

Phenylene Coupling of Methylene Sites. The Spin States of Bis(X–methylene)-*p*-phenylenes and Bis(chloromethylene)-*m*-phenylene

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Abstract: We judge the energetic sequence of spin states in substituted methylenes by *ab initio* multiconfigurational computations and, where feasible, density functional modeling techniques. The best of these calculations reproduce well-established singlet–triplet gaps in X–C–Y species, in which X can be phenyl and Y can be H, methyl, or chloro. Similar computations on *p*-phenylene-coupled Y–methylenes and meta-coupled Y–methylenes support the suggestion by Zuev and Sheridan that bis(chloromethylene)-*p*-phenylene has a singlet diradical ground state. However, despite the density functional computations' support for those authors' suggestion that bis(chloromethylene)-*m*-phenylene has a singlet ground state, we find that our best MCSCF calculations place the quintet ground state suggested by the simplest theory almost equal in energy to that singlet.

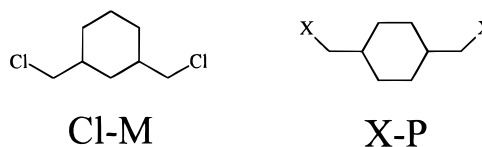
Introduction

The design of organic systems with high-spin ground states is an essential step in the production of organic materials with desirable magnetic properties.¹ High-spin ground states are found in systems which satisfy well-established criteria. These systems contain orbitals which are (nearly) degenerate, only partially occupied in (at least some) low-lying states, orthogonal perhaps by symmetry, and “coextensive”, so that each orbital has large amplitude on common atoms, and exchange integrals are substantial.²

Local methylene, nitrene, or other radicals with local spins can be assembled into large molecules with high resultant spin, if a reliable “ferromagnetic coupler” linking local spin sites can be incorporated. One of the most robust rules of thumb in design of high-spin molecules is that *m*-phenylene coupling tends to favor high-spin states (this is called ferromagnetic coupling) while *p*-phenylene coupling tends to favor low-spin states (called antiferromagnetic coupling).³ The first known organic spin quintet was formed by *m*-phenylene coupling of two methylenes.⁴ Later work showed that bisnitrene-*m*-phenylene systems also display a quintet ground state.⁵ More recent studies have focused on the relatively stable systems incorporating *m*-phenylene-coupled RNO fragment radicals.⁶ The limits of this guideline have been tested both experimentally⁷ and theoretically.⁸ It would appear that unless substituents severely

disrupt the π -interaction between local spins and the phenyl coupler,⁹ the rules apply regardless of the nature of substituents and survive the introduction of heteroatoms at the spin sites¹⁰ and even some charged units within the phenylene coupler.^{8,11} This stability seems remarkable in view of the fact that substituents alter the energetic order of spin states in simple (one-center) methylenes.

There is some suggestion that bis(chloromethylene)-*m*-phenylene has a singlet ground state¹² in contradiction to expectation, while the spin state of bis(chloromethylene)-*p*-phenylene is said to be “an open question.”¹³ In this work we characterize the spin states of bis(X-substituted methylene)-*p*-phenylene (X–P), and bis(chloromethylene)-*m*-phenylene (Cl–M) by *ab initio* computation.



Effects of Substitution on Spin State Preference in X,Y–Methylenes

In order to establish the trustworthiness of our computational methods, we describe a series of one-center carbenes. It is well known that high-level calculations are required for accurate evaluation of singlet–triplet gaps in single-center X–C–Y carbenes, though careful scaling of simple calculations can give useful estimates.¹⁴ Density functional methods seem remarkably effective,¹⁵ even in the difficult case of phenylcarbene,¹⁶ partly because they incorporate some recognition of correlation effects and partly because they display only minimal spin contamination

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Table 1. Singlet–Triplet Gaps^a and Relative Energetics^b of X–C–Y Methylenes

Singlet–Triplet Gaps						
species	gap			comparison	ref	
	C	L	B			
Cl–C–Cl	18.8	20	21	20.5	18	
H–C–Ph	–4.5	–7.5	–5.6	–4.3	15	
Cl–C–Ph	+4.5	+5.6	+7.3	singlet behavior	19	
Relative Energetics						
substituents	basis	model		gap		
Cl, Cl	3-21G*	R(O)HF		–8		
	3-21G*	CASSCF(2,2)		<1		
	3-21G*	CASSCF(2,6)		8		
	6-31G*	R(O)HF		–4		
	6-31G*	CASSCF(2,2)		9		
	6-31G*	CASSCF(2,6)		19		
	6-31G*	LSDA		20		
	6-31G*	BLYP		21		
	Orthogonal Phenyl					
Cl, Ph	3-21G*	R(O)HF		–19		
	3-21G*	CASSCF(2,2)		–10		
	6-31G*	R(O)HF		–15		
	6-31G*	CASSCF(2,2)		–2		
	6-31G*	CASSCF(6,6)		–3		
	6-31G*	LSDA		2		
H, Ph	6-31G*	BLYP		3		
	3-21G*	R(O)HF		–31		
	3-21G*	CASSCF(2,2)		–22		
	3-21G*	CASSCF(6,6)		–23		
	6-31G*	R(O)HF		–26		
	6-31G*	CASSCF(2,2)		–17		
Cl, Ph	6-31G*	CASSCF(6,6)		–16		
	6-31G*	LSDA		–14		
	6-31G*	BLYP		–14		
	Coplanar Phenyl					
	Cl, Ph	3-21G*	R(O)HF		–11	
		3-21G*	CASSCF(2,2)		–3	
6-31G*		R(O)HF		–6		
6-31G*		CASSCF(2,2)		+4		
6-31G*		CASSCF(6,6)		+4		
6-31G*		6-31LSDA		+6		
H, Ph	6-31G*	BLYP		+7		
	3-21G*	R(O)HF		–22		
	3-21G*	CASSCF(2,2)		–14		
	3-21G*	CASSCF(6,6)		–12		
	6-31G*	R(O)HF		–17		
	6-31G*	CASSCF(2,2)		–6		
6-31G*	CASSCF(6,6)		–5			
6-31G*	LSDA		–8			
6-31G*	BLYP		–6			

^a Values in kcal/mol. Basis: 6-31G*; methods C = CAS(6,6) except CAS(10,6) for Cl–C–Cl, L = LSDA, B = BLYP; positive sign places the singlet as the ground state. ^b Gap in kcal/mol; gap < 0 indicates ground triplet.

in their representation of high-spin states. UHF methods often suffer major contamination, reflected by the overestimate of the expectation value of the S^2 operator. This does have structural as well as energetic consequences.

We used the Gaussian suite of programs for all calculations.¹⁷ The results collected in Table 1 illustrate the generalizations that calculations (a) in small basis sets and (b) neglecting

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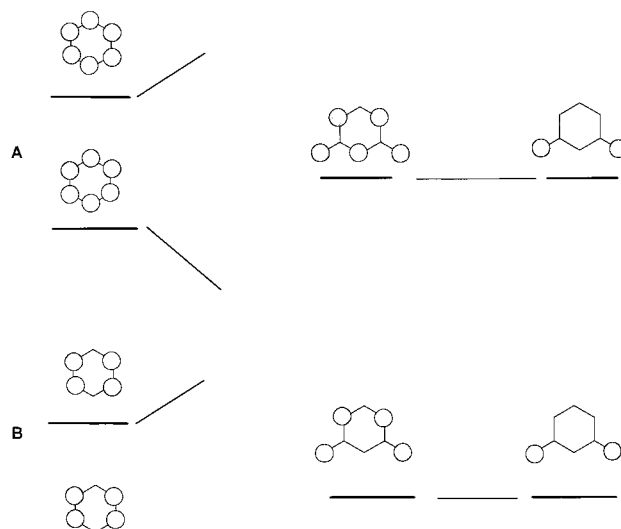


Figure 1. *m*-Phenylene coupling of π substituent sites leaves partly occupied π MOs degenerate. (A) Orbitals symmetric with respect to the plane exchanging the substituents. The nonbonding combination of π sites at methylene carbons remains nonbonding upon *m*-phenylene coupling. (B) Orbitals antisymmetric with respect to the plane exchanging the substituents. The nonbonding combination of π sites at methylene carbons remains nonbonding upon *m*-phenylene coupling.

configuration mixing exaggerate the stability of the triplet relative to the singlet state. The difficulties arise from the distinct configurations σ^2 (singlet) versus $\sigma\pi$ (triplet) which serve as a starting point, and the need to include substantial weights of the π^2 configuration in the singlet. Density functional theory does well in these systems where configuration mixing is not extensive, though it may be energetically significant. Our best calculations use the 6-31G* basis and multiconfigurational complete active space (CAS) methods defining as the CAS in the first case the methylene carbon's σ and π orbitals. This is described as CAS(2,2) in the table. The integers refer to the number of electrons correlated and the number of orbitals in the CAS, respectively. A more extensive space for phenyl- and phenylchlorocarbene includes the HOMO and LUMO near-degenerate pairs of orbitals on the phenyl fragment and the four π electrons in the HOMO orbitals. This is described as (6,6) in the table. In the case of dichlorocarbene, the CAS includes the four π and pseudo- π lone pair orbitals. The calculation correlates ten electrons (four lone pairs and the two electrons on the carbon) and is described as CAS(10,6) in the table. These and density functional calculations both in the local density approximation (LSDA) and with a gradient correction (BLYP) produce for phenylchlorocarbene a singlet–triplet gap of –7 to –12 mhartrees or –4 to –8 kcal/mol. The best reported computational result is –4.3 kcal/mol.¹⁸ (The negative sign means that the triplet is the ground state.) We have not discovered a high-level calculation of the singlet–triplet gap for (chlorophenyl)carbene, but its experimental behavior shows it to have a singlet ground state.¹⁹ Our best estimate of the gap is +7 to +11 mhartrees, or +4 to +7 kcal/mol, consistent with experimental behavior.

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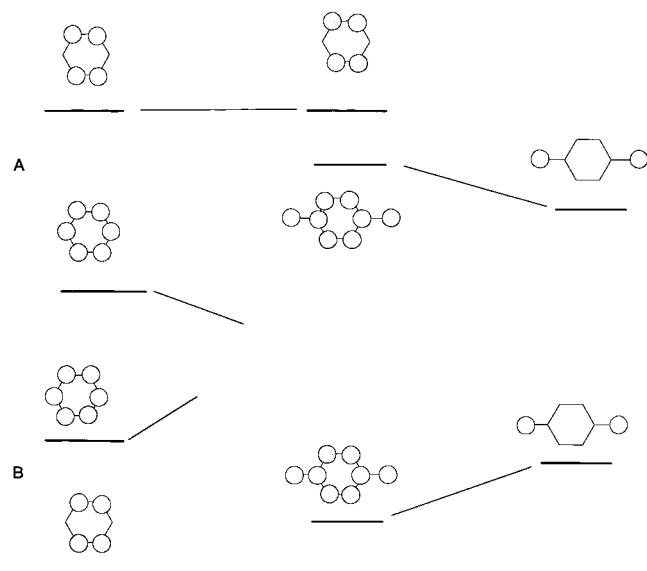


Figure 2. *p*-Phenylene coupling of π substituent sites splits partly occupied π MOs. (A) orbitals antisymmetric with respect to the plane exchanging the substituents. The nonbonding combination of π sites at methylene carbons is destabilized upon *p*-phenylene coupling. (B) Orbitals symmetric with respect to the plane exchanging the substituents. The nonbonding combination of π sites at methylene carbons is stabilized upon *p*-phenylene coupling.

Note that the phenyl- and (chlorophenyl)carbenes prefer an arrangement in which all atoms are coplanar, as opposed to an orthogonal arrangement in which the Cl–C–C plane bisects the phenyl plane. This stabilization can be attributed to enhanced conjugation in the all-planar species. The effect is captured even by methods which do not give a convincing estimate of the singlet–triplet gap. It is interesting to note that this preference is reversed in phenylnitrenium,¹⁶ which assumes an orthogonal geometry according to calculations of similar quality.

Coupling of Local Spins through the Benzene π System

Figure 1 shows that, according to the simplest perturbation analysis, the π and π^* molecular orbitals of benzene are approximately unshifted by admixture of orbitals at the meta sites. The persistence of near-degeneracy of the local partly occupied orbitals, and the admixture of the benzene orbitals which make the resultant MOs coextensive, together favor a high-spin state; e.g., xylylene has a triplet ground state.²⁰ In contrast (Figure 2), in *p*-phenylene coupling both the a_2 and the b_1 combination are altered in energy by interaction with the phenyl fragment MOs. In the perturbative view, the a_2 combination is elevated in energy by interaction with the like-symmetry π phenyl orbital while the b_1 combination is lowered in energy by interaction with the like-symmetry π^* phenyl level. This favors double occupancy of the stabilized level and a low-spin ground state.

Even the simplest theory of phenylene-coupled methylenes leads us to consider the assignment of four electrons to four MOs composed of methylene p and hybrid AOs, σ_{\pm} and π_{\pm} . Methylene (or nitrene) systems have weakly binding “lone pair” σ as well as π levels so that the local spin state at a methylene can be either a singlet or a triplet. The *m*-phenylene coupling aligns the local $S = 1$ angular momenta, producing a spin

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Chart 1

Orbital Modeling: Effects of Substituents and Bending

Coupling type	Metaphenylene	Paraphenylene
Effect on local methylene levels a_1, b_2, b_1, a_2	a_2 and b_1 pi degeneracy maintained	a_2 and b_1 pi degeneracy broken (b_1 stabilized, a_2 destabilized)
Effect of Substituents R on pi levels	Both a_2 and b_1 destabilized	Both a_2 and b_1 destabilized
Effect of Substituents R on pseudo-pi (sigma) levels	Both a_1 and b_2 destabilized	Both a_1 and b_2 destabilized
Effect of CCR Bending	Both a_1 and b_2 stabilized	Both a_1 and b_2 stabilized

Choices of Spin Multiplicity

Configuration	State	Remark
<i>Singlet</i>		
$a_1^2 b_2^2$	1A_1	Sigma levels stabilized by bending
para $a_1^2 b_1^2$ and $b_2^2 b_1^2$	1A_1	Sigma level stabilized by bending, stabilization from b_1 level; possible multiconfigurational quality to 1A_1
<i>Triplet/open</i>		
Predict 110 degree Ph - C - R angle.		
$a_1 b_2 b_1$	3A_2	Some stabilization of b_1 level (para)
$a_1 b_2^2 b_1$	3B_1	Some stabilization of b_1 level (para)
$b_1^2 a_2 a_1$	3A_2	Stabilization from b_1 level, canceled in part by a_2 (para)
$b_1^2 a_1 b_2$	3B_2	Substantial stabilization from b_1 level (para)
<i>Quintet</i>		
Predict intermediate Ph - C - R angle		
$a_1 b_2 b_1 a_2$	5A_1	No net orbital stabilization; exchange-stabilized
Predict 130 degree Ph - C - R angle.		

Table 2. Relative Energetics (kcal/mol) of Bis(X–methylene)-*p*-phenylenes

Bis(chloromethylene)- <i>p</i> -phenylene: 631G*				
method	5A_1	1A_1 multiconfig	3B_2 $b_1^2 a_1 b_2$	1A_1 $a_1^2 b_2^2$
R[O]HF	0	NonRep	+2.5	+18
CAS[4,4]	0	-11.3	-8.2	-5.0
CAS[8,8]	0	-27	-25	not available
DFT Results				
LSDA	0	NonRep	-29	-10
BLYP	0	NonRep	-26	-10
Bis(methylmethylene)- <i>p</i> -phenylene: 631G*				
method	5A_1	1A_1 $b_1^2(a_1^2 + b_2^2)$	3B_2 $b_1^2 a_1 b_2$	1A_1 $a_1^2 b_2^2$
R[O]HF	0	NonRep	<1	+31
CAS[4,4]	0	-12	-10	+15
DFT				
LSDA	0	NonRep	-29 ^a	+12
BLYP	0	NonRep	-18 ^a	+7
Bis(methylene)- <i>p</i> -phenylene: 631G* ^b				
method	5A_1	1A_1 $b_1^2(a_1^2 + b_2^2)$	3B_2 $b_1^2 a_1 b_2$	1A_1 $a_1^2 b_2^2$
R[O]HF	-306.245 766	NonRep	+1	+38
CAS[4,4]	-306.245 766	-20	-10	+14
DFT				
LSDA	-306.372 601	NonRep	-26	+12
BLYP	-308.054 515	NonRep	-30	+14

^a 3A_2 $b_1 b_2$ (high-lying in ROHF) lies at -8 kcal/mol according to LSDA or -5 kcal/mol according to BLYP. ^b Energy relative to 5A_1 reported in kcal/mol (nearest integer value).

quintet. The σ levels retain a high degree of localization, so they are not themselves coextensive. However, the phenyl coupling of the π component of the local spin forces the result.

Other degrees of freedom may influence the preferred spin state. Local methylene σ orbital energies will be elevated by their interaction with lone pairs on substituent R. This has little differential effect. However, the bending of the Ph–C–Cl angle makes an impact on the local σ hybrid. As this angle becomes smaller, the admixture of carbon s AOs stabilized those levels. This tends to favor low-multiplicity states with high occupancy of the stabilized levels. This is significant in both the *p*- and *m*-phenylene-coupled chloromethylenes.

These considerations are summarized in Chart 1. In short, orbital energies and multiconfigurational character and preferred

Table 3. Energetics (kcal/mol) of Bis(chloromethylene)-*m*-phenylenes (631-G*)^a

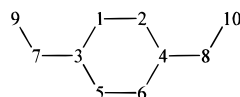
method	⁵ A ₁ b ₁ a ₁ b ₂ a ₂	¹ A ₁ multiconfig	³ B ₁ a ₂ b ₂ a ₁ ²	³ A ₂ a ₂ a ₁ b ₂ ²	¹ A ₁ a ₁ b ₂ ²
R[O]HF	0	NonRep	+83	+88	+15
CAS[4,4]	0	+1	+1	+10	-7
CAS[8,8]	0	+6	+14	+28	+1
LSDA	0	NonRep	-1	+8	-7
BLYP	0	NonRep	<1	+9	-9

^a Quintet energy taken as reference: energy for other states reported in kcal/mol relative to this value.

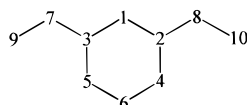
spin state all interact to tell a complex story of a balance struck among initial σ - π splitting, strength of *p*-phenylene coupling, substituent interactions with both σ and π , and extent of Ph-C-R bending. We would expect that chloro substitution *taken alone* would always favor a singlet state with small Ph-C-R angles, but the strong π coupling cannot be overlooked, as quantitative results will show.

In contrast, the persistent effective degeneracy of the π levels in bismethylene-*m*-phenylene drives the system to maximum multiplicity. The elevation of locally- σ methylene levels by interaction with chlorine's lone pairs (and opening of the Ph-C-Cl angle) allows them to approach degeneracy with the π levels as well, so that the main determinant of the favored state is the extent of exchange, in analogy to Hund's rules for atoms. This is maximal in the quintet, but according to simple theory substantially reduced in the singlet-coupled arrangement of four electrons in the same four molecular orbitals.

All of these qualitative notions need to be tested by quantitative calculations.

Table 4. Optimized CAS(8,8) Geometries for Dichloro Species^aA. Numbering Scheme for Bis(chloromethylene)-*p*-phenylenes

state	A = 1-2	B = 2-3	C = 3-5	D = 5-6	E = 3-7	F = 7-9
quintet	1.4036	1.3930	1.4140	1.3620	1.4517	1.6963
triplet	1.3518	1.4632	1.4697	1.3271	1.3466	1.6983
singlet	1.3549	1.4578	1.4659	1.3288	1.3532	1.6990
state	$\alpha = 2-1-3$	$\beta = 1-3-5$	$\gamma = 3-5-6$	$\delta = 5-3-7$	$\epsilon = 1-3-7$	$\phi = 3-7-9$
quintet	120.34	118.84	120.82	118.20	122.96	128.73
triplet	121.24	117.10	121.65	119.33	123.54	132.31
singlet	121.20	117.20	121.60	119.27	123.53	131.91

B. Numbering Scheme for Bis(chloromethylene)-*m*-phenylenes in Geometry I

state	A = 1-3	B = 3-5	C = 5-6	D = 3-7	E = 7-9	
quintet	1.3800	1.4168	1.4082	1.4202	1.6976	
triplet	1.3822	1.4070	1.4024	1.4522	1.7143	
singlet (open)	1.3821	1.4029	1.4013	1.4501	1.6965	
singlet (σ^4)	1.3948	1.4064	1.3908	1.4686	1.7407	
state	$\alpha = 2-1-3$	$\beta = 1-3-5$	$\gamma = 3-5-6$	$\delta = 5-3-7$	$\epsilon = 1-3-7$	$\phi = 3-7-9$
quintet	121.52	120.04	118.86	120.69	118.50	129.65
triplet	120.99	120.25	118.69	121.12	116.01	120.24
singlet (open)	121.30	119.85	119.23	120.55	118.20	128.80
singlet (σ^4)	121.93	118.48	120.42	128.34	113.18	112.79

^a Bond lengths in angstroms and bond angles in degrees.

Computational Methods for Phenylenes

For quantitatively reliable results in these systems a multi-configurational SCF treatment is required in principle, in which the active space is composed of σ and π local orbitals at the spin sites a₁ and b₂, and b₁ and a₂, respectively in *C*_{2v}-adapted form. Reported results were obtained in the 6-31G* basis set, a well-tested compromise between bulk and reliability. The complete active space was taken to be the four orbitals on the methylene sites in initial calculations, labeled CAS(4,4). The two highest occupied and two lowest unoccupied π MOs of the phenyl fragment were included as well in CAS(8,8) calculations.²¹

The stabilization by *p*-phenylene coupling of the b₁ π combination is decisive. The triplet and singlet in which the b₁ level is doubly occupied are the lowest energy structures: the two-configuration (a₁² + b₂²)b₁² singlet represents the ground state. The energy differences are remarkably indifferent to substitution (Table 2), with one exception. In every case the triplet, well represented by a₁¹b₂¹b₁², lies only 4.2–4.9 mhartrees (2.5–3.0 kcal/mol) above the favored singlet, while the quintet lies 17.9–20.4 mhartrees (10–12 kcal/mol) above that singlet. Remarkably, the high-spin state is more stable than the a₁²b₂² or σ^4 single-determinantal state for the chloro-substituted species; that σ^4 state is far less stable than other states for the methyl-substituted and unsubstituted species. Chloro substitution does not alter the conclusion that *p*-phenylene favors singlet spin coupling, but in view of the CASSCF estimate that a triplet lies only 4.2–4.9 mhartrees (2.5–3.0 kcal/mol) above the favored singlet state, one should not rule out the possibility that the triplet may be a participant in the chemistry of these species.

The results support the conjecture by Zuev and Sheridan that the system is well described as a σ,σ diradical.¹²

Preliminary calculations for unsubstituted and methyl-substituted analogs (Table 2) suggest that the singlet open shell state is only slightly more stable than the triplet. These systems may as well have considerable diradical character.

Zuev and Sheridan¹³ have also investigated the bis(chloromethylene)-*m*-phenylene, and suspect a singlet ground state, suggested by the IR spectrum showing strong absorptions near 1600 and 1150 cm^{-1} which is analogous with isophthaloyl chloride (apart from carbonyl bands). This argument is strengthened by the parallel analogy between the IR spectra of phenylchlorocarbene and benzoyl chloride. The UV spectrum of the bismethylene resembles the spectrum of phenylchlorocarbenes, and reactivity patterns are characteristic of singlet species.

The implication that the bis(chloromethylene)-*m*-phenylene has a singlet ground state is contrary to the simplest theories of spin coupling, and thus of considerable interest. Zuev and Sheridan¹³ report calculations in RHF constraint for this system, and find similarity between the observed and CI (single excitations) computed optical spectrum.

Aside on DFT

Density functional theory gives a coherent representation of the relative energy of spin states in one-center methylenes as we have seen, so we explored its representation of these two-center species. In Gaussian's treatment of DFT the charge density is represented as a sum of squares of Kohn-Sham orbitals of an idealized independent-electron system.²² As might be expected from this method's representation of the wave function, its treatment of strongly multiconfigurational systems is problematic. The multiconfigurational states are not representable in Gaussian-94's DFT package; one must choose one or another configuration as a starting point, and none by itself is even qualitatively correct. For this reason DFT's efforts to estimate the energy of multiconfigurational systems are omitted from the tables. For those species which are dominated by one determinant, we find reasonable results. The $a_1b_2b_1^2$ *p*-phenylene triplet B_2 is recognized in DFT as lower in energy than the essentially single-determinant A_1 quintet or the σ^4 singlet. The quintet is placed higher in energy than the σ^4 singlet only for the chloro-substituted system.

(21) Minato, M.; Lahti, P. M. (*J. Am. Chem. Soc.* **1997**, *119*, 2187) allude to calculations by A. S. Ichimura, as yet unpublished, on bisnitrene-*m*-phenylene. CAS(8,8) calculations in 6-31G* correctly predict the preference of this system for the 1A_g state over the $^3B_{1u}$ state, ca. 900 small cal/mol.

(22) Yang, W.; Parr, R. G. *Density Functional Theory*; Oxford University Press: New York, 1989.

The description of the *m*-phenylene states by density functional theory should be reliable insofar as states are representable primarily by a single configuration. This is the case for the σ^4 singlet favored by Zuev and Sheridan¹³ as well as the quintet predicted by simple theory. Density functional theory calculations place the quintet well above the σ^4 singlet, by 7 kcal/mol (LSDA) and 9 kcal/mol (BLYP).

CAS Calculations

Our CASSCF(8,8) computations on bis(chloromethylene)-*m*-phenylene (Table 3) show that two singlet states are of significance.

First, we find a low-lying singlet with a Ph-C-Cl angle near 130°, with five configurations figuring prominently in the wave function: The open shell A_1 singlet $a_2^2b_1^2(a_1\alpha b_2\alpha b_1\beta a_2\beta)$ has a coefficient of 0.43 in the ground state wave function, which also incorporates a set of four equally weighted (coefficient 0.40) closed shell configurations combined as $a_2^2b_1^2[a_1^2a_2^2 - b_2^2a_2^2 - a_1^2b_1^2 + b_2^2b_1^2]$.

The lowest singlet state, by 5 kcal/mol, has small Ph-C-Cl angles (ca. 113°) and is predominantly the closed shell $\sigma^4 a_1^2b_2^2$ structure. This is again the state favored by Zuev and Sheridan.¹³ The qualitative expectations listed in Chart 1—that is, that the greater the open shell character the greater the Ph-C-X bond angle—are roughly consistent with the detailed geometry from our best CAS(8,8) calculations for the bis(chloromethylene) species (Table 4).

We have found that the quintet of bis(chloromethylene)-*m*-phenylene, after correlation correction comparable to that for the singlets described above, is almost identical in energy with the closed shell singlet σ^4 favored by Zuev and Sheridan.¹³ CAS-(8,8) calculations place the quintet 400 small cal/mol below that singlet.

Conclusions

Our calculations provide a prediction that the robust *m*-phenylene spin-aligning coupling is sufficient to overpower the tendency of chloro-substituted methylenes to favor low-spin states, so that bis(chloromethylene)-*m*-phenylene has a low-lying quintet state. Similarly, bis(chloromethylene)-*p*-phenylene has a ground singlet state. In the latter species, a triplet state may be accessible, since the ground state is essentially a σ,σ diradical.

Supporting Information Available: Energetics and structures of all species mentioned in this paper (19 pages). See any current masthead page for ordering and Internet access instructions.

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