

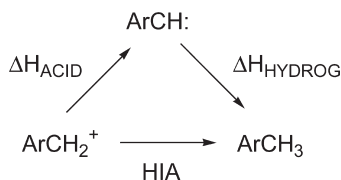
Correlations between Carbene and Carbenium Stability: Ab Initio Calculations on Substituted Phenylcarbenes, Nonbenzenoid Arylcarbenes, Heteroatom-Substituted Carbenes, and the Corresponding Carbocations and Hydrogenation Products[†]

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Calculations were completed at the G3MP2 level on a large group of carbon- and heteroatom-substituted carbenes (X-CH, singlets and triplets), carbenium ions (X-CH₂⁺), and their hydrogen addition products (X-CH₃). One series includes 11 *meta*- and 12 *para*-substituted phenylcarbenes, X = Ar. Gas-phase enthalpies of reaction were calculated for four processes: singlet–triplet enthalpy gaps of the carbenes, ΔH_{ST} ; enthalpies for deprotonation of the cations yielding singlet carbenes, ΔH_{ACID} ; hydride ion affinities of the carbenium ions, HIA; and enthalpies of hydrogenation of the singlet carbenes, ΔH_{HYDROG} . A plot of HIA vs ΔH_{HYDROG} values provides a direct comparison of substituent effects on the stabilities of the singlet carbenes and the corresponding benzylic cations. These effects are larger for the cations but are remarkably consistent over a wide range of reactivity: 166 kcal/mol in HIA. All four processes were analyzed according to the relative importance of polarizability, polar, and resonance effects. Polar and resonance effects are large and of similar magnitude for *meta* compounds. For the *para* compounds resonance effects are more dominant. Calculations were made on three nonbenzenoid arylcarbenes: Ar = cycloheptatrienyl⁺, cyclopentadienyl⁻, and cyclopropenyl⁺. The cyclopentadienyl⁻-substituted system fits the HIA vs ΔH_{HYDROG} correlation, but the other two fall well off the line, suggesting markedly different interactions are at play. A set of heteroatom-substituted carbenes and carbocations was also examined. Points for these groups lie well above the correlation line for the HIA vs ΔH_{HYDROG} plot defined by the aryl compounds, confirming that heteroatoms stabilize the singlet carbene proportionally more than the carbocation.

Introduction

Carbenes, including the relatively stable heteroatom carbenes, are important objects of study from both theoretical and practical points of view. The chemistry of singlet carbenes ranges from the electrophilic to the nucleophilic

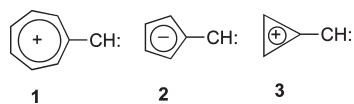
side of the electronic supply and-demand spectrum¹ and includes recent applications as ligands in organometallic catalysis of a number of useful synthetic processes,² of which

[†] This paper is dedicated to the memory of Yvonne Chiang Kresge
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C–C bond-forming cross-coupling reactions provide an example.^{3a} A very recent application of *N*-heterocyclic carbenes is their function as stabilizing electron-donating ligands in the formation of a metalloaromatic, octahedral array of six gallium atoms.^{3b} Protonation at the central carbon of a singlet carbene gives another important reactive intermediate, a carbenium ion. The ease of the reverse process, loss of a proton from a carbenium center, corresponds to the “ α -acidity” of the carbenium ion, a variant of the well established “ β -acidity” where loss of a proton furnishes an alkene. Factors affecting the stability of carbenium ions can also affect that of singlet carbenes, notably the electron-donating ability of attached groups.¹

In a previous study, experimental and computational work were combined to explore structural effects on the α -acidity of carbenium ions, including methyl⁺, other small alkyl⁺, benzyl⁺, and methoxylated carbocations.⁴ Equilibrium constants for hydrolysis of the carbocations (pK_R), hydration of the singlet carbenes (pK_{H_2O}), and the α -acidity of the carbocations (pK_a) appropriate to the aqueous phase were obtained. From a linear plot of pK_{H_2O} vs pK_R the effects of structural changes on carbene and carbocation stability were compared. Similarly, computed values for the hydride ion affinities of the carbocations (HIAs) and heats of hydrogenation of the singlet carbenes (ΔH_{HYDROG}) allowed the same comparison to be made for the gas phase. Although the slopes and intercepts of the two plots were quite different, the quality of the correlations was similar and both showed sharp deviations of the points for the methoxylated compounds, which indicated that the attached CH₃O group has a larger stabilizing effect on the carbene than on the carbocation compared with attached H, alkyl, and phenyl groups. We conjectured that this result is a general one for groups possessing an electron pair on the atom directly attached to the carbene or carbenium center. In this work, we look at all such row 2 and row 3 heteroatom substituents. To establish a baseline measure of electronic effects, we have extended our study to include 23 *meta*- and *para*-substituted phenylcarbenes and benzyl cations. Additionally, we examine three nonbenzenoid, aryl substituents: cycloheptatrienyl⁺, cyclopentadienyl[−], and cyclopropenyl⁺ furnishing carbenes 1–3.



We note at the outset the work of Geise and Hadad who reported a DFT computational study of the singlet–triplet gap for phenylcarbene and a variety of *ortho*-, *meta*-, and *para*-substituted phenylcarbenes.⁵ The same group has also examined substituent and solvent effects, experimentally and by computation, on the singlet–triplet gap for a series of phenylcarbomethoxycarbenes⁶ and 2-naphthylcarbomethoxycarbenes.⁷ Also relevant is a recent DFT study in

which steric factors affecting the singlet–triplet gap for mono- and diarylcarbenes were investigated.⁸

Methods and Results

All structures were built and optimized at HF/3-21 or HF/6-31G(d) levels using the MacSpartan Plus software package.⁹ Conformational preferences were established at these or higher levels, including G3MP2. All geometry optimizations were completed using the G3MP2 method. The GAUSSIAN 03 quantum mechanical package was used for all the higher level calculations.¹⁰ All structures reported here represent electronic energy minima except for structures identified as transition states, each of which has one imaginary frequency.

G3MP2 enthalpies and free energies at 298 K for the substituted phenyl compounds, in hartrees, are tabulated in the Supporting Information, Tables S1 (*meta* compounds) and S2 (*para* compounds). These tables also list the calculated point groups for all compounds. Reaction enthalpies and free energies are found in Tables 1 (*meta*) and 2 (*para*). The corresponding data for other sets, including the nonbenzenoid aryl compounds, are found in Table S3 and Table S4, and the heteroatom carbene data are in Table S4 and Table S5.

Substituted Phenyl Compounds: Geometries. In the carbene structures, the carbenic C–H bond is invariably coplanar with the ring to within 0.5°, usually to within 0.1°. It was necessary to investigate alternate conformations for a number of the carbenes because the rotational orientation of the substituent group relative to the carbenic C–H bond is a variable. For all of the *meta* carbenes, the C–H bond is directed away from the substituent. However, there are other rotational possibilities for some of the substituents. We report in the tables the results only for the most stable of the calculated conformers. Conformational preferences and other geometric features found by us agree well with those of Geise and Hadad.⁵ Conformational enthalpy differences are small, less than 0.2 kcal/mol.

The carbenic angle, $\Phi(\text{HCC})$, for the singlet carbenes is remarkably insensitive to the identity and position of the substituent, averaging $106.3^\circ \pm 0.04$ for 22 of the examples studied. For comparison geometries were also calculated for singlet methylene and previously reported aryl carbenes. Agreement with values in the literature was good; for example, we found the carbenic angle in ¹CH₂ to be 102.1° , whereas an experimental value of $\sim 102^\circ$ is reported.¹ Likewise, this angle in the triplet is almost invariant at $132.3 \pm 0.1^\circ$. The only exceptions are the anionic *m*- and *p*-oxy-substituted carbenes in which these angles are slightly smaller. Several other geometric parameters are systematically different between singlet and triplet carbene structures. For example, the carbenic C–H bond length in the singlets is almost constant at 1.112 Å, while for the triplets it is likewise almost constant, but shorter at 1.081 Å. The distance between the carbenic carbon and the aromatic

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TABLE 1. G3MP2 Enthalpies of Reaction for Meta-Substituted Phenylcarbenes and Benzyl Cations (kcal/mol)

substituent	substituent constants ^a			ΔH_{ST}^b	ΔH_{ACID}^c	HIA ^d	ΔH_{HYDROG}^e
	σ_α	σ_F	σ_{R+}				
O ⁻	NA	NA	NA	-8.2	359.0	-127.1	-87.2
NH ₂	-0.16	0.14	-0.52	1.53	266.4	-231.5	-98.
OH	-0.03	0.30	-0.38	1.70	260.3	-237.8	-99.1
SH	-0.55	0.28	-0.25	1.63	259.2	-239.4	-99.
CH ₃	-0.35	0.00	-0.08	1.63	262.6	-236.0	-99.6
H	0.00	0.00	0.00	2.13	259.9	-240.5	-99.4
F	0.13	0.44	-0.25	2.72	255.1	-244.6	-100.7
Cl	-0.43	0.45	-0.17	2.47	255.8	-243.9	-100.8
CHO	-0.46	0.31	0.00	2.24	254.0	-245.6	-100.6
CF ₃	-0.25	0.44	0.00	3.02	252.5	-247.9	-101.4
CN	-0.46	0.60	0.00	3.05	249.0	-252.1	-102.1
NO ₂	-0.26	0.65	0.00	3.38	248.6	-252.7	-102.4

^aGas-phase substituent constants for polarizability (α), polar (F), and electron-donating resonance (R+) effects: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. ^bEnthalpy difference between singlet and triplet carbenes; a positive value indicates the triplet is more stable. ^cEnthalpy of deprotonation of the benzylic cation forming the singlet carbene. ^dHydride ion affinity of the benzylic cation; addition of hydride forms the substituted toluene. ^eEnthalpy of hydrogenation of the singlet carbene to form the corresponding toluene.

TABLE 2. G3MP2 Enthalpies of Reaction for Para-Substituted Phenylcarbenes and Benzyl Cations (kcal/mol)

substituent	substituent constants ^a			ΔH_{ST}^b	ΔH_{ACID}^c	HIA ^d	ΔH_{HYDROG}^e
	σ_α	σ_F	σ_{R+}				
O ⁻	NA	NA	NA	-24.3	376.0	-87.5	-64.5
NH ₂	-0.16	0.14	-0.52	-4.05	280.9	-210.6	-92.5
OH	-0.03	0.30	-0.38	-1.70	269.6	-224.8	-95.5
SH	-0.55	0.28	-0.25	-0.04	269.7	-227.1	-97.8
CH ₃	-0.35	0.00	-0.08	0.78	265.6	-231.3	-98.0
CH ₂ F	-0.30	0.22	-0.03	1.5	261.5	-236.6	-99.1
H	0.00	0.00	0.00	2.13	259.9	-240.5	-99.4
F	0.13	0.44	-0.25	0.22	259.6	-237.5	-98.2
Cl	-0.43	0.45	-0.17	1.40	260.5	-237.4	-99.3
CHO	-0.46	0.31	0.00	4.52	254.3	-246.6	-101.9
CF ₃	-0.25	0.44	0.00	3.79	252.5	-249.0	-102.6
CN	-0.46	0.60	0.00	4.39	250.2	-251.2	-102.4
NO ₂	-0.26	0.65	0.00	4.98	248.4	-253.6	-103.0

^aGas-phase substituent constants for polarizability (α), polar (F), and electron-donating resonance (R+) effects: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. ^bEnthalpy difference between singlet and triplet carbenes; a positive value indicates the triplet is more stable. ^cEnthalpy of deprotonation of the benzylic cation forming the singlet carbene. ^dHydride ion affinity of the benzylic cation; addition of hydride forms the substituted toluene. ^eEnthalpy of hydrogenation of the singlet carbene to form the corresponding toluene.

ring shows almost no variation in the triplets, averaging 1.408 ± 0.002 Å, and is always longer in the singlets, ranging from 1.428 Å in the *p*-amino compound to 1.447 Å for the *p*-nitro carbene, consistent with the ability of the *para* substituent to act as a π -donor.⁵ In fact, this distance levels off at 1.447 Å for each of the substituents having a resonance substituent constant value, $\sigma_{R+} = 0.00$.¹¹ Again, the largest variations are found for the oxyanion substituent (O⁻): in the *p*-oxy singlet carbene this bond shortens to 1.395 Å. For the *meta*-singlet series a similar, but significantly smaller, trend is seen for this bond length except in the *m*-oxy triplet where it has lengthened to 1.455 Å. The gross differences between the C–H and C–C distances, singlet vs triplet, reported here can be ascribed to a greater amount of *s*-character in valences used by the triplet carbenic carbon. The trends observed by us are in good agreement with those found by Geise and Hadad.⁵

As for the benzyl cation and toluene sets, the bond between the ring carbon and the positive benzylic carbon in the cations is uniformly the shortest of all members of a set, especially for the good π -donors in the *para*-substituted cations. The range is not large, however, extending from 1.354 Å for the *p*-oxy

“cation” to 1.376 Å for the *m*-nitro cation. Of course, the *p*-oxybenzyl “cation” is actually a neutral compound, *p*-quinomethide. The C_{Ar}–CH₃ bond in the toluenes is the longest and is essentially constant at 1.505 Å.

With regard to C–C distances *within* the ring, those in the toluenes show the least alternation and serve as a reference by which to gauge the extent of bond length alternation in other compounds. Ring C–C distances in the benzylic cations show the most alternation, consistent with π -electron donation from the ring to the benzylic position, and most evident for the *p*-oxy and *p*-amino cations. Bond length alternation occurs in the carbenic structures too, and interestingly, these distances are consistently shorter and with slightly greater alternation in the triplet carbenes than in the singlets, presumably as a consequence of the interaction of unpaired spins with the aromatic π -system, an interaction which has been shown to reduce the aromatic ring current in the attached aryl groups.⁸

The Singlet–Triplet Gap, ΔH_{ST} : Comparisons with the Literature. The singlet–triplet enthalpy gaps are included in Tables 1 and 2. The trends are in qualitative agreement with those found by Geise and Hadad.⁵ A plot of our ΔH_{ST} against their ΔE_{ST} (B3LYP/6-311+G**//B3LYP/6-31G*) for the *meta*-substituted phenylcarbenes gives $\Delta E_{ST}(\text{GH}) =$

(11) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

$1.39\Delta H_{ST} + 2.89, r^2 = 0.955$. The point for the unsubstituted phenylcarbene lies off the correlation line established by the nine other substituents common to both studies. The *para*-substituted carbenes also show good agreement, with $\Delta E_{ST} = 1.09\Delta H_{ST} + 4.00$ ($r^2 = 0.960$ for 10 points). A gentle curvature in this plot is evident, and a quadratic fit is excellent with $r^2 = 0.993$. The most marked difference between the two studies is that the G3MP2 ΔH_{ST} values are uniformly somewhat more negative than the ΔE_{ST} values of Geise and Hadad. For example, $\Delta E_{ST} = 5.4$ kcal/mol for phenylcarbene and 0.7 kcal/mol for the *p*-amino derivative, while we find $\Delta H_{ST} = 2.1$ kcal/mol for phenylcarbene ($\Delta E_{ST} = 0.5$ kcal/mol) and $\Delta H_{ST} = -4.1$ kcal/mol ($\Delta E_{ST} = -4.9$ kcal/mol) for the *p*-amino substituent using the G3MP2 method. Woodcock et al. give an “empirically corrected” value, $\Delta H_{ST} = 2.75$ kcal/mol for phenylcarbene.⁸ Our *p*-hydroxy and sulfhydryl groups, like the *p*-amino, favor the singlet, albeit only slightly in the case of SH. The oxyanion substituent, not examined by Geise and Hadad, strongly favors the singlet with $\Delta H_{ST} = -24.3$ kcal/mol in the *para* position and -8.2 kcal/mol from the *meta* position.

In summary, beyond the fact that Geise and Hadad used electronic energy differences and we used enthalpy differences, the use of a different computational models results in a moderate negative shift in the ΔH_{ST} values calculated with the G3MP2 model. However, we reiterate that the qualitative trends are the same: electron-donating groups, especially the π -donors among *p*-substituents, stabilize the singlet more than the triplet state. These effects are further considered under substituent constant correlations below.

Substituent Constant Correlations, General. We have analyzed substituent effects on all four processes calculated in this study: ΔH_{ST} , ΔH_{ACID} , HIA, and ΔH_{HYDROG} . These processes are shown as Scheme 1.

In the analysis, we use the gas-phase substituent constants governing polarizability (σ_α), polar effects (σ_F), and π -electron donation by resonance (σ_{R+}) given by Hansch, Leo, and Taft.¹¹ Multiparameter correlations using these constants and based on eq 1 have proved useful in previous studies.^{4,13,14}

$$\Delta H = \rho_\alpha \sigma_\alpha + \rho_F \sigma_F + \rho_{R+} \sigma_{R+} \quad (1)$$

Such analyses allow the contributions of the different influences to be separated as indicated by the coefficients (ρ values) which are summarized in Table 3. For each correlation, a plot of the ΔH values predicted by the fit against those calculated by the G3MP2 method gave good agreement as indicated by near-unit slopes, by intercepts much smaller than the spread of data point values, as well as by near-unit r^2 values. In the *para* correlations, values for *p*-CH₂F and *p*-CHO were omitted as outliers. The CH₂F substituent has previously proved difficult to fit to computed values. The problem seems to lie with its σ_F value.¹⁵ We have

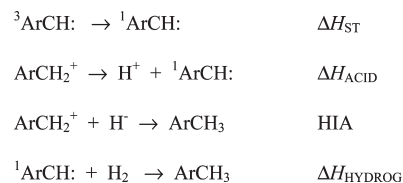
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(15) Calculations at the MP2/6-311+G** level on a series of carbocations, EWG-CH₂⁺, where EWG are electron withdrawing groups, shows that such cations are stabilized by bridging from a component of the EWG. Rotation of the CH₂⁺ unit to eliminate this interaction produces rotational transition states. The HIAs of these states are very well correlated by the σ_F constants of the EWGs with the exception of the CH₂F group.

SCHEME 1. Overview of Reactions



no explanation for the CHO group. However, it is important to note that even with inclusion of those points the r^2 values for the *para* compounds are quite respectable, ranging from 0.963 (for ΔH_{ST}) to 0.984 (for ΔH_{ACID}).

Substituted Phenyl Carbenes, ΔH_{ST} . Geise and Hadad plotted their calculated ΔE_{ST} values against solution phase σ_m values (*meta* substituents) and σ_p^+ values (*para* substituents).⁵ Good correlations were found with ρ values of 3.3 and 5.0, respectively, showing that both polar and resonance effects affect the singlet–triplet gap and that *para*-substituents have the greater effect. The results of our multiparameter fits for the *meta* and *para* sets are listed in Table 3.

In agreement with Geise and Hadad, we find that *para* substituents exert a strong resonance effect but also that polar effects are not negligible. For the *meta* substituents, both polar and resonance effects are important as they are in the original Hammett σ_m constants. The relative size of the polarizability sensitivity parameter in the *meta* correlation is surprisingly large; $\rho_\alpha = 0.95$, and constitutes 18% of the total effect. However, this could be a consequence of uncertainties arising from the very small range of calculated ΔH_{ST} (*meta*) values (see Table 1).

Substituted Phenyl Carbenes, ΔH_{ACID} . The acidity of a carbocation is measured by the ease with which it loses a proton from its α -carbon to form the singlet carbene; ΔH_{ACID} represents the calculated enthalpy change for this process.⁴ The results of the multiparameter fits of ΔH_{ACID} to eq 1 for *meta*- and *para*-substituted benzyl cations are given in Table 3.

It is noteworthy that in these correlations, as well as those for HIA (see below), polarizability has a significant influence, not as great as polar and resonance effects, but clearly important. This is especially true for the *para* substituents because the positive charge, formally on the benzylic carbon in the carbocation, can be relayed to the *para* position, proximate to the attached groups. A corollary, reinforced by the comparatively large negative ρ_{R+} values for ΔH_{ACID} and HIA, is that resonance effects are more important for the (reactant) carbocations than for the (product) singlet carbenes.

Substituted Phenylcarbenes, HIA. Table 3 also contains the results of the three-parameter substituent effect correlations for the hydride ion affinities of the *meta*- and *para*-substituted arylcarbenium ions. Sensitivity to polar and resonance effects are large and comparable for the *meta* HIA values, as they were for ΔH_{ACID} . For the *para* HIA values the absolute values of ρ are larger and the resonance effect is magnified as addition of a hydride ion not only neutralizes the cation but removes possibilities for conjugation between the substituent and the reaction center. As mentioned above for the *para* ΔH_{ACID} set, polarizability plays a relatively small but significant role in

TABLE 3. Summary of substituent effects on ΔH_{ST} , ΔH_{ACID} , HIA, and ΔH_{HYDROG} for arylcarbenes and their conjugate acid benzylic cations.^a

reaction	ρ_{α}	ρ_F	ρ_{R+}	n^b	slope, intercept, r^2
ΔH_{ST} (<i>meta</i>)	0.95	2.23	1.98	11	0.94, 0.14, 0.945
ΔH_{ST} (<i>para</i>)	0.08	3.91	13.27	10	1.00, 0.03, 0.995
ΔH_{ACID} (<i>meta</i>)	-1.89	-18.92	-16.51	11	0.99, 3.25, 0.990
ΔH_{ACID} (<i>para</i>)	-8.37	-21.94	-43.03	10	1.00, 0.75, 0.998
HIA (<i>meta</i>)	-3.75	-20.76	-22.28	11	0.98, -4.09, 0.990
HIA (<i>para</i>)	-10.07	-25.05	-60.78	10	1.00, 0.11, 0.999
ΔH_{HYDROG} (<i>meta</i>)	0.13	-4.28	-2.88	11	0.97, -3.18, 0.951
ΔH_{HYDROG} (<i>para</i>)	0.10	-5.64	-14.66	10	0.99, -0.98, 0.990

^aGas-phase substituent constants for polarizability (α), polar (F), and resonance (R+) effects taken from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. Slope, intercept, and r^2 values are for the plots of ΔH values predicted by the multiparameter substituent effect analysis, $\Delta H(\text{fit})$, y axis, vs those calculated by the G3MP2 method, $\Delta H(\text{G3})$, x axis. ^bNumber of data points.

enthalpies of hydride addition to *p*-substituted benzylic cations.

Substituted Phenyl Carbenes, ΔH_{HYDROG} . Lastly, Table 3 shows the substituent effects on the heats of hydrogenation of the singlet carbenes. For both *meta* and *para* compounds polarizability is insignificant since no charge change occurs upon hydrogenation of the singlet carbene to the methylarene. For the same reason, the other ρ constants are relatively small, somewhat resembling in absolute magnitude those for the singlet–triplet gaps. They are, however, opposite in sign because electron donors and acceptors have opposite effects on the stability of the singlet carbenes relative to the reaction products in the two cases. Donors cause ΔH_{HYDROG} to be less exothermic (by stabilizing the singlet carbene), while electron-withdrawing groups increase the singlet–triplet gap, in favor of the triplet, by selectively destabilizing the singlet carbene.⁵

Other Arylcarbenes. The study was extended to a series of nonbenzenoid arylcarbenes, the associated protonated species, and the products of hydrogenation of the singlet carbenes. Three nonbenzenoid aryl groups were considered, cycloheptatrienyl⁺, cyclopentadienyl⁻, and cyclopropenyl⁺. Calculated structures for the singlet and triplet carbenes are shown below in Figure 1. Reaction enthalpies are given in Table 4. In the case of Ar = cycloheptatrienyl⁺ and cyclopropenyl⁺, the carbenes and their hydrogenation products are cations, while the protonated carbenes are dications. For Ar = cyclopentadienyl⁻ the carbene and its hydrogenation product are anions, while the protonated singlet carbene is a neutral, fulvene. Cyclopropenylcarbene⁺, together with other C₃H₃⁺ isomers, has been implicated in computations related to mass spectrometric studies.^{16,17} No substituent correlations were possible with these carbenes, but as will be seen here (and in the Supporting Information, Table S3), some interesting and unusual features, both geometric and energetic, were found.

Heteroatom Substituted Carbenes. Calculations were also carried out for carbenes substituted with heteroatoms (X-CH), their conjugate acids (carbenium ions, X-CH₂⁺), and their hydrogenation products (X-CH₃), for X = NH₂, OCH₃, F, PH₂, SCH₃, and Cl. Two disubstituted carbenes, XY-C, where X = OCH₃, Y = CH₃, and X = Y = OCH₃, were also included.⁴ The nitrosocarbene O=N-CH is a special case, discussed below. For these carbenes, multiparameter substituent constant correlations were carried out on the four processes, ΔH_{ST} , ΔH_{ACID} , HIA, and ΔH_{HYDROG} , for seven

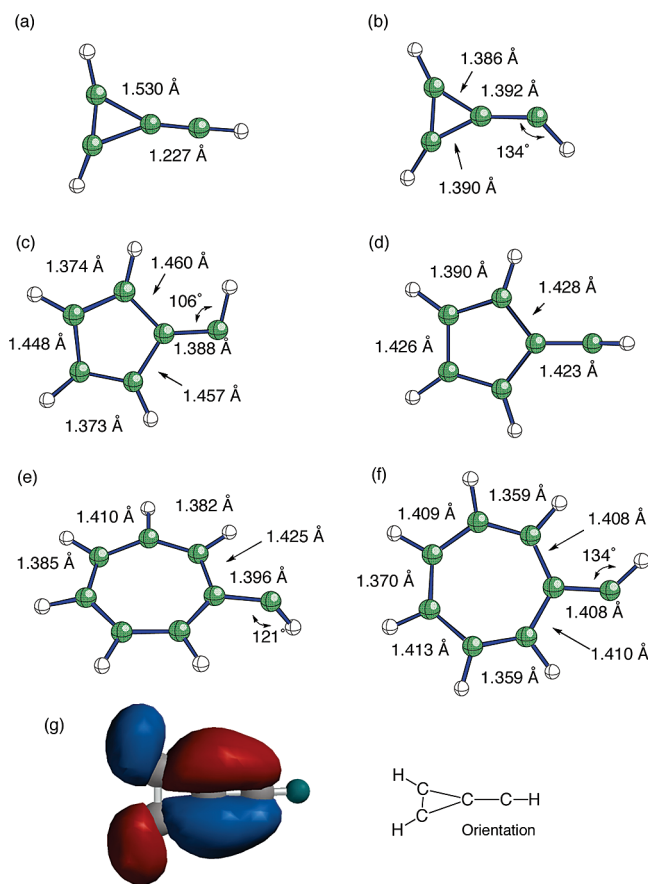


FIGURE 1. MP2/6-31G(d) structures for the singlet (left side) and triplet (right side) states of (a) and (b) cyclopropenylcarbene⁺, (c) and (d) cyclopentadienylcarbene⁻, and (e) and (f) cycloheptatrienylcarbene⁺. Structure (g) shows the HOMO - 1 for singlet cyclopropenylcarbene⁺.

of the heteroatom systems (relative to hydrogen) using the ΔH values in Table 5. The calculated values are recorded in Table 6. No substituent constant data are available for PH₂, and as will be discussed, the nitroso example completely contradicts expectations from its substituent constant values.

The correlations between the G3MP2-computed and three-parameter fit values are not as good as those for the aryl compounds shown in Table 3. Alternate sets of coefficients in which ρ values were varied by up to 15% gave correlations of similar quality. A probable cause of the poorer fit is that the substituent constants were evaluated for cases in which the substituents were remote from the reaction centers¹¹ rather than directly attached as in the present case.

(16) Schröder, D.; Loos, J.; Schwarz, H.; Thissen, R.; Roithova, J.; Herman, Z. *Int. J. Mass Spectrom.* **2003**, *230*, 113.

(17) Anand, S.; Schlegel, H. B. *J. Phys. Chem. A* **2005**, *109*, 11551.

TABLE 4. G3MP2 Enthalpies of Reaction and Activation for Reactions of Aryl Carbenes and Related Species and the Corresponding Carbocations (kcal/mol)

R in R-CH	ΔH_{ST}^a	ΔH_{ACID}^b	HIA ^c	ΔH_{HYDROG}^d	ΔH^e
phenyl	2.13	259.9	-240.5	-99.4	45.4 ^e
cycloheptatrienyl ⁺ (tropyli ⁺ , Tr ⁺)	9.2	137.2	-369.9	-108.2	22.6 ^e
cyclopentadienyl ⁻ (C ₅ H ₅ ⁻ , Cp ⁻)	-26.4	388.7	-70.0	-59.8	91.8
cyclopropenyl ⁺ (Cypro ⁺)	-20.7	53.4	-428.7	-83.2	14.7 ^f
cyclopropyl	-6.5	252.9	-241.2	-95.1	15.4 ^g , 31.2 ^h
cyclohexa-2,4-dienylidene ⁱ	3.2	267.3	-215.0	-83.4	-1.5 ^j
cyclohexa-2,5-dienylidene ^k	3.2	269.5	-215.1	-85.7	
vinyl ^l	8.2	242.8	-256.1	-100.1	7.0 ^m

^aEnthalpy difference between singlet and triplet carbenes; a positive value indicates the triplet is more stable. ^bEnthalpy of deprotonation of the cation forming the singlet carbene. ^cHydride ion affinity of the cation; addition of hydride forms the substituted toluene or other hydrocarbon. ^dEnthalpy of hydrogenation of the singlet carbene to form the corresponding toluene or other hydrocarbon. ^eEnthalpy of activation for rotation of the exocyclic CH₂ group to a position perpendicular to the ring plane; $\nu = 1031\text{ cm}^{-1}$ for Ar = phenyl, 591 cm^{-1} for tropyli⁺, 346 cm^{-1} for cyclopentadienyl⁻. ^fIn this case the enthalpy of activation is for rotation of the exocyclic CH₂ group from the more stable perpendicular conformation to the less stable position, coplanar with the ring; $\nu = 325\text{ cm}^{-1}$. ^gEnthalpy of activation for rotation of the exocyclic carbene CH group out of the bisected conformation; $\nu = 479\text{ cm}^{-1}$. ^hEnthalpy of activation for rotation of the exocyclic carbocation CH₂ group out of the bisected conformation; $\nu = 660\text{ cm}^{-1}$. ⁱFor singlet cyclohexa-2,4-dienylidene the carbocation is the benzenonium ion and the hydrogenation product is cyclohexa-1,3-diene. ^jEnthalpy of activation for the rearrangement of cyclohexa-2,4-dienylidene to benzene. The reaction enthalpy is -91.1 kcal/mol. ^kFor singlet cyclohexa-2,5-dienylidene the carbocation is the benzenonium ion, and the hydrogenation product is cyclohexa-1,4-diene. Isomerization of the 2,4-carbene to its 2,5-isomer has $\Delta H = 2.2\text{ kcal/mol}$. The 2,5-isomer isomerizes to cyclohexa-1,2,4-triene with $\Delta H = -17.6\text{ kcal/mol}$. ^lThe anti conformation of the triplet carbene is more stable than the syn by 0.3 kcal/mol. ^mEnthalpy of activation for rotation of the carbene CH unit about the vinyl unit in the anti conformer of the singlet; $\nu = 412\text{ cm}^{-1}$.

TABLE 5. G3MP2 Enthalpies of Deprotonation (ΔH_{ACID}) and HIA Values for Some Heterosubstituted Carbocations. Singlet-triplet Gaps (ΔH_{ST}) and Enthalpies of Hydrogenation (ΔH_{HYDROG}) for the Corresponding Carbenes

carbocation, X-CH ₂ ⁺	substituent constants ^a			ΔH_{ACID}	HIA	ΔH_{ST}	ΔH_{HYDROG}
	σ_α	σ_F	σ_{R+}				
H ^b	0	0	0	205.2	-314.5	9.4	-118.1
NH ₂	-0.16	0.14	-0.52	241.9	-217.1	-34.5	-60.0
OCH ₃ ^b	-0.17	0.25	-0.42	232.2	-238.9	-28.1	-70.2
OCH ₃ , CH ₃ ^{b,c}	-0.52	0.25	-0.50	242.5	-221.1	-32.7	-64.6
OCH ₃ , OCH ₃ ^{b,d}	-0.34	0.50	-0.84	235.6	-206.2	-59.8	-40.8
F	0.13	0.44	-0.25	199.1	-289.5	-14.6	-89.6
SiH ₃	NA	NA	NA	NA ^e	NA ^e	18.1	-117.4
PH ₂	NA	NA	NA	233.5	-249.3	-13.4	-83.9
SCH ₃	-0.68	0.25	-0.27	234.7	-233.9	-24.9	-69.7
Cl	-0.43	0.45	-0.17	212.9	-279.7	-6.9	-93.7
NO ^f	-0.25	0.41	~0.00	164.8	-255.9	-60.4	-21.7

^aSee ref 11. ^bSee ref 4. ^cThe carbocation is methoxymethylcarbenium ion; the listed substituent constants are the sums of those for the methoxy and methyl groups. ^dThis carbocation is dimethoxycarbenium ion; the listed substituted constants are the sum for two methoxy groups. ^eSilylmethyl cation, H₃Si-CH₂⁺, rearranges to methylsilyl cation, H₃C-SiH₂⁺ upon optimization. There are no listed substituent constants for the silyl group. Those for the trimethylsilyl group suggest that both polar and resonance effects are small; see ref 11. ^fThe singlet carbene is actually hydrogen cyanide N-oxide, H-C≡N-O, and the carbocation is best pictured as CH₂=N⁺=O.

TABLE 6. Summary of Substituent Effects on ΔH_{ST} , ΔH_{ACID} , HIA, and ΔH_{HYDROG} for Heteroatom Carbenes and Their Conjugate Acid Cations^a

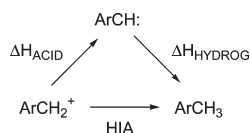
reaction	ρ_α	ρ_F	ρ_{R+}	n^b	slope, intercept, r^2
ΔH_{ST}	8.5	-3.0	75.8	8	0.98, -0.50, 0.978
ΔH_{ACID}	-32.2	-51.3	-53.6	8	0.94, 14.57, 0.936
HIA	-52.6	-51.6	-136.3	8	0.94, -14.89, 0.940
ΔH_{HYDROG}	-18.8	-2.6	-83.9	8	0.95, -4.00, 0.948

^aGas-phase substituent constants for polarizability (α), polar (F), and resonance (R+) effects taken from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. Slope, intercept, and r^2 values are for the plots of ΔH values predicted by the multiparameter substituent effect analysis, $\Delta H(\text{fit})$, y axis, vs those calculated by the G3MP2 method, $\Delta H(\text{G3})$, x axis. Good agreement is indicated by near-unit slopes, by intercepts much smaller than the spread of data point values, as well as by near-unit r^2 values. We estimate the ρ values to be accurate to within 15%. ^bNumber of data points.

In our case, it is reasonable to expect that the different types of interaction mechanisms, e.g., polar and resonance, are not completely independent, but influence each other. Note, for example, the negative ρ_F value for ΔH_{ST} . This seems to suggest that electron-withdrawing groups reduce ΔH_{ST}

contrary to experimental evidence. Fortunately, this number is a small one, its value and sign determined by the requirement of the fit, and in any case, it is overwhelmed by the resonance effect, diminishing its importance. Aside from this observation, the ρ values obtained are qualitatively sensible in

SCHEME 2



several respects. Their absolute magnitudes are large, reflecting the proximity of the substituent groups to the reaction centers, unmediated by a benzene ring.

Likewise the polarizability contributions are larger than those for the aryl systems, again a consequence of proximity. These contributions are especially exalted for ΔH_{ACID} and HIA, reactions in which ions are involved. Also, the contribution of polar effects are small for ΔH_{ST} and ΔH_{HYDROG} but much larger for the ionogenic reactions, as they should be. Finally, the slope, intercept, and r^2 values are satisfactory, allowing a modest degree of predictive power.

Discussion

The aim of this study was to examine the influence of wide variations in the structure of carbenes on their singlet–triplet energy gap (ΔH_{ST}) as well as on their stability and basicity, as measured by heats of hydrogenation (ΔH_{HYDROG}) and protonation ($-\Delta H_{\text{ACID}}$). As shown in Scheme 2, the latter two quantities may be combined in a thermodynamic cycle with the hydride ion affinity of the carbocation resulting from protonation of the carbene.

As described above, there is a satisfactory consistency between the singlet–triplet energy gaps calculated for substituted phenylcarbenes by G3MP2 methods in this work and by a high level DFT method in the literature.⁵ Moreover, we find excellent agreement between calculated G3MP2 HIA values and experimental HIAs reported for carbocations considered in this study.¹⁸ This gives grounds for confidence in further calculations focused on singlet carbenes and carbenium ions. Of principal interest here are carbenes substituted by heteroatoms or positively charged unsaturated groups such as tropylium. The unusual character of these carbenes may be assessed by comparison with those of the more straightforward reference group comprised of *meta*- and *para*-substituted phenylcarbenes.

In previous work, we pointed out that hydride ion affinities of carbocations and heats of hydrogenation of the corresponding singlet carbenes allow direct comparison of structural effects on the stabilities of the cations and the carbenes.⁴ A plot of values of ΔH_{HYDROG} against HIA for a number of mainly alkyl carbenes was found to be linear. The plot, updated to include cyclohexa-2,4- and cyclohexa-2,5-dienylidenes, vinylcarbene, and cyclopropylcarbene, is shown below in Figure 4 and has the slope, intercept, and correlation coefficient shown in eq 2. The correlation is good, indicating that structural changes affect the stabilities of the carbocation and singlet carbene in qualitatively

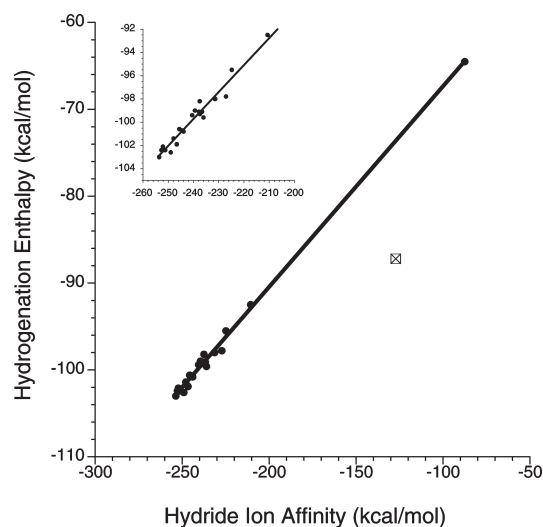


FIGURE 2. Plot of hydride ion affinity (HIA) for *meta*- and *para*-substituted benzylic cations vs ΔH_{HYDROG} , the enthalpies of hydrogenation for the corresponding singlet arylcarbenes. See eq 2. The outlier is *m*-O[−] and is not used in the fit. The inset is an expansion of the data in the lower left quadrant.

similar ways, albeit with greater sensitivity on the part of the carbocations.

$$\Delta H_{\text{HYDROG}} = 0.327\text{HIA} - 16.2, r^2 = 0.961, n = 9 \quad (2)$$

Although eq 2 is based mainly on alkyl carbenes, it also accommodates phenyl and diphenyl carbenes. The substituted phenylcarbenes of the present study, however, fit this correlation only approximately. They are better described by their own fit shown as Figure 2 and eq 3.

$$\Delta H_{\text{HYDROG}} = 0.231\text{HIA} - 44.3, r^2 = 0.995, n = 23 \quad (3)$$

The fit to eq 3 includes *meta* and *para* substituents in the phenyl group, as well as the point for the oxyanion substituent, O[−], in the *para* position, even though the benzylic “cation” in this case is actually the neutral *p*-quinomethide. The range of HIA values covered by the correlation is large: 46 kcal/mol without the *p*-O[−] substituent and 166 kcal/mol with it. The outlying point is for the *meta*-oxyanion substituent, which is seen to stabilize the benzylic zwitterion proportionately more than the singlet carbene. The negative deviation of this point is opposite to that found for the methoxycarbenes and represents the dominance of an electrostatic polar stabilization of the zwitterion and a relative lack of π -donation to the central carbon in either the zwitterion or the carbene. The slope and intercept of the plot in Figure 2 are virtually identical with a similar plot omitting the *p*-oxyanion point and with a plot using *only* data for *p*-substituents. The plot obtained from the *meta* points alone is relatively imprecise, possibly because the range of values, especially for ΔH_{HYDROG} , is very small.

Addition of the three nonbenzenoid aryl groups, cycloheptatrienyl⁺ (tropylium⁺), cyclopentadienyl[−], and cyclopropenyl⁺ (giving carbene structures 1–3) to Figure 2 is shown in Figure 3.

The cyclopentadienyl[−] point accurately fits the correlation line, despite the fact that the conjugate acid of cyclopentadienylcarbene[−] is not really a carbocation, but the neutral fulvene. It lies to the uppermost right of the Figure just above the point for the *p*-oxyanion substituent. These

(18) $\text{HIA}(\text{G3}) = 0.998 \text{HIA}(\text{exp}) - 0.29, r^2 = 0.999$. Experimental values were taken or calculated from data given in: Bartmess, J. E. In *NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology (http://webbook.nist.gov): Gaithersburg, MD, 2003.

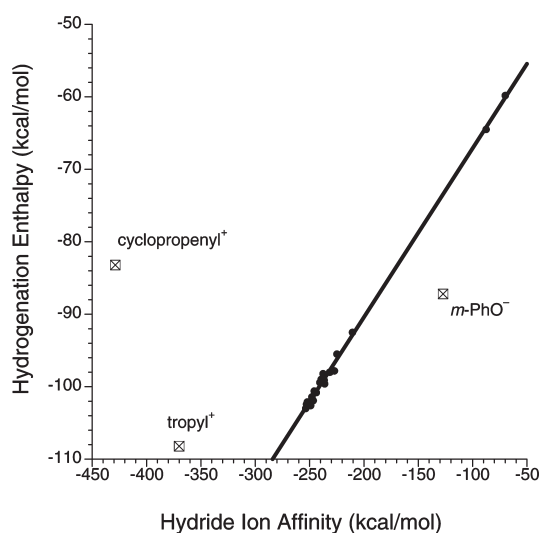


FIGURE 3. Plot of hydride ion affinity (HIA) for *meta*- and *para*-substituted benzylic cations and cyclopentadienyl-CH₂ (fulvene) vs ΔH_{HYDROG} , the enthalpies of hydrogenation for the corresponding singlet arylcarbenes. See eq 3. The outlying substituents are cycloheptatrienyl⁺, cyclopropenyl⁺, and *m*-oxyphenyl⁻.

two examples underline the point that aside from a relatively small polarizability contribution to the stabilization of the carbocations, π -electron donors can be expected to affect carbocations and singlet carbenes by very similar interaction mechanisms.

The outlying substituents not fitting the correlation line in Figure 3 are *m*-oxyphenyl⁻ (below the line), tropyli⁺ (lower left), and cyclopropenyl⁺ (middle left). The tropyli⁺ group behaves as might be expected from its electron-withdrawing, positive charge. The carbocation in this case is doubly charged, and the effect is to destabilize the cation (tropyli-CH₂)²⁺ even more than the singly charged singlet carbene.

It is noteworthy that the singlet–triplet gap for the tropyli⁺-substituted carbene, ΔH_{ST} , is 9.2 kcal/mol. Thus, it adheres to the generalization that electron withdrawing groups destabilize the singlet carbene more than they do the triplet.⁵ The singlet also shows an interesting geometric feature, considered possible by Geise and Hadad,⁵ namely, that the carbenic unit is perpendicular to the ring plane rather than coplanar with it. They suggested that electron-withdrawing groups might potentially favor this geometry but did not observe it in their study.

The cyclopropenyl⁺ point falls even further from the correlation line than the point for tropyli⁺. That is, this group either stabilizes the singlet carbene (C₃H₂-CH:)⁺ more than the corresponding dication (C₃H₂-CH₂)²⁺ or the dication is more destabilized (or both). In fact, the singlet seems to be stabilized. For one thing, the singlet–triplet gap for cyclopropenylcarbene⁺ favors the singlet, and by an unusually large amount: $\Delta H_{\text{ST}} = -20.7$ kcal/mol! This result does not appear to arise from a problem with the triplet, which has a planar C_s geometry with a carbenic H–C–C angle of 134.0°, the typical outcome for the triplets calculated in this study. Rather the singlet seems to be unusually stable. It has C_{2v} symmetry with a linear carbenic angle. The carbenic C–H bond is very short at 1.076 Å as is the exocyclic C=C bond at only 1.227 Å. The C=C bond within the ring is also short at 1.271 Å. The H–C=C angles

in the ring are spread to 163.3° rather than the ~150° angle expected by comparison with its hydrogenation product, methylcyclopropenyl⁺. In the geometric sense it has some of the character of both acetylene and a vinyl cation. In fact the n_pa charge distribution shows slightly more positive charge on the exocyclic C–H fragment (+0.51) than in the ring.

A final geometric feature also indicates something special about singlet cyclopropenylcarbene⁺. The two C–C bonds in the ring are highly elongated: 1.530 Å compared with 1.376 Å in methylcyclopropenyl⁺. This suggests that these two “bent” bonds interact with an empty p orbital on the carbenic carbon while the filled p orbital on that carbon back-bonds to the ring carbon. Visualization of the HOMO –1 orbital confirms the presence of this interaction; see Figure 1. Further support comes from calculations on singlet cyclopropylcarbene and cyclopropylcarbinyl cation (bisected forms). Like the cation,¹⁹ this carbene also shows the interaction of bent, elongated C–C ring bonds with the carbene center. Bond elongation (relative to distances in methylcyclopropane) is very small in the triplet and absent in the perpendicular form of the cation, a rotational transition state.²⁰

The doubly charged cyclopropenyl system, (C₃H₂-CH₂)²⁺, also shows some unusual features. The more stable form here, as for the carbene, is the bisected form, which is 14.7 kcal/mol more stable than the planar form (a rotational transition state). Relative to the planar transition state, the bisected ground state has a considerably shorter exocyclic C–C bond, 1.393 vs 1.473 Å, and longer ring C–C bonds at 1.402 vs 1.373 Å. These features indicate the availability of some stabilization through bent-bond interactions for this species as well.

It is appropriate to ask why the tropyli⁺ and cyclopropenyl⁺ carbenes are different: the triplet is favored for tropyli⁺ but the singlet for cyclopropenyl⁺. Additionally, the conjugate acid of the latter (C₃H₂-CH₂)²⁺ favors the bisected form while the planar conformation is preferred for (cycloheptatrienyl-CH₂)²⁺. Why doesn't the tropyli⁺ group offer the apparent advantages to the singlet that cyclopropenyl⁺ does? We suggest that participation by the ring C–C bonds, described above for the 3-membered ring, is absent or greatly diminished in the 7-membered ring, first of all because these bonds are not bent. In fact, the bonds are slightly longer in the singlet than in the triplet (or in methyltropylium⁺) but not by nearly as much as they are in the cyclopropenyl⁺ example. A natural bond order (NBO) analysis also suggests back-bonding for singlet cyclopropylcarbene⁺. This is indicated by a depletion in electron occupancy of the interacting bonds and also unusual hybridizations (i.e., sp hybridization in the ring-carbene bond and sp^{1.54} hybridization in the short ring bond). These features

(19) Good accounts of the large amount of experimental and computational work on the C₄H₇⁺ system are found in: Prakash, G. K. S.; Schleyer, P. v. R., Eds. *Stable Carbocation Chemistry*; Wiley-Interscience: New York, 1997. See: Saunders, M.; Jiménez-Vásquez, H. A., Chapter 9, pp 304–306. Sunko, D. E., Chapter 11, pp 370–372. (c) Myhre, P. C.; Yannoni, C. S., Chapter 12, pp 422–425.

(20) In methylcyclopropane, the relevant C–C bond lengths are 1.502 Å. In bisected singlet cyclopropylcarbene (the *anti* form is slightly favored) they are 1.566 Å. For the triplet they are 1.513 and 1.520, and in the singlet rotational transition state which lies 15.4 kcal/mol above the bisected form, they are 1.496 and 1.498 Å in length.

are absent in cycloheptatrienylcarbene⁺, for which it might also be true that such participation would compromise the aromaticity of the tropylium cation moiety more than it does the cyclopropenyl cation moiety. In summary, the balance of stabilizing and destabilizing forces is tipped differently in the two systems.

Heteroatom Carbenes. Carbenium ion centers directly attached to electronegative heteroatoms having, formally, a nonbonding valence electron pair are stabilized by the extra bonding resulting from sharing that pair with the carbon. Similarly, substituted carbenes (“heterocarbenes”) are also stabilized by this interaction, the singlet more than the triplet, leading to negative singlet–triplet gaps, the singlet being strongly favored.¹ A number of these carbenes have been isolated in recent years, and some have found use as ligands in organometallic-catalyzed reactions.^{2,3a} A recent paper by Amyes and co-workers reports quantitative experimental and calculated (DFT) results on the protonation at C-2 of several N-substituted heterocyclic carbenes (e.g., imidazol-2-ylidenes) giving the corresponding heterocyclic cations.²¹ Their paper includes rates of proton exchange and aqueous phase pK_a values as well as a discussion of substituent effects.

In previous work, we noted that compared with systems in which the carbene or carbenium centers are attached only to H, alkyl or phenyl groups, the attachment of methoxy groups provides extra stabilization to the singlet carbenes relative to the carbenium ions.⁴ This result was revealed by the HIA vs ΔH_{HYDROG} plot defined by the nonheteroatom points, eq 1, from which the methoxy points deviated substantially. It was inferred that this would be a general result since direct attachment of electronegative atoms, e.g., O, N, F, to the central carbon can stabilize both a carbocation and a carbene by lone-pair π -donation, but that the polar effect, while stabilizing for carbenes, is destabilizing for carbocations.^{4,12} We have checked this inference by extending the calculations to carbenes with substituents F, Cl, SCH_3 , NH_2 , and PH. Values of hydrogenation energies, ΔH_{HYDROG} , are plotted against hydride affinities, HIA, in Figure 4, which also includes the correlation for alkyl and aryl carbenes and the previously studied methoxy and dimethoxy carbenes.

It can be seen that all nine heteroatom points lie well above the HIA vs ΔH_{HYDROG} plot for nonaryl-substituted carbenes, with the dimethoxy and nitroso points far from the others. Without the latter two, the heteroatom groups define their own correlation shown in Figure 4 and described by eq 4. The deviation for dimethoxy is likely related to a greater impact from the saturation of resonance stabilization in the carbenium ion than the carbene. Nitroso is a special case and is discussed below.

$$\Delta H_{\text{HYDROG}}(\text{hetero}) = 0.444\text{HIA} + 33.7r^2 = 0.904 \quad (4)$$

Our earlier conjecture, that heteroatom carbenes have a measure of stability not available to their conjugate acid carbenium ions, is now confirmed, not only for second-row heteroatoms but for those in the third row as well. However, even among the heteroatom carbenes the behavior of the attached nitroso group stands out. It stabilizes the

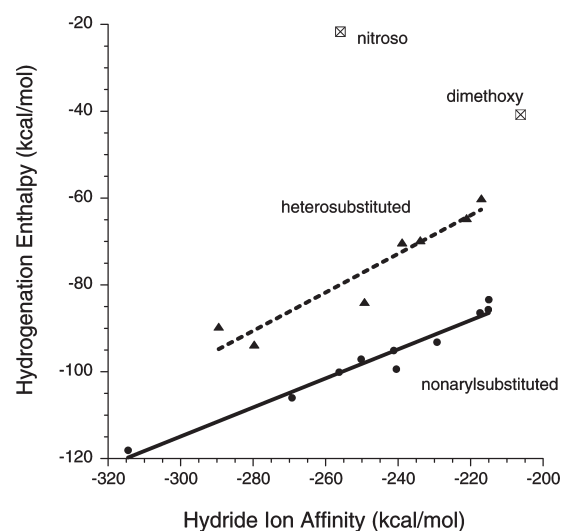


FIGURE 4. Plots of hydride ion affinity (HIA) for nonarylsubstituted carbocations (circles; see eq 2) and heterosubstituted carbocations (triangles) vs ΔH_{HYDROG} , the enthalpies of hydrogenation for the corresponding singlet carbenes. The nitroso and dimethoxy points are excluded from the fits.

carbenium ion, and particularly the carbene unusually well, especially considering its usual role as an electron-withdrawing group.¹¹ Geometric and other features for the C_2 carbocation suggest that it is best formulated as having strong π -participation from the lone pair on the nitrogen, that is, it resembles $(\text{CH}_2=\text{N}=\text{O})^+$ with a formal positive charge on nitrogen. The singlet–triplet gap is extraordinarily large, $\Delta H_{\text{ST}} = -60.4$ kcal/mol! The singlet is linear with a very short CN bond, 1.184 Å. It is, in fact, the simplest of the nitrile oxides, hydrogen cyanide *N*-oxide ($\text{H}-\text{C}\equiv\text{N}-\text{O}$). It is not really a carbene at all, but represents an extreme case of strong π donation from the nitrogen combined with strong back-bonding from carbon.

A closer look at the effect of attached heteroatoms on carbene and carbenium ion stability is afforded by calculated atomic orbital occupancies. Table 7 lists the natural atomic orbital occupancies (NAOO) in the formally unoccupied valence 2p orbitals of the central carbons of selected singlet carbenes and carbenium ions. These occupancies are complex, and determined by several factors, including the electronegativities and polarizabilities of the atoms attached to the carbene or carbenium centers. The requirement for electron donation is largely a consequence of the charge on the central carbon, with greater demand in the case of the carbenium ion. But the ratio of occupancy for the cation to that for the carbene is not constant; hence, a linear relationship between the two is not found.

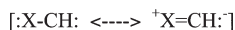
Several qualitative points can be made based on the data in Table 7. Thus, the heteroatoms are more proficient at π -donation toward carbenic centers than toward carbenium ions, particularly in the special case of nitroso. Among the other groups, those attached by atoms in the third row are better than those directly above them in the second row. With regard to valence bond depictions of these carbenes two principal structures are considered (4). With orbital occupancies greater than 0.5 one may regard the zwitterionic structure to be the better representation. Such is the case for

(21) Amyes, T. L.; Diver, S. R.; Richard, J. P.; Rivas, F. M.; Toth, K. J. *Am. Chem. Soc.* **2004**, *126*, 4366.

TABLE 7. Natural Atomic Orbital Occupancies (NAOO) at the Central Carbon for Selected Singlet Carbenes and Carbenium Ions^a

X, Y in carbene, XY-C	carbene	cation
nonheteroatom groups		
H, H	0.01	0.01
CH ₃ , H	0.14	NA ^b
CH ₃ , CH ₃	0.13	0.35
Ph, H	0.23	0.61
heteroatom groups		
NH ₂ , H	0.42	0.90
OCH ₃ , H	0.35	0.53
OCH ₃ , CH ₃	0.37	0.56
OCH ₃ , OCH ₃	0.49	0.68
F, H	0.22	0.63
SiH ₃	0.08	0.06 ^c
PH ₂ , H	0.73	0.91
SCH ₃ , H	0.52	0.79
Cl, H	0.28	0.54
NO, H	1.02, 1.02, 1.02 ^d	1.264 ^d

X = PH₂, SCH₃, and (almost) for NH₂. Attached OCH₃ does not make this mark.



4

In both the second and third rows the less electronegative elements deliver more π -electron density. The impact of attached heteroatoms on carbenium ion stability is determined by a combination of π -donation, σ -withdrawal, and electrostatics,²² and this work demonstrates that a similar combination of effects influences the stability of the singlet carbene. It is therefore important not to take the degree of double-bond character too literally as a measure of the stabilization imparted by π -participation because second-row X=C bonds are stronger than those from the third row and the destabilizing/stabilizing impact of σ -withdrawal or donation varies considerably for different heteroatoms.

Conclusions

Substituted phenylcarbenes, benzyl cations, and their close relatives comprise a coherent family of compounds within which electronic effects on carbene and carbenium ion stabilities can be systematically compared. This study shows, in agreement with earlier studies,^{5–7} that electron-withdrawing ring substituents increase the singlet–triplet gap, ΔH_{ST} . Electron donors, especially π -donors in the *para* position, decrease the gap, actually favoring the singlet in the case of the strongest π -donors: *p*-O[−], *p*-NH₂, *p*-OH, and (barely) *p*-SH at the G3MP2 level of computation. They do so by stabilizing the singlet more than the triplet.⁵

Substituent effects are very similar on the stabilities of aryl carbenes and their protonated singlets, that is, the benzylic cations. This is best shown by the linearity of a plot of the

hydride ion affinities, HIA, of these cations against the enthalpies of hydrogenation, ΔH_{HYDROG} , of the singlet carbenes. This plot covers 166 kcal/mol on the HIA axis. Noteworthy is the excellent fit for *p*-O[−] even though the change in charge from carbene to protonated carbene is −1 to 0 in this instance. The *m*-O[−], substituent, however stabilizes the protonated carbene, a zwitterion, disproportionately more than the carbene. The lack of π -donation from the *meta* position leaves the carbene without much help, but for the zwitterionic conjugate acid, a strong, stabilizing, electrostatic effect exists.

Three nonbenzenoid aryl groups were also evaluated: cycloheptatrienyl⁺, cyclopentadienyl[−], and cyclopropenyl⁺. The cationic substituents cause substantial departure from the HIA vs ΔH_{HYDROG} correlation line in the sense that they destabilize the conjugate acids (dications) more than the carbenes. Additionally, the singlet cyclopropenylcarbene⁺ is more stable than the triplet state by $\Delta H_{ST} = -20.7$ kcal/mol! The C_{2v} singlet is stabilized by electron donation from the ring's bent bonds, and further stabilized by back bonding from a filled carbene orbital to the ring. By contrast the cyclopentadienyl[−] point *does* fit the HIA vs ΔH_{HYDROG} correlation line (see Figure 3) underlining the large effect of π -donors on both carbene and conjugate acid stability. The cyclopentadienyl[−] group also strongly affects the singlet–triplet gap, favoring the singlet by $\Delta H_{ST} = -26.4$ kcal/mol.

For the *m*- and *p*-substituted phenyl compounds, quantitative assessment of substituent effects on four processes was accomplished by multiparameter fits using gas phase polarizability, polar, and resonance-donor substituent constants.¹¹ Good fits were obtained for ΔH_{ST} , ΔH_{ACID} (α -acidity: enthalpy of deprotonation of the cations), HIA, and ΔH_{HYDROG} . As expected, polarizability is important only for the processes in which charged species are involved, ΔH_{ACID} and HIA. Polar and resonance effects both make significant contributions to all four processes, similar in magnitude for *meta* groups, but with resonance dominating for the *para* groups; see Table 3.

Points for carbenes with heteroatom substituents lie well above the correlation line for the HIA vs ΔH_{HYDROG} plots defined by the other compounds, confirming that directly attached heteroatoms stabilize the singlet more than the carbenium ion. This is shown by Figure 4 and eq 4. The nitroso group, in contrast to expectations based on its substituent constant values,¹¹ is a surprisingly effective π donor when directly attached to an electron deficient center. The amount of π -electron donation provided by the heteroatoms to the formally unoccupied 2p orbital of carbenes and carbenium ions is given by calculated Natural Atomic Orbital Occupancies, NAOO. By this criterion third row heteroatoms donate π -electron density more than do the second row elements. However this does not necessarily mean that the third row elements provide more stabilization by this interaction because third row X=C double bonds are not as strong as those formed by second row elements.

Supporting Information Available: G3MP2 enthalpies and free energies, imaginary frequencies for transition states, point groups for all computed structures, npa charges for heteroatom carbenes and carbenium ions, and Cartesian coordinates for all computed structures reported here. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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