898 *J. Phys. Chem. A* **2005,** *109,* 898−904

Post-Hartree−Fock Studies on the Structure of Bis(ortho-substituted phenyl)methylenes†

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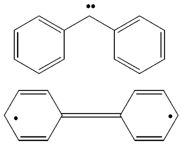
Received: June 18, 2004; In Final Form: November 17, 2004

Long-lived triplet bisarylmethylenes are now well-known. Experimental data (primarily ESR hyperfine parameters) suggest that the carbon framework of long-lived bisarylmethylenes approaches D_{2d} symmetry, as ortho-substitution forces the central angle to approach 180°. According to DFT modeling, the approach of the central angle to 180° is accompanied by a dramatic shortening of the central CC bonds and severe quinoid distortion of the phenyl rings. In contrast, X-ray investigation of bis(2,4,6-trichlorophenyl)methylene shows a structure closer to the carbene valence bond representation with less seriously distorted phenyl rings, a more acute central angle, and a longer bond from the methylene carbon to the aryl substituent. We address the difficulty of achieving a balance of cumulene and carbene character, treating the model systems diethynylmethylene, dicyanomethylene, and diisocyanomethylene by post-Hartree−Fock methods CAS and CCSD as well as DFT models, and applying the perturbation-corrected CAS methods to the chloro and methyl ortho-substituted bisphenyl carbenes.

Introduction

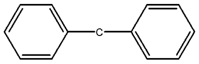
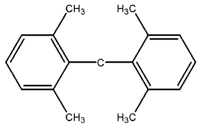
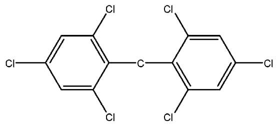
A variety of long-lived singlet methylenes are known,[1] but the search for stable triplet methylenes has proved more challenging. The leading candidates developed by Tomioka[2] are bisaryl species, mostly substituted bisphenylmethylenes.[3] It is possible to write two distinct Lewis structures for bisarylmethylenes. Besides placing the unpaired electrons on methylene leaving the rings conventionally aromatic, one may draw a cumulene connection between two cyclic radicals.



Clues to the structure of the long-lived triplets have been derived from the *D* and *E* parameters of the ESR spectra of these species.[4] The *D* value is related to the mean distance between unpaired electrons. A near-zero value of E/D suggests a cylindrical spin distribution, hence a near linear methylene. EPR data strongly imply that the bisaryl triplets respond to ortho-substitution by broadening the methylene angle from the ca. 150° estimated for triplet bisphenylmethylene.[5]

Since the issue of geometry of species representable as a combination of carbenic and diradical allenic structures has arisen in the discussion of the smaller species diethynylmethylene (**A**) and dicyanomethylene (**B**), we review and develop post-Hartree−Fock treatments of these species as well as bisisocyanomethylene, **C** (see Chart 1). CCSD and QCISD calculations are not feasible for the parent bisphenylmethylene **1** and two ortho-substituted species, bis(2,6-dimethylphenyl)methylene **2** and bis(2,4,6-trichlorophenyl)methylene **3**. However, we find some highly suggestive behavior in the small molecules that can guide our discussion of the bisarylmethylenes.

CHART 1: Species Discussed in This Paper

Model systems		Bisarylmethylenes	
A	HCC—C—CCH	**1**	
B	NC—C—CN	**2**	
C	CN—C—NC	**3**	

Methods for computational characterization of methylenes are well developed.[6] Density functional modeling has provided reliable descriptions for Tomioka's long-lived bisarylmethylenes[7] and many other carbenes[8] and nitrenes.[9] For most bis(ortho-substituted phenyl)methylenes DFT modeling displays broadening of the central angle compared to the bisphenyl carbene, and predicts drastic shortening of the central carbon to aryl carbon bond distance relative to that of unsubstituted species.[7] This is attended by a severe quinoid distortion of the aromatic rings.

Kawano et al.[10] report X-ray estimates of a central bond angle of 142° and (not quite equivalent) central bond lengths near 1.43 Å for bis(2,4,6-trichlorophenyl)methylene triplet. The DFT model produces a C_2-symmetric structure, a central bond angle of 160°, and central bond lengths of 1.375 Å (see details in Table 1.) This suggests that DFT methods may overestimate the importance of the linear allenic diradical structure and underestimate the weight of the carbenic structure.

Open shell and especially diradical systems generally need careful treatment.[11] It seems particularly important to avoid

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

10.1021/jp0473467 CCC: $30.25 © 2005 American Chemical Society
Published on Web 01/14/2005

TABLE 1: X-ray and DFT Structures for Diazo Precursor to Bis(2,4,6-trichlorophenyl)methylene (3) and X-ray and DFT Structures for 3[a]

Bis(2,4,6-trichlorophenyl)diazomethane

source	geometric parameters (unit) ⟹	N−N distance (Å)	C0−N distance (Å)	C0−C1 distance (Å)	C1−C0−C1′ angle (deg)	C2−C1−C0−C1′ torsion (deg)
X-ray		1.136	1.323	1.480	127.1	70.2
B3LYP/6-31G(d)		1.140	1.313	1.480	126.3	64.8

Bis(2,4,6-trichlorophenyl)methylene

source	geometric parameter (unit) ⟹	C0−C1 distance (Å)	C1−C0−C1′ angle (deg)	C2−C1−C0−C1′ torsion (deg)	E (hartrees)
X-ray (disordered)		1.437, 1.423	142		
B3LYP/6-31G(d) T$\sigma\pi$		1.375	160.0	90	−3258.8642089
B3LYP/6-31G(d) Sσ^2		1.403	131.4	101	−3258.8438813
UB3LYP/6-31G(d) S$\sigma\pi$		1.363	180.0	90	−3258.8530353

[a] C0 is the central (methylene) carbon, and C0−C1 is the central bond distance from the methylene carbon to either of two equivalent aryl carbons. C1−C0−C1′ is the central bond angle. T$\sigma\pi$ is a label for the triplet state in which the odd electrons are assigned respectively to orbitals on the central carbon of type σ (A in point group C_2) and π (B in C_2). S$\sigma\pi$ is the corresponding open shell singlet, represented in this case by broken symmetry UB3LYP. Sσ^2 is the closed shell singlet with both electrons paired and assigned to the σ (A) orbital.

serious contamination of the spin state, while allowing open shell character in singlets. We use CAS methods primarily, since its multiconfigurational wave function can represent open shell singlets and guarantees valid spin states. Practical limitation to small active spaces requires that one exercise careful judgment so that the right electrons are correlated. In the large bisarylmethylene systems of interest here, the minimum meaningful calculation embraces two orbitals for the two carbenic electrons. This calls for ROHF and CAS(2,2) calculations for the triplet and singlet states, respectively. The Gaussian suite of programs provides an MP2 correction to the ROHF energy, and a similar dynamic correction to CAS calculations.

For more thorough treatment of nondynamical correlation, we can treat the two electrons formally assigned to the carbene center and at least one additional π electron pair from each ethynyl, cyano, isocyano, or aryl substituent (6 electrons in 4 or more orbitals). The next level of effort would correlate four π electrons from each substituent with the two electrons of the carbene center (10 electrons in 6 or more orbitals). Further nondynamic correlation can be achieved by expanding the virtual active space, e.g., placing the 6 correlated electrons in 8 orbitals or the 10 electrons in 10 orbitals.

Computational Methods and Software

We used Gaussian 98W[12] on NT and Windows 2000 Pro PC systems, and PQS software on PQS Linux systems.[13] NBO analyses[14] were available in both software suites. CAS calculations began from verified minimum energy structures produced by ROHF or B3LYP. If optimization by these methods converged to high-symmetry structures, that high symmetry was presumed in all later CCSD, QCISD, and CAS calculations. CAS extreme points were not verified as minima owing to the computational demands of vibrational calculations in CAS.

Discussion

Small π-Acceptor Substituted Triplet Carbenes (^{3}A, ^{3}B, ^{3}C). Tables 2−4 display properties of the species we take as models for bisphenylcarbenes. Early RHF calculations[15] treated linear $HC_{2n+1}H$, apparently without verification by diagnostic vibrational calculations. B3LYP/6-31G(d) optimization produces a linear structure for **^{3}A** while strongly spin-contaminated MP2 and pure-spin-triplet ROHF methods produce a bent structure.[16] CCSD/DZP treatment[17] produces a linear form with a very low frequency (40 cm^{-1}) deformation, while QCISD[17] leaves the system bent. Our CCSD/6-31G(d) and QCISD/6-31G(d) calculations which begin with the strongly bent ROHF geometry favor a weakly bent structure with a central angle near 172° to an optimized linear form, but by less than 0.2 kcal/mol. CAS(6,6) and CAS(10,10) calculations favor a severely bent form with central angles of 143° and 153°, respectively. One notes that the linearized CAS(10,10) structure has substantially shorter central bonds than the equilibrium bent form. This suggests substantial participation by the cumulene diradical valence bond structure.

TABLE 2: Post-Hartree−Fock Representations of Bisethynylmethylene ^{3}A[a]

model chemistry	bond lengths (Å)	angle (deg)	$\langle S^2 \rangle$; Sc
ROHF/6-31G(d)	1.3900, 1.1924	135.9	2.00
CAS(6,6)/6-31G(d)	1.3343, 1.2395	143.3	2.00
CAS(10,10)/6-31G(d)	1.3358, 1.2349	153.0	2.00
[CAS(10,10)/6-31G(d)]	[1.3019, 1.2405]	[180.0]	2.00
B3LYP/6-31G(d)	1.3090, 1.2440	180.0	2.08
MP2/6-31G(d)	1.3177, 1.2193	172.7	2.67/2.34
CCSD/6-31G(d)	1.3225, 1.2445	172.2	
QCISD/6-31G(d)	1.3230, 1.2453	172.2	2.78/2.47

[a] Bracketed entries refer to linear forms.

TABLE 3: Post-Hartree−Fock Representations of Biscyanomethylene ^{3}B[a]

model chemistry	bond lengths (Å)	central angle (deg)	$\langle S^2 \rangle$
ROHF/6-31G(d)	1.4025, 1.1375	132.7	2.00
CAS(6,8)/6-31G(d)	1.3722, 1.1567	139.0	2.00
[CAS(6,6)/6-31G(d)]	[1.3394, 1.1485]	[180.0]	2.00
CAS(10,10)/6-31G(d)	1.3647, 1.1741	141.4	2.00
[CAS(10,10)/6-31G(d)]	1.3269, 1.1835	[180.0]	2.00
B3LYP/6-31G(d)	1.3162, 1.1940	180.0	2.08
MP2/6-31G(d)	1.3812, 1.1466	136.8	2.51
CCSD/6-31G(d)	1.3477, 1.1905	152.9	2.45
QCISD/6-31G(d)	1.3481, 1.1932	152.6	

[a] Bracketed entries refer to linear forms.

TABLE 4: Post-Hartree−Fock Representations of Triplet Bisisocyanomethylene ^{3}C

model chemistry	bond lengths (Å)	central angle (deg)	$\langle S^2 \rangle$
ROHF/6-31G(d)	1.3408, 1.1634	125.6	2.00
B3LYP/6-31G(d)	1.2989, 1.2066	127.2	2.18
MP2/6-31G(d)	1.3351, 1.1911	129.6	2.21
CCSD/6-31G(d)	1.3239, 1.2015	129.6	2.03
QCISD/6-31G(d)	1.3247, 1.2033	129.6	2.03

TABLE 5: Illustration that B3LYP/6-31G(d) Overestimates Stability of Cumulene Double Bonds Relative to Localized Triple and Single Bonds[a]

species	B3LYP/6-31G(d)	CCSD/6-31G(d)	QCISD(T)[c]
methylacetylene $CH_3{-}CCH$	−116.6532701	−116.2684833	−116.359666
allene $CH_2{=}C{=}CH_2$	−116.6576762	−116.2668647	−116.356558
energetic preference	allene 3.0 kcal/mol	methylacetylene 1.0 kcal/mol	methylacetylene 0.8 kcal/mol
methylnitrile $CH_3{-}CN$	−132.7549284	−132.3567318	−132.445283
ethylideneimine $CH_2{=}C{=}NH$	−132.7111412	−132.3016999	−132.395368
preference	methylnitrile 27.5 kcal/mol	methylnitrile 36.4 kcal/mol	methylnitrile 31.3 kcal/mol
methylisonitrile $CH_3{-}NC$	−132.7165728	−132.3165899	−132.406690
unnamed ylide[b] $CH_2{=}N{=}CH$	−132.6696751	−132.2544591	−132.348210
preference	methylisonitrile 29.4 kcal/mol	methylisonitrile 39.0 kcal/mol	methylisonitrile 36.7 kcal/mol

[a] Absolute energies in hartrees; relative energies as noted in table. [b] No CA name has been assigned to the structure as written here; a nitrile ylide has the same atom sequence, but a different connectivity and formal charge assignment. [c] Computed in the G2(MP2) sequence: QCISD(T)/6-311G(d,p)//MP2/6-31G(d).

The biscyanomethylene triplet ^{3}**B** was predicted by noncorrelated methods to be strongly bent,[18] but DFT produces a linear structure.[19−21] Post-Hartree−Fock studies reported for this system[20,21] were explicitly acknowledged to begin with the linear B3LYP-optimized linear forms; CAS and CCSD calculations with that starting point would not find a minimum energy bent form. CCSD/6-31G(d) and QCISD/6-31G(d) optimization beginning with the ROHF bent structure produces a central angle of 152°. Our CAS(6,6)/6-31G(d) calculations show the bent form to be >30 kcal/mol more stable than the linear form; extending the active space brings the two forms closer in energy but still favors the bent form.

Triplet bisisocyanomethylene ^{3}**C** is bent; all methods yield central angles in the range 125−130°. Bond lengths for all correlated models agree within 0.01 Å, and spin contamination is minimal, by comparison with the other species.

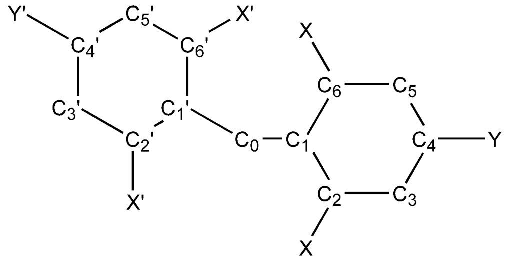

Figure 1. Numbering scheme for bisphenylmethylenes.

DFT, CCSD, and QCISD(T) calculations (the latter a part of the G2(MP2) sequence) on C_3H_4 isomers methylacetylene and allene (Table 5) suggest that B3LYP has a definite bias in favor of cumulated double bonds over adjacent single and triple bonds. This bias in favor of cumulenic double bonds suggests that we might expect a bias of DFT toward allenic structures over carbenic structures in other contexts, such as the bisarylmethylenes of interest here.

Bisphenylmethylene (^{1,3}1). The DFT and post-Hartree−Fock characterization of bisphenylcarbene, **1**, is summarized in Tables 6−8. See Figure 1 for a general labeling scheme.

B3LYP/6-31G(d) modeling of bisphenylmethylene shows a triplet preference, by 7 kcal/mol. Relative to the closed shell singlet described in B3LYP/6-31G(d), the triplet species has shorter C0−C1 and C0−C1′ bond lengths, accompanied by an expanded C1−C0−C1′ angle. The phenyl ring is considerably distorted, with C1−C2 bonds lengthened to 1.43 Å and C2−C3 bonds shortened to 1.38 Å. Structures by B3LYP/6-311G-(d,p)[22] are nearly indistinguishable.

NBO analysis assigns 1.430 α spins to the methylene carbon in ^{3}**1**, and 0.285 α spins to each phenyl ring. The NBO analysis assigns 0.218 α spins to each ortho carbon and 0.204 α spins to each para position, 0.089 *β* spins to each meta position, and 0.149 *β* spins to each attachment site.

TABLE 6: DFT Models for Bisphenylmethylene

species: symmetry	model chemistry	*E* (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**1**: C_2	B3LYP/6-31G(d)	−501.3042674	0	1.4036	142
^{1}**1**: C_2	B3LYP/6-31G(d)	−501.2931408	7	1.4346	119
^{1}**1**: C_2	UB3LYP/6-31G(d)	−501.2972662	4.4	1.4234	127
^{3}**1**: C_2[a]	B3LYP/6-311G(d,p)	−501.424280	0	1.400	143
^{1}**1**: C_2[a]	B3LYP/6-311G(d,p)	−501.415070	5.8	1.431	119

[a] Reference 22.

TABLE 7: Minimally Correlated Models and MP2 Corrections for Bisphenylmethylene for Species 1[a]

species: symmetry	model chemistry	*E* (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**1**: C_2	ROHF/6-31G(d)	−498.0335179	0	1.4529	134
^{1}**1**: C_2	CAS(2,2)/6-31G(d)	−498.0251819	5	1.4686	117
^{3}**1**: D_2	ROHF/6-31G(d)	−498.0120418	12	1.4264	180
^{3}**1**: C_2	ROMP2 (FULL)//ROHF /6-31G(d)	−499.6969	<1	[1.415][b]	[136][c]
^{3}**1**: C_2	ROMP2 (FULL)//ROHF/6-31G(d)	−499.6970	0	[1.415]	[140][d]
^{1}**1**: C_2	CAS(2,2)+MP2//CAS(2,2)/6-31G(d)	−499.6763463	13	[1.4686][e]	[117][e]

[a] C_2 symmetry is assumed. Bracketed values of geometric parameters C0−C1 (the central bond distances) and C1−C0−C1′ (the central bond angle) are estimates from our coarse pattern search. Unbracketed values are from fully optimized structures. MP2 corrections to ROHF and CAS involve all electrons (FULL). The pattern search varies the C0−C1 distance from 1.31 to 1.49 Å, in steps of 0.03 Å. In this scan all geometric parameters are optimized in ROHF/6-31G(d) except the C1−C0 distances. ROMP2/6-31G(d) energies evaluated at those ROHF/6-31G(d) geometries are used for the estimation of the optimum C0−C1 distance. The basis is always 6-31G(d). [b] This is the optimized C0−C1 distance according to the pattern search described in the text. [c] This is the ROHF/6-31G(d)-optimized angle at the central bond distances 1.415 Å. [d] We estimated the optimum-energy angle by interpolation in a series of single-point ROMP2 energies. These single-point calculations used ROHF geometries optimized at values of the central C1−C0−C1′ angle ranging from 130° to 150° in 5° steps, keeping the central bond distances fixed at 1.415 Å. [e] CAS22+MP2 energies are evaluated at the geometry of the CAS(2,2)/6-31G(d) optimized singlet species.

TABLE 8: Larger Active Space CAS Calculations for Species 1

species: symmetry	model chemistry	E (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**1**: C_2	CAS(6,6)/6-31G(d)	−498.0666154	-0-	1.4336	136
^{1}**1**: C_2 vertical	CAS(6,6)/6-31G(d)	−498.0325030	21	[1.4336]	[136]
^{1}**1**: C_2 optimized	CAS(6,6)/6-31G(d)	−498.0455861	13	1.4543	118

TABLE 9: DFT Characterization of the ^{1,3}2 Species Bis(2,6-dimethylphenyl)carbene

state: symmetry	model chemistry	E (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**2**: C_2	B3LYP/6-31G(d)	−658.5754775		1.3730	179
^{1}**2**: $C_2\,\sigma^2$	B3LYP/6-31G(d)	−658.5581084	12.1	1.4125	131
^{1}**2**: $C_2\,\sigma\pi$	UB3LYP/6-31G(d)	−658.5682389	4.5	1.3730	179

TABLE 10: Minimally Correlated ROHF and CAS(2,2) Models for Bis(2,6-dimethyl)carbene, ^{1,3}2[a]

state: symmetry	model chemistry	E (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**2**: C_2	ROHF/6-31G(d)	−654.173075	0	1.459	138
^{3}**2**: D_{2d}	ROHF/6-31G(d)	−654.158577	9.1	1.4280	180
^{1}**2**: C_2	CAS(2,2)/6-31G(d)	−654.156083	11	1.4662	121
^{1}**2**: D_{2d} closed shell	CAS(2,2)/6-31G(d)	−654.107882	40[a]	[1.4280]	180
^{1}**2**: D_{2d} open Shell	CAS(2,2)/6-31G(d)	−654.125506	30	1.3730	180

[a] Label “a” identifies an energy relative to the D_{2d} triplet. Geometric parameters are for optimized geometries within specified symmetry except when explicitly constrained [marked with brackets]. The structure is reoptimized with respect to other degrees of freedom.

TABLE 11: MP2 Corrections to Minimally Correlated ROHF and CAS(2,2) Models for Bis(2,6-dimethyl)methylene, ^{1,3}2

state: symmetry	model chemistry	E (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**2**: C_2	ROMP2/6-31G(d)	−656.401870	0	1.40[a]	141[b]
^{1}**2**: C_2	CAS(2,2)+MP2/6-31G(d)	−656.373425	18	1.46[a]	121

[a] Obtained by interpolating ROMP2 energy calculations at a series of ROHF geometries optimized at values of central bond distances ranging from 1.37 to 1.46 Å in 0.03 Å steps. [b] Obtained by interpolating ROMP2 values at 1.40 Å and a series of central angles ranging from 130° to 150° in 5° steps.

Our alternative modeling (see Table 7) begins with the uncorrelated ROHF method for the triplet, and CAS(2,2) for the singlet. This minimal or zero-correlation treatment produces pure spin states. The optimized bond lengths obtained from these methods are much longer than those produced by DFT, and the central angles more acute. ROMP2 permits an estimate of the effects of dynamic correlation. Lacking analytical derivatives for the ROMP2 calculations, we performed a limited pattern search for the C_2 triplet structure. In a line search on the central bond distance, we evaluated ROMP2/6-31G(d) energies at a sequence of C1−C0 distances. The structures at each point were ROHF/6-31G(d) geometries optimized with the C0−C1 bond distance fixed. The ROMP2 energy values made clear that the central bond is shortened by dynamic correlation, to about 1.415 Å. A line search on the C1−C0−C1′ angle with that distance held fixed and the structure otherwise optimized in ROHF at each value of the central angle showed that the central angle would expand as the central bond distance decreased.

We estimate $R(\mathrm{C0{-}C1}) = 1.415$ Å and C1−C0−C1′ = 140°. This agrees reasonably with the DFT bisphenylmethylene description of the central geometry (1.40 Å, 143°). However, we see no great distortion of the phenyl rings in these calculations, such as is characteristic of the DFT modeling. Forcing D_{2d} symmetry costs 13.5 kcal/mol in ROHF, and shortens the central bond distance by almost 0.03 Å. The ROHF calculation still places most of the α spin at the central carbon in D_{2d} symmetry.

Expanding the active space to include the two electrons at the methylene carbon and two electrons from each phenyl defines a CAS(6,*n*) calculation with some nondynamic correlation (Table 8). This has a minor effect. At the CAS(6,6) triplet geometry, the lowest singlet (ca. 21 kcal above the triplet) is the closed-shell state. This argues against ascribing diradical character to the bisphenylmethylene.

Bis(2,6-dimethylphenyl)methylene (^{1,3}2). Methyl substitution at the ortho-positions forces the geometry of triplet bis(2,6-dimethylphenyl)methylene (^{3}**2**) toward D_{2d}. An increase of central angle C1−C0−C1′ from 140° to almost 180° is predicted in the DFT model (see Table 9). The bending potential is very soft, and the deformation from 180° to 160° costs only about 0.1 kcal/mol. The central bond distances are shortened to about 1.38 Å as the central angle broadens. The phenyl rings are again strongly quinoid-distorted in DFT.

Minimally correlated ROHF and CAS(2,2) calculations (Table 10) yield longer central bonds and more acute central angles than B3LYP predicts. The impact of the ortho substitution is modest according to these models. Constraining the symmetry to D_{2d} costs 9 kcal/mol in ROHF, and shortens the central bond distance by about 0.03 Å. The interplay between angle broadening and bond lengths confirms the view that a cumulene structure is close in energy to the carbene structure when steric influences force near-D_{2d} symmetry.

Correction of the minimally correlated model for ^{1,3}**2** by ROMP2 and CAS(2,2)+MP2 [shown in Table 11] has the expected effect of shortening the central C0−C1 bond distance for the triplet. Our interpolation, performed as already described in the parent system, puts that value at about 1.41 Å. This approximate minimum-energy bond length is almost identical with that modeled by ROMP2 for the unsubstituted bisphenylmethylene. A line search on the central angle with the central bond distance held fixed at 1.410 Å indicates that the central angle expands to about 144°. This is only a few degrees greater than the value an equivalent calculation produces for the unsubstituted bisphenylmethylene. Of course this limited search

TABLE 12: CAS(6,6) Treatment of Species ^{1,3}2

state: symmetry	model chemistry	E (hartrees)	E_{relative} (kcal/mol)	C0−C1 (Å)	C1−C0−C1′ (deg)
^{3}**2**: C_2	CAS(6,6)/6-31G(d)	−654.2020754	0	1.4290	142
^{1}**2**: C_2	CAS(6,6)/6-31G(d)	−654.1431504	37[a]	[1.4290]	[142]
^{1}**2**: C_2	CAS(6,6)/6-31G(d)	−654.1656244	23	1.4626	122
^{3}**2**: D_{2d}	CAS(6,6)/6-31G(d)	−654.1811246	13	1.42081	[180]
^{1}**2**: D_{2d} $(x^2 - y^2)$	CAS(6,6)/6-31G(d)	−654.1494127	33[b]	[1.42081]	[180]
^{1}**2**: D_{2d} $(x^2 - y^2)$	CAS(6,6)/6-31G(d)	−654.1602975	26	1.3302	[180]

[a] Vertical energy gap from ground C_2-symmetric ^{3}**2** to ^{1}**2** = 37 kcal/mol. Equilibrium energy gap from ground C_2-symmetric ^{3}**2** to ^{1}**2** = 23 kcal/mol. Triplet barrier to $C_2 \rightarrow D_{2d}$ = 13 kcal/mol. [b] Vertical energy gap from D_{2d} triplet to singlet = 20 kcal/mol. Singlet barrier to $C_2 \rightarrow D_{2d}$ = 4 kcal/mol.

TABLE 13: Minimally Correlated and MP2-Corrected Structures and Singlet−Triplet Gaps for Species 3[a]

state: symmetry	model chemistry	C0−C1 (Å)	C1−C0−C1′ (deg)	^{3}**3** to ^{1}**3** gap (kcal/mol)	E (hartrees)
^{3}**3**: C_2	ROHF/	1.4524	137.6		−3251.407089
^{1}**3**: C_2	CASSCF(2,2)	1.4694	120.7	14	−3251.384858
^{3}**3**: C_2	ROMP2//ROHF	[1.41]	143		−3253.94409
^{1}**3**: C_2	RMP2/	1.4525	123	11	−3253.92600

[a] The central C0−C1 distances and the central C1−C0−C1′ angle are fully optimized in all but ROMP2 calculations on the triplet. In this case the optimum distance and angles are estimated by interpolation in a coarse pattern search with 5° steps in C1−C0−C1′ from 130° to 150° and 0.03 Å steps in C0−C1 (=C0−C1′) from 1.37 to 1.46 Å, with geometries otherwise optimized in ROHF. The basis is always 6-31G(d).

TABLE 14: Bis(2,4,6-trichlorophenyl)methylene in Extended Active Space

state: symmetry	model chemistry	C0−C1 (Å)	C1−C0−C1′ (deg)	^{3}**3** to ^{1}**3** gap (kcal/mol)	E (hartrees)
^{3}**3**: C_2	CASSCF(6,6)/6-31G(d)	1.4298	140.5	−0-	−3251.441205
^{1}**3**: C_2	CASSCF(6,6)/6-31G(d)	[1.4298]	[140.5]	24	−3251.403479
^{1}**3**: C_2	CASSCF(6,6)/6-31G(d)	1.4664	120.9	16	−3251.416379

has not provided a very precise estimate of the central geometry, but the results so far bear no resemblance to the near D_{2d} form favored in DFT modeling and offer little prospect of accord between the models.

Full geometry optimization in CAS(6,6) yields a moderately shortened central bond distance and a slightly broadened central bond angle relative to ROHF structures, without the striking quinoid distortion of the phenyl rings which is so prominent a feature of the DFT modeling (see Table 12).

The D_{2d} singlet requires two determinants for correct qualitative representation, the highest energy two electrons being assigned to $e_x^2 - e_y^2$. The D_{2d} singlet in CAS(6,6) correlates smoothly with the bent form, also closed shell. The D_{2d}-constrained triplet lies 13 kcal/mol higher than the bent triplet, and the D_{2d} singlet lies 20 kcal/mol higher than the D_{2d} triplet. The structures of singlet and triplet are quite different in C_2 or D_{2d} symmetry, confirming that this species is not to be interpreted as a diradical.

In the CAS modeling the ortho-methyl substitution has minor effects on the central bond distance and the central angle. The ROMP2 and CAS(6,6) methods disagree only in minor ways. There remains a serious discrepancy between the DFT structure and the results of these alternative post-Hartree−Fock models.

Hexachlorinated Species ^{1,3}3. We now consider the discrepancy between DFT modeling of bis(2,4,6-trichlorophenyl)methylene ^{1,3}**3** and the structural data from X-ray studies on that species derived from the diazo precursor in situ. DFT modeling of the singlet precursor matches the X-ray structure well. Table 1 summarizes DFT calculations on the methylene. In the now-familiar pattern the B3LYP triplet has a shortened C0−C1 distance and a wider C1−C0−C1′ bond angle, similar to many other bis(ortho-substituted phenyl)methylenes. Accompanying these changes is a severe quinoid distortion of the benzene ring's normal hexagon. The C1−C2 and C1−C6 distances are extended to 1.43 Å and the C2−C3 and C5−C6 bonds are shortened to 1.38 Å.

According to the X-ray data,[10] the central bond distances are longer and the central bond angle is more acute than B3LYP predicts. The reported X-ray structure does not show any symmetry, while all calculations predict C_2 symmetry. The X-ray structure suggests that the two central bonds are slightly different in length and that the benzene rings differ in structure from one another and from their usual near-perfect 6-fold symmetry.[23] Kawano et al.[10] ascribe the discrepancies in torsion and central angles to packing effects in the solid, a suggestion given plausibility by the soft potential opposing such motion. A referee makes the more specific suggestion that Cl···Cl interactions in the solid have important effects.

ROHF/6-31G(d) gives a C_2-symmetric reference structure with a C1−C0−C1′ angle of 138°, very close to the central angle taken up in ROHF by the 2,6-dimethyl and unsubstituted species (see Table 13). The minimally correlated CAS(2,2) singlet is closed shell and displays a more acute angle, 121°.

Interpolation in a sequence of ROMP2/6-31G(d)//ROHF/6-31G(d) energy values for ^{3}**3** produced a minimum-energy distance of ca. 1.41 Å, and a C1−C0−C1′ angle near 143°. X-ray estimates of the central bond distances and angle are near 1.43 Å and 141°.

Extending the active space has a modest effect on the computed geometry (see Table 14). The CAS(6,6)/6-31G(d)-optimized C0−C1 bond distance is moderately shortened relative to the ROHF/6-31G(d) value, to a value of about 1.43 Å. This value is very close to that reported in the X-ray study and contrasts strikingly with the much shorter CC bond distances produced in the B3LYP modeling.

A series of CAS(6,6)+MP2/6-31G(d)//CAS(6,6)/6-31G(d) energy calculations, interpolated to yield an estimate of the optimum geometry, suggests a shortening of the central bond

TABLE 15: Details of Computed Geometries for ^{3}3 by DFT and Post-HF Methods[a]

parameter (Å and deg)	source of value					
	DFT	ROHF	ROMP2	CAS66	CAS66+MP2	CAS1010
C0−C1	1.375	1.4524	1.40	1.43	1.40	1.420
C0−C1′	1.375	1.4524	1.40	1.43	1.40	1.420
C1−C0−C1′	160	138	143	141	143	142
C1−C2 &	1.4388	1.3975	1.4022	1.4116	1.4170	1.413
C6−C1	1.4375	1.3980	1.4016	1.4159	1.4200	1.417
C2−C3 &	1.3836	1.3810	1.3800	1.3766	1.3738	1.388
C5−C6	1.3828	1.3800	1.3791	1.3700	1.3686	1.367
C3−C4 &	1.3990	1.3808	1.3810	1.3882	1.3834	1.388
C4−C5	1.3988	1.3803	1.3806	1.3814	1.3888	1.393
C1′-C2′ &	1.4388	1.3975	1.4022	1.4116	1.4170	1.413
C1′-C6′	1.4375	1.3980	1.4016	1.4159	1.4200	1.417
C2′-C3′ &	1.3836	1.3810	1.3800	1.3766	1.3738	1.388
C5′-C6′	1.3828	1.3800	1.3791	1.3700	1.3686	1.367
C3′-C4′ &	1.3990	1.3808	1.3810	1.3882	1.3834	1.388
C4′-C5′	1.3988	1.3803	1.3806	1.3814	1.3888	1.393
C2−C1−C6	115	116	118	116	115	116

[a] The numbering scheme is specified in Figure 1. All calculations assume C_2 symmetry and use the 6-31G(d) basis set. All computed structures are optimized by gradient search except for ROMP2 and CAS66+MP2 for which no analytical gradients are available. Structures for ROMP2 and CAS66+MP2 are obtained by interpolation in a grid of ROMP2/6-31G(d)//ROHF/6-31G(d) and CAS(6,6)+MP2/6-31G(d)//CAS(6,6)/6-31G(d) energy values at specified values of the C0−C1 length and C1−C0−C1′ angles. Results are detailed in the Supporting Information.

distance from about 1.43 Å to about 1.40 Å, and an opening of the C1−C0−C1′ angle to near 144°. This is the calculation in which we place the greatest confidence, and which we would set against experimental data.

We conducted geometry optimization of ^{3}**3** in CAS(10,10)/6-31G(d), and as Table 15 shows, the further extension of the active space beyond CAS(6,6)/6-31G(d) had little impact on the geometry. We can conjecture that the correlation correction by MP2 on CAS(10,10) would not produce a structure significantly different from that we have seen for MP2 corrections on CAS(6,6).

B3LYP, RMP2/ROMP2, and all CASSCF calculations agree that the triplet is the ground state. The estimates of the singlet−triplet gap are consistent, 13−16 kcal/mol regardless of method. CAS confirms that the lowest excited state at the optimized triplet geometry is the closed shell singlet, placing it 16 kcal/mol above the triplet. This species cannot be considered a diradical.

Our post-Hartree−Fock modeling produces structures that disagree with the DFT structures of Kawano's methylene ^{3}**3** in ways already illustrated for the parent and bis(2,6-dimethylphenyl)methylenes. No post-Hartree−Fock modeling suggests so serious a quinoid deformation of the phenyl ring as does DFT, and no such method produces so nearly linear a central angle and so short a central bond length. B3LYP and CAS+MP2, which include both nondynamical and dynamical corrections, produce the shortest bond distance estimates—both shorter than the X-ray study suggests. There are other serious disagreements among experimental, DFT, and our post-Hartree−Fock representations of the phenyl rings. Reliable estimation of the bond lengths in the phenyl ring is impeded by difficulty of analysis of X-ray data for the disordered crystals. Any attempt to match the X-ray data beginning with our computed structures would be of great interest.

Conclusions

Minimally correlated ROHF and CAS(2,2) methods and similar calculations in extended active spaces predict structures of bis(2,6-disubstituted phenyl)methylene triplets in serious disagreement with DFT models. For the parent (unsubstituted) system post-Hartree−Fock results agree generally with DFT values of central bond length and angle, but the severe quinoid distortion of the phenyl rings and the very broad central angles produced by DFT modeling of the bis(2,6-disubstitutedphenyl) species are not found in these alternative schemes. The molecular structure for bis(2,4,6-trichlorophenyl)methylene obtained by X-ray analysis agrees more closely with the CAS or ROHF + MP2 modeling than with DFT modeling, but significant discrepancies persist. It may be worthwhile to reexamine the X-ray data in light of the structures computed here.

Acknowledgment. The PQS system was generously made available to C.T. by W. Dean Harman. NSF grant CHE-9807375 to W.D.H. made possible the purchase of this system. Thanks to the Chemistry Department at the University of Virginia, which provided equipment and travel support to C.T. The continuing encouragement and assistance of the Body Foundation is acknowledged with gratitude. I am grateful for encouragement by H. Tomioka of the Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan, and for communication of unpublished information by M. Kawano, Department of Applied Chemistry, University of Tokyo, Graduate School of Engineering, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

Supporting Information Available: Tables and graphs of the energies of bisarylmethylene structures included in the post-Hartree−Fock grids. This material is available free of charge via the Internet at http://pubs.acs.org.

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