meta substituent	σ_m	triplet spin density	triplet atomic charge	singlet atomic charge
NH_2	−0.16	1.52	−0.16	−0.11
CH_3	−0.069	1.52	−0.16	−0.10
H	0.000	1.52	−0.16	−0.10
OCH_3	0.115	1.52	−0.16	−0.10
CO_2CH_3	*d*	1.53	−0.15	−0.09
OH	0.121	1.52	−0.16	−0.10
F	0.337	1.53	−0.14	−0.09
Cl	0.391	1.52	−0.15	−0.09
CF_3	0.430	1.53	−0.14	−0.08
CHO	*b*	1.52	−0.15	−0.09
NC	*b*	1.53	−0.14	−0.08
CN	0.560	1.53	−0.14	−0.08
NO_2	0.710	1.53	−0.13	−0.07

[a] For the B3LYP/6-311+G**//B3LYP/6-31G* wave function. [b] σ_m value is not available.

that of the para-substituted system. The σ_m values (Table 4) should be appropriate for the study of meta-substituted phenylcarbenes, as the lack of conjugation decreases the ability to transmit the electronic effect of these substituents from the meta position. There is a good linear correlation between ΔE_{ST} and σ_m, and this leads to a ρ value of 3.3. This confirms that mesomeric stabilization via conjugation to the aromatic π system and inductive effects are both important factors in the stabilization of substituted phenylcarbene. However, the more pronounced effect observed in the para-substituted cases indicates that mesomeric stabilization via conjugation to the aromatic π system is the dominant source of the observed electronic effect in the para systems.

In this light, the atomic charge on the carbene center for the singlet states and charge and spin density for the triplet states show interesting trends (Table 5). In a manner similar to the para cases, the triplet spin density calculated at the carbene position for the meta-substituted species shows no correlation to the corresponding linear free energy scale (σ_m). One very surprising observation made by Wasserman and co-workers[49] relates to the observed *D* parameter in nitro-substituted phenylcarbenes. Phenylcarbene has a *D* value of 0.5098. para-Nitrophenylcarbene, as one would expect from the electron-withdrawing nature of the nitro group, has a smaller *D* value (0.4859), and the unpaired electron is delocalized throughout the ring. This is reflected in our calculations of the triplet spin density at the carbene center for the parent phenylcarbene and *p*-nitrophenylcarbene, which yield values of 1.52 and 1.49 e$^-$, respectively. *m*-Nitrophenylcarbene is observed to have a *D* value (0.5230) that is greater than the parent phenylcarbene. This result is also revealed in our calculations, as the calculated triplet spin density for *m*-nitrophenylcarbene is 1.53 e$^-$, slightly larger than that of phenylcarbene.

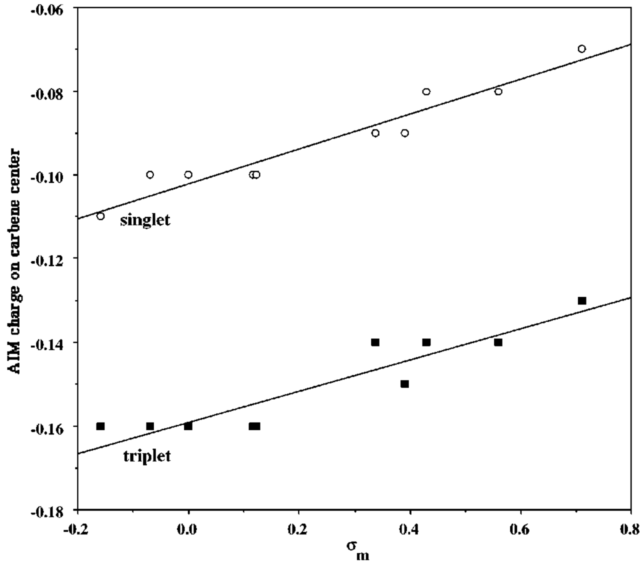

Figure 5. LFE relationship of the charge on the carbene carbon versus σ_m in the singlet and triplet meta-substituted phenylcarbenes at the B3LYP/6-311+G**//B3LYP/6-31G* level.

Similar to the para-substituted species, the meta-substituted species show a correlation between the charge on the carbene center in the triplet state and σ_m (Figure 5). The charge on the carbene center of the singlet carbene also shows a reasonable correlation to σ_m (Figure 5), with one notable characteristic. In this case, each slope is 0.04. The fact that these slopes are identical indicates the importance of mesomeric interaction in the para systems, and confirms that inductive effects will be very similar in both the singlet and triplet species. This explains the small effect observed by meta-substitution.

C. Ortho-Substituted Phenylcarbenes. Ortho-substituted phenylcarbenes provide a complication not encountered in the meta and para cases due to the spatial proximity of the substituent to the reactive carbene center. All attempts to optimize structures with formyl, carbomethoxy, and nitro substituents with the carbene anti or syn to the ortho substituent resulted in the formation of a bicyclic heterocycle (as illustrated for the formyl case in Scheme 1). C_s-Symmetric structures that were calculated (in an attempt to avoid this insertion process) were transition states, with the vibrational mode for the imaginary frequency depicting a rotation about the (carbene-carbon)−(ipso-carbon) bond axis. Displacement along this normal mode in either direction (±5%), followed by careful optimizations (opt = calcall), mono-

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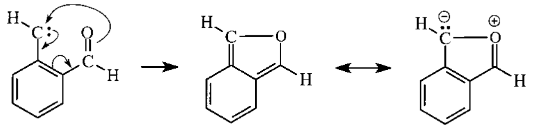
[49] Trozzolo, A. M.; Wasserman, E. Structure of Aryl Carbenes. In *Carbenes*; Moss, R. A., Jones, M. J., Jr.; Wiley: New York, 1975; Vol. II, Chapter 5, p 185.

Scheme 1



Scheme 2

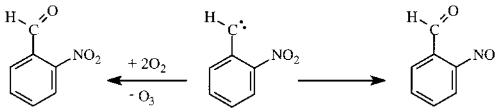


Table 6. ΔE_{ST} for Ortho-Substituted Phenylcarbenes[a]

ortho substituent	B3LYP/ 6-31G* [b]	B3LYP/6-311+G**// B3LYP/6-31G* [c]
NH_2	−3.7	−4.4
OH	3.1	−0.6
OCH_3	4.4	3.3
CH_3	6.8	5.3
H	7.3	5.4
F	6.4	5.1
Cl	8.4	6.6
CF_3	10.5	9.1
CN	10.6	9.0
NO_2	*d*	*d*
CHO	*d*	*d*
CO_2CH_3	*d*	*d*
NC	9.3	7.8

[a] Values are given in kcal/mol. [b] Fully optimized geometries. [c] Single-point energy using the B3LYP/6-31G*-optimized geometry. [d] Singlet state could not be obtained without rearrangement (see text).

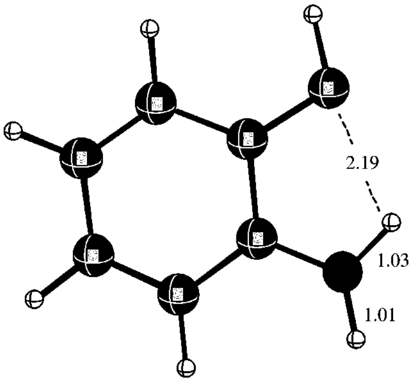
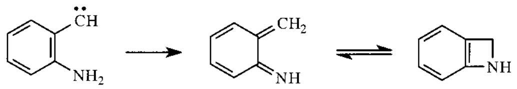
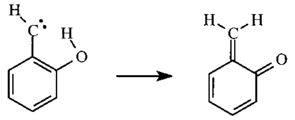


Figure 6. Hydrogen-bonding conformation of C_s-symmetric ortho-aminophenylcarbene. Distances are shown in angstroms.

Scheme 3



Scheme 4



tonically lead to the heterocycle (Scheme 1). Experimental preparation of the ortho isomer of carbomethoxyphenylcarbene does not yield a free carbene, but rather gives an ylide, formed from an intramolecular reaction analogous to the one shown in Scheme 1.[50] In this work, the *o*-nitrophenylcarbene also yielded the ylide upon optimization, but a different product was observed experimentally. When synthesized in the presence of an ortho nitro group, phenylcarbene undergoes O-transfer, as illustrated in Scheme 2, and this process probably occurs via a heterocyclic ylide.[51] Products consistent with the free carbene can be trapped as 2-nitrobenzaldehyde in 20% oxygen-doped argon matrixes, but direct spectroscopic characterization of the carbene was not possible (Scheme 2). For the other substituents considered here, we were able to obtain minima for both the singlet and triplet carbenes, and the data are shown in Table 6.

In general, ortho substitution has a smaller effect on the calculated ΔE_{ST} (Table 6) than does para substitution, except for the special cases of *o*-aminophenylcarbene and *o*-hydroxyphenylcarbene. The range for the energy gap from *o*-methoxy to *o*-trifluoromethylphenylcarbene is only 5.8 kcal/mol (ranging from 3.3 to 9.1 kcal/mol). The large ΔE_{ST} observed for *o*-trifluoromethylphenylcarbene may be due to an unfavorable steric interaction between the substituents and the carbene center as well as the electron-withdrawing nature of the CF_3 group. *o*-Aminophenylcarbene shows a very unique behavior. It is calculated to have a ΔE_{ST} that is 7.7 kcal/mol less than ortho-methoxyphenylcarbene, and the amino group provides an energetic preference for the singlet state. The origin of this effect is a hydrogen bond formed between the amino substituent and the lone pair on the singlet carbene. As seen in Figure 6, the amino group is nearly planar at the nitrogen center, with one of the N−H bonds oriented directly toward the carbene center. There is a lengthening of the N−H bond oriented toward the carbene center (1.03 versus 1.01 Å for the N−H bond oriented away from the carbene center). Experimental efforts to isolate this carbene by photolysis ($\lambda = 544$ nm, argon, 11 K) of 2-aminophenyldiazomethane produced 6-methylene-2,4-cyclohexadien-1-imine.[3,52] This was converted to a benzazetine upon irradiation at shorter wavelength (Scheme 3). Searches for a minimum energy structure for the hydroxyl case with the O−H bond oriented toward the carbene center resulted in the formation of the quinone-type structure shown in Scheme 4. In light of the observed experimental behavior in studying *o*-aminophenylcarbene, this computational difficulty is not a surprise. What is interesting, though, is that the lowest energy structure that was located for *o*-hydroxyphenylcarbene was the syn-syn isomer, where the carbenic H and hydroxyl group H are directed toward one another.

The geometry of the singlet carbene is greatly affected by ortho substitution, particularly in *o*-aminophenylcarbene. Here, participation of the lone pair on the carbene carbon in the aforementioned hydrogen bond to the amine hydrogen allows for a larger C−C−H bond angle about the carbene carbon, which widens to 109.0°. For the rest of the molecules (in which all but *o*-methoxyphenylcarbene favor the syn isomer), this angle varies from 106.1° (*o*-trifluoromethylphenylcarbene) to 110.5° (*o*-hydroxyphenylcarbene).

D. Regioisomer Stability. As mentioned in the Introduction, many theoretical studies of the rearrangement of phenylcarbene have afforded quite a detailed

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(50) Murata, S.; Ohtawa, Y.; Tomioka, H. *Chem. Lett.* **1989**, 853.

(51) Tomioka, H.; Ichikawa, N.; Komatsu, K. *J. Am. Chem. Soc.* **1992**, *114*, 8045.

(52) Sander, W.; Morawietz, J. *Tetrahedron* **1993**, *34*, 1913.

Table 7. Relative Energies of the Regioisomers of Substituted Phenylcarbenes[a,b]

substituent	ortho	meta	para
	singlet carbenes		
NH_2	−4.7	6.7	0.0
OH	−1.5	3.7	0.0
OCH_3	1.9	3.9	0.0
CH_3	1.2	1.3	0.0
F	1.1	2.3	0.0
Cl	2.0	1.4	0.0
NC	0.9	1.0	0.0
CF_3	2.5	−0.7	0.0
CO_2CH_3	*c*	−1.1	0.0
CN	0.5	−0.3	0.0
CHO	*c*	−1.3	0.0
NO_2	*c*	−0.8	0.0
	triplet carbenes		
NH_2	−1.0	0.8	0.0
OH	0.6	0.0	0.0
OCH_3	0.6	0.0	0.0
CH_3	−0.1	0.1	0.0
F	0.6	−0.2	0.0
Cl	0.9	0.4	0.0
NC	1.0	1.2	0.0
CF_3	1.9	0.6	0.0
CO_2CH_3	1.2	1.5	0.0
CN	1.1	1.6	0.0
CHO	1.4	2.2	0.0
NO_2	2.6	1.9	0.0

[a] All values are given in kcal/mol and include scaled zero-point vibrational energy corrections. [b] Values correspond to the single-point energy calculated at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory and includes a scaled ZPE correction. [c] The singlet state could not be obtained without rearrangement (see text).

description of the C_7H_6 potential energy surface.[13−15] There have been many photochemical studies of ring expansion of phenylcarbenes to cycloheptatetraenes by Chapman et al.[53−57] While this rearrangement process is certainly affected by the stability of the starting phenylcarbene, it is not our intention here to revisit these surfaces, which would surely be complicated by the presence of substituents. Rather we will present, briefly, a view of the relative stability of each regioisomeric phenylcarbene.

The relative energies of the regioisomeric substituted phenylcarbenes are given in Table 7. For simplicity, the para species is chosen as the reference for each case. The meta-substituted singlet states show a very interesting, and intuitively satisfying trend. In the cases of para substitution by π donors, the para-substituted species is more stable than the meta-substituted species. This satisfies the valence orbital argument, where the singlet state should resemble an electron-deficient carbocation, with an empty p-orbital conjugated to the aromatic ring. Thus, substituents that can stabilize carbocationic centers by resonance interaction should also preferentially stabilize the singlet carbene when the substituent is in the para position, but not in the regioisomeric meta isomer. Electron-withdrawing substituents (both inductively and mesomerically electron-withdrawing) are expected to destabilize the singlet state. This effect should also be greater in the para position, as resonance interaction is expected to enhance this effect. This is exactly what is observed, as the meta isomers are more stable than the para-substituted singlet phenylcarbenes when the substituents are electron withdrawing. (It is also worth noting here that there is potentially another rotamer in which the C−H bond of the carbene is oriented perpendicular to the plane of the aromatic ring. In the case of electron-withdrawing substituents, this rotamer may potentially be a preferred conformation of the carbene. Attempts were made to find such structures computationally, but in all cases, the only minimum energy structures were ones in which the carbene C−H bond was coplanar with the aromatic ring.)

The meta-substituted triplet states are consistently equal in energy to or higher in energy than the para-substituted isomers, with the one exception of *m*-fluorophenylcarbene. It is not clear why this should be, but the difference is small (0.2 kcal/mol). These results are consistent with our calculations in which the triplet spin density on the carbene carbon in all cases is greater for the meta isomer than for the para analogue. This indicates less delocalization of the unpaired electron into the π system in the meta-substituted species, which should lead to a higher energy triplet isomer.

Perhaps the most striking feature of Table 7 is the instability of the ortho-substituted phenylcarbenes compared to either the meta- or para-substituted isomers (with the exception of singlet *o*-amino and *o*-hydroxylphenylcarbene and triplet *o*-amino and *o*-methylphenylcarbene). As noted earlier, the ability of ortho-aminophenylcarbene to form a hydrogen bond between the amino hydrogen and the lone pair on the carbene center, is the reason for the increased stability of this species.

IV. Conclusions

Gas-phase calculations predict that phenylcarbene is sensitive to substituent effects for groups located ortho, meta, and para to the carbene center, and the ortho and meta substituents provide a much smaller effect on the singlet−triplet energy gap except when a proximity interaction with the carbene center is possible. LFE analyses suggest that the sensitivity is comparable to that observed in substituted phenylnitrenium ions.[21] In light of these results, it may be more appropriate to consider that the difference in stabilization between CH_2 and C_6H_5CH and between NH_2^+ and $C_6H_5NH^+$ is due to the instability difference between the parent molecules (CH_2 and NH_2^+) rather than a greater interaction with the π system on the part of phenylnitrenium ion over phenylcarbene. This becomes clear when one considers that on going from methylene to phenylcarbene, the carbene center in the singlet state gains 0.07 e^-, whereas the triplet state loses 0.02 e^-.

In fact, ΔE_{ST} for the para-substituted derivatives correlates well with σ_p^+, implying that electron-donating/withdrawing resonance interactions between the empty π orbital on the carbenic carbon and the substituent groups resembles that of strongly electron-deficient centers. This is consistent with our conception of the valence orbital interactions of phenylcarbene, where the empty carbene π orbital is stabilized and destabilized by

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(54) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973.

(55) Chapman, O. L.; Abelt, C. J. *J. Org. Chem.* **1987**, *52*, 1218.

(56) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J. P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456.

(57) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 501.

the same types of interactions that affect carbocationic centers. Interactions can be so significant that they may change the multiplicity of the ground electronic state, as in the case of ortho-aminophenylcarbene. Similar trends have been experimentally observed in para-substituted phenylethylidenes (X−Ph−C−CH_3) with a variety of para substituents (CF_3, Br, H, OCH_3).[7] In heptane as a solvent, the ΔG_{ST} at 298 K was found to be 3.5, 3.0, 2.3, and 1.4 kcal/mol for CF_3, Br, H, and OCH_3, respectively. This trend (excluding para Br, which was not calculated in this work) agrees qualitatively with our results.

It is also noted that, when provided spatial proximity (as in the ortho case), significant interaction with the carbene center can lead to bicyclic structures, ylides, and hydrogen-bonding structures, all of which have a significant effect on the structure and electronic properties of these species.

Acknowledgment. The authors would like to thank the National Science Foundation (CHE-9733457) and the Ohio Supercomputer Center for their support of this work. We also thank Professor Matthew Platz (Ohio State University) for helpful discussions.

Supporting Information Available: Energies, enthalpies, free energies, Cartesian coordinates, harmonic frequencies, and tables of selected geometric parameters for all species. NPA results for atomic properties for the para- and meta-substituted phenylcarbene. This material is available free of charge via the Internet at http://pubs.acs.org.

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