Stabilities of Carbenes: Independent Measures for Singlets and Triplets

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Ⓢ *Supporting Information*

ABSTRACT: Thermodynamic stabilities of 92 carbenes, singlets and triplets, have been evaluated on the basis of hydrogenation enthalpies calculated at the G3MP2 level. The carbenes include alkyl-, aryl-, and heteroatom-substituted structures as well as cyclic 1,3-diheteroatom carbenes. Over a wide energy range, a good correlation is seen between the singlet–triplet gaps and the hydrogenation enthalpies of the singlets, but there are some clear outliers, which represent cases where the triplet has unusual stability or instability. By use of hydrogenation enthalpies, separate carbene stabilization enthalpy scales (CSEs) have been developed for singlets and triplets, and these highlight structural features that affect the stability of each. The treatment also allows estimates of aromaticity in cyclic carbenes. In this way, imidazol-2-ylidene is estimated to have an aromatic stabilization energy of about 20 kcal/mol.
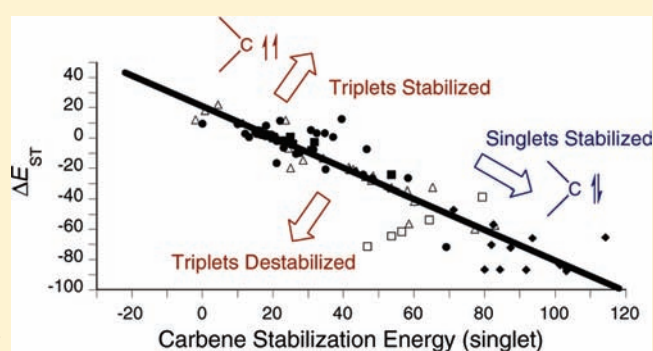
INTRODUCTION

An important guide to understanding the chemistry of reactive intermediates is the development of measures of their relative stability. For carbanions and carbocations, proton and hydride affinities, respectively, have proven to be useful and widely accepted properties for this purpose. In the case of carbenes, no single property has achieved a comparable status. The singlet–triplet energy or enthalpy gap, ΔE_{ST} or ΔH_{ST}, has been employed in some instances, but it is a composite of factors that affect the singlet and triplet independently.[1] By comparison, heats of hydrogenation (ΔH_{HYDROG}) should provide a better qualitative gauge for carbenes because addition of two hydrogens to the carbenic carbon replaces all carbene characteristics in the conversion to a saturated carbon center.[2]

We report here G3MP2 calculations on a large number of carbenes as well as their hydrogenation products.[3] The results point to a strong correlation between $\Delta H_{HYDROG(singlet)}$ and ΔH_{ST} and offer insights into factors that stabilize both singlet and triplet carbenes. The calculations focus on thermodynamic stabilities and neglect the extensive literature on experimental and computational investigations of kinetics and the character- ization of transition states for carbene reactions.[4] Our principal goal is to illustrate an easily implemented computational method for the independent assessment of singlet and triplet carbene stabilization energies (CSEs), based on calculated enthalpies of hydrogenation for the carbenes. We also point out the existence of a useful, qualitative correlation between enthalpies of hydrogenation and the singlet–triplet enthalpy gap, ΔH_{ST}, and discuss

the origin of an apparent maximum in this gap of about 85 kcal/mol. Although ΔE_{ST} is most useful in experimentally assessing the relative stability of spin states, ΔH_{ST} has been used here when comparisons are made to other enthalpy values. All computed enthalpies refer to 298 K.

Continuing interest in carbene chemistry is exemplified in a recent thematic issue of *Chemical Reviews*.[5] A focus of this interest has been N-heterocyclic carbenes. Recent reports of these carbenes include synthesis of an unusual gallium complex,[6] isolation of an "abnormal" carbene structure stable at room temperature,[7] and catalytic employment of a sterically crowded N-heterocyclic carbene in the synthesis of a tri-iron, tricyclooc- tatetraene complex.[8] A beta-issue of *Journal of the American Chemical Society* is devoted to the many uses of N-heterocyclic carbenes.[9]

METHODS AND RESULTS

Structures of carbenes and the hydrocarbons formed by their hydro- genation were built and optimized at HF/3-21G or HF/6-31G(d) levels by use of the MacSpartan Plus software package.[10] Conformational preferences were established at these or higher levels, including G3MP2. All geometry optimizations were completed via the G3MP2 method. The GAUSSIAN 03 quantum mechanical package was used for all the higher-level calculations.[3] All structures reported here represent electro- nic energy minima except for structures identified as transition states

Table 1. G3MP2 Singlet−Triplet Energy Gaps for Selected Carbenes and Carbene Stabilization Enthalpies for Singlet and Triplet Carbenes at 298 K[a]

carbene	ΔE_{ST} (G3MP2), kcal/mol	ΔE_{ST} (lit.),[b] kcal/mol	CSE (singlet), kcal/mol	CSE (triplet), kcal/mol
Type 1: Alkyl, Alkenyl, and Alkynyl Carbenes[18]				
1 CH₂	9.4	9.0 (exp)	0	0
2 CH₃CH	3.0	2.3	12.1	5.6
3 (CH₃)₂CH−CH	0.6		13.2	4.4
4 (CH₃)₂C	−1.0	−2.5	21.0	9.7
5 H₂C=CH−CH	8.2	6.4	18.0	16.8
6 HC≡C−CH	11.8		22.0	24.0
7 (HC≡C)₂−C[19]	13.5		39.5	42.7
8 cyclopropylidene	−16.8	−12.9,[20] −3.8,[21] −14.1[22]	21.0	−5.1
9 cyclobutylidene	−10.5	−5.9[21]	26.5	6.7
10 cyclopentylidene	−10.0	−8.7[23]	27.6	8.3
11 cyclopropenylidene	−71.6	−70,[24] −52.3[22]	69.1	−12.0
12 cyclopropylcarbinylidene	−6.5		23.0	7.1
13 cyclobut-1-en-3-ylidene	−24.1	25[25]	45.6	12.1
14 cyclopent-1-en-1-ylidene	−7.6		31.5	14.5
15 2,4-cyclohexadienylidene	3.2	3.0	34.7	28.5
16 2,5-cyclohexadienylidene	3.2	3.1	32.4	26.2
17 6,6-dimethylcyclohexa-2,4-dienylidene	5.3		30.7	26.6
18 spiro[2.5]octa-4,6-dien-8-ylidene	−7.3		46.6	29.8
19 spiro[2.5]octa-4,7-dien-6-ylidene	0.9		37.0	27.9
Type 2: Selected Aryl Carbenes[26]				
20 PhCH	2.32	2.3 (kinetic estimate),5.4[17]	18.7	11.4
21 PhCCH₃	1.0	2.0 (kinetic estimate)[27]	24.9	16.3
22 3-nitrophenyl	3.58	7.8	15.7	9.7
23 4-nitrophenyl	5.10	10.3	15.1	10.7
24 3-hydroxyphenyl	1.91	5.3	19.0	11.3
25 4-hydroxyphenyl	−1.33	1.7	19.6	11.5
26 3-aminophenyl	1.73	5.2	19.2	11.3
27 4-aminophenyl	−3.51	0.7	25.6	12.1
28 3-oxyphenyl⁻	−8.02		30.9	13.3
29 4-oxyphenyl⁻	−24.10		53.6	19.9
Type 3: Acyclic Heteroatom and Cyano Carbenes				
30 H₂NCH	−40.8		58.1	14.2
31 (NH₂)₂C	−57.1	−52.6, −53.2[22]	82.9	16.1
32 HOCH (anti)	−25.4	−28.0[28]	46.3	11.2
33 CH₃OCH	−27.8		47.9	10.4
34 CH₃OCCH₃	−32.6		53.5	11.4
35 (CH₃O)₂C[29]	−59.8	−53.0	77.3	8.1
36 FCH	−14.6	−14.7 (exp)[13]	28.5	4.5
37 F₂C	−56.2	−56.7 (exp)[13]	58.7	−6.9
38 SiH₃CH	18.1	18.1[30]	0.7	9.4
39 (SiH₃)₂C	22.1	24.7[31]	4.4[31]	17.0[31]
40 H₂PCH	−13.3	−6.6[32]	34.2	11.4
41 HSCH (anti)	−20.4	−13.8[32]	42.7	12.7
42 CH₃SCH	−24.8		48.4	14.1
43 ClCH	−6.9	−6.4 (exp)[13]	24.4	8.1
44 Cl₂C	−21.7	−20.5 (exp)[13]	43.7	12.5
45 (NH₂)₂CCH⁺	11.9	14.1[33]	−2.0	0.7
46 cyanocarbene	10.0	17.0[34]	11.5	12.0
47 dicyanocarbene	12.2	16.4[35]	23.6	25.9
48 nitrocarbene[36]	NA	NA	NA	0.7
49 dinitrocarbene[37]	−20.0		25.0	−4.1
50 aminocyanocarbene	−31.9		65.3	23.5
51 aminonitrocarbene	−41.5		60.1	9.2
Type 4: Five-Membered, Cyclic 1,3-Diheteroatom Carbenes[c]				
52 imidazol-2-ylidene	−85.5	−84.5	103.1	8.0
53 4,5-dihydroimidazol-2-ylidene	−72.3	−69.4	81.9	2.3
54 N,N′-dimethylimidazol-2-ylidene	−87.5		103.2	6.2
55 4,5-dimethylimidazol-2-ylidene	−83.5		101.4	8.4
56 4,5,N,N′-tetramethylimidazol-2-ylidene	−86.1		103.6	7.9
57 imidazol-5-ylidene	−64.9		114.3	39.6
58 1,3-dioxol-2-ylidene	−86.1		84.4	−11.6
59 1,3-dioxolan-2-ylidene	−72.5		80.0	−2.1
60 oxazol-2-ylidene	−86.3		91.8	−4.4

Table 1. Continued

carbene	ΔE_{ST} (G3MP2), kcal/mol	ΔE_{ST} (lit.),[b] kcal/mol	CSE (singlet), kcal/mol	CSE (triplet), kcal/mol
61 4,5-dihydrooxazol-2-ylidene	−70.2		81.9	2.3
62 4,5,N,N′-tetrasilylimidazol-2-ylidene	−82.4		101.2	8.8
63 1,3-diphosphole-2-ylidene	−26.2		48.1	12.6
64 1,3-diphospholan-2-ylidene	−21.1		43.2	11.8
65 1,3-dithiol-2-ylidene	−56.5		82.5	16.2
66 1,3-thiolan-2-ylidene[38]	−47.0		71.2	14.6
Type 5: Small-Ring Aza- and Diazacarbenes[c]				
67 diazirene-3-ylidene	−33.1	−32.3[22]	56.5	14.0
68 diazirane-3-ylidene	−55.1	−67.0[22]	63.1	−10.8
69 1,3-diazetidin-2-ylidene	−63.0		79.4	7.2
70 azet-2-ylidene	−39.0		46.8	−1.9
71 azetidin-2-ylidene	−46.9		64.3	8.0

[a] A negative value for ΔE_{ST} indicates the singlet is more stable. Where there are several stable conformations, the most stable is used. Calculated values for ΔE_{ST} and ΔH_{ST} are extremely well correlated, with the former averaging 0.2 kcal/mol more positive: $\Delta E_{ST} = 1.00\Delta H_{ST} + 0.18$, $r^2 = 1.00$. [b] Literature values for ΔE_{ST} are found in a number of sources. Most values listed here are computational and were obtained by a variety of methods. Experimental results (exp) are noted. Unless otherwise noted, literature values, both experimental and computational, were taken from the recent compilations listed in refs 1c,1e,17 and especially ref 1f. [c] Where cis and trans isomers exist, the more stable of the two is used for the ΔH calculations.

(ts), each of which has one imaginary frequency. Several of the carbenes were also calculated at the MP2/6-311+G** and B3LYP/6-311++G** levels. The resulting structures are in good agreement with the G3MP2 structures in terms of both symmetry and individual geometric parameters. Significant spin contamination was detected at the Hartree–Fock (HF) level for the triplets of diethynylcarbene, **7**, and dicyanocarbene, **47** (as well as for triplet diphenylcarbene, not used in this study). We therefore urge caution in the interpretation of our results for these carbenes (singlet and triplet states).

G3MP2 enthalpies and free energies at 298 K in hartrees are tabulated for all 88 carbenes, their conjugate acid carbenium ions, and their hydrogenation products in Tables S1–S4 in the Supporting Information. These tables also list the calculated point groups for all members of each set. Also in the Supporting Information, Table S5 lists Cartesian coordinates for the compounds and Table S6 includes calculated values of ΔH_{ST} and ΔH_{HYDROG} for singlet carbenes as well as hydride ion affinities (HIA) and ΔH_{ACID} values for the carbenium ion conjugate acids of the singlet carbenes. Our ΔH_{ST} and ΔE_{ST} values are very well correlated: $\Delta E_{ST} = 1.00\Delta H_{ST} + 0.18$, $r^2 = 1.00$.

Calculated values of ΔE_{ST} for 71 selected carbenes are shown in Table 1, in which the carbenes studied are listed and numbered (selected structures of cyclic species are given in Scheme 1). Table 1 also shows calculated values of ΔE_{ST} from the literature for many of the carbenes. Computational results in the literature were obtained with a variety of basis sets and methods and are in good qualitative accord with ours. Only in a few cases are experimental values available.[11] For CH_2,[12] HCF,[13] and CF_2,[13] experimental gas phase values of $\Delta E_{ST} = 9.0$, −14.7, and −57 kcal/mol, respectively, agree well with calculated values. Similarly good agreement is found for PhCH, estimated by kinetic measurements as $\Delta G_{ST} = 2.3$ kcal/mol in acetonitrile solution.[14,15] A high-level calculated value for H_3SiCH[16] at 18.1 kcal/mol is in exact agreement with our G3MP2 result.

We also call attention to the good agreement between our calculated geometries for the carbenes and those in the recent literature, in terms of both symmetry and individual parameters (bond angles and distances). This is noted in the references cited in Table 1. Among structures deserving further comment are the 1,3-heterocyclic carbenes grouped in Table 1 as type 4. Except for the 4,5-dihydro addition products of imidazol-2-ylidene (**53**) and oxazol-2-ylidene (**61**), all the singlets of this class have planar rings, those with like heteroatoms at positions 1 and 3 having exactly or virtually C_{2v} symmetry. By contrast, all the triplets as well as the 2,2-dihydro addition products have nonplanar rings, puckered or envelope-shaped. In fact a planar, C_{2v} conformation for ^{3}imidazol-2-ylidene is a *transition state*, lying $\Delta H^{\ddagger} = 18.7$ kcal/mol above the puckered triplet ground state. Additionally, excepting only the oxazole example, nitrogens in 1,3-heterocyclic triplets are

pyramidal. Further distortions include the C—C bonds in both the dioxole (**58**) and oxazole (**60**) triplets, which are not double bonds. The carbons are pyramidal and the C—C distances are 1.521 and 1.522 Å, respectively. Finally, bond length alternation in the ring is pronounced in these triplets and not so in the singlets. As discussed below, this is consistent with the fully conjugated singlets being aromatic while the triplets are definitely not aromatic.

■ DISCUSSION

The 71 carbenes listed in Table 1 are divided into five groups of representative structures, including (1) alkyl, alkenyl, and alkynyl carbenes; (2) aryl carbenes; (3) acyclic heteroatom and cyano carbenes; (4) five-membered, cyclic 1,3-diheteroatom carbenes; and (5) small-ring aza- and diazacarbenes. It is important to note that although we will refer to all of them as carbenes in the text, some may be better described by other resonance forms, particularly as ylides or cumulenes. Values of ΔE_{ST}, the energy separation between singlet and triplet carbenes, are listed together with experimental or previously computed values as well as carbene stabilization energies (see below).
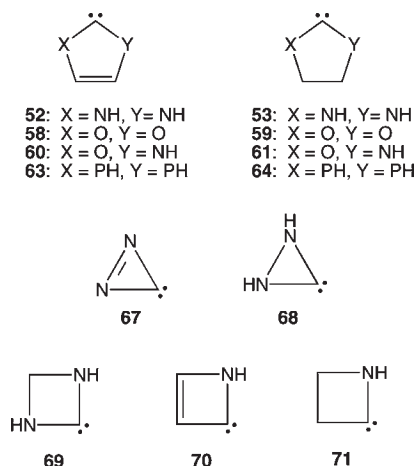
Figure 1a shows that ΔH_{ST} and $\Delta H_{HYDROG(singlet)}$ track each other well through more than 100 kcal/mol on both axes, yielding the correlation line of eq 1. A similar result would occur if ΔE_{ST} were used for the plot. Values from our previous study of aryl-substituted carbenes are included to give a total of 92 data points.[26] Although the correlation is subject to considerable scatter, it is improved by neglect of obvious outliers. These represent examples for which the triplet is unusually stable or unstable. The slope and intercept of the correlation line are hardly affected by removal of these examples. Considering the wide range of structures embraced, the correlation is a remarkably good one. In contrast, comparison of ΔH_{ST} with $\Delta H_{HYDROG(triplet)}$ yields essentially a scatter plot (Figure 1b).

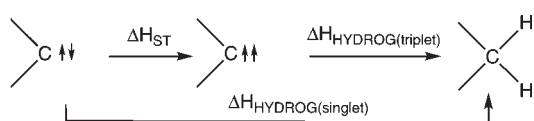$$\Delta H_{ST} = -1.04\Delta H_{HYDROG(singlet)} - 101.2$$
$$r^2 = 0.916, n = 92 \qquad (1)$$

The slope of the plot in Figure 1a is close to 1.0. This suggests that structural effects stabilizing singlet carbenes are eliminated not only by hydrogenation at the carbenic carbon but also to a

Scheme 1

52: X = NH, Y= NH
58: X = O, Y = O
60: X = O, Y = NH
63: X = PH, Y = PH

53: X = NH, Y= NH
59: X = O, Y = O
61: X = O, Y = NH
64: X = PH, Y = PH

67

68

69

70

71

Scheme 2

Figure 1. Plots of ΔH_{ST} against (a) $\Delta H_{HYDROG(singlet)}$ and (b) $\Delta H_{HYDROG(triplet)}$ for 92 carbenes. Values are given in kcal/mol. See Table 1 for type definitions.

significant extent by transformation to the triplet state. A strong implication is that $\Delta H_{HYDROG(singlet)}$ and ΔH_{ST} are primarily probing factors stabilizing the singlet carbene. The plot for $\Delta H_{HYDROG(triplet)}$ in Figure 1b suggests no correlation and it is evident that the hydrogenation enthalpy covers a much more limited range; that is, the impact of structure on triplet stability is more limited.

Why should this be the case? An answer is evident from consideration of the thermodynamic cycle of Scheme 2 (spin conservation is ignored in this thermodynamic cycle). Here the hydrogenation of the singlet is broken into two steps: (1) conversion to the triplet and (2) hydrogenation of the triplet. For a one-to-one correlation between $\Delta H_{HYDROG(singlet)}$ and ΔH_{ST}, the cycle requires that the energy associated with the second step, $\Delta H_{HYDROG(triplet)}$, should be roughly constant. Indeed, with a few exceptions, the data in Figure 1b show this to be the case with an average value, $\Delta H_{HYDROG(triplet)} = -99 \pm 10$ kcal/mol, for a large majority of the carbenes (71 of 92, including previously studied examples). This is a reasonable value and corresponds to an average of about 100 kcal/mol for each of the C—H bonds formed by hydrogenation of the triplet.

This behavior indicates that the singlet is much more sensitive to substituents than the triplet, so the impact of substituents on triplet stability is obscured on the scale of Figure 1a. For example, when triply bonded substituents are excluded (see below), the extremes of ΔH_{HYDROG} for the triplet are -91.6 kcal/mol for $(CH_3)_2Si$ or vinyl-substituted carbenes and -120.7 kcal/mol for cyclopropenylidene. By contrast, $\Delta H_{HYDROG(singlet)}$ shows a much wider variation from -14.5 kcal/mol for 4,5,N,N-tetramethylimidazol-2-ylidene, **56**, to -120.1 kcal/mol for the protonated amidino-substituted carbene $NH_2{}^+=C(NH_2)CH$, **45** (Table S6, Supporting Information).

Substituent effects and other factors affecting singlet—triplet separation energies have been discussed extensively in the literature.[1]
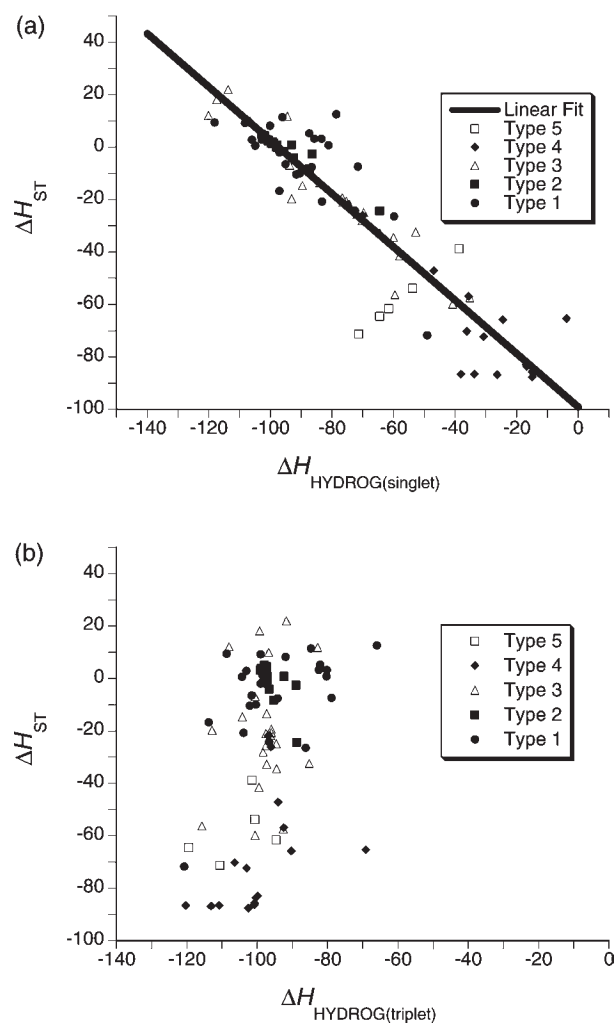
The structures in Table 1 were chosen to illustrate these factors, which are reviewed below in assessing the main sources of deviations from the correlation. To facilitate comparisons, the table includes carbene stabilization enthalpies (CSEs), measured as the difference in heat of hydrogenation of a carbene (CR_1R_2) from the value for the parent methylene as shown in eq 2.[39] The CSE values represent substituent effects (of R_1 and R_2) on stabilities of carbenes, with the unsubstituted (singlet or triplet) CH_2 taken as reference. Just as departures from the correlation line given by eq 1 reflect variations in the heat of hydrogenation of the triplet, strict adherence to the correlation would imply a constant CSE value. The -99 ± 10 kcal/mol "average" heat of hydrogenation of the triplet noted above is 10 kcal/mol below the value for CH_2 and therefore implies an "average" CSE of 10 ± 10 kcal/mol for the triplet. From inspection of the right-hand column of Table 1, it is clear that many values fall in the range 0—20 kcal/mol and that values outside this range are easily identified by their negative values or values greater than 20, corresponding to unusually stable or unstable triplets.

$$CSE(R_1R_2) = \Delta H_{HYDROG}(CR_1R_2) - \Delta H_{HYDROG}(CH_2) \quad (2)$$

The utility of the CSEs can be demonstrated with a comparison of CF_2 and $(CH_3O)_2C$. ΔE_{ST} is nearly the same for the two

carbenes, but their CSE values indicate that stabilization of the singlet is nearly 20 kcal/mol greater for $(CH_3O)_2C$ than for CF_2. This is consistent with the greater electron-donating capability of the methoxy group. The similarity of the singlet−triplet separation energies is derived from destabilization of the CF_2 triplet, probably as a result of conflict between Bent's rule[40], favoring a smaller carbenic bond angle for the more electronegative fluorine atoms, and the preference for larger bond angles in triplet carbenes. Thus the F−C−F angle in the CF_2 triplet is only 120°, whereas 130° is typical.

A readily identifiable influence on the heat of hydrogenation of the triplet carbene is the C−H bond dissociation energy (BDE) of its corresponding hydrogenation product. In fact, triplet stabilization energies yield a satisfactory correlation with bond dissociation energies for a selection of simple species (with known BDE) representing types 1, 2, and 3 carbenes. The slope of the plot is close to unity (1.1) and the correlation coefficient $r^2 = 0.92$. Ethynyl substituents are excluded from the correlation because they show enhanced stability for the triplet, possibly because the triplet can be considered to be interacting with both π-bonds.

In the following sections of the paper, trends in singlet and triplet carbenes are discussed in a systematic way on the basis of several types of substituent effects: (1) hyperconjugation/delocalization, (2) ring strain effects, (3) π-donor and π-acceptor effects, and (4) aromaticity.

Hyperconjugation/Delocalization. It is well documented that attached alkyl groups stabilize singlet carbenes relative to the triplet state.[1] The CSE values for the alkyl-substituted carbenes show that singlets are markedly stabilized by alkyl groups, but triplets gain only modest stabilization. In contrast, silyl groups (**38** and **39**) have almost no stabilizing effects on singlets and modest stabilizing effects on triplets. This leads to a large singlet/triplet gap. With π-conjugating groups, vinyl and ethynyl, the effects on singlets and triplets are comparable and the singlet/triplet gap is similar to CH_2; in all cases, triplet ground states are observed.[1f,41] In the systems that offer additional delocalization, such as diethynylcarbene (**7**) and 2,4- and 2,5-cyclohexadienylidenes (**15** and **16**), the stabilization of the triplet is sufficiently great to cause appreciable positive deviations from the correlation line of Figure 1a. For diethynylcarbene (**7**), the stabilization of the triplet is the largest in this study (CSE = 42.7 kcal/mol). However, it adopts a linear, cumulene-like structure and consequently lacks some of the carbene characteristics found in other species.[42] It is also noteworthy that among electron-withdrawing substituents (type 3 carbenes in Table 1), the cyano- and dicyanocarbenes (**46** and **47**)[32,35] show similar characteristics to the corresponding ethynyl carbenes, in that the cyano groups equally stabilize the singlet and triplet states and produce geometries similar to those seen in the ethynyl species.

According to the calculations, phenyl substituents show a greater stabilization for the singlet than triplet carbenes (type 2 carbenes in Table 1). As expected, π-electron-donating p-substituents significantly favor the singlet, and between the p-nitro- and p-amino-substituted phenyl carbenes, the calculated value of ΔE_{ST} decreases by 9 kcal/mol.[26]

Ring Strain Effects. It is also well documented that constraints on the carbenic angle, X−C−Y, affect the relative stabilities of singlet and triplet carbenes.[1c,1f,43] Without such constraints, singlets typically have carbenic angles near 105° while those for triplets are over 130°.[1c,1f,17,26] Increasing the bulk of X and Y opens the angle and favors the triplet, while compression of the carbenic angle favors the singlet. This is apparent in cyclopropylidene (**8**)[22,44], where the singlet is stabilized by 21.0 kcal/mol

(the same extent as for singlet dimethylcarbene) whereas the triplet is destabilized by 5.1 kcal/mol (as opposed to 10 kcal/mol stabilization for dimethylcarbene), leading to a mild negative deviation from the correlation of ΔH_{ST} in Figure 1. The diaza analogue of cyclopropylidene is diazirane-3-ylidene, **68**, for which destabilization of the triplet is even larger, with CSE = −10.8 kcal/mol (in contrast with the 16.1 kcal/mol stabilization for triplet diaminocarbene). This effect is much less evident in four- and five-membered rings where the triplet CSEs are within a few kilocalories per mole of the values for acyclic analogues.

Among the cyclic π-conjugated carbenes, cyclopropenylidene, **11**, shows a larger singlet stabilization energy than other π-conjugated carbenes, consistent with its well-recognized aromatic character.[24] There is no indication of aromaticity in the triplet, which again shows a larger destabilization (−12 kcal/mol) relative to CH_2 than cyclopropylidene (−5 kcal/mol) and a correspondingly larger deviation from the correlation line of Figure 1a. This is likely driven by one of the carbene's unpaired electrons being forced into a formally antibonding π-orbital (if analogous orbitals to those in the singlet are assumed).

π-Donor and π-Acceptor Effects. Polar effects are overridden by π-donation to the singlet carbenic carbon as exemplified by substituents NH_2, CH_3O, and F among the type 3 carbenes in Table 1. Aside from carbenes with aromatic character, π-donation leads to the most stabilized singlets in the data set. These are also systems where one expects a strong influence from an ylide resonance form with a formal π-bond to the carbenic carbon. The CSE(singlet) values for the heteroatom carbenes, **30** (N), **40** (P), **32** and **33** (O), and **41** and **42** (S), as well as those for the five-membered cyclic 4,5-dihydro-1,3-dihetero-2-ylidenes, **52** (N), **63** (P), **58** (O), and **65** (S), show that whereas the difference between stabilization by nitrogen and phosphorus is large, that between oxygen and sulfur is not. A similar result was obtained by Schreiner et al.[38] in their study of the corresponding six-membered diheterocarbenes. They point out that these differences parallel those found for heteroatom-substituted carbenium ions as well.[45] Also illustrated in these data is that two π-donating substituents are very much more effective than one. For example, the first methoxy substituent provides a CSE(singlet) of 47.9 kcal/mol, which grows to 77.3 kcal/mol with the addition of the second methoxy group. With the exception of fluorine substituents, the triplet also is mildly stabilized by π-donors. Fluorine generally is poor at stabilizing unpaired electrons, and as already discussed, CF_2 is exceptional, resulting in a significant negative deviation from the correlation of Figure 1a. Irikura et al.[13] previously have discussed the competing effects of σ-withdrawal/π-donation by substituents like fluorine. Weaker π-donation effects, also referred to above, are exerted by substituents at the para position of a phenyl carbene. This is expressed quantitatively by the greater resonance reaction constant, $\rho_R^+ = 13.3$, than polar constant, $\rho_F = 3.9$, reported in an earlier paper for ΔH_{ST}.[26]

As an example of an electron-withdrawing substituent, cyano has a modest effect on singlet carbene stability (about the same as an alkyl group). In contrast, the amidinium ion moiety $[(NH_2)_2\text{-}CH^+]$ in **45** destabilizes the singlet and is the only substituent group with a negative singlet CSE. Here, the powerful electron-withdrawing capabilities of the cationic group push the carbene toward its alternative resonance form, in this case a vinylic cation.[33]

Singlet nitrocarbene (**48**) rearranges to nitrosocarbaldehyde,[36] precluding calculation of CSE(singlet). The triplet CSE value is unusually small, signifying little or no stabilization by the nitro group, which does not engage in a neighboring, bridging interaction in this case. In this respect nitrocarbene resembles cationic

3385

dx.doi.org/10.1021/ja1071493 |*J. Am. Chem. Soc.* 2011, 133, 3381–3389

diaminomethylcarbene, $(NH_2)_2CCH^+$ (**45**),[33] suggesting that the nitro and $(NH_2)_2C^+$ moieties, isoelectronic with one another, are behaving simply as inductive electron-withdrawing groups. These two substituents are among the very few in this study that have little or no effect on carbene stability relative to CH_2. Finally, dinitrocarbene (**49**) is unique in the heteroatom category. In the singlet, an oxygen from one of the nitro groups bridges to the carbenic carbon (it does so even more strongly in dinitrocarbenium ion). Consequently, singlet dinitrocarbene is better characterized as an N-oxide of an oxazirine. In the triplet this interaction is missing; the nitro groups are symmetrical, have normal nitro geometry, and are twisted with respect to one another. Here two nitro groups are seen to be slightly destabilizing.

Aminocyanocarbene (**50**) and aminonitrocarbene (**51**) provide possible examples of what Bertrand[1d] calls D—C—W carbenes, in which a π donor (D) is combined with a π acceptor (W). For both carbenes the singlet is strongly favored and CSE (singlet) values are large, reflecting the dominant influence of π donation by the amino group. In principle, this interaction can be supplemented by interaction of the carbenic lone pair with a vacant π orbital in the cyano or nitro group.[1d] In the case of aminocyanocarbene, the CSE of the singlet is somewhat less than the sum of the CSEs for an amino group and a cyano group, indicating that there is no cooperativity in the stabilization of the singlet. In addition, the singlets have little or none of the allenic character described by Bertrand. The compounds do not approach linearity, the carbenic angle being just 111° in ^{1}**50** and 104.6° in ^{1}**51**. The amino and nitro groups in ^{1}**51** are both planar and define a dihedral angle of 24° rather than the ~90° required by an allenic geometry.

Aromaticity. The potential influence of aromaticity on the stability of singlet carbenes and the magnitude of ΔE_{ST} is illustrated principally by the heterocyclic carbenes of type 4. Examples include carbenes based on the imidazole, 1,3-dioxole, and oxazole ring systems. The influence of aromaticity can be judged by comparison with corresponding dihydro ring systems. Thus 4,5-dihydroimidazol-2-ylidene (**53**), in which the formal C4═C5 double bond of the parent imidazole ring (**52**) has been saturated, still strongly favors the singlet state but by a smaller amount than for the imidazolyl carbene itself. Similar differences are shown by the O,O (**58**, **59**) and O,N (**60**, **61**) entries. On the basis of comparison of ΔE_{ST} values, up to 15 kcal/mol may be assigned to the effect of aromaticity on ΔE_{ST}, if it is assumed that the effect is present in the singlets but absent in the triplets. In comparison, the 1,3-diphosphorus system shows only a 4 kcal/mol difference in ΔE_{ST} between the parent (1,3-diphosphole, **63**) and dihydro (1,3-diphospholane, **64**) ring systems. The nonplanarity of the ring and other geometric features also indicate very little aromatic character for singlet 1,3-diphosphole-2-ylidene.
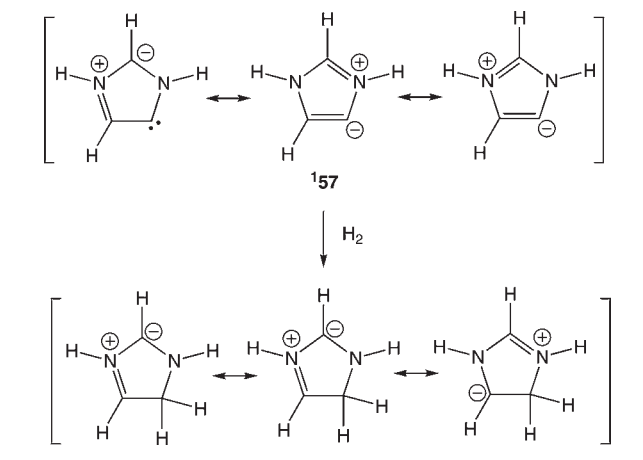

52   **53**
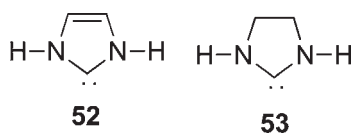
A more accurate assessment of aromaticity is provided by heats of hydrogenation and CSE values because the stability of the triplets are also affected by forming cyclic, conjugated systems. For imidazol-2-ylidene (**52**), ΔH_{HYDROG} and CSE for the singlet are ~21 kcal/mol greater than that for its 4,5-dihydro singlet derivative (**53**), while the corresponding values for the triplets

are greater by just 6 kcal/mol in the saturated system. For the oxazole pair, **60** versus **61**, there is approximately 10 kcal/mol extra stabilization for the singlet but ~7 kcal/mol *destabilization* for the triplet. For the dioxole pair, **58** versus **59**, the numbers are just 4.4 kcal/mol extra stabilization for the singlet and 9.5 kcal/mol destabilization for the triplet. For the second-period elements, diminished stabilization of the singlet and destabilization of the triplet by increasingly electronegative heteroatoms in the order O,O > O,N > N,N is indicated. Thus, although there is aromatic stabilization of singlets **52**, **58**, and **60**, the degree of aromaticity is not equal for all three. The N,N system (imidazol-2-ylidene) possesses the most aromatic character (21 kcal/mol based on CSE values) and the O,O system (1,3-dioxol-2-ylidene) the least. This conclusion is supported by geometric evidence. For example, bond length extension upon hydrogenation at the carbenic carbon is greater for **52** than for **58**. Greater π participation by nitrogen than by oxygen is a well-known property, demonstrated, for example, by their relative σ_R^+ values.[46] Also pertinent is the general agreement, based on a variety of properties, that simple N-heterocycles, such as pyrrole, are more aromatic than the corresponding O-heterocycles, such as furan.[47] Comparisons of the saturated ring systems to acyclic analogues such as $(CH_3O)_2C$ and $(NH_2)_2C$ indicate that, in contrast to all-carbon five-membered rings, cyclization sharply destabilizes the triplet by enforcing what must be an unfavorable interaction between the unpaired electrons on the carbene and the heteroatom lone pairs. Again, these results highlight the value of considering the effects on the singlet and triplet separately rather than as the composite quantity ΔE_{ST}.

We have also looked at the core structure of Bertrand and Frenking's "abnormal" N-heterocyclic carbene, imidazol-5-ylidene (**57**).[7] In this case, the singlet is less stable than the isomeric 2-ylidene singlet (^{1}**52**) by 19.4 kcal/mol, while the triplets have almost the same stability.[48] This result also indicates that ^{1}**57** is 19.4 kcal/mol more basic than ^{1}**52**, since protonation leads to the same product in each case. The CSE values are very large for **57** because the reference state (i.e., product of hydrogenation at the carbenic carbon) has an unfavorable, ylide structure. Here the CSE values are *not* particularly useful because the structure of the hydrogenation product does not correlate well with the carbene. This is in part due to the fact that ^{1}**57** is undoubtedly better described as an ylide rather than a carbene (Scheme 3). Unlike imidazol-2-ylidene, the carbene resonance form of imidazol-5-ylidene formally retains charge separation (that is, is an ylide) and has no advantage with respect to conventional ylide resonance forms. In fact, the carbene resonance form requires sacrificing a formal π-bond in the ring as well as a carbon octet and should be viewed as a small contributor (i.e., ^{1}**57** is an ylide, not a carbene). The decreased stability of ^{1}**57** relative to ^{1}**52** does not arise from a loss of aromatic character, however. NICS(0) values for the two are about the same: −14.2 and −14.7, respectively, for the 2-ylidene and the 5-ylidene, both very similar to values for pyrrole and imidazole (−13.6 and −13.1, respectively).[47e]

For cyclopropylidene and cyclopropenylidine[22,24] singlet carbenes, a large difference in CSE values (48 kcal/mol) suggests a much larger "aromatic" stabilization than for the heterocyclic carbenes. The overall stabilization of singlet cyclopropenylidine is smaller than for the heterocycles because it lacks the stabilization provided by π-donation from the adjacent heteroatoms. Nonetheless, the level of stabilization is impressive for a hydrocarbon and its NICS(0) value of −16.8[22] also suggests significant aromaticity.
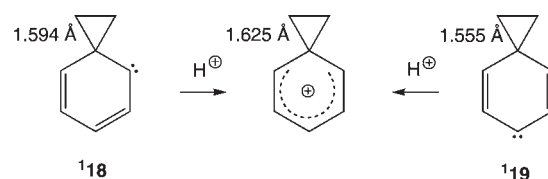
Scheme 3

Figure 2. Computed bond lengths (MP2/6-31G*) for spiro carbenes and analogous phenonium ion.

Figure 3. MP2/6-31G* geometries of singlets **70** and **71**.

The unusually large CSEs for the singlets of 2,4-cyclohexadienylidene and 2,5-cyclohexadienylidene (**15** and **16**) may be an indicator of incipient hyperconjugative aromaticity in these structures.[49] Support for this idea comes from results for carbenes bearing a cyclopropyl moiety attached to the carbenic carbon. Cyclopropylcarbene (cyclopropylcarbinylidene, **12**) has CSE(singlet) = 23.0 kcal/mol, 9.8 kcal/mol greater than that of isopropylcarbene, **3**, consistent with the exalted electron-donating ability of a cyclopropyl group toward an adjacent, electron-deficient center compared with that of ordinary alkyl groups. The cyclopropyl effect is magnified in spiro[2.5]octa-4,6-dien-8-ylidene, **18** (Figure 2). Its CSE(singlet) is 46.6 kcal/mol, 15.9 kcal/mol greater than that for 6,6-dimethylcyclohexa-2,4-dienylidene, **17**, demonstrating an enhanced hyperconjugative effect. Further support comes from comparison of spirocarbene **18** with its isomer spiro[2.5]octa-4,7-dien-6-ylidene (**19**), in which the carbenic carbon, C6, is *not* adjacent to the cyclopropyl group. Isomer **19** is 8.8 kcal/mol less stable than **18**. Effective conjugation of the cyclopropyl group with its carbenic carbon would require significant ylide character, placing electron deficiency at C8. Evidently such character is of minor importance. In isomer **18**, ylide character is not required and the stabilizing hyperconjugative interaction is effective. A small cyclopropyl effect in **19** may be inferred from the fact that its CSE(singlet) value is 4.6 kcal/mol greater than that of 2,5-cyclohexadienylidene, **16**.

The attribution of aromaticity to singlet cyclic carbenes is reinforced by a search for the implied opposite property, antiaromaticity. Comparison of heats of hydrogenation or CSE values for the singlet four-membered azet-2-ylidene ring, **70**, and corresponding saturated azetidin-2-ylidine, **71**, indicates a greater stabilization of the *saturated* molecule by 17.5 kcal/mol (structures in Figure 3). This value is an indication of antiaromatic character. The effect on ΔE_{ST} is moderated by a destabilization of the triplet by about 9 kcal/mol in the unsaturated system. In the singlet carbene of **70** (C_1 symmetry), antiaromaticity can be avoided or lessened by a structural deformation: the nitrogen is pyramidal, the ring is folded, and the N—C bond is long at 1.50 Å, almost the same as that in its 2,2-dihydro hydrogenation product and much longer than in **71**. However, a price must be paid for this deformation, namely, diminished stabilization by π-donation. For comparison, the replacement of the adjacent NH unit in azet-2-ylidene with a CH_2 group results
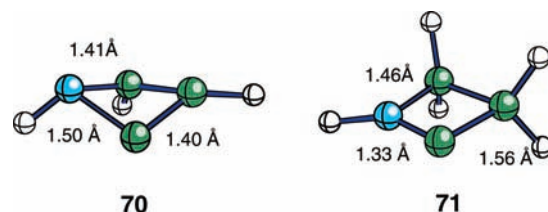
in cyclobut-1-en-3-ylidene (**13**) and a system where no compromise involving antiaromaticity is necessary. Singlet **13** retains a stabilizing allylic interaction[50] between the carbene center and the C=C double bond; thus ΔE_{ST} becomes *more* negative (by 14 kcal/mol) and CSE(singlet) *larger* (by 19 kcal.mol) than for its saturated analogue cyclobutylidene (**9**). It may seem surprising that in singlet **9** the transannular distance is not lengthened compared to that in **71** but shortened to 1.711 Å. This result, however, is due to a different interaction, a hyperconjugative donation from the distal CH_2 unit, resulting in elongated H_2C—CH_2 single bonds (to 1.608 Å) and shortened C—CH_2 bonds (to 1.445 Å).[21a,51] Both of these effects are magnified in the conjugate acid of **9**, the bicyclobutonium ion.

Maximum for ΔE_{ST}? An intriguing question is whether there are maximum values for singlet−triplet gaps and CSEs for carbenes? Our data for ΔE_{ST} level off at about 85 kcal/mol for aromatic heterocyclic species such as imidazol-2-ylidene,[52] and CSEs for singlets level off at about 100 kcal/mol for the same species. Perhaps a more pertinent question is, at what point is a singlet carbene so stabilized that it can no longer be considered a carbene? Except for the "abnormal" imidazol-5-ylidene (**57**, see above), an arbitrary but reasonable cutoff is ∼65−75 kcal/mol of stabilization, the typical strength of a π-bond. With this level of stabilization, a resonance form with a formal π bond to the carbenic carbon is a better descriptor. By this criterion all of the type 4 singlets, with the exception of the phosphorus compounds, are classified as π-bonded ylides, e.g., $^{+}N{=}C^{-}$, rather than as carbenes. Excepting the phosphorus entry, the 4,5-dihydro-1,3-diheterocarbenes have singlet CSE values averaging about 80 kcal/mol, a quantity near to that of a π-bond. The aromatic carbenes have singlet CSE values about 20 kcal/mol larger. This provides one estimate of the contribution of aromaticity to the stability of these carbenes.

We suggest, therefore, that $\Delta E_{ST} \cong -85$ kcal/mol and a singlet CSE $\cong 100$ kcal/mol are maxima and represent situations where the singlet benefits from a fully formed π-bond and/or aromaticity. However to exhibit the chemical behavior that one associates with reactive singlet carbenes, the CSE value must be substantially lower, most likely less than 60 kcal/mol. By this definition, none of the 1,3-heterocyclic carbenes, with the exception of the phosphorus systems, are deemed "true" carbenes and they are better viewed as ylides.

SUMMARY

A good correlation between ΔH_{ST} and $\Delta H_{HYDROG(singlet)}$ spans a remarkably wide energy range and includes a large number and a wide variety of carbenes. Outliers represent systems where the triplet is unusually stable or unstable. Factors that affect singlet and triplet spin states individually are conveniently expressed in terms of carbene stabilization energies (CSEs), based on enthalpies of hydrogenation. We have shown previously that good correlations exist between substituent effects on the stabilities of singlet carbenes and carbocations, both species strongly stabilized by attached electron-donating groups.[18,26,53] Here we show that, in contrast, *triplet* carbene stability is *not* strongly affected by electron-donating groups. In fact, CSE(triplet) values correlate well with radical stabilities as measured by relative C−H bond dissociation energies of the corresponding carbene hydrogenation products. Combining an analysis of CSE values with inspection of the correlation between ΔH_{ST} and $\Delta H_{HYDROG(singlet)}$ provides a convenient framework for exploring and displaying constitutional effects on carbene stabilities.

ASSOCIATED CONTENT

S **Supporting Information.** Complete ref 3 and six tables, containing G3MP2 enthalpies, free energies, and point groups; Cartesian coordinates for the computed structure sets; and ΔH_{ST} and $\Delta H_{HYDROG(singlet)}$ values for carbenes and including HIA and ΔH_{ACID} values for carbenium ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

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3388

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3389

dx.doi.org/10.1021/ja1071493 |*J. Am. Chem. Soc.* 2011, 133, 3381–3389