Carbene Stabilization by Aryl Substituents. Is Bigger Better?

H. Lee Woodcock,*,†,‡ Damian Moran,*,†,§ Bernard R. Brooks,‡
Paul v. R. Schleyer,*,† and Henry F. Schaefer III†

*Contribution from the Center for Computational Chemistry, University of Georgia, Athens,
Georgia 30602-2525, Computational Biophysics Section, Laboratory of Computational Biology,
National Heart Lung and Blood Institute, National Institutes of Health, Bethesda, Maryland
20892, and School of Chemistry, University of Sydney, Sydney, NSW 2006 Australia*

Received December 13, 2006; E-mail: hlwood@nih.gov; dmoran@chem.usyd.edu.au; schleyer@chem.uga.edu

Abstract: The geometries and relative stabilities of the singlet and triplet states of phenyl- (C_s), diphenyl-(C_2), 1-naphthyl- (C_s), di(1-naphthyl)- (C_2), and 9-anthryl-substituted (C_s) carbenes were investigated at the B3LYP/6-311+G(d,p) + ZPVE level of density functional theory. The singlet−triplet energy separations (ΔE_{ST}), 2.7, 2.9, 3.4, 3.7, and 5.7 kcal/mol, respectively, after including an empirical correction (2.8 kcal/mol) based on the error in the computed singlet−triplet gap for methylene versus experiment, are in good agreement with available experimental values. Consistent with literature reports, triplet di(9-anthryl)carbene has a linear, D_{2d} symmetrical, allene structure with 1.336 Å C=C bond lengths and considerable biradical character. B3LYP favors such cumulene biradical structures and triplet spin states and predicts a large (>15 kcal/mol) "di(9-anthryl)carbene" singlet−triplet (biradical) energy gap. The resonance stabilization of both singlet and triplet carbenes increases modestly with the size of the arene substituent and overall, (di)arylcarbenes, both singlet and triplet, are better stabilized by bigger substituents. For example, methylene is stabilized more by a naphthyl than a phenyl group (singlets, 26.6 versus 24.4; and triplets, 20.9 versus 18.1 kcal/mol, respectively). The carbene geometries are affected by both steric effects and arene−carbene orbital interactions (σ−p and p−π). For instance, the central angles at the carbene are widened by a second arene group, which leads to increased s-character and shorter carbene bond lengths (i.e., C̈-C, C̈-H). In general, the aromaticity of the substituted rings in triplet carbenes is most affected by the presence of the unpaired electrons.

1. Introduction

Carbenes are divalent carbon species having two nonbonded electrons, either with parallel (e.g., triplet methylene,[1−3] **1**) or paired spins (e.g., singlet dimethylcarbene, **2**). These reactive intermediates are frequently characterized using IR, UV−visible, and, in the case of triplets, EPR spectroscopy.[4−7] The later is a particularly powerful technique, as EPR zero-field splitting (ZFS) parameters give details of both the separation between the carbene nonbonded electrons (D value) and of the carbene bond angle (E value). The ZFS D and E parameters for methylene, phenylcarbene (**3**),[8,9] diphenylcarbene (**4**),[8−14] 1-naph-

thylcarbene (**5**),[15,16] di(1-naphthyl)carbene (**6**),[17] 9-anthrylcarbene (**7**)[15] and di(9-anthryl)carbene (**8**)[18−20] are summarized in Table 1. It is apparent from the values in Table 1 that aryl groups have more modest effects on D values than their corresponding E values with the latter changing dramatically for different substituents. Theoretical predictions of carbene molecular and electronic structure provide a powerful complement to ZFS measurements, as computed carbene bond angles providing qualitative insights into E values, while calculations of carbene electron delocalization shed light on observed D values.

The accurate determination of the energy separation, ΔE_{ST}, between singlet and triplet carbene states (colloquially termed

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Table 1. Triplet Carbene Zero-Field Splitting Parameters *E* and *D* (cm^{-1})

Carbene	D	E	Carbene	D	E
methylene (^{3}**1**)	0.69	0.003	Di(1-naphthyl)carbene		
phenylcarbene (^{3}**3**)[8,9]	0.5150	0.0251	Nascent, bent[17]	0.3157	0.0109
diphenylcarbene (^{3}**4**)[8,9]	0.4055	0.0194	Relaxed, linear (^{3}**6**)[17]	0.2609	0.0051
1-naphthylcarbene			9-Anthrylcarbene (^{3}**7**)[15]	0.3008	0.0132
s-*E*-conformer (^{3}**5**)[15]	0.4555	0.0202	Di(9-anthryl)carbene		
s-*Z*-conformer[15]	0.4347	0.0208	Nascent, bent[20]	0.1038	0.0000
			Relaxed, linear (^{3}**8**)[20]	0.0890	0.0000
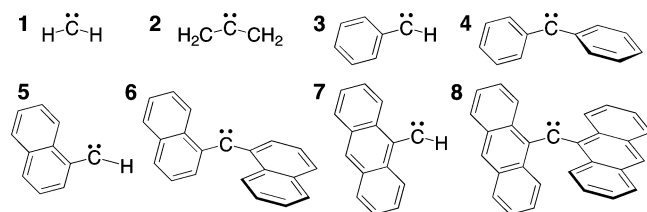
Figure 1. Compounds studied here: methylene (**1**), dimethylcarbene (**2**), phenylcarbene (**3**), diphenylcarbene (**4**), 1-naphthylcarbene (**5**), di(1-naphthyl)carbene (**6**), 9-anthrylcarbene (**7**), and di(9-anthryl)carbene (**8**).

the S−T "gap") has long challenged experimentalists and theoreticians alike. The fundamental S−T gap of methylene (Figure 1) is the most famous example.[3,21−29] The S−T gap of phenylcarbene[30−37] also has been much debated; determinations range from 2 to 7 kcal/mol.[30−37] However, the results of laser flash photolysis experiments (ΔE_{ST} = 2.3 kcal/mol)[35,36] and high level ab initio computations (2.4 kcal/mol at CCSD(T)/DZP// CISD/DZP[38] and 2.5 kcal/mol at CCSD(T)/cc-pVDZ//B3LYP/ 6-31G(d))[39] have narrowed the generally accepted S−T range of **3** to within 2−3 kcal/mol.[40] Estimates of the singlet−triplet energy separation of diphenylcarbene[30,34,41,42] range from 2 to 6 kcal/mol.[30,34,41,42] We calculated a diphenylcarbene S−T gap of 5.8 kcal/mol earlier,[41] but the B3LYP/6-311G(d,p) level employed is known to overestimate singlet−triplet energy

separations (vide infra); indeed, the benchmark laser flash photolysis S−T gap of **4** is 2.6 kcal/mol.[30]

As density functionals do not include a Coulomb correlation term, nor do they treat nondynamic electron correlation accurately, they underestimate the stability of singlet species relative to their triplet forms intrinsically.[43] Because the size of our larger systems precludes the application of more sophisticated correlated multireference treatments (e.g., CASPT2, CISD, geminal methods), we overcame the problem of singlet energy underestimation by employing an empirical correction, ΔE_{corr}, based on the difference between the experimental methylene singlet and triplet energy separation (9.05 kcal/mol)[42] with that computed at the same theoretical level. For example, this empirical correction improves the B3LYP/TZ2P 2-propylidene (dimethylcarbene) S−T separation, −0.2 kcal/mol (favoring the singlet), to −2.5 kcal/mol, which is very close to the high level MRCI+Q values of −2.6 to −3.1 kcal/mol.[42] In addition to the lack of multireference singlet state electronic descriptions, density functional theory (DFT) suffers from the overestimation of the cumulene-type delocalization[44] found in aryl-substituted carbenes, particularly the triplet diaryl species. The DFT bias for allene-like structures of the bisanthryl carbenes may be responsible for its remarkable B3LYP-optimized triplet D_{2d} geometry with a 180° ∠C−C̈−C central angle, dramatically shortened central C̈−C bond lengths (1.336 Å), and severely quinoid-distorted aryl rings.[45,46] In contrast, ROHF and CAS-(2,2) methods predict triplet di(9-anthryl)carbene geometries in better agreement with experiment (e.g., less seriously distorted aryl rings) and longer C−C̈ bonds.[46]

Aryl substituent effects on carbenes are dramatic because arene interactions with both the p and sp^2 carbene orbitals are involved (Figure 2). We reported earlier that a 1-naphthyl substituent stabilizes the singlet 6−7 kcal/mol more than the triplet state.[47] A previous study by McKellar et al.[28] showed that a single phenyl substituent reduces the S−T gap of methylene significantly but that a second phenyl group has little further effect. Prompted by experimental efforts to characterize aryl group effects on carbenes,[48] we now employ isodesmic equations (Figure 3) to evaluate and compare the phenyl, naphthyl, and anthryl stabilization energies of singlet (Stab$_S$) and triplet (Stab$_T$) mono- and disubstituted methylenes. The experimental phenyl- and diphenylcarbene S−T values[41] are compared with our empirically corrected computed values. The 1-naphthylcarbene,[47] di(1-naphthyl)carbene, 9-anthrylcarbene,

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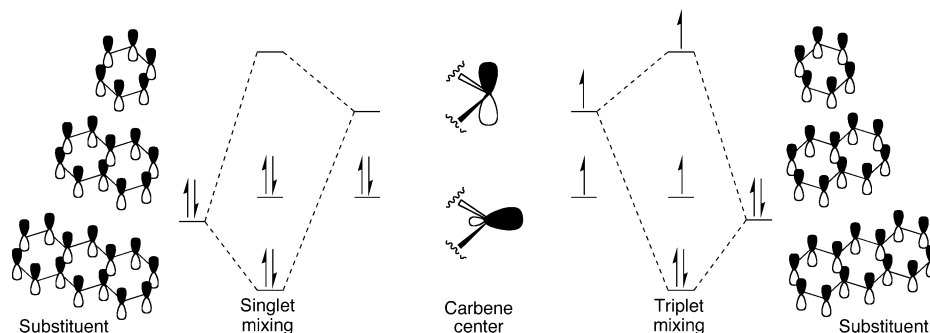
Figure 2. The interaction between a carbene p AO and the π MO's (shown schematically) of the first aryl-substituents. Because the carbene p-orbital is unoccupied, the singlets are stabilized more than the triplets, which have singly occupied carbene orbitals. The second aryl substituent (which results in twisted geometries) does not differentiate between singlet and triplet appreciably.
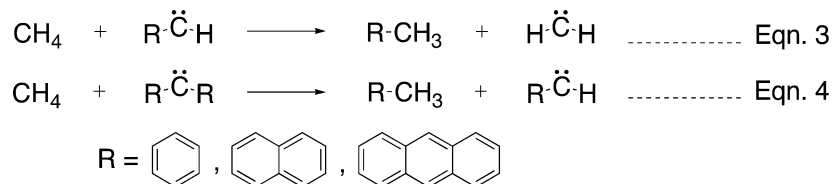

Figure 3. Isodesmic equations used to evaluate the methylene stabilization due to mono- (eq 3) and di- (eq 4) phenyl, 1-naphthyl, and 9-anthryl substitutions. Equation 4 gives the additional stabilization of the second aryl group.

and di(9-anthryl)carbene S−T gaps also have been evaluated. Computed nucleus independent chemical shifts (NICS)[49−51] indicate the aromatic character of the aryl groups of carbenes **3**−**8**. We employed the widely tested B3LYP functional, as numerous examples[41,42,47,52] demonstrate its success in evaluating carbene S−T gaps and NICS values.[53−56]

2. Methods

Quantum chemical computations principally employed Q-Chem's[57] restricted (singlet) and unrestricted (triplet) B3LYP DFT.[58,59] UBS-B3LYP and ROB3LYP energies were calculated using Gaussian 03.[60] Kohn−Sham orbitals[61] were employed along with the 6-31G(d) and 6-311+G(d,p) basis sets.[62] Numerical integration in Q-Chem[57] employed the SG-1 grid, which is comprised of 50 radial and 194 angular points (50,194).[63] B3LYP/6-31G(d) structures were confirmed to be stationary points on the potential energy hypersurface (all real vibrational frequencies for minima; one imaginary frequency for transition structures). The B3LYP/6-311+G(d,p) energies were cor-

rected with B3LYP/6-31G(d) zero-point vibrational energies (ZPVEs). Unless otherwise noted, ZPVE corrected B3LYP/6-311+G(d,p) results are discussed throughout the text. Orbital populations were analyzed using natural bond order (NBO) analysis (Version 4),[64] as implemented in Q-Chem.

The CHARMM program package[65] and the Replica Path Method,[66] which maps discretized reaction pathways via a root-mean-square deviation (rmsd) restraint function, were employed to explore carbene isomerizations. In particular, both the "endo" to "exo" interconversion and the θ_{CCC} bending surface, respectively, of singlet and triplet di(1-naphthyl)carbene were examined.

The corrected energy separations, ΔE_{ST}, between singlet and triplet carbene states, employing the difference between the computed and experimental methylene values,[42,62] were determined using eqs 1 and 2 below

$$\Delta E_{corr} = (\ddot{C}H_2\ \Delta E_{ST})^{DFT} - (\ddot{C}H_2\ \Delta E_{ST} = 9.05\ kcal/mol^{28})^{Exp} \tag{1}$$

$$\Delta E_{ST} = (R_1\ddot{C}R_2\ \Delta E_{ST})^{DFT} - \Delta E_{Corr} \tag{2}$$

In addition to the primary goal of achieving accord with experiment, the empirical correction also improves agreement between different levels of theory. For example, the ∼2 kcal/mol difference between the S−T gap calculated for **3** at B3LYP/6-31G(d) and B3LYP/6-311+G-(d,p), is reduced to just 0.4 kcal/mol when the correction is applied.

NICS were computed at the B3LYP/6-311+G(d,p) level of theory using Gaussian 03.[60] NICS are absolute magnetic shieldings computed at selected points in space with their signs inverted to conform to the chemical shift convention. Using the geometric centers of each unique carbon atom ring (NICS(0)), we evaluated the **zz**-tensor (which is perpendicular to the ring planes) of the magnetic shielding (so-called

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Table 2. Optimized[a] Carbene Bond Lengths (r_a and r_b, Å) as Well as Bond (θ) and Torsion Angles (ϕ)[b]

molecule	spin	r_a	r_b	$\theta°$	$\phi°$
methylene	^{1}**1** (C_{2v})	1.114	1.111	101.55	-
	^{3}**1** (C_{2v})	1.080	1.075	135.36	-
dimethylcarbene	^{1}**2** (C_2)	1.471	1.471	112.60	-
	^{3}**2** (C_{2v})	1.468	1.468	133.73	-
phenylcarbene	^{1}**3** (C_s)	1.437	1.109	106.96	0.00
	^{3}**3** (C_s)	1.389	1.081	135.67	0.00
diphenylcarbene	^{1}**4** (C_2)	1.431	1.431	119.54	58.46
	^{3}**4** (C_2)	1.399	1.399	142.88	53.67
1-naphthylcarbene	^{1}**5** (C_s)	1.430	1.106	106.73	0.00
	^{3}**5** (C_s)	1.377	1.080	135.48	0.00
di(1-naphthyl)carbene	^{1}**6** (C_2)	1.416	1.416	121.62	68.94
	^{3}**6** (C_2)	1.378	1.378	173.62	87.31
9-anthrylcarbene	^{1}**7** (C_s)	1.418	1.101	109.72	0.00
	^{3}**7** (C_s)	1.354	1.077	139.31	0.00
di(9-anthryl)carbene	^{1}**8** (C_2)	1.359	1.359	147.28	78.71
	^{3}**8** (D_{2d})	1.336	1.336	180.00	90.00
di(9-anthryl)diazomethane	**9** (C_2)	1.491	1.491	128.23	91.00

[a] B3LYP/6-311+G(d,p). [b] See Figure 6 for details.

NICS(0)$_{zz}$).[49,50] Aromatic molecules have negative isotropic NICS, while antiaromatic molecules have positive values.[55,56,67−71]

3. Results and Discussion

Geometries. Phenylcarbene (^{1}**3** and ^{3}**3**), 1-naphthylcarbene (^{1}**5** and ^{3}**5**), and 9-anthrylcarbene (^{1}**7** and ^{3}**7**) favor planar structures that maximize delocalization between the vacant or partially filled carbene p-orbital and the adjacent arene π-system. In contrast, diphenylcarbene (^{1}**4** and ^{3}**4**), di(1-naphthyl)carbene (^{1}**6** and ^{3}**6**), and di(9-anthryl)carbene (^{1}**8**) are severely strained in planar symmetries due to aryl-bumping and carbene-ring orbital repulsion. Instead, they adopt twisted C_2-propeller-like or D_{2d}-perpendicular conformations (Table 2). In the case of carbenes with multiple conformers such as **5** and **6** (see below), the lower energy isomers of these carbenes have been employed. Comparison between our B3LYP/6-311+G(d,p) predicted geometries and literature reports on the experimentally determined structural parameters of arylcarbenes **3−8** generally reveals good agreement between experiment and theory. The experimental carbene angles of triplet phenylcarbene, diphenylcarbene, 1-naphthylcarbene, and 9-anthrylcarbene range from ~135 to 140°[72] and are in good agreement with the triplet carbene angles for **3−5,7**. As previously noted, di(9-anthryl)carbene is predicted to have a linear carbene angle both experimentally (E ~ 0)[20,72,73] and computationally.[45,46]

As is well-known from EPR spectroscopy,[15] there are two 1-naphthylcarbene hydrogen orientations; both structures were considered here. The anti-orientation of the 1-naphthylcarbene hydrogen is 0.96 (^{1}**5**) and 0.76 (^{3}**5**) kcal/mol more stable than the syn-orientation, which has unfavorable H−H bumping. In addition, three di(1-naphthyl)carbene singlet minima (Figure 4)

and two di(1-naphthyl)carbene triplet minima were located using the replica path method followed by refinement via unrestrained optimizations or transition state searches. The singlet di(1-naphthyl)carbene with an exoconformation benefits considerably from strain relief and is lowest in energy, as compared with the "up-down" and "endo" conformers. The C_2-symmetric "linear" triplet minimum of di(1-naphthyl)carbene is approximately isoenergetic with the "bent" conformer, indicating the energy potential describing the carbene angle is very flat. Tukada[17] studied di(1-naphthyl)carbene using ESR and reported that it has a linear carbene angle with naphthyl rings in a perpendicular orientation. We have, therefore, used the "linear" triplet minimum of di(1-naphthyl)carbene for subsequent computations. In the ^{3}**8** D_{2d} symmetric minimum, the carbene CCC angle is exactly 180°; the anthryl groups are perfectly perpendicular (ϕ torsion 90°). Trindle[45] describes "two extreme cases of the bonding" in bisaryl triplet carbenes: a spin-delocalized carbene and a cumulenic diradical. The UB3LYP/6-311+G(d,p) optimized geometry of triplet di(9-anthryl)carbene has the latter character, in agreement with Trindle's CAS computations[45] and, more importantly, in agreement with the very small D and E values of ^{3}**8**.[20,72,73]

As noted by Xie et al.,[47] carbene center CC bond lengths are affected by repulsion between substituent σ-bonds and the adjacent carbene occupied-orbitals. As a result, the $r(C−C_a)$ distance between the carbene center and phenyl ring (Figure 5) is substantially longer in ^{1}**3** (1.437 Å) than in ^{3}**3** (1.389 Å) (Table 2), as the carbene-substituent σ-sp^2 repulsion[47] is greater for the singlet, which has a doubly occupied sp^2 orbital in-plane with the phenyl σ-bond. Similarly, the 1.430 Å C−C$_a$ bond length in ^{1}**5** is 0.055 Å longer than the corresponding 1.377 Å length in ^{3}**5**. Likewise, there is 0.064 Å difference in bond lengths between ^{1}**7** (1.418 Å) and ^{3}**7** (1.354 Å).

The central CC bonds of the singlet disubstituted carbenes are also longer than in their triplet counterparts. For instance, the difference between ^{1}**4** (1.431 Å) and ^{3}**4** (1.399 Å) $r(C−C_a)$ bond lengths ($\Delta r = 0.032$ Å) is less than between ^{1}**3** and ^{3}**3** ($\Delta r = 0.048$ Å). Compared with the monosubstituted species, σ-sp^2 destabilization is expected to be less significant for disubstituted carbenes, as their twisted, propeller-like structures minimize this carbene-substituent orbital interaction. However, steric interactions between adjacent aryl groups may also be important.

The variations in the θ_{CCC} bond angles (Figure 5) reflect the relative stabilities of the singlet carbenes among each other and to their triplet states. For instance, θ_{CCC} for ^{1}**4** (119°) is 12° larger than ^{1}**3**, while θ_{CCC} is wider in ^{3}**4** (143°) than in ^{3}**3** (136°). Greater singlet carbene θ_{CCC} angles have less favorable s-p orbital mixing (Figure 2).[74] Hence, triplet carbenes typically are more stable when θ_{CCC} is large. Hence, the differences between ^{1}**3** and ^{1}**4** and between ^{3}**3** and ^{3}**4** carbene bond angles is consistent with the ^{1}**4**−^{3}**4** versus ^{1}**3**−^{3}**3** relative energy separations. Optimized ^{1}**8** has a propeller-like C_2-symmetric structure; the carbene bond angle ($\theta_{CCC} = 147°$) is much wider than those of ^{1}**4** or ^{1}**6**. In addition to steric repulsion between the adjacent anthryl-substituents, strong arene-carbene overlap helps widen the ^{1}**8** θ_{CCC} angle, because the increased carbene σ-character shortens the C−C$_a$ bond and thereby increases the repulsion between the substituents.

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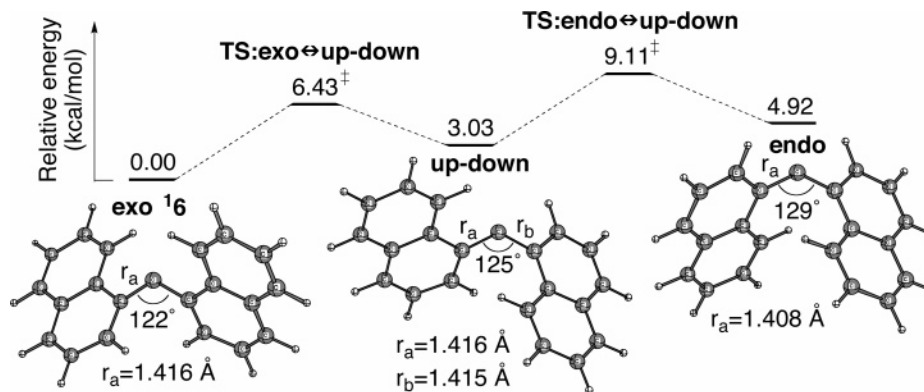
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Figure 4. Optimized singlet di(1-naphthyl)carbene (^{1}**6**) has three B3LYP/6-31G(d) minima. The C_2-symmetric exo-structure (^{1}**6**) is 3.03 kcal/mol more stable than the C_1-symmetric up-down-conformer, and 4.92 kcal/mol more stable than the C_2-symmetric endo-conformer (B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) + ZPVE).
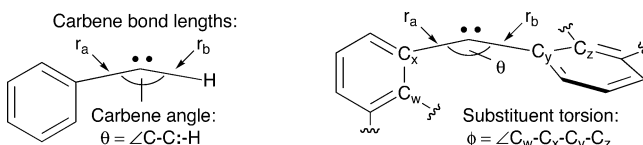

Figure 5. Definition of important geometric parameters in mono- and disubstituted arylcarbenes.

Singlet−Triplet Energy Separations. Table 3 summarizes our empirically corrected S−T energy differences (ΔE_{ST}) for carbenes **3**−**8** along with the raw (uncorrected) singlet−triplet energy separations ([S−T]) for reference. By definition (see eqs 1 and 2), the correction is based on the difference between our computed [S−T] value for methylene (11.89 kcal/mol) and its accurately determined experimental singlet−triplet energy difference of 9.05 kcal/mol.[28] This empirical correction is 2.84 kcal/mol at the B3LYP/6-311+G(d,p) + ZPVE level. Our corrected phenylcarbene ΔE_{ST} (2.7 kcal/mol) is close to the experimental value of 2.3 kcal/mol.[35,36] Likewise, our ΔE_{ST} for **4** (2.9 kcal/mol, Table 3) is in equally good agreement with the experimental 2.6 kcal/mol separation.[30] This agreement is much better than that of our previous, 5.8 kcal/mol estimate,[41] as the latter was not corrected. Experimental 1-naphthylcarbene and di(1-naphthyl)carbene S−T gaps are not available, but our ΔE_{ST} separations for **5** (3.4), **6** (3.7), and **7** (5.7 kcal/mol) should be reasonably reliable.

While a single phenyl substituent reduces ΔE_{ST} by 6.3 kcal/mol relative to methylene, the reductions due to the larger 1-naphthyl (5.7) and 9-anthryl (3.7 kcal/mol) groups (ΔE_{sub}, Table 4) actually are smaller. Surprisingly, the second aryl substituents have very little further effect (less than 0.4 kcal/mol) on ΔE_{ST} for diphenyl and di(1-naphthyl)carbene. However, these comparisons (Table 4) hide the fact (analyzed further below), that the larger 1-naphthyl and 9-anthryl groups stabilize both the singlet and especially the triplet carbene more than phenyl due to increased resonance stabilization. The same is true for diaryl-substitution. The difference in ΔE_{ST} between 1-naphthyl and di(1-naphthyl)carbene is only 0.3 kcal/mol.

The much larger difference in [S−T] (>7 kcal/mol) between 9-anthryl- with di(9-anthryl)carbene is spurious. Trindle[45] noted that about 65% of the unpaired electron spin density of the di-(9-anthryl)carbene triplet is displaced from the carbene carbon to the 10 and 10′ positions of the anthryl rings (Figure 6). Indeed, ^{3}**8** prefers D_{2d} symmetry with a linear (180.0°) carbene angle and allene-like central C=C bond lengths (1.336 Å). The triplet

is 2.2 kcal/mol more stable than the broken-symmetry UBS-B3LYP/6-311+G(d,p) open-shell singlet with $<S^2>$ = 1.1 (computed using the triplet geometry). UB3LYP, which among other general problems[75] overestimates the stability of both cumulene structures and the triplet spin state, predicts an anomalously large energy [S−T] difference (15.7 kcal/mol) between singlet and triplet states of **8**. Note that this difference does not include our 2.8 kcal/mol empirical [S−T] correction, as ^{3}**8** has a greater degree of delocalized biradical than of triplet carbene character. While the spin contamination of this linear triplet biradical is minor ($<S^2>$ = 2.1), the ROB3LYP/6-311+G(d,p) energy is 5.2 kcal/mol higher than the UB3LYP/6-311+G(d,p) optimized triplet energy, both at the latter geometry. Applying this larger correction reduces the singlet carbene and biradical triplet energy difference of **8** from 15.7 (UB3LYP) to 10.5 kcal/mol (ROB3LYP).

Trindle[45] attempted to diminish the triplet biradical character of di(9-anthryl)carbene;1,1′-di(CF$_3$) substitution decreased the carbene angle from 180 to 155°, but had little effect on the unpaired electron distribution. We optimized model structures of ^{3}**8** having constrained central bond lengths and angles, but delocalization of the spin-density to the anthryl groups remained almost complete. However, we did have some success when we predicted the di(9-anthryl)carbene S−T gap using the optimized geometry of di(9-anthryl)diazomethane, with the N$_2$ moiety removed (without further geometry optimization) to produce a so-called "nascent" structure. This approach was inspired by Tomioka and co-workers,[20] who in explaining their observations of di(9-anthryl)carbene introduced a species that "is generated in rigid matrices at very low temperature, it should have the geometry dictated by that of a precursor." In their case, the precursor was di(9-anthryl)diazomethane.[20] And indeed, when the singlet−triplet gap of **8** is calculated using the so-called nascent geometry for both singlet and triplet species, a [S−T] gap of 7.8 kcal/mol (not ZPVE corrected) is predicted. This is much more consistent with the other S−T gaps in Table

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Table 3. Corrected Carbene Singlet−Triplet Energy Separations (ΔE_{ST}, kcal/mol)[a]

molecule	ΔE_{ST}	[S−T]	molecule	ΔE_{ST}	[S−T]
phenylcarbene (**3**)	2.75	5.59	diphenylcarbene (**4**)	2.94	5.78
1-naphthylcarbene (**5**)	3.40	6.24	di(1-naphthyl)carbene (**6**)	3.74	6.58
9-anthrylcarbene (**7**)	5.67	8.51	di(9-anthryl)carbene (**8**)	[b]	15.70
			ROB3LYP (³**8**)	[b]	10.51[c]
			³**8** nascent		7.76[d]

[a] As the uncorrected B3LYP/6-311+G(d,p) (B3LYP/6-311+G(d,p)//B3LYP/6-31G(*d*) + ZPVE) [S−T] gaps overestimate these separations, the [S−T] values have been adjusted by the 2.84 kcal/mol difference between the experimental and computed S−T gap (at the same level) for methylene (the correction is 2.84 kcal/mol at B3LYP/6-311+G(d,p)). [b] The allene-like triplet biradical ³**8** is not a carbene, and it is not meaningful to adjust the [S−T] energy separation using the error between the experimental and computed methylene S−T gap. [c] ROB3LYP/6-311+G(d,p)//UB3LYP/6-31G(d) + ZPVE. [d] The nascent S−T gap does not include ZPVE. For reference, the 9-anthrylcarbene vibrationless (i.e., not ZPVE corrected) S−T gap is 7.81 kcal/mol.

Table 4. Enthalpies (kcal/mol) of the Isodesmic Reactions That Evaluate the Effect of Adding Aryl Groups to Methylene[a]

	$E_{sub}^{(\uparrow\downarrow)}$	$E_{sub}^{(\uparrow\uparrow)}$	ΔE_{sub}[b]		$E_{sub}^{(\uparrow\downarrow)}$	$E_{sub}^{(\uparrow\uparrow)}$	ΔE_{sub}[c]
[structure]	24.4 (¹**3**)	18.1 (³**3**)	6.3	[structure]	15.8 (¹**4**)	16.0 (³**4**)	−0.2
[structure]	26.6 (¹**5**)	20.9 (³**5**)	5.7	[structure]	18.6 (¹**6**)	19.0 (³**6**)	−0.4
[structure]	30.5 (¹**7**)	26.8 (³**7**)	3.7	[structure]	21.5 (¹**8**)	- (³**8**)	-

[a] See Figure 3 for details of eqs 3 and 4. [b] $\Delta E_{sub} = E_{sub}^{(\uparrow\downarrow)} - E_{sub}^{(\uparrow\uparrow)}$; these data are derived from the difference between ΔE_{ST} for methylene and the monosubstituted carbenes in Table 3. [c] These data are based on the differences between the mono- and disubstituted carbene ΔE_{ST} values in Table 3.
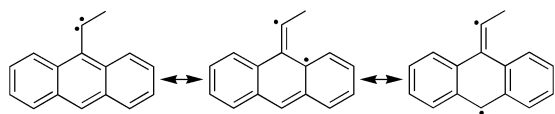
Figure 6. Resonance contributors for triplet 9-anthrylcarbene emphasizing the spin delocalization onto the central ring of anthracene.

Figure 7. Optimized singlet and triplet structures of **4**, **6**, and **8**. In general, the structures demonstrate that the p−π conjugation of diarylcarbenes is incomplete, as not all the ring atoms lie in a plane perpendicular to a carbene p-orbital.

3, particularly the singlet−triplet gap of **7** (7.8 kcal/mol without ZPVE correction).

Substituent Effects. Aryl groups stabilize carbenes significantly. However, p−π arene conjugation stabilizes the vacant p-orbitals of singlet carbenes more than the singly occupied p-orbitals of the triplet states. The mono- and disubstitution effects, evaluated using isodesmic eqs 3 and 4 (Figure 3), are summarized in Table 4. The p−π conjugation of arylcarbenes is maximized when all the atoms lie in the same plane, and this may not be the case when there are two bulky substituents (see Figure 7). Consequently, the effect of the second aryl group may be quite different from the first, which is readily confirmed by comparing the *D*-parameter values in Table 1. Relative to methylene ($D = 0.69$ cm^{-1}) for example, a second phenyl-substituent (³**4**, $D = 0.41$ cm^{-1}) decreases the *D*-parameter less than the first phenyl-substituent (³**3**, $D = 0.52$ cm^{-1}).

For instance, phenyl stabilizes ¹**3** by 24.4 and ³**3** by only 18.1 kcal/mol. The vacant carbene ¹**3** p-orbital interacts more effectively with the ring π-system than the singly occupied carbene p-orbital in ³**3**. In contrast to this 6.3 kcal/mol difference favoring ¹**3** over ³**3**, the second phenyl groups in ¹**4** and ³**4** stabilize both equally (by approximately 16 kcal/mol each; see eq 4, Figure 3). The ring−ring torsion angle values (ϕ, Figure 5), which are a measure of the twist of the substituent rings relative to each other, are 58 and 54° for ¹**4** and ³**4**, respectively. Neither value is ideal for optimal orbital interactions between

the carbene-center and substituent (see Figure 7). Both the phenyl groups in ¹**4** would need to be coplanar to maximize electron-density donation into the vacant carbene p-orbital. While both phenyl-rings in ³**4** would need to be perpendicular for maximum overlap with the adjacent singly occupied carbene orbitals. Despite the greater substituent stabilization-effect for ¹**3**, ³**3** has a shorter carbene bond length (1.437 Å versus 1.389 Å). This is because of carbene-substituent σ-sp² repulsion,[47] as discussed below.

The 1-naphthyl group stabilizes ¹**5** and ³**5** by 26.6 and 20.9 kcal/mol, respectively, relative to methylene. These 1-naphthyl effects are 2−3 kcal/mol greater than those for phenyl, due to the greater resonance stabilization of the larger arene. Like ¹**3**, the 1-naphthyl substituent stabilizes ¹**5** 5.7 kcal/mol more than ³**5**. The second 1-naphthyl group stabilizes ¹**6** and ³**6** by 18.6 and 19.0 kcal/mol, respectively (Table 4). The first aryl substituent stabilizes carbenes more than the second. This attenuation is more pronounced for the singlets. In contrast with the C_2-twisted disubstituted singlet carbenes, the planar C_s monosubstituted singlet carbenes have optimum planar geometries for arene π-interaction with the aligned carbene p-orbital.

Table 5. B3LYP/6-311+G(d,p) Strain Energies (kcal/mol) Due to Substituting Methylene with Phenyl, 1-Naphthyl, or 9-Anthryl Groups at the Constrained Angles of the Parents[a]

phenyl-	strain	1-napthyl-	strain	9-anthryl-	strain
^{1}3	0.70	^{1}5	0.65	^{1}7	1.4
^{3}3	0.00	^{3}5	0.01	^{3}7	0.22
diphenyl-		di(1-naphthyl)-		di(9-anthryl)-	
^{1}4	8.66	^{1}6	10.02	^{1}8	18.53
^{3}4	0.70	^{3}6	1.32	^{3}8	8.82

[a] B3LYP/6-311+G(d,p) partially optimized geometries.

Table 6. B3LYP/6-311+G(d,p) Singlet and Triplet Carbene NICS(0)$_{zz}$ Values (ppm)

|	^{1}3	^{3}3		^{1}4	^{3}4
A–ĊH	−10.4	−2.3	A–Ċ⟨⟩	−9.4	−3.7
	^{1}5	^{3}5		^{1}6	^{3}6
A / B (Ċ–H)	−5.5 / −13.4	+2.6 / −10.8	A / B Ċ	−3.5 / −12.6	+5.4 / −9.7
	^{1}7	^{3}7		^{1}8	^{3}8
A / B / C (ĊH)	−9.3 / −2.8 / −10.0	−5.9 / +9.2 / −5.8	A / B / C Ċ	−6.3 / +5.2 / −6.5	−4.5 / +14.5 / −4.5

Furthermore, the steric strain in the large disubstituted carbenes (e.g., **6**) destabilizes the singlets in particular (vide infra).

Isodesmic eq 3 (Figure 3) shows that the 9-anthryl stabilizations of ^{1}**7** and ^{3}**7** are 30.5 and 26.8 kcal/mol, respectively. Hence, 9-anthryl is the most stabilizing aryl-substituent considered. The NICS values for the central rings of the 9-anthryl carbenes (particularly for ^{3}**7**) are significantly less than for the adjacent rings, indicating a significant reduction in their diatropic ring currents (see below). The substantial overlap between the carbene and 9-anthryl orbitals results in some quinoid character of the central anthryl-rings. Like the phenyl and 1-naphthyl carbenes, ^{1}**7** is stabilized more than ^{3}**7** but only by 3.7 kcal/mol. The unusually small difference is due to the exceptional ability of the 9-anthryl group to resonance stabilize ^{3}**7** (Figure 4). Note that there is a similar loss in net stabilization of singlet over triplet when comparing the isodesmic equations for **3** (6.3 kcal/mol) and **5** (5.7 kcal/mol), which is due to the additional resonance stabilization of a naphthyl group as compared to a phenyl group.

Substituent Strain Effects. The steric interactions involving the aryl substituents were investigated by constraining the phenyl, 1-naphthyl, and 9-anthryl carbene angles to the 102° (singlet) and to the 135° (triplet) HCH angles of ĊH$_2$. The energies resulting from the partial optimization of these constrained species are compared with those of the unconstrained optimizations (Table 5). With the exception of ^{3}**8** and to a lesser extent ^{3}**6**, all the triplets are virtually strain free, as the unconstrained and constrained θ_{HCC} angles are large and nearly the same. The model singlet phenyl (^{1}**3**) and 1-naphthyl (^{1}**5**) carbenes with much smaller 102° θ_{HCC} angles are strained by only ca. 0.7 kcal/mol due to the "bumping" between the carbene hydrogen and the adjacent aryl CH group. The steric environments in ^{1}**3** and ^{1}**5** are essentially the same, as are their fully optimized θ_{HCC} angles (107°). The somewhat more demanding steric environment of ^{1}**7** (the relaxed θ_{HCC} angle is 110°) only increases the strain to 1.4 kcal/mol. However, in disubstituted carbenes, the magnitude of the strain predicted for the singlet species is very large (>9 kcal/mol), which explains why (as shown in Table 4) a second substituent stabilizes a singlet carbene much less than the first substituent (cf $E_{sub}^{(\dagger)}$ for ^{1}**5** [26.6 kcal/mol] versus ^{1}**6** [18.6 kcal/mol]). Overall, strain favors the triplets and increases the monosubstituted carbene S−T energy separations modestly (≤1.2 kcal/mol). The disubstituted singlets are destabilized much more by carbene angle strain than their equivalent triplet species.

Carbene Substituent Rotational Barriers. The p−π conjugation between the unoccupied (singlet) or singly occupied (triplet) carbene p-orbital and the π arene system is "switched-off" in the rotational transition structures. Instead, the π arene system interacts (less effectively, due to the smaller overlap) with the doubly or singly occupied carbene sp^2 orbital. Indeed, the rotational transition structures ^{1}**3TS** and ^{3}**3TS**, with 90° ring-Ċ−H dihedral angles are 11.73 and 3.30 kcal/mol higher in energy than ^{1}**3** and ^{3}**3**, respectively (Figure 8). The greater loss of p−π conjugation for the vacant p-orbital of ^{1}**3TS** than for the singly occupied p-orbital of ^{3}**3TS** during rotation is largely responsible for the 8.43 kcal/mol difference.

Similarly, the transition structures ^{1}**5TS** and ^{3}**5TS** correspond to rotational barriers of 12.89 and 3.58 kcal/mol for ^{1}**5** and ^{3}**5**, respectively (Figure 8). The ^{3}**5** barrier to syn−anti interconversion is somewhat lower than the reported experimental range, which "must be greater than 4.5−6.3 kcal/mol."[16] The loss of
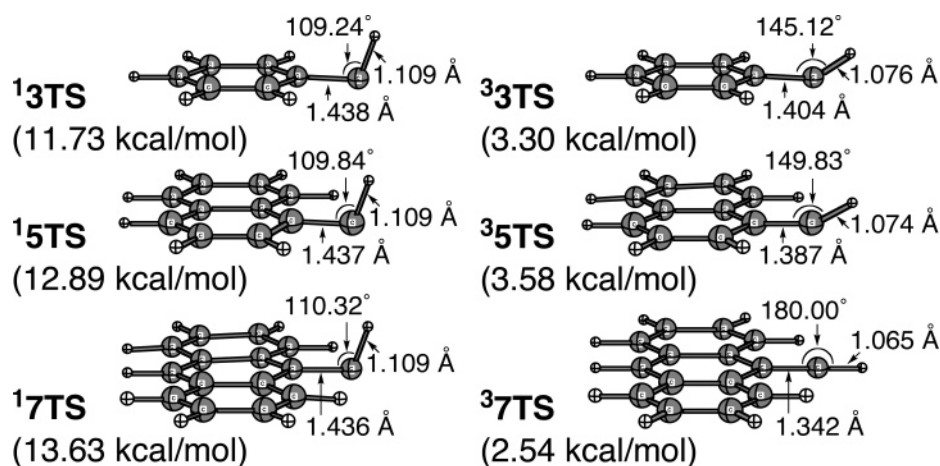
Figure 8. Structural features and rotational barriers (in parentheses) of singlet and triplet carbene rotational transition states.

^{1}**3TS** (11.73 kcal/mol) — 109.24°, 1.109 Å, 1.438 Å
^{3}**3TS** (3.30 kcal/mol) — 145.12°, 1.076 Å, 1.404 Å
^{1}**5TS** (12.89 kcal/mol) — 109.84°, 1.109 Å, 1.437 Å
^{3}**5TS** (3.58 kcal/mol) — 149.83°, 1.074 Å, 1.387 Å
^{1}**7TS** (13.63 kcal/mol) — 110.32°, 1.109 Å, 1.436 Å
^{3}**7TS** (2.54 kcal/mol) — 180.00°, 1.065 Å, 1.342 Å

p$-\pi$ stabilization is responsible for much of the 9.31 kcal/mol energy difference between [1]**5TS** and [3]**5TS**. Likewise, the [1]**7**→ [1]**7TS** (13.63) and [3]**7**→ [3]**7TS** (2.54 kcal/mol) ([3]**7TS**) rotational barriers differ by 11.09 kcal/mol. Because of the linear θ_{CCC} angle and allene-like structure of [3]**7TS**, the [3]**7**→ [3]**7TS** rotation results in the unusually large ring-carbene bond shortening of 0.012 Å.

Nucleus Independent Chemical Shifts. In general, the aromatic ring currents of the substituent aryl groups of **3**−**8** (Table 6) are most strongly affected by the presence of the unpaired electrons from triplet carbenes (see Figure 4). This is highlighted by comparing the NICS values for the monosubstituted carbenes, such **3** and **5**, where the 8.1 ppm difference between the singlet and triplet values shows a dramatic disruption of the aromatic ring current in both [3]**3** and [3]**5**. Indeed, the positive NICS(0)$_{zz}$ values for the carbene-attached rings of the substituent groups of [3]**5**,[3]**6**, and [3]**7** indicate complete loss of aromaticity. Focusing on the singlet species, it is interesting to note that the NICS values monotonically increase in going from [1]**3** (-10.4 ppm) to [1]**8** ($+5.2$ ppm). With the exception of [3]**3**, there is the same trend for the carbene-attached rings of the substituent groups of the triplet species.

4. Conclusions

The inherent DFT underestimation of singlet carbene energies (nondynamic correlation problem) has been corrected empirically by the error (at the same DFT level) in the singlet−triplet energy separation of methylene. When this correction is applied to the B3LYP/6-311+G(d,p) + ZPVE mono- and disubstituted carbene energies, the resulting phenyl- (C_s), diphenyl- (C_2), 1-naphthyl- (C_s), di(1-naphthyl)- (C_2) and 9-anthryl-substituted (C_s) methylene ΔE_{ST} values, 2.7, 2.9, 3.4, 3.7, and 5.7 kcal/mol, respectively, are in excellent agreement with the available experimental and highest level theoretical data. Although no trend is apparent in these ΔE_{ST} values, both singlet and triplet carbene stabilizations follow the order of increasing size of these aryl groups. But there are complicating features.

While phenyl-, 1-naphthyl-, and 9-anthryl-substituents stabilize triplet carbenes considerably (>15 kcal/mol), the singlets are stabilized even more (>24 kcal/mol). This effect reduces, but does not overcome, the inherent preference of the parent methylene for the triplet ground state. Consequently, all the mono- and diaryl-carbenes also have triplet ground states. While the additional stabilization of a second aryl-substituent is nearly the same as the first for the triplets, steric effects of the second

group attenuate the additional stabilization of the singlets due to ring twisting Consequently, the singlet−triplet energy separations tend to be larger for the di- than for the monosubstituted carbenes. The NICS values of both the singlet and the triplet carbenes indicate that the p$-\pi$ net stabilizing interactions reduces the aromaticity of the arylcarbene substituents. The triplets exhibit substantial spin delocalization into the aromatic rings.

The rotation barriers of the singlet monosubstituted carbenes ([1]**X**−[1]**XTS**, $X = $ **3**, **5**, **7**), 11.7, 12.9, and 13.6 kcal/mol, respectively, are much larger than those of the corresponding triplets ([3]**X**−[3]**XTS**, $X = $ **3**, **5**, **7**), 3.3, 3.6, and 2.5 kcal/mol, respectively. This also demonstrates the importance of the greater p$-\pi$ stabilization in the planar singlet ground states, which is lost during rotation. The triplet barriers involve small differences in interactions involving singly occupied orbitals. The greater flexibility of the [3]**XTS** structures allow the carbene angles to widen more easily to reduce steric repulsions.

Overall and in response to the title question, bigger substituents are better at stabilizing both singlet and triplet arylcarbenes. For the monosubstituted carbenes, the effect is greatest for the singlet species. However, for the disubstituted carbenes, the singlet and triplet species are stabilized to approximately the same extent: the increased strain of the singlet diarylcarbenes effectively counteracts their electronic stabilization advantage relative to their triplet counterparts.

Supporting Information Available: Complete refs 57 and 60, Cartesian coordinates and energies of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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