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Tuning Effects for Some Cyclic Aromatic Carbenes Bearing Remote Amino Groups

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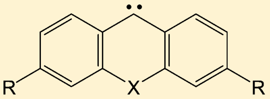
Supporting Information

ABSTRACT: Yamamoto and co-workers synthesized two cyclic aromatic carbenes with remote amino groups. Here we theoretically studied related compounds to explore tuning effects on the singlet−triplet splitting by variations of functional groups. For the Yamamoto compound, the lowest singlet state lies 15.7 kcal/mol below the lowest triplet. The singlet−triplet separation is reduced by ∼7 kcal/mol when the dimethylamino groups are replaced by H. In one set of carbenes, when X = O, we substitute S, Se, Te, SO, SeO, and TeO for X; the resulting Δ*E*(S−T) predictions are 9.9, 7.3, 3.9, 4.3, 2.3, and −0.1 kcal/mol, respectively. A different set of X fragments yields triplet electronic ground states with Δ*E*(S−T) values of −8.6 (X = BH), −6.8 (X = AlH), −7.2 (X = GaH), −7.5 (X = InH), and −7.0 kcal/mol (X = TlH). We also predicted Δ*E*(S−T) with $N(CH_3)_2$ replaced by PH_2, AsH_2, SbH_2, BiH_2, BH_2, CH_3, OH, and F. Of all the molecules considered, that with $N(CH_3)_2$ replaced with BH_2 and X = BH most favors the triplet state, lying 13.7 kcal/mol below the singlet. Finally, we have relocated the $N(CH_3)_2$ and NH_2 groups from the (3, 6) positions to the (4, 5), (2, 7), and (1, 8) terminal ring positions, with very interesting results.



1. INTRODUCTION

Carbenes, which may assume either a singlet or a triplet electronic state ground state, are generally too reactive to be isolated. The early synthesis of a free singlet carbene by Arduengo in 1991 (**A** in Figure 1),[1] however, marked a watershed for stable singlet carbenes and introduced the ongoing advances in N-heterocyclic carbene (NHC) chemistry.[2−10] For Arduengo-type free carbenes, a key factor for their remarkable stability is the neighboring electron-rich nitrogen atoms, whose electrons are donated into the vacant p orbital at the carbene center.[11,12] Further explorations have revealed that replacement of the α heteroatoms with the carbene carbon is not uniquely sufficient for stabilizing singlet carbenes. Subsequently, a new class of carbenes in which no heteroatom is located in positions α to the carbene carbon has grown extensively in recent years, these species being described as "remote" carbenes.[13]

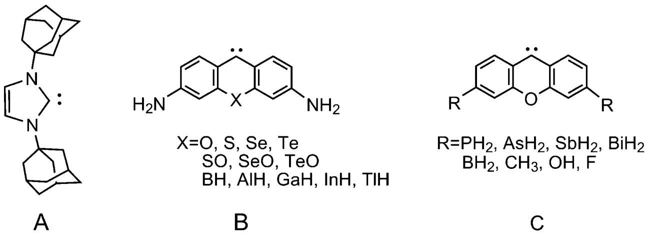


Figure 1. Early isolated N-heterocyclic carbene (NHC) of Arduengo (**A**), some novel cyclic aromatic carbenes (**B**), and X = O structures with the amino groups replaced with PH_2, AsH_2, SbH_2, BiH_2, BH_2, CH_3, OH, and F (**C**).

For cyclic aromatic carbenes,[14−20] potential scaffolds for ligands associated with transition metal catalysts, the bridging heteroatom plays a significant role with respect to the ground state multiplicity (singlet or triplet). This became clear from the seminal study by Schuster and co-workers, in which the authors observed the photophysical reactions of 9-mesityl-9,10-dihydro-9-boraanthrylidene[21] and 9-xanthylidene.[22]

In 2012, Yamamoto's group made further significant discoveries[23] involving what we shall call cyclic aromatic and remote (R = NH_2) carbenes (**CANC**) with the attachment of amino groups to conjugating positions of the carbene skeleton (structure B in Figure 1). Yamamoto synthesized the 3,6-bis(dimethylamino)-9-xanthylidene and 3,6-piperidinyl-9-xanthylidene Pd(II) complexes. In their research, Yamamoto also performed some computations on model compounds with methyl groups attached to the nitrogen atoms. Selecting X = NMe, O, S, SO, and BMes, they investigated the tuning effects of the aryl ring and found that singlet states are favored when electron-donating groups (NMe group or O or S atoms) are introduced at position X, while electron-withdrawing groups, for example, SO and BMes, preferentially lower the triplet states.

More comprehensive theoretical studies of the electronic structures of the **CANC** have not yet been reported. Here we undertake a systematic theoretical study of compounds of the general type synthesized by Yamamoto (structure **B** in Figure 1) to establish tuning effects involving the aryl rings on the ground state spin multiplicity and energetics of the **CANC**. To improve our understanding of the electronic effects of the remote nitrogen atoms, we also explore the analogous cyclic aromatic carbenes (**CAC**) without amino groups. Also considered are cyclic aromatic and remote carbenes (R =

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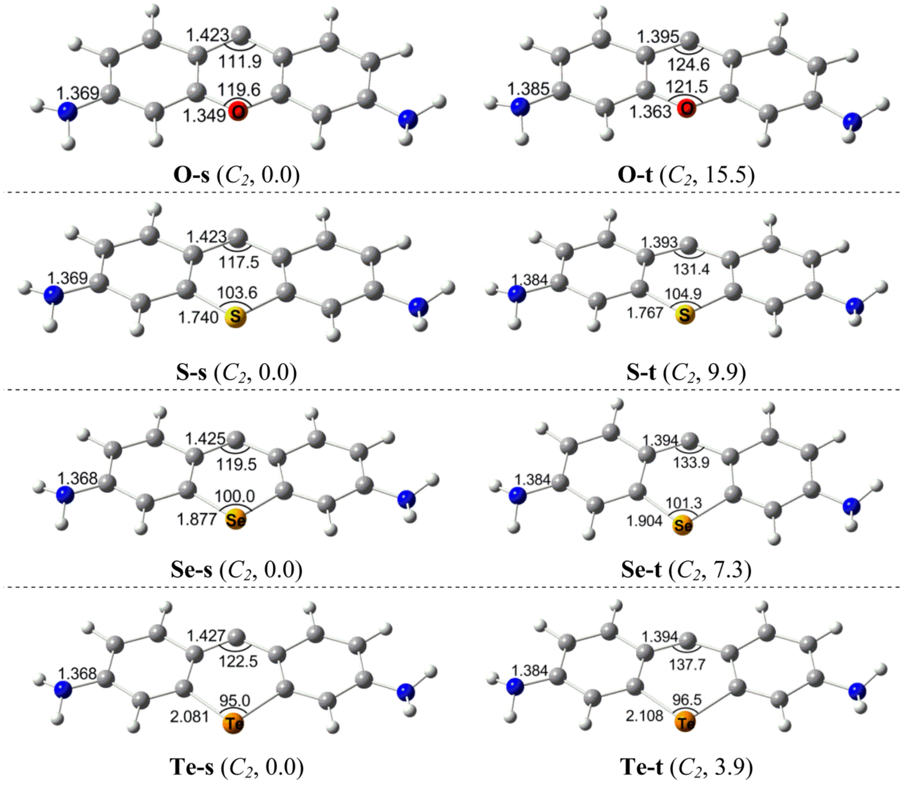
Figure 2. Side views of the C_2 *trans* conformation (left) and C_s *cis* conformation (right) for the X = O, S, Se, and Te species. The C_s conformers for structures **O-s**, **S-s**, and **Se-s** lie above the analogous C_2 conformers by ∼0.01 kcal/mol.



O-s (C_2, 0.0) **O-t** (C_2, 15.5)

S-s (C_2, 0.0) **S-t** (C_2, 9.9)

Se-s (C_2, 0.0) **Se-t** (C_2, 7.3)

Te-s (C_2, 0.0) **Te-t** (C_2, 3.9)

Figure 3. Equilibrium geometries and relative energies (kilocalories per mole) for the C_2 symmetry singlet and triplet aromatic carbenes with bridging X = O, S, Se, and Te.

PH_2, AsH_2, SbH_2, BiH_2, BH_2, CH_3, OH, and F) (**CARC**) in which the NH_2 groups are replaced (structure **C** in Figure 1). A range of interesting molecular structures and energetics is revealed, with an eye on future experimental studies with viable new cyclic aromatic carbenes.

2. COMPUTATIONAL DETAILS

All geometries of the singlet and triplet spin states are optimized with the hybrid meta-GGAs functional M06 developed by Truhlar's group.[24] For the H, C, B, Al, Ga, N, P, As, O, S, and Se atoms, the correlation-consistent cc-pVTZ basis sets were adopted.[25−27] For the In, Tl, Sb, Bi, and Te atoms, the Stuttgart-Cologne MCDHF (multiconfiguration Dirac−Hartree−Fock adjusted) effective core potentials (ECP) and the corresponding correlation-consistent cc-pVTZ-PP basis sets were employed.[28−31] With these ECPs, 28 core electrons ($1s^22s^22p^63s^23p^63d^{10}$) are embodied in the effective cores for In, Sb, and Te and 60 core electrons ($1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}$) for Tl and Bi. The singlet−triplet separation of the simplest carbene:CH_2 at the M06/cc-pVTZ level of theory was predicted to be −10.0 kcal/mol, in good agreement with the experimental value of −9 kcal/mol.[32]

Structural optimizations were performed with Gaussian09.[33] Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The ultrafine grid, i.e., the pruned (99, 590) grid, was used for the computation of two-electron integrals.

3. RESULTS AND DISCUSSION

The optimized **CANC**, **CAC**, and **CARC** structures are shown in Figures 2−8. The **CANC** structures are designated **X-m**, where **X** represents the bridging heteroatom. The letter **m** designates the spin state, i.e., **s** for singlets and **t** for triplets. These theoretical predictions are classified into three groups: X = O, S, Se, and Te as group I; X = SO, SeO, and TeO as group II; and X = BH, AlH, GaH, InH, and TlH as group III.

3.1. Molecular Structures. *3.1.1. Group I (X = O, S, Se, and Te)*.

The group I (X = O, S, Se, and Te) molecules reveal two conformations, with C_2 and C_s symmetries, with different orientations of the two amino groups (side views depicted in Figure 2). Both are genuine minima with all real vibrational frequencies. Generally, the C_2 conformations, because of the separation of the two lone pairs, are slightly preferred (by 0.01 kcal/mol) over the C_s structures, and thus, the C_2 species are mainly discussed in this section (Figure 3 and Tables 1 and 2).

Among the group I molecules, the singlet states have lower energies than the analogous triplets. For the X = O species, Yamamoto singlet state structure **O-s** is predicted to lie 15.5 kcal/mol below triplet state **O-t**. To be certain we were realistically modeling the Yamamoto compounds,[23] we replaced the parent NH_2 groups with $N(CH_3)_2$ and found a ΔE(S−T) of 15.7 kcal/mol. The singlet−triplet separations (Figure 3 and Table 1) for **S-s** versus **S-t**, **Se-s** versus **Se-t**, and **Te-s** versus **Te-t** are reduced monotonically to 9.9, 7.3, and 3.9 kcal/mol,

Table 1. Symmetries, Singlet−Triplet Separations [Δ*E*(S−T) = *E*(triplet) − *E*(singlet) (in kilocalories per mole)], Spin Expectation Values ($\langle S^2\rangle$), HOMO and LUMO Energies (in electronvolts), and HOMO−LUMO Gaps (in electronvolts) for Aromatic Carbenes

	symmetry	Δ*E*(S−T)	$\langle S^2\rangle$	HOMO	LUMO	gap
O-s	C_2	15.5 (13.7)[a]	0	−4.83	−1.51	3.33
O-t	C_2		2.04	−3.90	−0.13	3.77
S-s	C_2	9.9 (8.0)[a]	0	−4.69	−1.59	3.10
S-t	C_2		2.04	−3.94	−0.38	3.57
Se-s	C_2	7.3	0	−4.63	−1.64	2.99
Se-t	C_2		2.05	−3.98	−0.32	3.66
Te-s	C_2	3.9	0	−4.51	−1.67	2.84
Te-t	C_2		2.05	−3.98	−0.57	3.41
SO-s	C_s	4.3 (3.0)[a]	0	−5.05	−2.16	2.90
SO-t	C_s		2.05	−4.52	−0.72	3.80
SeO-s	C_s	2.3	0	−5.05	−2.21	2.84
SeO-t	C_s		2.05	−4.58	−0.82	3.76
TeO-s	C_s	−0.1	0	−4.96	−2.21	2.76
TeO-t	C_s		2.05	−4.55	−0.96	3.59
BH-s	C_s	−8.6 (−9.6)[a]	0	−4.73	−2.60	2.13
BH-t	C_s		2.05	−4.61	−1.25	3.36
AlH-s	C_s	−6.8	0	−4.40	−2.19	2.21
AlH-t	C_s		2.04	−4.28	−1.18	3.10
GaH-s	C_s	−7.2	0	−4.44	−2.30	2.14
GaH-t	C_s		2.04	−4.31	−1.29	3.02
InH-s	C_s	−7.5	0	−4.31	−2.20	2.11
InH-t	C_s		2.04	−4.20	−1.45	2.76
TlH-s	C_s	−7.0	0	−4.28	−2.13	2.15
TlH-t	C_s		2.05	−4.17	−1.38	2.79

[a] B3LYP/6-31G(d) results from ref 23.

respectively, consistent with the level of electron donation decreasing in the following order: O > S > Se > Te. Bourissou and co-workers suggested that the larger the absolute Δ*E*(S−T) value of a carbene, the more likely it is to be synthesized.[34] By this criterion, the **O-s** structure is most stable, consistent with the homologous 3,6-bis(dimethylamino)-9-xanthylidene and 3,6-piperidinyl-9-xanthylidene Pd(II) complexes that have been synthesized and isolated.[23]

For the singlet structure **O-s**, the two C−C bond distances adjacent to the carbene center are predicted to be 1.423 Å, reasonably close to the experimental values of 1.431(7) and 1.410(7) Å for the analogous palladium structure determined by X-ray crystallography.[23] The C−C−C carbene angle for **O-s** is predicted to be 111.9°, somewhat smaller than the experimental value of 116.0(5)° for the palladium complex.[23] The deviation of 4° may come from the difference between the free carbene and the metal complex. With the transition from singlet **O-s** to triplet **O-t**, the equilibrium geometrical parameters undergo significant changes, the C−C bond length decreasing to 1.395 Å and the C−C−C angle increasing to 124.6°. This is of course consistent with triplet carbenes having central bond angles that are larger than those of the corresponding singlets.[35]

Similar trends in structural predictions are found from **S-s** to **S-t**, from **Se-s** to **Se-t**, and from **Te-s** to **Te-t**; that is, the C−C bond distances are 1.423, 1.425, and 1.427 Å for **S-s**, **Se-s**, and **Te-s**, respectively, while they decrease by ~0.03 Å for the corresponding triplets. In the order **O**, **S**, **Se**, and **Te**, the C−C−C angles monotonically increase from 111.9° to 122.5° for the singlets and from 124.6° to 137.7° for the triplets. The C−C−C carbene angle is an important factor in determining their

Table 2. Symmetries, Singlet−Triplet Separations [Δ*E*(S−T) = *E*(triplet) − *E*(singlet) (in kilocalories per mole)], Central C−C−C Angles (in degrees), C−C Distances (in angstroms), C−X Distances (in angstroms), and NBO Atomic Charges for Aromatic Carbenes

	symmetry	Δ*E*(S−T)	C−C−C	C−C	C−X	charge(C)	charge(X)
O-s	C_2	15.5	111.9, *116.0(5)*[a]	1.423, *1.431(7), 1.410(7)*[a]	1.349	−0.09	−0.45
O-t	C_2		124.6	1.395	1.363	0.20	−0.48
S-s	C_2	9.9	117.5	1.423	1.740	−0.09	0.40
S-t	C_2		131.4	1.393	1.767	0.21	0.32
Se-s	C_2	7.3	119.5	1.425	1.877	−0.09	0.50
Se-t	C_2		133.9	1.394	1.904	0.21	0.44
Te-s	C_2	3.9	122.5	1.427	2.081	−0.09	0.70
Te-t	C_2		137.7	1.394	2.108	0.21	0.64
SO-s	C_s	4.3	115.7	1.431	1.785	−0.05	1.30
SO-t	C_s		128.8	1.398	1.780	0.22	1.28
SeO-s	C_s	2.3	117.5	1.434	1.931	−0.05	1.43
SeO-t	C_s		131.6	1.398	1.942	0.23	1.43
TeO-s	C_s	−0.1	120.0	1.435	2.125	−0.05	1.73
TeO-t	C_s		135.7	1.397	2.134	0.23	1.73
BH-s	C_s	−8.6	117.2	1.435	1.541	−0.02	0.58
BH-t	C_s		129.7	1.390	1.535	0.27	0.47
AlH-s	C_s	−6.8	124.1	1.442	1.931	−0.06	1.53
AlH-t	C_s		138.4	1.397	1.935	0.24	1.46
GaH-s	C_s	−7.2	124.1	1.440	1.945	−0.06	1.23
GaH-t	C_s		138.5	1.396	1.946	0.25	1.16
InH-s	C_s	−7.5	127.0	1.439	2.142	−0.06	1.31
InH-t	C_s		142.4	1.396	2.146	0.24	1.24
TlH-s	C_s	−7.0	127.1	1.439	2.200	−0.07	1.16
TlH-t	C_s		142.9	1.396	2.203	0.24	1.10

[a] Crystal structure for the 3,6-piperidinyl-9-xanthylidene Pd(II) complex of Sugawara, Kojima, and Yamamoto.[23]

possible application as ligands for transition metal catalysts. Schoeller et al. in their computational studies on (phosphino)(silyl)carbenes concluded that a wider carbene bond angle discourages complexation to a metal, a process that was otherwise energetically costly.[36,37] Therefore, singlet state structures **O-s**, **S-s**, **Se-s**, and **Te-s** with smaller carbene angles should be more suitable candidates for transition metal catalysts compared with the corresponding triplet **O-t**, **S-t**, **Se-t**, and **Te-t** structures considered in this research.

3.1.2. Group II (X = SO, SeO, and TeO). For our group II molecules, the M06 method predicts genuine minima of C_s symmetry ($^2A''$ state) with all real vibrational frequencies. The corresponding structures constrained to C_2 symmetry are predicted to be transition states, each with one substantial imaginary frequency and each higher in energy by 20.1−47.5 kcal/mol than the corresponding C_s structures. Following the corresponding normal modes, the C_1 *trans* conformers are obtained. The resulting energies are much lower, but still higher than those of the C_s *cis* conformers, though not much. For X = SO, SeO, and TeO, the C_1 structures lie above the C_s structures by 0.05, 0.12, and 0.14 kcal/mol, respectively.

The C_s symmetry structures possess the remarkable arched conformation revealed by the side view in Figure 4. The angles of the XO out of the CXC plane (O−O−P angle) are 57.9°, 63.9°, and 68.5° for **SO-s**, **SeO-s**, and **TeO-s**, respectively. For the corresponding triplet states, the OOP angles are slightly larger, 59.5°, 64.3°, and 68.2° for **SO-t**, **SeO-t**, and **TeO-t**, respectively. The C−C bond lengths adjacent to the carbene carbon atom in **SO-s**, **SeO-s**, and **TeO-s** are 1.431, 1.434, and 1.435 Å, respectively, roughly 0.01 Å longer than those in the **X-s** structures (X = O, S, Se, and Te). These C−C bond lengths are 1.398, 1.398, and 1.397 Å from **SO-t** to **TeO-t**, shorter by ∼0.03 Å compared with those of the analogous singlets. The C−C−C carbene angles are predicted to be 115.7°, 117.5°, and 120.0° for singlet structures **SO-s**, **SeO-s**, and **TeO-s**, respectively, while they are larger for the triplets (128.8°, 131.6°, and 135.7°, respectively). This suggests that singlet state structures **SO-s**, **SeO-s**, and **TeO-s** should strengthen the ability of the **CANC** to bind with transition metals, similar to the case in group I.

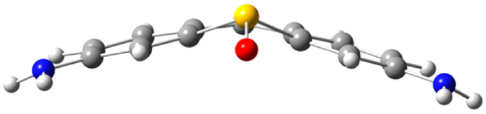
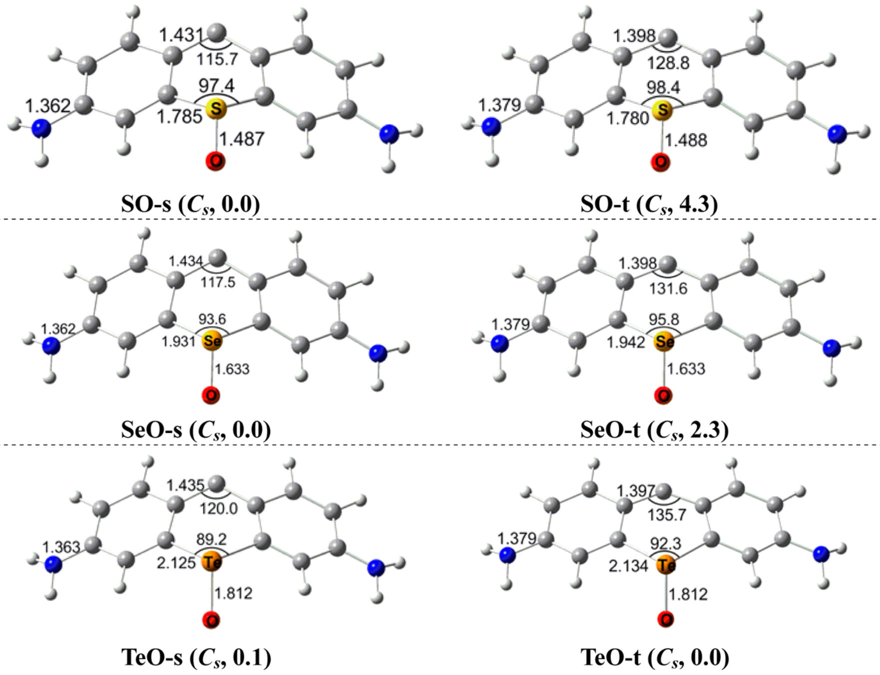


Figure 4. Side view of the C_s conformations of the group II compounds for which X = SO, SeO, and TeO.

The singlet−triplet separations are further reduced to ΔE(S−T) values of 4.3 and 2.3 kcal/mol for X = SO and SeO, respectively. When X = TeO, the ΔE(S−T) value changes sign, and the energy of singlet **TeO-s** becomes 0.1 kcal/mol higher than that of triplet **TeO-t**. This favoring of the triplet may be due to the weaker electron-donating group TeO, compared with the SO and SeO bridges (Figure 5).

3.1.3. Group III (X = BH, AlH, GaH, InH, and TlH). In our group III molecules, the singlet state structures with C_s symmetry adopt less bent conformations (side view in Figure 6), while the triplet structures are almost planar. The C_s singlet and triplet structures are all predicted to be genuine minima, with no imaginary vibrational frequencies. Similar to the case for group II, the C_2 singlet structures are characterized as transition states with high energies. Similar to the case for group II, after following the corresponding normal modes, the C_1 *trans* conformers have energies much lower and close to those for the C_s *cis* conformers. However, they are still marginally higher than those of the C_s conformers. For structures with X = BH, AlH, GaH, and InH, the C_1 conformers lie above the C_s structures by ∼0.01 kcal/mol, and by 0.004 kcal/mol for TiH (Figure 7).

The triplet structures lie significantly lower in energy than the singlets for this group. The planarity of the triplet states



SO-s (*C*$_s$, **0.0**) **SO-t** (*C*$_s$, **4.3**)

SeO-s (*C*$_s$, **0.0**) **SeO-t** (*C*$_s$, **2.3**)

TeO-s (*C*$_s$, **0.1**) **TeO-t** (*C*$_s$, **0.0**)

Figure 5. Equilibrium geometries and relative energies (kilocalories per mole) for the X = SO, SeO, and TeO systems.

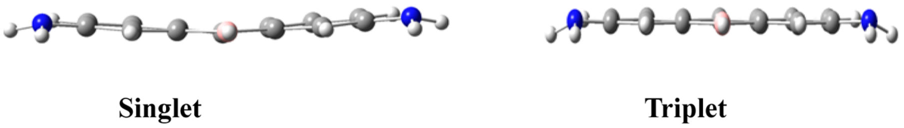


Figure 6. Qualitative side views of the singlet (left) and triplet electronic states (right) for the X = BH, AlH, GaH, InH, and TlH systems.

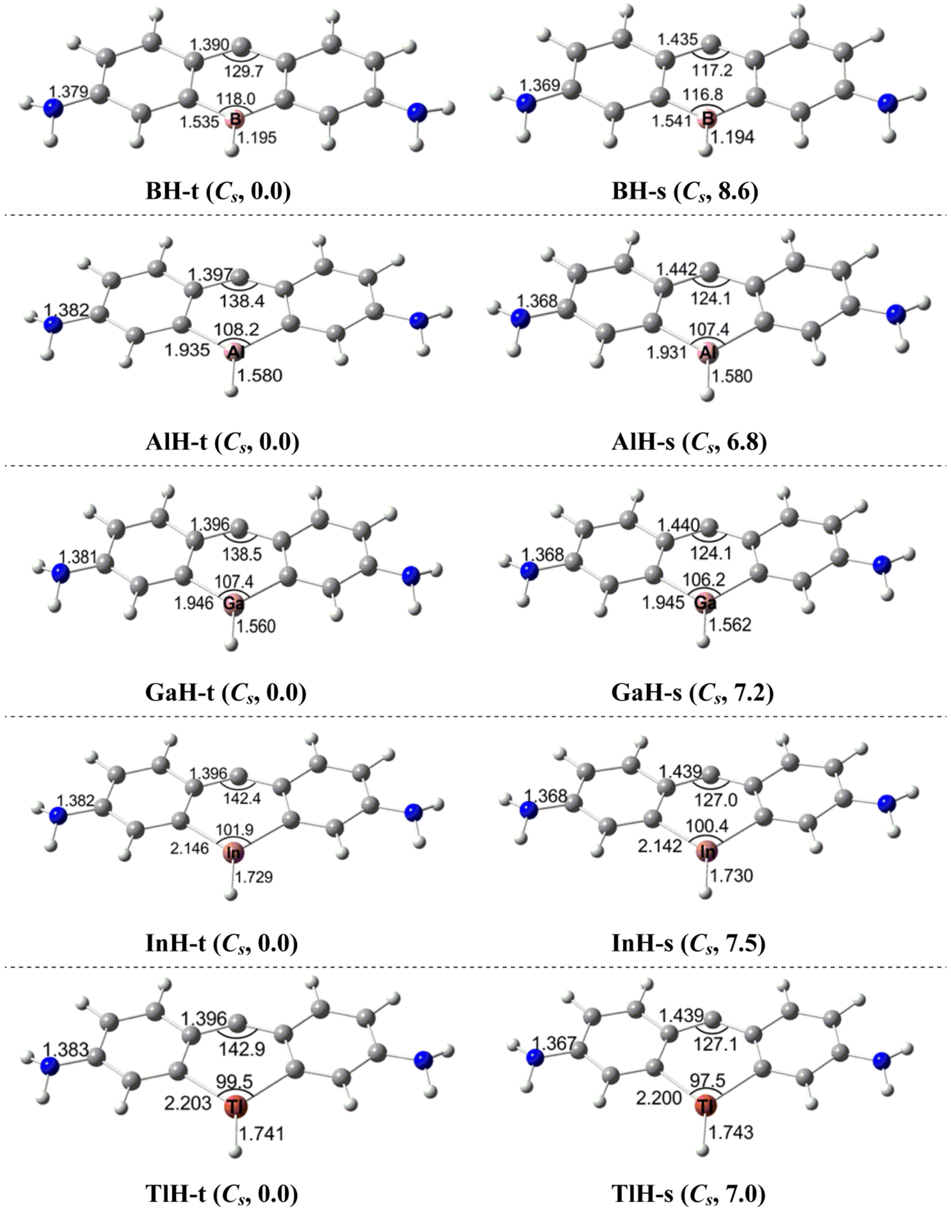


Figure 7. Equilibrium geometries and relative energies (kilocalories per mole) for the bridging X = BH, AlH, GaH, InH, and TlH carbenes.

may contribute to their favorability, compared with the arched conformations of the singlet states. The carbene C−C bond distances in the triplet minima (1.390−1.397 Å) are shorter than those for the singlet distances (1.435−1.442 Å) for **BH-s**, **AlH-s**, **GaH-s**, **InH-s**, and **TlH-s**, similar to the case for groups I and II. The C−C−C triplet carbene angles for **BH-t**, **AlH-t**, **GaH-t**, **InH-t**, and **TlH-t** fall in the range of 129.7−142.9°, which is significantly wider than the range for the singlets, which vary from 117.2° to 127.1°. This again suggests that the triplet structures may be poorer donors of electrons to transition metals, even though the triplet states lie lower in energy for these X moieties.

The singlet−triplet splittings range from −8.6 to −6.8 kcal/mol, of course rather different from the predictions for groups I and II. This reversal is mainly due to the shift from the electron-donating groups (O, S, Se, and Te) and weak electron-withdrawing groups (SO, SeO, and TeO) to the electron-withdrawing groups (BH, AlH, GaH, InH, and TlH). As expected, the BH moiety has the greatest electron-withdrawing potential, with its ΔE(S−T) value being −8.6 kcal/mol. This agrees qualitatively with the observation by Schuster et al. in 1984 that direct irradiation leads first to the singlet 9-mesityl-9,10-dihydro-9-boraanthrylidene, which quickly collapsed to the triplet, with an absolute free energy difference, ΔG(S−T), of >5.2 kcal/mol.[21]

3.2. HOMO−LUMO Gaps. The energy of the highest occupied molecular orbital (HOMO, α orbital for triplets) has sometimes been regarded as a good indication of the character of the carbenes.[38] The HOMO energies (Table 1) of the group I molecules (−4.83 to −4.51 eV for singlets and −3.98 to −3.90 eV for triplets) are generally higher than those for group II (−5.05 to −4.96 eV for singlets and −4.58 to −4.52 eV for triplets) and group III (−4.73 to −4.28 eV for singlets and −4.61 to −4.17 eV for triplets). Consequently, group I may be more basic, a result of the replacement of the electron-donating groups O, S, Se, and Te.

The HOMO−LUMO gap may sometimes be correlated with the kinetic stability of a molecule.[39,40] Among our three groups of molecules, the HOMO−LUMO gaps indicate that the group I structures may be more kinetically stable (2.84−3.33 eV), whereas the group III structures (2.11−2.21 eV) may be the least kinetically favorable.

3.3. Comparison with Carbenes without a Remote Nitrogen. To assist in our understanding of the remarkable experimental stability associated with the remote nitrogen atoms, the analogous cyclic aromatic carbenes without amino groups are investigated, with the bridging groups X = O, S, Se, Te, SO, and BH. Comparisons of the singlet−triplet splittings between the two types of structures are listed in Table 3. The ΔE(S−T) values for the **CAC** species are generally lower than those for the **CANC** structures by 7 kcal/mol. The largest singlet−triplet splitting, 15.5 kcal/mol, between **O-s** and **O-t**, is significantly reduced to 8.2 kcal/mol for the O′ species (9-xanthylidene), in agreement with the experimental finding that the singlet carbene 9-xanthylidene ground state was lower than the triplet state by at least 4 kcal/mol.[22] Furthermore, for the tellurium species, the ground state shifts from the singlet to triplet, and the singlet−triplet splitting value changes from 3.9 to −3.5 kcal/mol. A similar situation occurs for the SO species, with the singlet−triplet splitting changing from 4.3 to −3.2 kcal/mol. Finally, the splitting for the BH′ system becomes larger, decreasing from −8.6 to −12.5 kcal/mol. Therefore, the participation of the remote nitrogen atoms greatly promotes the viability of the singlet state carbenes.

Table 3. Symmetries, Singlet−Triplet Splittings [ΔE(S−T) = E(triplet) − E(singlet) (in kilocalories per mole)] for Species with Different X Moieties (see Figure 1B)[a]

X	symmetry	ΔE(S−T)
O	C_2	15.5
O′	C_{2v}	8.2
S	C_2	9.9
S′	C_{2v}	2.8
Se	C_2	7.3
Se′	C_{2v}	−0.03
Te	C_2	3.9
Te′	C_{2v}	−3.5
SO	C_s	4.3
SO′	C_s	−3.2
BH	C_s	−8.6
BH′	C_s	−12.5

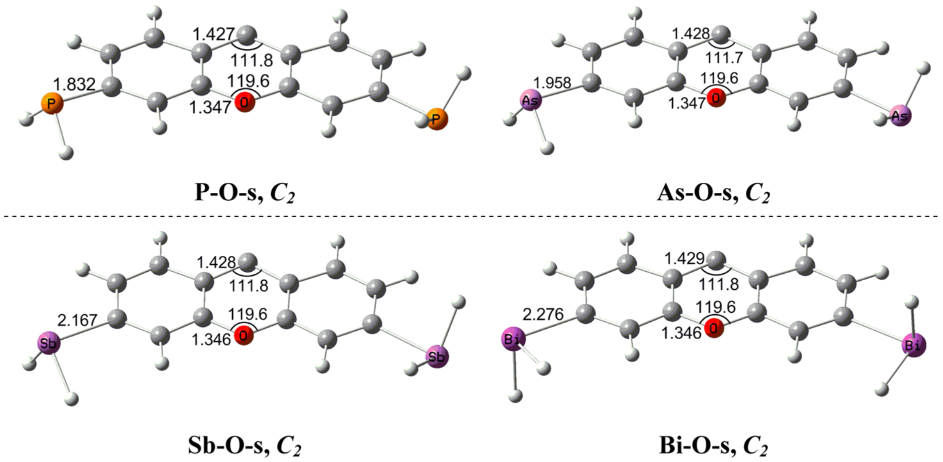
[a] The species with amino groups replaced by H are labeled with primes.

We have also investigated the X = O systems with NH_2 replaced by BH_2, CH_3, OH, and F. The ΔE(S−T) predictions are 0.7, 10.0, 13.6, and 10.9 kcal/mol, respectively. Again, the NH_2 group favors the singlet states.

3.4. Replacement of NH_2 with PH_2, AsH_2, SbH_2, and BiH_2. The cyclic aromatic carbenes with remote R = PH_2, AsH_2, SbH_2, and BiH_2 rather than NH_2 are also considered only for the X = O species (designated **R-O**). The replacement of NH_2 with PH_2, AsH_2, SbH_2, and BiH_2 notably decreases the singlet−triplet splittings. The ΔE(S−T) values are 8.6, 8.4, 6.8, and 7.5 kcal/mol for **P−O**, **As−O**, **Sb−O**, and **Bi−O** systems, respectively. The singlet global minimal structures are reported in Figure 8. The replacement with PH_2, AsH_2, SbH_2, and BiH_2 has little influence on the predicted singlet C−C−C carbene angles (~112°) or the carbene C−C bond distance (~1.43 Å). Thus, **P-O-s**, **As-O-s**, **Sb-O-s**, and **Bi-O-s** may be inclined to bind to transition metals. The obvious geometrical change occurs for the R−C distance, monotonically increasing from 1.832 Å (PH_2) to 2.276 Å (BiH_2). Simultaneously, the lone pairs belonging to the R atoms are no longer perpendicular to the cyclic aromatic rings, especially for **Bi-O-s**. This is mainly due to the fact that the higher the energy required for the hypothetical sp^3 hybridization of P, As, Sb, and Bi, the more difficult the conjugation between the cyclic aromatic rings and the P, As, Sb, and Bi lone pairs. As a consequence, the singlet−triplet separations are smaller than those for the analogous R = NH_2 structures.

3.5. The "Best" Triplet Molecule. As noted above, the carbene triplet electronic state is favored by replacement of R = NH_2 with R = H [ΔE(S−T) = 15.5 → 8.2 kcal/mol]. In addition, the replacement of X = O with X = BH also favors the triplet [ΔE(S−T) = 15.5 → −8.6 kcal/mol]. Assuming the two effects to be additive, one might suggest a singlet−triplet separation of −8.6 kcal/mol − 7.3 kcal/mol = −15.9 kcal/mol. In fact, for the R = H, X = BH system, the predicted ΔE(S−T) is −12.5 kcal/mol, nearly as large as the value of −9 kcal/mol found for CH_2. For the R = BH_2, X = BH system, the triplet state is even more favored, lying 13.7 kcal/mol below the singlet.

3.6. Repositioning of Amino Groups. Of the compounds considered thus far, the original Yamamoto compound, for which R = $N(CH_3)_2$ and X = O, has the largest singlet−triplet separation (15.7 kcal/mol). In terms of a standard numbering system, the Yamamoto structure may be labeled the 3,6-bis(dimethylamino)xanthene carbene. Now let us revert from the dimethylamino substitutents to the simple R = NH_2. The predicted structures of the analogous singlet structures for the four NH_2 positions are seen in Figure 9. Initially, we might have assumed the Yamamoto compound (3,6) to be the lowest-lying diamino-xanthene and to have the lowest total energy. In fact, Figure 9 shows the 1,8 structure to lie 9.0 kcal/mol below the 3,6 structure. For the four isomers shown in Figure 9, the predicted singlet−triplet energy differences are 22.3 (1,8), 7.8 (2,7), 7.5 (4,5), and 15.5 (3,6) kcal/mol. Thus, with Yamamoto's $N(CH_3)_2$ ligands replaced by NH_2, we predict the largest ΔE(S−T) value yet found. Therefore, in Figure 10, we report the relative energies of the four singlet isomers with Yamamoto's $N(CH_3)_2$ ligands, and indeed, with these substituents, Yamamoto's 3,6 structure has the lowest energy. Although the 1,8 structure lies lowest with R = NH_2, with R = $N(CH_3)_2$ the obvious steric challenge (Figure 10, bottom panel) reverses the energetic ordering. Even so, the 1,8



P-O-s, C_2 **As-O-s, C_2**

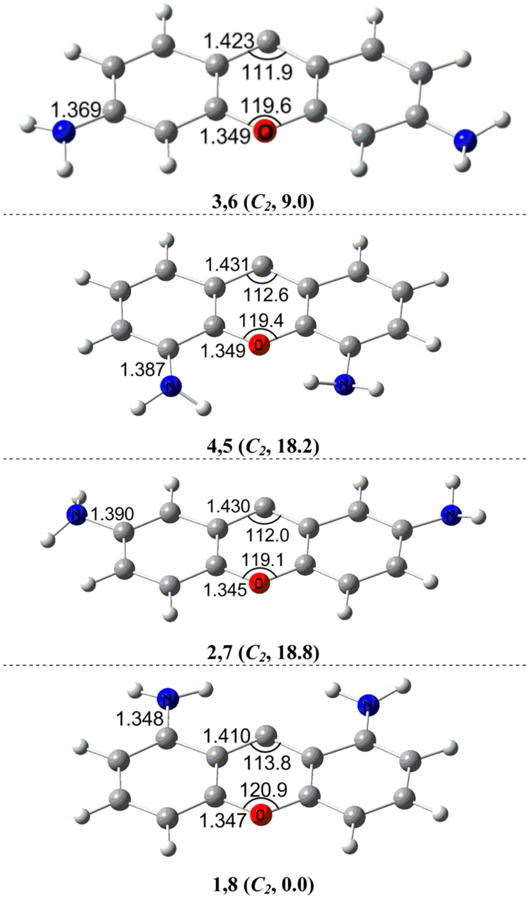
Sb-O-s, C_2 **Bi-O-s, C_2**

Figure 8. Singlet equilibrium geometries with remote R = PH_2, AsH_2, SbH_2, and BiH_2 carbenes.

Table 4. Symmetries, Singlet−Triplet Splittings [ΔE(S−T) = E(triplet) − E(singlet) (in kilocalories per mole)] for the Species Seen in Figure 1C

	symmetry	ΔE(S−T)
P-O	C_2	8.6
As-O	C_2	8.4
Sb-O	C_2	6.8
Bi-O	C_2^{a}	7.5

[a] C_2 for singlet and C_{2v} for triplet.



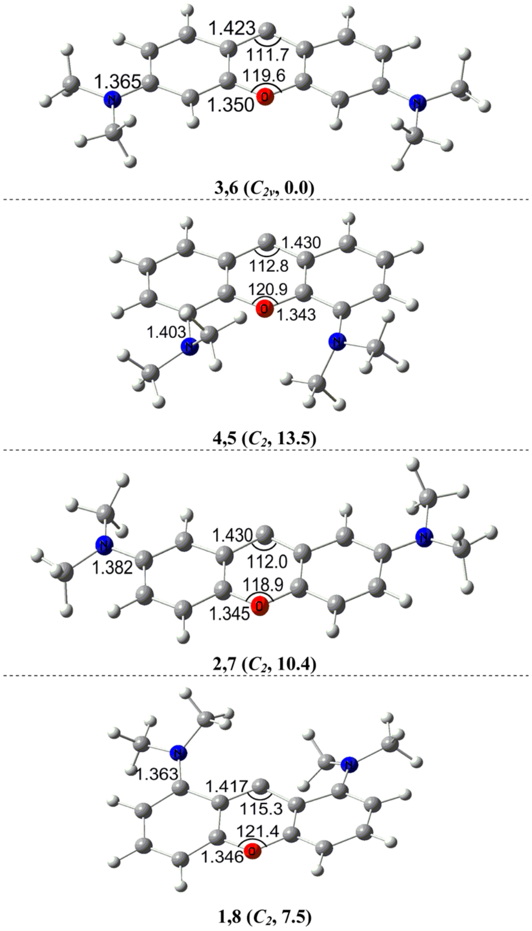
3,6 (C_2, 9.0)

4,5 (C_2, 18.2)

2,7 (C_2, 18.8)

1,8 (C_2, 0.0)

Figure 9. Structures and relative energies (kilocalories per mole) of the diamino-xanthene carbenes.



3,6 (C_{2v}, 0.0)

4,5 (C_2, 13.5)

2,7 (C_2, 10.4)

1,8 (C_2, 7.5)

Figure 10. Structures and relative energies (kilocalories per mole) of the bis(dimethylamino)-xanthene carbenes.

structure lies only 7.5 kcal/mol above Yamamoto's synthesized 3,6 compound.

For the R = $N(CH_3)_2$ structure, the ΔE(S−T) value are 8.9 (1,8), 7.9 (2,7), 8.4 (4,5), and 15.7 (3,6) kcal/mol. Thus, the Yamamoto compound has the lowest energy of the R = $N(CH_3)_2$ structures; it also has the largest singlet−triplet separation, making it most susceptible to complexation by transition metals.

4. CONCLUDING REMARKS

The synthetic research of Sugawara, Kojima, and Yamamoto[23] has produced two fascinating new cyclic aromatic carbenes incorporating remote amino groups (structure **B** in Figure 1). Here we demonstrate that the bridging moiety X on the central ring has a significant tuning effect on the aromatic carbene singlet−triplet energy difference, considered central for coordination to a transition metal. When X = O, S, Se, and Te (electron-donating groups), we predict singlet ground state ΔE(S−T) values from 15.5 to 3.9 kcal/mol. When X = SO, SeO, and TeO (weak electron-withdrawing groups), the ΔE(S−T) predictions decrease, from 4.3 to −0.1 kcal/mol. When X = BH, AlH, GaH, InH, and TlH (electron-withdrawing groups), the electronic ground states are triplets, with ΔE(S−T) values in the range of −8.6 to −6.8 kcal/mol. The remarkable experimental stability engendered by the remote nitrogen atoms has been corroborated with ΔE(S−T) values for the species with the dimethylamino groups replaced with remote H, NH_2, PH_2, AsH_2, SbH_2, BiH_2, BH_2, CH_3, OH, and F groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total energies for the aromatic carbenes (Table S1), optimized coordinates for molecular structures determined here (Tables S2−S81), and harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) (Tables S82−161). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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