DFT Studies of Biarylcarbenes and the Carbene−Biradical Continuum[†]

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We use electronic structure modeling, mainly density functional methods, to characterize a variety of long-lived bisaryl triplet carbenes. The bisaryl systems have a triplet ground state, favored by a substantial delocalization of the spin into the aromatic rings. One can imagine two extreme cases of the bonding in these species, representable as valence isomers. In the first case, spin delocalization is minor and incidental; the spin is predominantly located on the central carbene carbon. In the second case, spins are separated by large distances and are found primarily on the aromatic rings; the rings are linked by an allenic bridge. The bisphenyl carbenes tend toward the first limit. They can be kinetically stabilized by ortho substituents which shield the reactive center and para substituents which protect that site which has substantial spin density. The bond angle at carbene is opened from about 142° (the B3LYP/6-31G* value for the parent bis(phenyl)carbene) to 160° or more by these substituents. Bisanthryl carbenes illustrate the second extreme, favoring a D_{2d} structure and possessing a low-lying open shell singlet state. A hypothetical phenyl-9-anthrylcarbine lies between the carbine and diradical extemes. The same principle which guides the design of stabilized diphenylcarbene carbenes and substitution of reactive sites by bulky protective groups serves to stabilize the bis-9-anthrylcarbene biradical.

Introduction

A variety of long-lived singlet carbenes are known,[1] but the search for stable triplet carbenes has proved more challenging. The leading candidates developed by Tomioka[2] are bis(aryl) species, mostly derivatized bis-(phenyl)carbenes.[3] The lifetime of the bis(phenyl)carbenes have been extended by substituents which alter the geometry and shield the centers with abundant spins. Examples are listed in Chart 1.

It is possible to write two distinct Lewis structures for bisaryl carbenes. Besides placing the unpaired electrons on carbene and leaving the rings conventionally aromatic, one may draw a cumulene connection between two weakly coupled cyclic radicals. Such biradicals can be recognized by a spatial separation of spins or a low-lying open shell $\sigma\pi$ singlet,[9] in which two of the natural orbitals have occupancies close to one.

[†] A preliminary version of this work was presented at the International Symposium on Reactive Intermediates and Unusual Molecules, Nara, Japan, September 2001.

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CHART 1. Long-Lived Triplet Species

Structure	Lifetime
Diphenylcarbene	2 μs
(2,6-dibromo-4-tert-butylphenyl)(2',6'-bis(trifluoromethyl)-4'-isopropylphenyl)carbene[4]	16 min
Alkylated Diphenylcarbenes [5]	
Bis (2,4,6-trimethylphenyl)carbene	160 ms
Bis (2,3,5,6-tetramethylphenyl)carbene	410 ms
Bis (2,6-dimethyl-4-tert-butyl phenyl)carbene	500 ms
Chlorinated Diphenylcarbenes[6]	
Bis (2,4,6-trichlorophenyl)carbine	18 ms
Bis (perchlorophenyl)carbene	28 ms
Brominated Diphenylcarbenes [7]	
Bis (2,4,6-tribromophenyl)carbene	1 sec
Bis (4-methyl-2,6-dibromophenyl)carbene	0.2 sec
Bis (4-tert-butyl-2,6-dibromophenyl)carbene	16 sec
Bis (4-tert-butyl-2,3,6-tribromophenyl)carbene	16 sec
Anthrylcarbenes[8]	
Bis (9-anthryl)carbene	0.5 μs
Bis (10-phenyl-9-anthryl)carbene	19 min

Clues to the structure of triplet carbenes have been derived from the D and E parameters of the ESR spectra of these species.[10] The D value is related to the mean
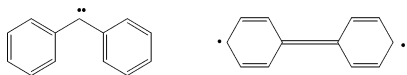
distance between unpaired electrons. A near-zero value of E/D suggests a cylindrical spin distribution. This is ordinarily taken to suggest a near linear carbine, but the possibility of rotational averaging cannot be overlooked.[11] EPR data strongly imply that the bisarylcarbene triplets respond to ortho-substitution by broadening the carbene angle from the ca. 150° estimated for triplet bisphenyl-carbene.[12] On the question of the position of a low-lying open shell $\sigma\pi$ singlet, the data are silent.

Calculations can provide estimates of singlet and triplet structures for these carbenes, the relative energies of the two spin states, and a notion of the spin distributions. Combined with the considerable experimental data in hand, such computational modeling can enhance our understanding of these elusive and interesting systems. Here we present density functional models for a variety of bisarylcarbenes, listed in Chart 2.

Technical Issues, Modeling Methods, and Software

In this paper, we present computational models for some of the long-lived triplet carbenes reported by Tomioka and co-workers. Methods for computational characterization of carbenes are well developed,[13] but the modeling of carbenes is not perfectly straightforward. Spin contamination can cast doubt on the quality of computational results. $\langle S^2 \rangle$ is an exact quantum number for the ROHF method, but this method contains no correlation correction. UHF and MP2 treatments of

triplet carbenes generally suffer from serious spin con-tamination. Density functional modeling is generally not seriously undermined by poor $\langle S^2 \rangle$ values and has provided reliable descriptions for a number of carbenes and nitrenes.[14]

The lowest singlet of a carbene may be an open-shell $\sigma\pi$ state, a biradical with orbital occupancy analogous to the triplet state. This was an important step in the understanding of phenyl nitrene behavior.[15] Singlet bi-radicals generally need careful treatment.[16] DFT, widely successful in a variety of chemical contexts and well tested for systems such as phenylcarbenes and some phenylnitrenes,[17] may not be suitable for the description of singlets that might be biradicals. In the limit of isolated spins, such singlets require two configurations for a qualitatively correct representation by familiar wave function methods.[18] Though it is possible to effect an approximate representation of an open shell singlet by broken symmetry unrestricted calculations using a single determinant, such methods do not represent a well-defined spin state. The fact that currently available functionals are not thoroughly tested for open shell systems makes advisable a careful comparison of DFT results with the geometric and energetic estimates from independent correlation-corrected methods with at least qualitatively correct multiconfigurational character, such as complete active space (CAS) calculations.[19]

All species are described here by density functional calculations in the familiar B3LYP hybrid gradient-corrected method combining the hybrid exchange func-tional of Becke and the correlation functional of Lee, Yang, and Parr. All reports refer to the 6-31G* basis set except for the brominated systems; for these we used the 6-311G* basis. In cases for which there seemed to be a possibility of low-lying open shell singlet biradical states, we estimated the energy of that state by a symmetry-breaking unrestricted density functional method. In the limit of independent alpha and beta spins, this method produces a single determinant with $S_z = 0$ and S^2 expectation value 1.0; that is, a 50–50 mixture of singlet and triplet states with the same MOs for both states. In UHF wave function calculations the energy difference between this unrestricted single determinant "singlet" and the unrestricted single determinant triplet in the limit of small coupling between spins is half of the value computed with a proper two-determinant representation of the singlet and the single-determinant of the triplet, again with the same orbitals thoughout. To test the suggestions of the unrestricted calculations in certain

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(9) International Union of Pure and Applied Chemistry, Organic Chemistry Division Commission on Physical Organic Chemistry, Glossary of Terms Used in Physical Organic Chemistry (IUPAC Recommendations 1994) Prepared for publication by P. Müller, Dé-partement de Chimie Organique, Université de Genève, CH-1211 Genève 4, Suisse; World Wide Web version prepared by Gerard P. Moss, Department of Chemistry, Queen Mary University of London, Mile End Road, London, E1 4NS, UK [g.p.moss@qmul.ac.uk] with the assistance of Charles L. Perrin [cperrin@ucsd.edu] http://www.chem-.qmul.ac.uk/iupac/gtpoc/. Also IUPAC Class Names 1993. IUPAC: Organic Chemistry Division. Glossary of Class Names of Organic Compounds and Reactive Intermediates Based on Structure, now published in _Pure Appl. Chem._ **1995**, _67_, 1307–1375. Biradicals are defined as "An even-electron molecular entity with two (possibly delocalized) radical centers which act nearly independently of each other." Species in which the two radical centers interact significantly are often referred to as "biradicaloids". If the two radical centers are located on the same atom, the species are more properly referred to by their generic names: carbenes, nitrenes, etc. The lowest energy triplet state of a biradical lies below or at most only a little above its lowest singlet state (usually judged relative to kT, the product of the Boltzmann constant k and the absolute temperature T). The states of those biradicals whose radical centers interact particularly weakly are most easily understood in terms of a pair of local doublets. The term is synonymous with "diradical". IUPAC Photochemical Glossary 1992. IUPAC: Organic Chemistry Division: Commission on Photochemistry. Glossary of Terms Used in Photochemistry. Draft 1, provisional.

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(18) The Kohn–Sham determinant of orbitals for noninteracting electrons is in principle capable of representing the exact density and thus will accommodate many-configurational effects. Currently avail-able approximate functionals may not describe systems demanding a multi-configurational representational in wave function methods.

(19) A clear discussion is provided by: Jensen, F. _Computational Chemistry_; Wiley: New York, 1999.

CHART 2.   Species Described in This Work

A: C_2-symmetric species

Index: Systematic name
1:     bisphenylcarbene
2a: bis(2,6-dichlorophenyl)carbene
2b: bis(2,4,6-trichlorophenyl)carbene
3:     bis(2,6-dimethylphenyl)carbene
4a: bis(2,6-dibromophenyl)carbene
4b: bis(2,4,6-tribromophenyl)carbene
4c: bis(4-methyl-2,6-tribromophenyl)carbene
4d: bis(4-*tert*-butyl-2,6-dibromophenyl)carbene
5a: bis(2,3,6-tribromo-4-methylphenyl)carbene
5b: bis(2,3,6-tribromo-4-tert-butylphenyl)carbene

B: Unsymmetric bisphenylcarbenes

6a	2,6-di(trifluoromethyl)-4-alkylphenyl-2,6-dibromo-4-alkylphenylcarbene
6b	2,6-di(trifluoromethyl)-4-methylphenyl-2',6'-dibromo-4'-methylphenylcarbene
6c	2,6-di(trifluoromethyl)-4-iso-propylphenyl-2',6'-dibromo-4'-tert-butylphenylcarbene

C: Bis anthryl systems

7a:	bis(9-anthryl)carbene
7b:	bis(10-phenyl-9-anthryl)carbene
7c:	bis(2-trifluoromethyl-9-anthryl)carbene

D: Fragments and a composite system

8:	9-anthryl methyl radical
9:	phenylmethyl radical
10:	phenyl-9-anthrylcarbene
11:	2,6-dichlorophenylmethyl radical

cases, we employ a complete active space (CAS) model, which ensures exact expectation values of S^2.

To characterize the spin distribution, we use Weinhold's natural bond orbital analysis[20] for all DFT densities. This generally yields reasonable assignments of α- and β-spin charges to individual atoms.

B3LYP calculations were performed with Gaussian 98W[21] on NT and Windows 2000 PC systems and with PQS software on PQS Linux systems.[22] NBO analyses[23] were available in both software suites. CAS calculations began from verified minimum energy structures produced by R(O)HF or DFT. If DFT or ROHF optimization converged to high-symmetry structures, that symmetry was presumed in all later CAS calculations. CAS extreme points were not verified as minima owing to the computational demands of vibrational calculations in CAS.

These systems have very soft potentials governing the central angle and the torsion defining the mutual orientation of the aromatic rings. This requires careful optimization under stricter than usual criteria. We found that refinement with a computed force constant matrix

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(22) Parallel Quantum Solutions software versions 2.2 and 2.3.

(23) NBO Version 3.1 NBO 4.0 is implemented in PQS software and in version A.9 of Gaussian 98.

TABLE 1. Treatment of Parent Bisphenylcarbene (Species 1) Density Functional Values for Relative Energies and Key Geometric Parameters for Unsubstituted Species 1

species: model	rel E (kcal/mol)	C0–C1 (Å)	C1–C0–C1′ (deg)	C6–C1–C1′-C6′ (deg)
^{3}**1**: UB3LYP/6-31G*	0	1.4036	142	65
^{1}**1**σ^2: B3LYP/6-31G*	7	1.4346	119	58
^{1}**1**$\sigma\pi$: UB3LYP/6-31G*	8.4	1.4234	127	59
^{3}**1**: UB3LYP/6-311G(d,p)	0	1.400	143	68
^{1}**1**σ^2: B3LYP/6-311G(d,p)	5.8	1.431	119	59
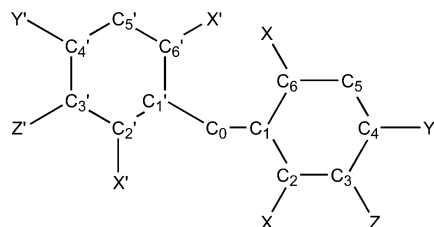
FIGURE 1. Numbering scheme and substituent labels shown define the family of bis(ortho-substituted phenyl)carbenes.
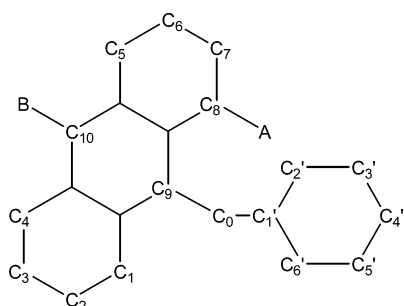
FIGURE 2. Phenylanthrylcarbene numbering scheme defines both the phenyl and anthryl substituents' skeletons.

after preliminary conjugate gradient optimization gave reliable structures.

Density Functional Calculations on Bisarylcarbenes

Labeling schemes are presented in Figures 1 and 2. Selected geometric parameters, NBO spin densities, and energy values are included in the summary tables discussed in the following text. Full characterization of the species described here is provided in the Supporting Information, which contains summary tables as well as log files from Gaussian and PQS calculations.

I. The Parent System Bisphenylcarbene. The DFT characterization of bisphenylcarbene is summarized in Table 1. The position numbers are as shown in Figure 1.

B3LYP/6-31G* modeling of bisphenylcarbene (species **1**) shows a triplet preference, by 7 kcal/mol over the σ^2 singlet. There are notable differences in structure between singlet and triplet bisphenylcarbenes ^{1}**1** and ^{3}**1**. Relative to the closed shell σ^2 singlet described in B3LYP/6-31G*, the triplet species has shorter C0–C1 and C0–C1′ bond lengths, accompanied by an expanded C1–C0–C1′ angle, as shown in Table 1 and the fuller tables in the Supporting Information. This is not the only remarkable geometric feature; the phenyl ring is considerably distorted, with C1–C2 bonds lengthened to 1.43 Å and C2–C3 bonds shortened to 1.38 Å, a severe "quinoid" deformation consistent with some C0–C1 double-bond character and some odd electron amplitude at the para

position of the phenyl rings. These results may be compared with those already reported by Schaefer et al., who used an extended 6-311G** basis in their B3LYP calculations. The larger basis produces a lesser S–T gap and slightly different geometry for the triplet; the triplet's primary angle remains 143°, and the torsion angle between the aromatic rings becomes 68°. The distortions of the aromatic rings suggested in calculations in the modest and extended bases are nearly indistinguishable.

NBO analysis assigns spins to the atomic centers. The α spin at the carbene carbon C0 is 1.430 electrons, showing that a considerable delocalization into the phenyl rings (0.285 α spins each) has taken place. The NBO analysis assigns 0.218 α spins to each ortho carbon and 0.204 to the para positions. Spin polarization is permitted in unrestricted B3LYP/6-31G*, and we find 0.089 β spins at meta positions and 0.149 β spins at the attachment sites.

The usual implementation of DFT does not represent an open-shell singlet well, but we may get an impression of the importance of this state by determining the unrestricted (UB3LYP) broken symmetry $\sigma\pi$ form. For comparison, we quote results for parent CH$_2$. The UB3LYP/6-31G* energy of the unrestricted single-determinant "singlet" $\sigma\pi$ methylene, $-39.140\,067\,76$ hartrees, is 6.3 kcal/mol above the UB3LYP/6-31G* $\sigma\pi$ triplet. From the limiting behavior already noted, we would estimate that the $\sigma\pi$ singlet lies at least 12 kcal/mol above the triplet for CH$_2$ and hence well above the closed-shell σ^2 singlet. The expectation value of S^2 in the UB3LYP "singlet" is 0.732, which can be taken as an index of the extent of triplet admixture and of diradical character. It must then be no surprise that the C1–C0–C1′ angle for the unrestricted $\sigma\pi$ "singlet" is slightly greater (113°) than is assumed by the σ^2 singlet, 110°.

In bisphenylcarbene, the C1–C0–C1′ angle for the unrestricted $\sigma\pi$ UB3LYP "singlet" is slightly greater (127°) than is assumed by the σ^2 singlet, 119°. Its expectation value of S^2 is 0.659, and its energy relative to the UB3LYP $\sigma\pi$ triplet is 8.4 kcal/mol. We would infer that bisphenylcarbene has no more diradical character than CH$_2$ and consider that neither bisphenylcarbene nor unsubstituted carbene need be considered a biradical.

II. Symmetric Bis(substituted-phenyl)carbenes. The broad structural features predicted by DFT calculations are shared by most of the long-lived species investigated by Tomioka. Regardless of the substituents, according to B3LYP/6-31* the C0–C1 distance is in the neighborhood of 1.37 Å and the phenyl rings are quinoid-distorted and roughly orthogonal; the skeleton approaches an approximately D_{2d} symmetry. Detailed results appear in the Supporting Information, Summary Tables 1 and 2. We consider chloro, methyl, and bromo systems in the following sections.

TABLE 2. Geometric Parameters of Kawano's Chloro Species and Its Diazo Precursor[a]

(a) Precursor to Species **2b**

geometric parameter	N to N (Å)	C0 to N (Å)	C0 to C1 (Å)	C1−C0−C1′ (deg)	torsion (deg)
X-ray	1.136	1.323	1.480	127.1	70.2
B3lyp/6-31G*	1.140	1.313	1.480	126.3	64.8

(B) Bis(2,4,6-trichlorophenyl)carbene, Species **2b**

geometric parameter	C0 to C1 C0 to C1′ (Å)	C1−C0−C1′ (deg)	torsion (deg)	E(rel) (kcal/mol)	$\langle S^2 \rangle$
X-ray (disordered)	1.437, 1.423	142	missing		
3 2b: UB3LYP/6-31G*	1.375	160.0	90	0	2.02
1 2b: B3LYP/6-31G*	1.403	131.4	101	13	0
1 2b: UB3LYP/6-31G*	1.355	180	90	7	0.87

[a] Triplet energy = −3258.8642326 hartrees.

Hexachlorinated Species. Kawano et al.[6] have presented structural data from Xray studies on bis(1,3,5-trichlorophenyl)carbene derived from the diazo precursor in situ. DFT modeling of the singlet precursor matches the X-ray structure well (Table 2A).

Irradiation leaves a nitrogen-free fragment, presumably the bis(1,3,5-trichlorophenyl)carbene. Table 2B summarizes DFT calculations on the carbene.

Compared with the parent **3 1**, **3 2b** in B3LYP/6-31G* has a shortened C0−C1 distance and a wider C1−C0−C1′ aryl−carbene−aryl bond angle, similar to the **3 6** system. Accompanying these changes is the familiar quinoid distortion of the benzene ring from a regular hexagon. The C1C2 and C1C6 distances are extended to 1.43 Å and the C2C3 and C5C6 bonds are shortened to 1.38 Å.

We see a substantial discrepancy between the structure of **3 2b** revealed by the Xray investigation and the structure of **3 2b** represented by the B3LYP model (Table 2B). The C_2 symmetry found in computational modeling is not deduced from the X-ray data, and the geometry around C0 disagrees with the model; the X-ray data implies longer C0−C1 bond lengths and a more acute C1−C0−C1′ angle. Kawano et al. ascribe the discrepancies in torsion and bend angles to packing effects in the solid, a suggestion given plausibility by the soft potential opposing such motion. The CC bond length disagreements are not so easily dismissed. We address this problem in a future paper. Here we will establish that the broad central angle and short central bond lengths are found in the DFT modeling of similar experimentally known species with alkyl and bromo substituents.

Methylated Species. Methyl substitution at the ortho positions also opens the C1−C0−C1′ central angle of bisphenylcarbene from 142° to more than 160°, increases the singlet−triplet gap, shortens the central bond distances, and brings the near-D_{2d}-symmetric cumulene triplet closer to the C_2-symmetric ground-state triplet.

According to B3LYP/6-31G* modeling (Table 3), replacement of chloro with the larger methyl substitution at all four ortho positions shifts the structure further toward the D_{2d} structure, with all that this implies. The C1−C0−C1′ angle increases to 180°. The B3LYP/6-31G* C0−C1 distance found in B3LYP/6-31G* is 1.3730 Å. Comparing this with the values 1.4036 Å in biphenylcarbene, and 1.3753 Å in the chloro system, we see the influences of size and spin delocalization. The greater steric requirement of methyl relative to chloro drives the structure toward D_{2d}, and closer to the cumulene biradi-

TABLE 3. Characterization of the Bis(2,6-dimethylphenyl)carbene (^{1,3}3)[a]

bis(2,6-dimethylphenyl)-carbene states	rel energy (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
1 3: B3LYP C_2 σ^2	12.1	1.4125	131
3 3: B3LYP/6-31G* $\sigma\pi$	0	1.3730	179
1 3: UB3LYP broken symmetry $\sigma\pi$	7.0	1.3630	179

[a] Triplet energy = −658.575 272 4 hartrees; the vertical closed shell singlet lies at +19 kcal/mol. The open shell UB3LYP "singlet" has $\langle S^2 \rangle = 1.0625$; cf. $\langle S^2 \rangle = 0.7141$ for bisphenylmethylene.

cal structure, but that same requirement seems to counterbalance the tendency to shorten the central C0−C1 bonds. The D_2-symmetric form, with enforced 180° central angle, is less than 0.1 kcal/mol higher in energy than the strictly optimized C_2-symmetric form.

The (σ^2) singlet to triplet gap, which was 7 kcal/mol in bisphenylcarbene, becomes 12 kcal/mol in both bis(2,4,6-trichlorophenyl)carbene and bis(2,6-dimethylphenyl)carbene.

Delocalization of spin into the aromatic substituents is more extensive when the system approaches D_{2d} symmetry. According to NBO analysis assignment the alpha spin at the central carbon in bis(2,6-dimethylphenyl)carbene has declined to 1.20 electrons, as compared with 1.27 for the chloro substituted system and 1.430 for the parent bisphenylcarbene. The spin amplitude at the para position is +0.270 α spins, to be compared with the analogous +0.210 α spins for bothe the unsubstituted and ortho chloro-substituted phenyl)carbene. This system is still not a biradical according to the criterion that an open shell $\sigma\pi$ singlet should be closely comparable in energy to the triplet state.

Brominated Species. Tomioka et al. have recently described a family of brominated bisphenylcarbenes, which are relatively long-lived triplet species. Ortho substituents block access to the carbene carbon, so the formation of ethylenes by dimerization occurs only slowly.[7,24] The sterically crowded triplets do not react with benzene solvent but do dimerize, coupling at the para carbons where spin amplitude is large. A bulky para group hinders access to that reactive site. The lifetime for a para-*tert*-butyl species is greater than the lifetime for the para-bromo compound, which is greater than the lifetime of the *p*-methyl compound.

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TABLE 4. Bis(brominated phenyl)carbene: B3LYP Structure and S−T Gap

species vs property	C0−C1 (Å)	C1−C0−C1′ (deg)	S − T gap (kcal/mol)
4a: bis(2,6-dibromophenyl)carbene	1.364	180	13
4b: bis(2,4,6-tribromophenyl)carbene	1.362	180	13
4c: bis(2,6-dibromo-4-methylphenyl)carbene	1.364	177	12
4d: bis(2,6-dibromo-4-*tert* butylphenyl)carbene	1.364	180	13
5a: bis(2,3,6-tribromo-4-methylphenyl)carbene	1.364	178	13
5b: bis(2,3,6-tribromo-4-*tert* butylphenyl)carbene	1.366	173	12

TABLE 5. B3LYP Characterization of Trifluoromethylated Triplet Carbene 6

species	model	C0−C1 (Å)	C0−C1′ (Å)	C1−C0−C1′ (°)	E(rel) (kcal/mol)	α spin at C0
^{3}**6a**	B3LYP/6-311G(d,p)	1.368	1.368	176	0	
^{1}**6a**	B3LYP/6-311G(d,p)	1.393	1.403	134	12.2	
^{3}**6b**	B3LYP/6-311G(d)	1.363	1.365	180	0	1.20
^{1}**6b**	B3LYP/6-311G(d)	1.395	1.402	134	12.7	
^{3}**6c**	B3LYP/6-311G(d)	1.364	1.365	173	0	1.19
^{1}**6c**	B3LYP/6-311G(d)	1.394	1.404	133	12.0	

TABLE 6. Species with the Bis(9-anthryl)carbene Skeleton[a]

species	A	B	NBO spin at C0 and C10	
^{3}**7a**: bis(9-anthryl)carbene	H	H	0.712	0.442
^{3}**7b**: bis(10-phenyl-9-anthryl)carbene	H	phenyl	0.707	0.443
^{3}**7c**: bis(1-trifluoromethyl-9-anthryl)carbene	CF$_3$	H	0.704	0.436

[a] A and B are substituents at the 1 and 10 positions on the 9-naphtyl fragment. Spins are expressed as α electrons.

Our B3LYP/6-311G* calculations are summarized in Table 4. The systems are forced very near to D_{2d} symmetry by the steric demands of the bromine substituents. The central angles for the *asymmetrically* substituted tribromophenylcarbenes are significantly bent from 180°, illustrating the softness of that bend. Central bond lengths are essentially unaffected by meta and para substitutions. Substitution at the meta site has a subtle structural effect. As the maximum achievable symmetry is reduced from D_{2d} to C_2, the distances from the carbene carbon to the ortho bromines depart from near-equality; we call these CBr(Br) and CBr(H). Our B3LYP/6-31G* calculations show that CBr(Br) = 3.05 Å and CBr(H) = 3.14 Å, as suggested by the notion of "buttressing" and captured even by semiempirical calculations.

NBO analysis of the B3LYP densities for the family of bis(2,6-bromophenyl)carbenes places about 1.2 α spins at the carbene carbon and about 0.24 α spins at the para position. This is consistent with the spin distribution of the whole series of ortho-substituted and near-D_{2d} symmetry bisphenylcarbenes. The gap between the closed-shell, geometry-optimized σ^2 singlet and the geometry-optimized triplet is also almost constant, 13 kcal/mol, within this family of substituted phenylcarbenes.

III. The *o*-Trifluoromethyl-Substituted Carbene and Variants. Tomioka[4] reports an "almost bottleable" carbene, 2,6-dibromo-4-*tert*-butyl-phenyl-2′.6′-bis(trifluoromethyl)-4′-isopropylphenylcarbene. The design principle at work is that steric crowding protects the vulnerable centers at the central carbon, the ortho positions, and the para positions of the aromatic rings. This species has a half-life of about 16 min at room temperature and is long-lived at −40 °C. Results of computational modeling on this species **6a** and simplified variants **6b** and **6c** are collected in Table 5.

According to published B3LYP/6-311G(d,p) calcula-tions,[25] Tomioka's triplet **6a** has a considerably shortened C0 to C1 distance (1.368 Å in ^{3}**6a**, to be compared to 1.39 and 1.40 Å in ^{1}**6a** and 1.42 Å in the parent bisphenyl-carbene singlet ^{1}**1**). The angle C1−C0−C1′ angle is almost linear (176° in ^{3}**6a**, 134° in ^{1}**6a**, 143° in the parent unsubstituted triplet ^{3}**1**). The aromatic rings in species ^{3}**6** are nearly orthogonal, though the torsional potentials governing the relative orientation of the aromatic rings are very flat.

There is evidently substantial spin delocalization into aryl rings; about 40% of the spin we might assign to C0 is accepted by the aromatic substituents. The singlet triplet gap according to the 6-311G(d,p) calculation is 12.2 kcal/mol, about twice the value for the unsubstituted bisphenylcarbene. Simplifying the alkyl groups to methyl or hydrogen leaves the geometry of singlet and triplet and the singlet−triplet gap unaffected, but of course would influence the kinetic stability of the carbene by failing to block the para positions. As observed already for the parent ^{3}**1** and substituted systems, B3LYP/6-31G* produces a strong quinoid distortion in the phenyl rings, with the C1C2 bonds extended to 1.43 Å and the C2C3 bonds shortened to about 1.38 Å.

Bisanthryl Systems. The longest-lived bisarylcar-benes reported by Tomioka are built with 9-anthryl substituents.[8] Our DFT and CAS calculations show that these systems, **7a**, **7b**, and **7c**, are qualitatively different from the bis(substituted phenyl)carbenes. As shown in Table 6, the anthryl fragments accept all but 35% of the spin we might have assigned to the central carbon. The displacement of spin from the carbene carbon into the anthryl rings' 10 and 10′ positions is substantial. This may be understood as the consequence of the very stable isolated 6π electron aromatic segments formed when the central ring is disrupted. Devising the longest-lived

(25) Woodcock, H. L.; Moran, D.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **2001** *123* 4331.

TABLE 7. B3LYP and CASSCF Parameters for Species ^{3}7a, Bis(9-anthryl)carbene

model	rel E (kcal/mol)	C0−C9 (Å)	C9−C0−C9′ (deg)
B3LYP C_s singlet	15	1.3683	143.8
UB3LYP-broken symmetry	1.5	[1.3413]^a	[180.0]^a
B3LYP-triplet	−0−	1.3413	180.0
CAS singlet (open shell)	(<0.5)	1.3293	180.0
CAS-triplet	−0−	1.3313	180.0

^{a} The broken symmetry singlet was not geometry-optimized.

bisaryl triplet yet known, Tomioka et al. blocked reaction at the 10, 10′ positions by phenyl substitution. The DFT representation of bis(10-phenyl-9-anthryl)carbene ^{3}**8b** displays D_{2d} symmetry and the C0−C9 distance typical of a CC double bond, 1.3413 Å.

The DFT closed-shell singlet has C0−C1 distance 1.3617 Å, C_2 symmetry, and a central angle C9−C0−C9′ of 147° (see Table 7). The triplet is favored by 15 kcal/mol over the closed-shell singlet. The UB3LYP/6-31G* broken-symmetry "singlet" with $\langle S^2 \rangle = 1.1201$ lies only 1.5 kcal/mol above the UB3LYP triplet and shares its D_{2d} symmetry. An open-shell singlet is shown by CAS(6,6) calculations beginning at the D_{2d} triplet CAS(6,6) minimum energy structure to be very nearly degenerate with the triplet. The CAS closed shell singlet, a strongly bent C_2-symmetric structure, can be captured beginning with the DFT singlet geometry but lies 35 kcal/mol above the D_{2d} triplet.

We made an attempt to disrupt the fused anthryl-methyl radical structure of the triplet, by introducing a CF$_3$ substituent at the 1, 1′ positions (species **7c**). This induces an appreciable change in the C9−C0−C9′ angle, to 155°. The torsion angles are also strongly disturbed, taking on values 60, 130, 130, and 93°. Although the soft modes respond to the substitution, the C0−C1 bond length, 1.3480 Å, is hardly altered from the unsubstituted reference system. This suggests that no major disturbance in the cumulene biradical character was accomplished. The NBO assignment of spin to the carbene carbon hardly changes upon substitution, leaving no doubt that this system is still a biradical.

Carbenes as Fused Phenylmethyl and Anthryl-methyl Fragments

The Fragment Radicals. The bis(9-anthryl)carbenes seem to be well characterized as orthogonally fused 9-anthrylmethyl radicals. To judge the accuracy of this simple characterization for aryl-substituted carbenes more generally, we study the species 9-anthrylmethyl radical = ^{2}**8**, the phenylmethyl radical ^{2}**9**, and the fragments fused into the unsymmetric species phenyl-9-anthrylcarbene ^{3}**10**. (See Figure 2 for numbering in this species.)

The ground states differ considerably. In the anthryl system, the odd electron is dispersed primarily through the aryl ring, while in the phenyl system the odd electron resides mainly on the exo CH$_2$. The length of the bond from ring C to CH$_2$ in the anthryl species is 1.37 Å, a bit longer than a typical CC double bond distance. The CH$_2$-ring distance in the phenylmethyl radical is very close to the value observed in bisphenylcarbene, ca. 1.40 Å.

It is possible to force an assignment of that odd electron to a $^2A_2$ level of the six-membered ring; this produces the high-energy valence isomer ^{2}**9*** phenylmethyl* which has a misleading resemblance in geometry to the anthryl radical's favored structure. The difference is in the symmetry of the states populated in the exo-double-bonded structures (Table 8).

A comparison of the geometry of phenyl and 9-anthryl fragments in the methyl radicals and in the fused carbene (Table 9A) shows a general similarity of structure across environments. The spin distribution for these species (Table 9B) shows significant differences only in the immediate neighborhood of the fusion center C0.

Triplet bisanthrylcarbene ^{3}**7** as already noted displays a D_{2d} symmetry and a central C0−C1 bond distance typical of a CC double bond. The C0−C9 distance in 9-anthrylmethyl radical ^{2}**8** is about 0.035 Å longer, but the very short distance is restored in the triplet phenyl-9-anthrylcarbene ^{3}**10**, as is the orthogonality of the aromatic rings.

The spin distribution in the 9-anthryl fragments in the carbenes is almost unchanged from that seen in the radical ^{2}**8**. The density functional method permits spin polarization, so that the anthryl fragment responds to the alpha spin at C0 with a substantial beta spin at the attachment site C9. The amplitudes at C9 are different in ^{3}**10** from the values observed in other systems which have only anthryl species. This must be traced to the greater independence of the anthryl fragment and the relatively strong coupling accomplished by phenyl.

The phenyl fragment responds to changes in environment. Although the structure of the phenylmethyl fragment is well preserved in bisphenylcarbene ^{3}**1**, as shown in Table 10A, the unsymmetric carbene ^{3}**10** displays a severely shortened C0−C1 distance.

The spin distribution is still more sensitive to environment, as shown in Table 10B. We mention only the α spin amplitude at the C4 (para) site, since that has implications on the kinetic stability of bisphenylcarbenes

TABLE 8. 9-Anthrylmethyl Radical ^{2}8, Phenylmethyl Radical ^{2}9, and Its Excited state ^{2}9*

species	^{2}**8**: 9-anthrylmethyl	^{2}**9**: phenylmethyl	^{2}**9***: phenylmethyl
symmetry	$^2B_1$	$^2B_1$	$^2A_2$
relative E (kcal/mol)	0	0	100, 79
R(C0 to ring) for ROHF, B3LYP (Å)	1.3317, 1.3705	1.4489, 1.4065	1.3506, 1.3616
spin locale	10 position of anthryl with delocalization	exo-CH$_2$ with delocalization	phenyl ring
structural characterization	bisphenyl methyl radical plus ethylene	phenyl ring plus CH$_2$ radical	pentyl radical plus ethylene
DFT spin density at C0 and ring sites	0.434 at C-0	0.726 at C-0	
	0.427 at C-10	0.244 at C-4	

TABLE 9.

(A) Geometry for Anthryl Systems in **7a**, **9**, and **10**

index	C0−C1	C0−C9′	C1−C0−C9′	torsion 1	torsion 2
³**10**	1.4187	1.3437	180	90	90
²**9**		1.3752			
³**7a**	1.3412	1.3412	180	90	90

(B) Anthryl Fragment Spin Distribution
According to NBO in **7**, **8**,[a] and **10**

species	C9	C10	C1, C8	C2, C7	C3, C6	C4, C5	C4a	C9a
³**10**	−193	436	−0.84	−141	−078	122	−100	204
²**8**	−148	444	−089	137	−081	122	−100	182
³**7b**	−148	428	−091	142	−82	124	−101	174

[a] In species **8**, the 9-anthrylmethyl radical, there is α spin amplitude at the *exo*-methyl radical site C0 of 435 millielectrons (me).

TABLE 10.[a]

(A) Geometry for Phenyl Fragments in **1**, **9**, and **10**

species	C0−C1	C1−C2	C2−C3	C3−C4
³**10**	1.3720	1.425	1.382	1.387
²**9**	1.406	1.427	1.386	1.402
³**1**	1.403	1.426	1.388	1.401

(B) Phenyl Fragment Spin Distribution According to NBO
in **1**, **9**, and **10**

species	C1′	C2′, C6′	C3′, C5′	C4′
³**10**	−144	220	−104	244
²**9**	−162	254	−112	266
³**1**	−150	210	−093	207

[a] Entries are in millielectrons; positive values refer to α spin, negative values to β spin. In species **9**, the phenyl methyl radical, there is an α spin amplitude at the *exo*-methyl radical site C0 of 727 millielectrons (me).

TABLE 11.[a]

(A) Geometry for 2,5-Dichloro-Substituted Phenyl Fragments in **11** and **2** (Distance in Å)

species	C0−C1	C1−C2	C2−C3	C3−C4
²**11**	1.3999	1.4368	1.3844	1.3985
³**2a**	1.3778	1.4361	1.3850	1.3987

(B) Spin Distribution According to NBO for 2,5-Dichloro-Substituted Phenyl Fragment in **11** and **2**

species	C1′	C2′, C6′	C3′, C5′	C4′
²**11**	−155	214	−106	241
³**2a**	−174	236, 229	−105, 106	233

[a] In species **11**, the 2,6-dichlorophenyl methyl radical, there is an α spin amplitude at the *exo*-methyl radical site C0 of 712 millielectrons (me).

generally. The C4 α spin is largest in the phenylmethyl radical ²**9** (266 me) and is substantially reduced in the bisphenylcarbene ³**1**.

Effect of Substitutions on the Fragments' Similarity in Carbene and Radical. The question arises to what extent the longer-lived bis(ortho-substituted phenyl)carbenes, which begin to approach the D_{2d} form, can be represented as essentially independent fused phenylmethyl radicals. The results showed in Table 11 allow comparison of the geometry and spin distribution in the 2,6-dichlorophenyl methyl radical ²**11** and the bis-(2,6-dichlorophenyl)carbene ³**2a**.

Apart from a substantial shortening of the central C0−C1 bond length in the carbene, the structures of the

CHART 3. DFT Spin Distribution and Central Angle in Bisarylcarbenes

Species	α Spin at C0	α Spin at C4 or C10	Central angle
Ideal Carbene (or CH2)	2.0	--	135
1: Bisphenylcarbene	1.430	0.207	142
2a: Bis(2,6-dichlorophenyl)carbene	1.297	0.233	159
2b: Bis(2,4,6-trichlorophenyl)carbene	1.262	0.223	162
3a: Bis(2,6-dimethylphenyl)carbene	1.239	0.258	164
3b: Bis(2,4,6-trimethylphenyl)carbene	1.238	0.249	161
4a: Bis(2,6-dibromophenyl)carbene	1.217	0.243	180
4b: Bis(2,4,6-tribromophenyl)carbene	1.184	0.238	180
4c: Bis(2,6-dibromo-4-methylphenyl)car-bene	1.202	0.245	177
4d: Bis(2,6-dibromo-4-*tert*-butylphenyl)car-bene	1.205	0.248	180
5a: Bis(2,3,6-tribromo-4-methylphenyl)carbene	1.197	0.244	178
5b: Bis(2,3,6-tribromo-4-t-butylphenyl)carbene	1.206	0.248	173
Intermediate Case			
10: Phenyl-9-anthrylcarbene	0.995	0.435anthryl, 0.246phenyl	180
Independent 9-anthrylmethyl radicals	0.868	0.436	180
7a: Bis(9-anthryl)carbene	0.712	0.442	180
7b: Bis(10-phenyl-9-anthry)carbene	0.707	0.443	180
7c: Bis(2-trifluoromethylanthryl)carbene	0.703	0.436	156
Ideal Spin-isolated Biradical	**0.0**	**1.0**	**180**

fragment radical and the fused carbene agree closely. More notably, the spin distribution in the 2,6-dichlorophenyl fragments in the radical ²**11** and the carbene ³**2a** agree much more closely than do unsubstituted and fragment species. We are led to the conjecture that the extended life of triplets associated with the shift in structure from the strongly bent C_2 parent bisphenylcarbene toward D_{2d} symmetry is linked to the decoupling of the radical fragments.

Summary and Conclusions

We can summarize our work with the help of Chart 3, which contains some data to bring to bear on the question whether the design and preparation of longlived carbenes is a triumph of stabilization of biradicals or carbenes.

Biradicals can be characterized by local and weakly interacting spins, with nearly degenerate triplet and open shell singlet states. Bisphenylcarbene is computed to be a triplet "carbene" with localized spin subject to aryl perturbations. About 70% of the spin density is located on the carbene carbon. The unrestricted $\sigma\pi$ open shell "singlet" ($\langle S^2 \rangle = 0.714$) lies well above the triplet, and has a structure very different from the optimized triplet geometry.

When substituents on the phenyl ring linearize the bisphenylcarbene triplet, spin is more extensively exported from the carbene carbon into the aromatic rings, leaving about 60% of the alpha spin at the carbene center. The lowest energy singlet state of bis (2,6-dimethylphenyl) carbene is still a (HOMO)² closed-shell with that HOMO located primarily on C0. The closed shell singlet state has a substantial admixture of the (LUMO)² configuration characteristic of carbenes. This system is

CHART 4

Species	CH$_2$	1	2	3	10	7a
$\langle S^2 \rangle$	0.7321	0.6591	0.8715	1.0625	1.0964	1.0901
σπS-T kcal/mol	6.3	8.4	7.0	4.5	2.5	1.5

clearly better described as a carbene rather than a biradical.

DFT calculations show this same general behavior throughout the family of bis (2,6-dichloro- and 2,6-dibromophenyl)carbenes, which can all be characterized as carbenes stabilized by spin donation to (substituted) phenyl substituents. Systems with 9-anthryl substituents are quite different. DFT characterization of the phenyl-methyl and anthrylmethyl radical shows that the anthryl system is a much more effective acceptor of odd spins. The mixed system phenylanthrylcarbene resembles a triplet coupled fusion of the two radicals. Its unrestricted open-shell "singlet" state is close to the independent-spin diradical limit of equal weights of sp triplet and singlet as the spin expectation value ($\langle S^2 \rangle = 1.014$) shows, but is less stable than the triplet state. This leads us to surmise that even though 50% of the triplet spin is withdrawn from the carbene carbon, the resulting system should not be called a biradical. Approximate unrestricted calculations on broken-symmetry "singlet" open shell species shows a rough correlation between "singlet"-triplet gap and diradical character as reflected by $\langle S^2 \rangle$ near 1.0, the limit for independent spins (Chart 4).

The 9-anthryl-, 1-trifluoromethyl-9-anthryl-, and the 10-phenyl-protected 9-anthryl substituents are computed to leave only about 35% of the α spins at the carbene carbon. The dispersal of spin suggests that the system is a biradical; and the very low-lying open shell singlet revealed by CAS calculations leaves little doubt that the bisanthryl systems must be considered biradicals. The combination of the 10-phenyl system with oxygen to yield the bis(10-phenyl-9-anthryl)ketone recalls the reactivity of triplet carbenes. This is the basis for Tomioka's view that the persistent 9-anthryl-substituted species are properly considered and named carbenes.[26] Still there is considerable spin amplitude at the carbene carbon in the hydrocarbon, and we can imagine a flow of spin toward this site as oxygen approaches. This small reagent is not likely to encounter difficulty in finding the central carbon.

The issue of terminology should not distract from the success of the experimental project, in which by the most persistent effort and imaginative design, the lifetime of intrinsically reactive species has been extended by many orders of magnitude.

DFT calculations are clearly helpful in illuminating the trends and differences within sets of similar aryl-substituted carbenes and have guided experimental ventures, but there is reason to be skeptical of some aspects of DFT modeling of these triplet systems. Structural data are available for the bis (2,4,6-trichlorophenyl)-carbenes. The data suggests that DFT calculations exaggerate the shortening of the central bonds and the extent of linearization of the carbene. That is, DFT models may be biased toward the cumulene limit. We report further post-Hartree–Fock calculations in a forthcoming report, addressing this conflict. There we show that the smallest-active space treatments, ROHF and CASSCF(2,2) with perturbative refinements provide a better match than does DFT to the data for the trichlorophenyl carbene. CAS calculations with larger active spaces and MP2 corrections, on chloro, methyl, and unsubstituted bis aryl carbenes, predict shorter central bonds for ortho-substituted species, tending toward support of the DFT modeling.

Supporting Information Available: Tables of selected structural parameters, Gaussian archive files, and PQS log files define coordinates and energy for all species. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034753Q

(26) From ref 8, "One of the best known reactions of triplet carbenes is their interaction with oxygen to form the corresponding ketones, which involves carbonyl oxide formation. In contrast, diradicals react with oxygen to give oxidation products mainly derived from the corresponding peroxides. When **1b** [bis 9-(10-phenyl)anthryl]diazomethane] was irradiated in the presence of oxygen, bis [9-(10-phenyl)-anthryl]ketone was formed. Laser flash photolysis studies showed the presence of a broad transient absorption at 505 nm ascribable to the carbonyl oxide. Moreover, whereas ^{3}**2a** [triplet di(9-anthryl)carbene] aggregated into a trimer, ^{3}**2b** [9-(10-phenyl)anthryl]carbene] produced a carbene dimer (**4**) through coupling of two molecules at their carbene centres. These observations, and the fact that we observed the main decay pathway of persistent triplet carbenes in solution to be dimerization, suggest that even though the free electrons in ^{3}**2b** are extensively delocalized, it is considered more appropriately as a carbene than a diradical."