p-Phenylbisphosphinidene and Its Carbene and Nitrene Analogues: An ab Initio Study

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Density functional and complete active space (CAS) SCF and CASPT2 calculations have been performed to investigate structural and electronic features of *p*-phenylbisphosphinidene and the analogous *p*-phenylbisnitrene, *p*-phenylbismethylene, *p*-phenylbis(fluoromethylene), and *p*-phenylbis(chloromethylene) molecules. Similar to the other species investigated, with the exception of *p*-phenylbis(fluoromethylene), *p*-phenylbisphosphinidene exhibits an open-shell singlet diradical ground state with a quinone-like structure. The singlet−triplet energy gap, computed with CASPT2 on CASSCF(10,10)/6-31+G* optimized structures, amounts to 1.78 kcal/mol. At the DFT (B3LYP/6-31+G*) level a value of 5.14 kcal/mol is obtained. Due to the highly multiconfigurational character of the *p*-phenylbisphosphinidene singlet and triplet wave functions, the DFT treatment becomes less accurate. Going to *p*-phenylbisnitrene, *p*-phenylbis(chloromethylene), *p*-phenylbis(fluoromethylene), and *p*-phenylbismethylene energies are better described by DFT calculations as the triplet wave functions have only one and the singlet wave functions exactly two leading configurations. The calculated singlet−triplet energy gaps are found to lie in a range of 1.3−2.2 kcal/mol at both DFT and CASPT2 levels of theory. *p*-Phenylbis(fluoromethylene) is a special case in the series as it has a closed-shell singlet ground state. The multiconfigurational treatment shows, however, that the singlet diradical state is very close in energy to the closed-shell singlet, even though the stability of the diradical is somewhat overemphasized by this method. The relative energies and the respective IR spectra are also discussed.

1. Introduction

Biradicals and biradical-like structures are important intermediates in a variety of photochemical and thermal processes of organic species. Especially, molecules with two or more radical centers coupled to each other via a phenyl ring as linking unit have been very actively investigated by means of both experimental and theoretical methods. The reason for such a vivid interest is on one hand the search for organic magnetic materials and on the other hand the wish to gain fundamental insights into electron spin interactions.[1−3] Using qualitative arguments it can be shown that if two biradical centers such as two carbene or carbene-like units are meta positioned on the phenyl ring, the highest spin state is expected to result, namely a quintet. Molecules such as *m*-phenylbismethylene[4] or *m*-phenylbisnitrene[4] are thus regarded as promising building blocks for organic magnets.

In contrast para-phenyl substituted systems, in which conjugation via the ring π-system is possible, were rather neglected as they have stable low-spin ground states. In the last years, however, some para coupled phenylenebiscarbene systems, i.e., *p*-phenylbis(chloromethylene)[5,6] ($C_6H_4(CCl)_2$) and *p*-phenylbis-(fluoromethylene)[7] ($C_6H_4(CF)_2$), have been explored both experimentally and theoretically and very recently the successful synthesis and spectroscopic description of *p*-phenylbismethylene[8,9] ($C_6H_4(CH)_2$) and *p*-phenylbisnitrene[10] ($C_6H_4N_2$) has been reported. The characterization of these very reactive molecules is not straightforward and is usually based on a combination of low-temperature spectroscopic measurements (IR and UV−vis) and reactivity patterns, which are not in all cases consistent and/ or conclusive. Due to the existence of a singlet ground state,

ESR spectroscopy cannot be applied unless low lying triplet states are thermally accessible. In this respect, ab initio calculations have successfully been applied[6−13] to help in establishing and characterizing the ground electronic state, to aid the interpretation of spectra, and to predict the energy gaps between the ground and excited states.

Until now the above-mentioned compounds, with the exception of *p*-phenylbis(fluoromethylene), have been found to have an open-shell singlet diradical ground state with a quinone-like structure. The presence of a double bond between the ring carbon and the exocyclic carbene or nitrene ligand usually induces characteristic bands in the IR spectra. In the case of the fluoromethylene analogue the reactivity pattern points to a singlet closed-shell state. The recorded vibrational spectrum confirms this but there are nevertheless weak bands present in the range where the resonance of the respective exocyclic double bond is expected. However, these bands were interpreted as possible combination bands of the closed-shell singlet.[7] For *p*-phenylbis(chloromethylene) the experimental results point toward a diradical, but the spin state could not be clearly established.[5] Subsequent CASSCF(8,8) calculations[6] yielded a singlet diradical ground state lying 2 kcal/mol below the corresponding triplet state. The very recently synthesized *p*-phenylbisnitrene[10] has been very carefully studied both by experiment and by DFT and CASPT2 calculations and was also found to have a singlet diradical ground state. The calculations place the triplet state 1.9 kcal/mol above the open-shell singlet while the measured energy splitting varies between 0.58 and 0.82 kcal/mol depending on the solvent employed.

In contrast to its singly substituted analogue, *p*-phenylbis-phosphinidene ($C_6H_4P_2$), the heavier congener of *p*-phenylbis-nitrene, has so far neither been experimentally nor theoretically investigated. Ab initio studies of phenylphosphinidene[14,15] found

p-Phenylbisphosphinidene and Some of Its Analogues

*J. Phys. Chem. A, Vol. 104, No. 17, 2000* **4023**

a triplet ground state with a ca. 22 kcal/mol higher lying closed-shell singlet state and an open-shell singlet state nearby. The P−C bond length of the ground state of Ph−P is, with 1.824 Å, in the range of a typical single bond. The benzene ring is slightly disturbed in this system by a shortening of the central C−C bond and a marginal lengthening of the other C−C distances.[14] In this context, a few questions of interest are the following. What kind of influence can we expect from a second phosphinidene function in para position? Does it have features very similar to the above-mentioned compounds? Will the lower electronegativity of phosphorus (2.19) as compared to nitrogen (3.04) produce any noticeable effects? In an attempt to provide some elements of answers to these questions, high level ab initio computations for this yet uncharacterized species have been carried out with the hope of facilitating future experimental interpretations. Furthermore we will compare them to *p*-phenylbisnitrene, as well as to *p*-phenylbismethylene and two of its halogenated analogues.

2. Computational Details

All structures were optimized at the density functional (DFT) and at the complete active space SCF (CASSCF) level of theory. For the DFT optimizations, the B3LYP functional as implemented in Gaussian98[16] and 6-31+G* basis sets were used. The vibrational frequencies were positive in all cases, and the zero-point energies have also been computed using DFT. Within the framework of unrestricted Hartree−Fock formalism (UHF) to obtain the singlet diradical structures, broken-symmetry calculations were initially performed. According to their resulting $<S^2>$ values of 1.11−1.18, they correspond to an almost equal mixture of both singlet and triplet state. Consequently the respective diradical singlet energies are underestimated (if the singlet lies lower in energy) and a crude estimate of the singlet−triplet energy gap could be obtained by adding about 50% of the original value before the zero-point energy correction. This method is also known as sum method.[17−19] Only *p*-phenylbisphosphinidene exhibits a very high $<S^2>$ value of 1.66 in the broken-symmetry singlet state, and also the triplet state is a difficult case for the UHF-DFT optimization. Hybrid functionals can yield excellent agreement with experiment for the singlet−triplet splittings in spin-coupled transition metal systems.[20,21] However, there exist also indications that in some cases of small to moderate multiconfigurational character pure DFT functionals would lead to an improved description.[22] In the case of *p*-phenylbisphosphinidene the BLYP functional would not only reduce the $<S^2>$ value to 1.27, but also yield a smaller S−T splitting. Nevertheless, a multiconfigurational treatment of these states is crucial for an accurate description of this molecule.

For this purpose, CASSCF optimizations with 6-31+G* basis sets have been considered. The active space consists of 10 electrons in 10 active orbitals, namely, the π orbitals of the ring carbons and the pπ and pσ orbitals of the respective radical centers. Most of the carbene structures were optimized in C_{2h} symmetry. The bisphosphinidene and the bisnitrene structures were treated in D_{2h} symmetry.

For the computation of the energy splittings at the CASSCF-(10,10) and CASPT2 level, the larger atomic natural orbital (ANO-L) basis sets[23,24] have been employed. For phosphorus and chlorine the basis set consists of 5s, 4p, 2d, and 1f functions, for carbon, nitrogen, and fluorine of 4s, 3p, and 1d functions, and of 3s and 1p functions for hydrogen. In the CASPT2 calculations all valence electrons, 1s H, 3s and 3p of P and Cl, and 2s and 2p of C, N, and F were correlated. In some cases a level shift between 0.1 and 0.3 au was necessary to get rid of intruder states.[25] Additionally a g1 corrected zeroth-order
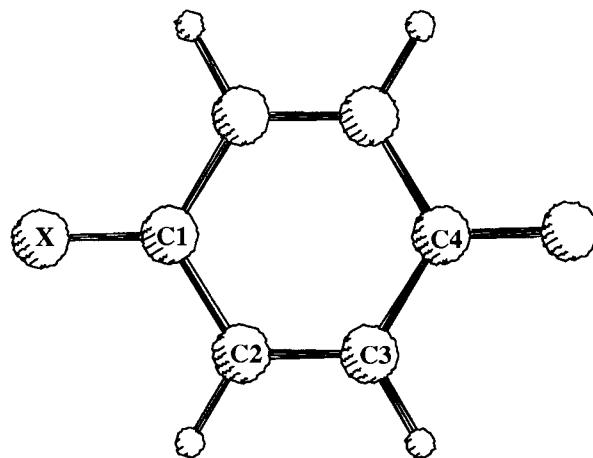
Figure 1. Atom labeling of the X−C$_6$H$_4$−X molecules with X = P, N, CH, CF, CCl.

Hamiltonian[26] was used in the CASSCF/CASPT2 calculations to ensure a balanced treatment of wave functions dominated by closed-shell configurations versus those with open-shell configurations. The zero-point energy corrections are based on DFT (UB3LYP/6-31+G*) computed vibration modes. All CASSCF/CASPT2 calculations were performed with the program MOLCAS-4.1.[27]

The atom numbering of the C$_6$H$_4$X$_2$ (X = P, N, CH, CF, CCl) structures are sketched in Figure 1. The complete active space orbitals are illustrated in Figure 2 for the *p*-phenylbisphosphinidene (or nitrene). For the methylene analogues only the four magnetic orbitals are depicted in Figure 3. The other active space orbitals have the same character as depicted in Figure 2. Orbitals π_1 to π_3 have in all configurations an occupation of about 2 and the occupation of orbitals π_6 to π_8 remains in all cases around 0. The four relevant magnetic orbitals are denoted π_+ ($=\pi_4$), π_- ($=\pi_5$), σ_+ ($=\sigma_1$), and σ_- ($=\sigma_2$). The π_+ orbital is formed by a bonding and the π_- orbital by an antibonding combination of the respective ligand p-orbital with the π system of the benzene ring. Consequently the degeneracy of the two orbitals is lifted in contrast to the σ_+ and the σ_- combinations, which are very close in energy. The five most important possibilities to distribute the 4 electrons of both diradical centers into the four orthogonal orbitals (π_+, π_-, σ_+, σ_-) are termed as follows: the singlet open-shell diradical, the triplet and the quintet state are denoted $^1[\sigma^2\pi^2]$, $^3[\sigma^2\pi^2]$, and $^5[\sigma^2\pi^2]$, respectively. These three states are dominated by the following configurations:

$$^1[\sigma^2\pi^2]...(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_+)^2[c_1(\sigma_+)^2+c_2(\sigma_-)^2]$$

$$^3[\sigma^2\pi^2]...(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_+)^2(\sigma_+)^1(\sigma_-)^1$$

$$^5[\sigma^2\pi^2]...(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_+)^1(\sigma_+)^1(\sigma_-)^1(\pi_-)^1$$

Two additional states, $^1[\sigma^4]$ and $^3[\sigma^3\pi^1]$, have been considered but could only be localized for the carbene compounds. Double occupation of the ligand pσ orbitals (π_+ and π_- are empty) yields the closed-shell singlet state ($^1[\sigma^4]$). The promotion of one electron to one of the π orbitals, usually π_+, results in an unsymmetric triplet ($^3[\sigma^3\pi^1]$) structure. For all the *p*-phenylenebismethylene geometries, a trans arrangement has been considered.

3. Results and Discussion

3.1. Geometries. The discussion of the X−C$_6$H$_4$−X geometries focuses on two main features. (A) What influence has
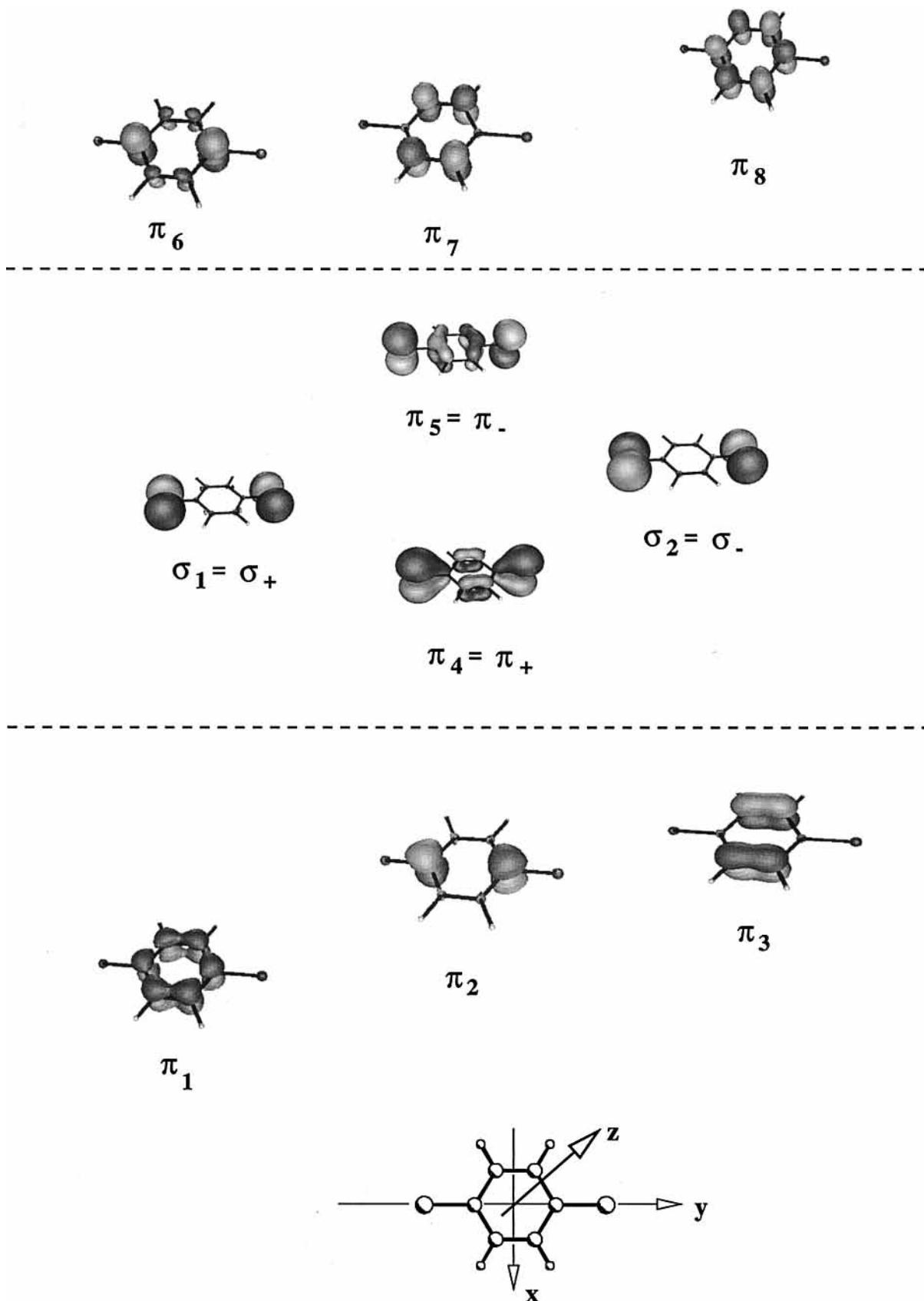
Figure 2. The 10 active space orbitals of the *p*-phenylbisphosphinidene and *p*-phenylbisnitrene species.

the occupation of the respective nonbonding σ orbitals and the π orbitals of the diradical centers? (B) Are the geometry parameters of the aryl ring related to the ligand electronegativity?

In agreement with experiment,[5,8,10] we find that *p*-phenyl-bismethylene, *p*-phenylbis(chloromethylene), and *p*-phenylbis-nitrene form quinone-like structures in the ground state. The X–C1 bond lengths, collected in Table 1, corroborate this

p-Phenylbisphosphinidene and Some of Its Analogues

J. Phys. Chem. A, Vol. 104, No. 17, 2000 **4025**
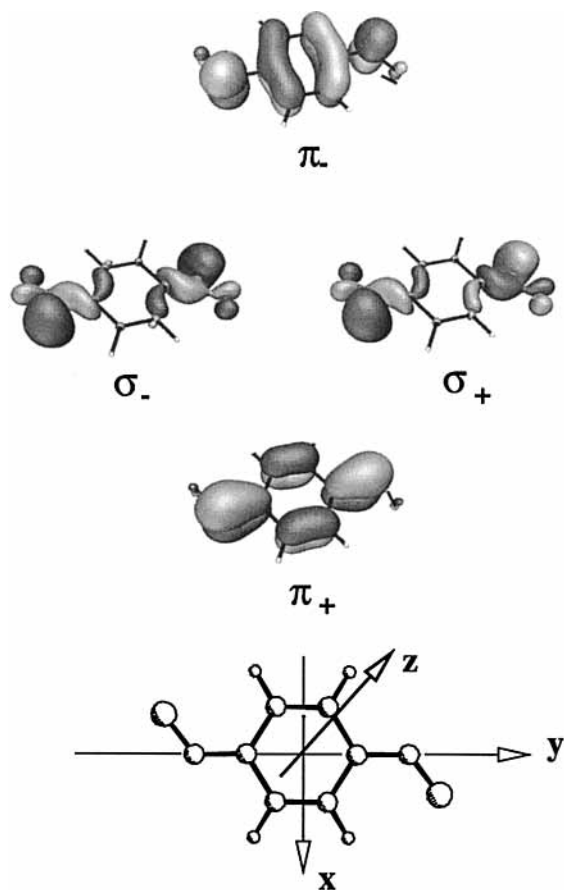
Figure 3. Relevant molecular orbitals of the *p*-phenylbismethylene, *p*-phenylbis(fluoromethylene), and *p*-phenylbis(chloromethylene) molecules.

TABLE 1: Geometry Parameters of the *p*-phenylbisdiradical Structures Having an Open-Shell Singlet State Computed at the DFT UB3LYP/6-31+G* and CASSCF(10,10)/6-31+G* Level of Theory[a]

X	(y−C)	X−C1	C1−C2	C2−C3	C3−C4	(y−C−C1)
UHF-B3LYP(pseudo-wave function for open-shell singlet)						
H		1.087	1.398	1.398	1.398	
P		1.761	1.433	1.376	1.433	
N		1.277	1.475	1.347	1.475	
HC	1.083	1.343	1.462	1.354	1.467	136.6
FC	1.324	1.351	1.456	1.354	1.462	128.0
ClC	1.688	1.352	1.461	1.355	1.458	133.7
CASSCF						
P		1.773	1.430	1.380	1.430	
N		1.282	1.468	1.351	1.468	
HC	1.072	1.354	1.460	1.356	1.462	132.3
FC	1.313	1.354	1.458	1.356	1.456	126.5
ClC	1.648	1.356	1.458	1.357	1.458	135.0

[a] All bond lengths are given in Å, the bond angles in degree. The notation of the atoms is according to Figure 1, with y = H, F, or Cl of the methylene ligand.

qualitative picture. It should be stressed that the UHF-DFT calculations do not properly describe the open-shell singlet state, but rather a mixture of both relevant singlet and triplet states with $\langle S^2 \rangle$ around 1.0 for the UHF wave functions. Strictly speaking, they are not wave functions for diradical states. However, for the sake of comparison, in going from one to the other system, we have recorded the parameters derived from these pseudo-singlet wave functions. It can be expected that the qualitative trend of changes is valid. On the other hand, because in most cases considered here both diradical singlet and triplet states are close in energy, only a few kcal/mol

TABLE 2: Composition of the Singlet $^1[\sigma^2\pi^2]$, Triplet $^3[\sigma^2\pi^2]$, and Quintet Wave Functions of *p*-Phenylbisphosphinidene and *p*-Phenylbisnitrene[a]
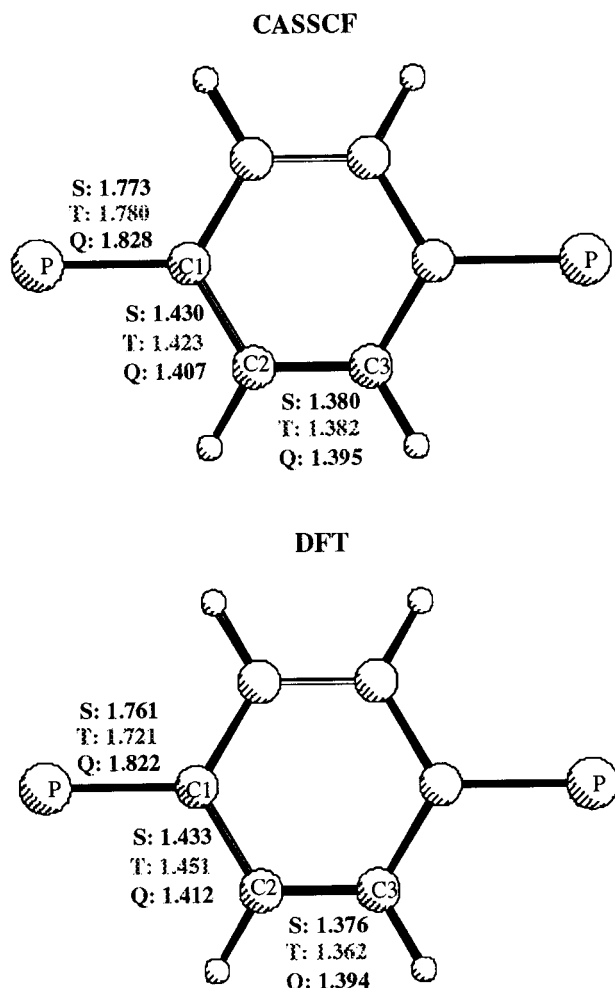
	p-phenylbisnitrene	*p*-phenylbisphosphinidene
$^1[\sigma^2\pi^2]$	40% $\pi_+^2\sigma_+^2$	29% $\pi_+^2\sigma_+^2$
	38% $\pi_+^2\sigma_-^2$	26% $\pi_+^2\sigma_-^2$
		9% $\pi_+^1\sigma_+^1\sigma_-^1\pi_-^1$
		9% $\sigma_+^2\pi_-^2$
		8% $\sigma_-^2\pi_-^2$
$^3[\sigma^2\pi^2]$	79% $\pi_+^2\sigma_+^1\sigma_-^1$	49% $\pi_+^2\sigma_+^1\sigma_-^1$
		15% $\pi_-^2\sigma_+^1\sigma_-^1$
		11% $\pi_+^1\sigma_+^2\pi_-^1$
$^5[\sigma^2\pi^2]$	83% $\pi_+^1\sigma_+^1\sigma_-^1\pi_-^1$	87% $\pi_+^1\sigma_+^1\sigma_-^1\pi_-^1$

[a] Only the four relevant orbitals are listed as the others stay either almost doubly or unoccupied.

separate them, the geometry parameters are equally comparable. Comparison with the corresponding results computed using the proper CASSCF(10,10) wave functions (Table 1) indicates that this is indeed the case. Overall, we would like to warn the reader not to attach too much importance on the absolute values obtained from the pseudo-singlet DFT calculations, but rather on the qualitative trend. The C−C1 bond lengths of the methylenes (1.354−1.356 Å) as well as the N−C1 distance of 1.282 Å in *p*-phenylbisnitrene are in the range of typical double bonds. On the other hand, for *p*-phenylbisphosphinidene the result is ambiguous, as the calculated value of 1.773 Å is somewhere between a typical P−C double bond (1.68 Å) and a P−C single bond as in phenylphosphinidene (1.82 Å). Compared to the phenylphosphinidene counterpart *p*-phenyl-bisphosphinidene also has a more pronounced influence on the benzene ring: a further shortening of the central C−C bond and a simultaneous elongation of the remaining C−C ring distances results in the alternating quinoid-like structure, even if the latter is less pronounced than in the other investigated species. An inspection of the *p*-phenylbisphosphinidene open-shell singlet wave function as obtained by CASSCF(10,10) calculations shows that, next to the two expected configurations, $\pi_+^2\sigma_+^2$ and $\pi_+^2\sigma_-^2$, three configurations stemming from excitations to the π_- orbital (see Table 2) contribute to the wave function. Occupation of the energetically less favorable π_- orbital, as in all $^5[\sigma^2\pi^2]$ quintet states, results in an elongation of the X−C bond.

Although all singlet diradicals exhibit qualitatively the same kind of orbital interactions, the ring bond lengths differ quite strongly from each other and from the undisturbed benzene ring (Table 1). The strongest deviations from unperturbed benzene (C1−C2 +0.077 Å, C2−C3 −0.051 Å) are found in the *p*-phenylbisnitrene molecule, followed by *p*-phenylbismethylene, *p*-phenylbis(chloromethylene), and *p*-phenylbis(fluoromethyl-ene), and finally *p*-phenylbisphosphinidene. The same trend is detected for the amount of electron withdrawal by the respective ligand from the carbon C1 atom. The Mulliken population shows an electron deficiency of 0.31, 0.28, and 0.12 electrons on C1 for *p*-phenylbisnitrene, *p*-phenylbismethylene, and *p*-phenyl-bisphosphinidene, respectively. This ordering relates directly to the Pauling electronegativity of 3.04 for nitrogen, 2.55 for carbon, and 2.19 for phosphorus. The halogenated methylenes are with 0.22 and 0.21 withdrawn electrons in about the same range as methylene.

The $^3[\sigma^2\pi^2]$ state is characterized by the reorientation of one of the electrons in the nonbonding ligand σ orbital. Consequently, we do not expect any major effects on the aryl ring

CASSCF

DFT

Figure 4. Bond lengths of the *p*-phenylbisphosphinidene $^1[\sigma^2\pi^2]$ (S), $^3[\sigma^2\pi^2]$ (T), and $^5[\sigma^2\pi^2]$ (Q) states obtained by CASSCF(10,10)/6-31+G* and DFT UB3LYP/6-31+G* optimizations.

system for this state. Bond lengths alterations of only ±0.01 Å are computed in all cases with the exception of the DFT optimized *p*-phenylbisphosphinidene triplet state. Here, a priori unexpected large deviations (up to 0.06 Å) were obtained between the DFT and CASSCF optimized geometries. Figure 4 depicts the bond lengths of the optimized $^1[\sigma^2\pi^2]$ (S), $^3[\sigma^2\pi^2]$ (T), and $^5[\sigma^2\pi^2]$ (Q) states of the *p*-phenylbisphosphinidene molecule calculated at the DFT and CASSCF level. The multiconfigurational character of the triplet phosphinidene partly explains why UHF-DFT may be less apt in the treatment of its $^1[\sigma^2\pi^2]$ and $^3[\sigma^2\pi^2]$ states, while it works fine for the other analogues. In Table 2 the $^1[\sigma^2\pi^2]$, $^3[\sigma^2\pi^2]$, and $^5[\sigma^2\pi^2]$ wave functions of *p*-phenylbisphosphinidene and *p*-phenylbisnitrene are compared. All configurations with weights higher than 5% are listed. The difference is immediately apparent. The $^3[\sigma^2\pi^2]$ wave function is multiconfigurational only in *p*-phenylbisphosphinidene, where it contains three different configurations with weights of 49%, 15%, and 11%. Obviously the π_- orbital becomes much easier occupied in the phosphinidene compound. This is also confirmed by the orbital energies, as obtained from the CASPT2 calculations on the respective $^1[\sigma^2\pi^2]$ CASSCF optimized structures (Table 3).

For the formation of the quintet state one electron is promoted from π_+ to the π_- orbital, thus weakening the bond between ligand and aryl system and mitigating the disturbance of the aromatic ring. Although the carbon bonds of the ring system are not equidistant as in benzene, the difference between the

TABLE 3: Relative Orbital Energies (eV) of the Four Most Important Orbitals As Obtained by CASSCF and CASPT2 Calculations on the $^1[\sigma^2\pi^2]$ States[a]

ligand	π_+	σ_+	σ_-	π_-
P	0 (1.43)	1.33 (1.04)	1.60 (0.96)	3.42 (0.58)
N	0 (1.80)	4.35 (1.02)	4.57 (0.98)	9.90 (0.21)
HC	0 (1.78)	3.00 (1.03)	3.25 (0.97)	8.71 (0.23)
FC	0 (1.74)	2.81 (1.01)	3.02 (0.98)	7.87 (0.26)
ClC	0 (1.75)	2.33 (1.02)	2.50 (0.98)	8.32 (0.26)

[a] The occupation of the respective orbital is given in parentheses.

C−C distances has decreased to less than 0.01 Å. The length of the exocyclic R−C1 bond approaches the value of a single bond.

Only in the case of the methylene ligands was it possible to optimize the closed-shell singlet, $^1[\sigma^4]$, and the unsymmetric triplet, $^3[\sigma^3\pi^1]$, structures. These states are energetically high lying for *p*-phenylbismethylene and *p*-phenylbis(chloromethylene). However, for *p*-phenylbis(fluoromethylene) the closed-shell structure becomes the ground state. Since in this state none of the ligand π orbitals is occupied, only a single bond between the methylene ligand and the aryl ring is formed. Consequently, the ring system remains almost undisturbed. Due to the fact that the σ orbitals are now doubly occupied, the HC−C1, FC−C1, and ClC−C1 bond angles decrease from around 130° to 110°. The $^3[\sigma^3\pi^1]$ triplet state is an intermediate between the $^3[\sigma^2\pi^2]$ and the $^1[\sigma^4]$ states and, as such, exhibits the structural features of both states. One of the X−C1 (X = CH, CF, CCl) bond angles is around 130° and the other one approximately 110°.

3.2. Energetics. In contrast to the geometric parameters of the different electronic X−C_6H_4−X states the energetic ordering and spacing between the states is quite strongly dependent on the level of theory. In this respect *p*-phenylbisphosphinidene and *p*-phenylbis(fluoromethylene) attract most attention, as their computational treatment becomes problematic either in the course of the DFT or the CASSCF/CASPT2 treatment (see further). In all cases except for *p*-phenylbis(fluoromethylene), both DFT and CASSCF/CASPT2 methods predict two low-lying electronic states, namely the $^1[\sigma^2\pi^2]$ and the $^3[\sigma^2\pi^2]$ state with a very small energy separation. Their relative energy is related to the Heisenberg coupling constant, *J*, via the formula $\Delta E_{T-S} = -2J$, which is taken as a measure for the strength of ferromagnetic or antiferromagnetic interaction. All our investigated X−C_6H_4−X species have a singlet diradical ground state and are thus antiferromagnetic. In case of a small singlet−triplet gap, the corresponding energy separation may be established by thermal excitation to the triplet state and via ESR measurement. For *p*-phenylbis(phenylmethylene)[28,29] these methods were applied to determine a ΔE_{S-T} of 0.58 and 0.85 kcal/mol, respectively. Of all molecules considered in the present study, *p*-phenylbisnitrene is the only one where a singlet−triplet energy separation has been experimentally determined.[30,31] Table 4 and Table 5 show the relative energies obtained at the DFT level (with and without energy correction due to the use of the broken-symmetry pseudo-singlet approach), at the CASSCF(10,10), the CASPT2, and the g1-corrected CASPT2 level, which we consider to be the most accurate. First we will shortly discuss the DFT results and then the results obtained by CASSCF and CASPT2 calculations.

While the measured singlet−triplet splittings of *p*-phenylbisnitrene,[30,31] which are solvent dependent between 0.58 and 0.82 kcal/mol, and also of *p*-phenylbis(phenylmethylene), are well below 1 kcal/mol, the DFT results yield singlet−triplet

p-Phenylbisphosphinidene and Some of Its Analogues

J. Phys. Chem. A, Vol. 104, No. 17, 2000 **4027**

TABLE 4: Relative Energies for *p*-Phenylbismethylene, *p*-Phenylbis(fluoromethylene), and *p*-Phenylbis(chloromethylene) in kcal/mol[a]

molecule	state	UB3LYP	CASSCF	CASPT2	CASPT2+g1
$C_6H_4-(CH)_2$	$^1[\sigma^2\pi^2](^1A_g, C_{2h})$	0	0	0	0
	$^3[\sigma^2\pi^2](^3B_u, C_{2h})$	1.45(2.30)[a]	1.61	2.17	2.00
	$^3[\sigma^3\pi^1](^3A'', C_s)$	19.4 (20.2)[a]	28.3	27.6	27.0
	$^5[\sigma^2\pi^2](^5A_g, C_{2h})$	25.9 (26.7)[a]	27.0	25.6	27.2
	$^1[\sigma^4](^1A_g, C_i)$	30.8 (31.6)[a]			
$C_6H_4-(CCl)_2$	$^1[\sigma^2\pi^2](^1A_g, C_{2h})$	0	0	0	0
	$^3[\sigma^2\pi^2](^3B_u, C_{2h})$	1.58 (2.32)[a]	1.66	2.21	2.19
	$^3[\sigma^3\pi^1](^3A'', C_s)$	7.04 (7.78)[a]	17.4	14.2	14.2
	$^1[\sigma^4](^1A_g, C_i)$	9.29 (10.0)[a]	18.2	20.3	19.6
	$^5[\sigma^2\pi^2](^5A_g, C_{2h})$	23.7 (24.5)[a]	25.6	22.8	22.1
$C_6H_4-(CF)_2$	$^1[\sigma^4](^1A_g, C_{2h})$	0	0	1.74	1.52
	$^3[\sigma^3\pi^1](^3A, C_1)$	6.77	13.3	5.32	7.06
	$^1[\sigma^2\pi^2](^1A_g, C_{2h})$	8.71 (7.89)[a]	0.69	0	0
	$^3[\sigma^2\pi^2](^3B_u, C_{2h})$	10.1	2.12	1.80	1.82
	$^5[\sigma^2\pi^2](^5A_g, C_{2h})$	33.8	27.3	24.8	24.8

[a] Values corrected under the assumption of a 50% overestimation of the singlet energy due to the use of the broken-symmetry approach.

TABLE 5: Energy Splittings for *p*-Phenylbisnitrene and *p*-Phenylbisphosphinidene in kcal/mol[a]

molecule	state	UB3LYP	CASSCF	CASPT2	CASPT2+g1
$C_6H_4-N_2$	$^1[\sigma^2\pi^2](^1A_g, D_{2h})$	0	0	0	0
	$^3[\sigma^2\pi^2](^3B_{1u}, D_{2h})$	1.29 (2.02)[b]	0.72	1.48	1.84
	$^5[\sigma^2\pi^2](^5A_g, D_{2h})$	33.1 (33.8)[b]	39.0	32.7	30.0
$C_6H_4-P_2$	$^1[\sigma^2\pi^2](^1A_g, D_{2h})$	0	0	0	0
	$^3[\sigma^2\pi^2](^3B_{1u}, D_{2h})$	5.14	2.27	2.29	1.78
	$^5[\sigma^2\pi^2](^5A_g, D_{2h})$	8.82	7.47	10.2	11.4

[a] All relative energies include the zero-point energy correction calculated at the DFT level. [b] Corrected values.

electronic energy gaps between 1.29 and 1.58 kcal/mol for *p*-phenylbisnitrene, *p*-phenylbismethylene, and *p*-phenylbis-(chloromethylene). If we take the error introduced by the broken-symmetry calculation into account, the ΔE_{S-T} gap further increases to 2.02−2.32 kcal/mol. However, for the comparison to the measured S−T splittings it is more appropriate to use free energy differences instead of the electronic ones. With values of 0.46 kcal/mol (0.95 kcal/mol) for *p*-phenylbisnitrene, 0.78 kcal/mol (1.52 kcal/mol) for *p*-phenylbis(chloromethylene), and 0.87 kcal/mol (1.59 kcal/mol) for *p*-phenylbismethylene we are in the desired range below 1 kcal/mol, where the values corrected by the sum method are given in parentheses. The $^5[\sigma^2\pi^2]$ state of these molecules lies 23−34 kcal/mol higher in energy. In *p*-phenylbismethylene the $^1[\sigma^4]$ state is highest in energy (31 kcal/mol), while the $^3[\sigma^3\pi^1]$ triplet, at 19.4 kcal/mol, is lower than the quintet state. According to Davidson[32] the quintet state of the *p*-phenylbismethylene should be more stable than the $^1[\sigma^2\pi^2]$ state. This is contradicted by our and all other previous theoretical and experimental[8,9] results. Substitution of the methylene hydrogen by chlorine stabilizes both $^3[\sigma^3\pi^1]$ and $^1[\sigma^4]$ states, such that they are only 7 and 9 kcal/mol above the ground state. In *p*-phenylbis(fluoromethylene) this stabilization is even stronger and causes the $^1[\sigma^4]$ state to become the ground state, with the unsymmetric triplet, $^3[\sigma^3\pi^1]$, as lowest lying excited state (6.77 kcal/mol) followed by the $^1[\sigma^2\pi^2]$ state at 8.7 kcal/mol. The $^3[\sigma^2\pi^2]$ state is found 10 kcal/mol higher than the ground state which has a large energetic gap of 23 kcal/mol to the $^5[\sigma^2\pi^2]$ state. It is well-known that the fluorine atom stabilizes the closed-shell singlet carbene relative to other high-spin states.[33−35]

The problem case for the DFT calculations is, as mentioned before, the *p*-phenylbisphosphinidene molecule with its highly multiconfigurational singlet and triplet wave functions (see Table 2). The calculated singlet−triplet energy separation of 5.14 kcal/mol reflects these problems. This large error is partly caused by the hybrid functional and could be somewhat reduced, if instead a pure DFT functional would be used.[22]

At the CASPT2 level, a considerably smaller value of 1.78 kcal/mol is calculated. Only the $^5[\sigma^2\pi^2]$ state has a single leading configuration. This molecule is also found to have a remarkably low-lying quintet state (9 kcal/mol). The latter is also confirmed by the CASSCF/CASPT2 calculations.

To accurately account for both static and dynamic correlation effects, additional CASSCF(10,10) and CASPT2 calculations have been performed on CASSCF optimized structures. In the case of *p*-phenylbismethylene, *p*-phenylbis(chloromethylene), and *p*-phenylbisnitrene the multiconfigurational treatment does not alter the ordering of the states although it changes the energetic spacing. In particular, both the $^1[\sigma^4]$ and $^3[\sigma^3\pi^1]$ states are moved to higher values. The CASPT2+g1 calculated singlet−triplet gap is always located between the corrected and the uncorrected DFT values. While for *p*-phenylbisnitrene the singlet−triplet energy separation computed at the CASSCF level (0.72 kcal/mol) compares well with the observed values (0.58−0.82 kcal/mol) it has to be emphasized that a crucial part of the correlation effects, namely the dynamic correlation, is still missing. Its inclusion increases the ΔE_{S-T} to 1.48 or 1.84 kcal/mol using the g1 corrected zeroth-order Hamiltonian. The CASPT2+g1 results indicate that *p*-phenylbisphosphinidene, the heavier congener of *p*-phenylbisnitrene, has a comparable singlet−triplet energy separation of 1.78 kcal/mol. The main difference to the nitrene analogue and also to the methylenes (see Table 4) is the exceptionally low lying quintet state. Consequently the configurations which combine the σ and π_- orbitals obtain larger weights in the respective wave functions of the bisphosphinidene species. The weaker interactions of the phosphinidene ligands with the phenyl ring, as compared to the nitrene and carbene analogues, can be traced to a general lack of conjugation between the phosphorus 3p and the carbon 2p orbitals. Similar observations have been reported in a thorough study of vinylnitrene and vinylphosphinidene by Parasuk and Cramer.[36]

The *p*-phenylbis(fluoromethylene) molecule turns out to be the problematic case for the CASPT2 calculations. In agreement

TABLE 6: Unscaled UB3LYP/6-31+G* Frequencies in cm^{-1} and Relative Intensities (%) of the $^1[\sigma^4]$ and $^1[\sigma^2\pi^2]$ Singlet States of *p*-Phenylbis(fluoromethylene)^a

$^1[\sigma^4]$	$^1[\sigma^2\pi^2]$
	492 (6)
792 (20)	776 (10)
856 (14)	806 (21)
1026 (7)	
1096 (90)	
1144 (31)	1125 (59)
	1166 (80)
1213 (100)	
1372 (8)	1321 (6)
1431 (10)	1443 (26)
1521 (9)	
	1633 (100)

^{a} Only vibration modes with more than 5% intensity are listed.

with experiment and the DFT results, CASSCF yields a $^1[\sigma^4]$ ground state. However, now the $^1[\sigma^2\pi^2]$ diradical singlet state appears as the lowest lying excited state at only 0.69 kcal/mol above the closed-shell ground state, followed by $^3[\sigma^2\pi^2]$ (2.12 kcal/mol). The $^3[\sigma^3\pi^1]$ triplet becomes twice as high in energy with 13.3 kcal/mol. Inclusion of dynamic correlation via CASPT2+g1 computations stabilizes the singlet diradical, such that it becomes the ground state, lying 1.52 kcal/mol below the closed-shell singlet state, closely followed by the $^3[\sigma^2\pi^2]$ state (1.82 kcal/mol). This preference for the biradical state is a well-known inherent error of the CASPT2 treatment,[37] and the energy differences obtained in this work are within the CASPT2 error limits. The use of the g1 corrected zeroth-order Hamiltonian helps but is not sufficient to obtain a balanced treatment of closed- and open-shell states in this case. Increasing the basis set by augmenting the fluorine and carbon basis set with one additional s, p, d, and f function and the hydrogen basis with another p function decreases the energy separation between closed-shell and diradical singlet. The $^1[\sigma^2\pi^2]$ singlet is still the ground state, but the energy difference to the closed-shell minimum shrinks to 0.74 kcal/mol. Thus it seems that while CASPT2 overemphasizes the singlet diradical stability, DFT overestimates the stability of the $^1[\sigma^4]$ singlet ground state. Because of the small energy separations involved, we believe that although the $^1[\sigma^4]$ is certainly the ground state of the fluorinated species, the $^1[\sigma^2\pi^2]$ state must be very close in energy. This would also explain the appearance of the respective typical peaks in the IR spectrum (see below).

3.3. Vibrational Frequencies. Two important methods for the experimental characterization of these very reactive compounds are infrared resonance spectroscopy (IR) on one hand

and electron spin resonance (ESR) on the other hand. While IR allows for a distinction between closed-shell and diradical singlet states by their structural differences, ESR permits the discrimination of singlet diradical and triplet states, as the singlet is ESR silent. The closed-shell and biradical singlet state of the $X-C_6H_4-X$ molecules can be clearly distinguished on the basis of specific characteristic peaks in the IR spectra. Thus the shorter bond to the exocyclic ligand gives rise to a typical bond stretch vibration mode between 1500 and 1700 cm^{-1} (1495 cm^{-1} in *p*-phenylbismethylene, 1606 cm^{-1} in *p*-phenylbis(chloromethylene) and 1633 cm^{-1} in *p*-phenylbis(fluoromethylene) as obtained by DFT calculations for the pseudo-singlet states). However, the interpretation of these spectra is not always unambiguous. In the case of *p*-phenylbis(fluoromethylene), Zuev and Sheridan[7] report weak bands in the region characteristic for the biradical, which they assign to possible combination bands of the $^1[\sigma^4]$ structure. According to the results from our calculations, pointing to a small energy difference between both singlets, these bands might actually be caused by the presence of small amounts of the diradical. The rest of the bands listed in Table 6 would also fit into the experimental spectrum,[7] but some of the peaks might partly be hidden by other bands stemming from the precursor substances. Although the validity of the UHF-DFT results for the open-shell singlet states remain questionable, the results can be trusted on a qualitative basis, as the structures of the carbene pseudo-singlets very strongly resemble those of the CASSCF computations.

Compared to the spectra of *p*-phenylbismethylene and its halogenated analogues, the spectra of *p*-phenylbisphosphinidene and *p*-phenylbisnitrene look rather simple. The *p*-phenylbisphosphinidene vibrational modes together with their intensities are listed in Table 7. The strongest vibrational mode (19) is the CH out-of-plane bending mode at 816 cm^{-1}. The same mode has been established to be 776 cm^{-1} for the triplet C_6H_5P ground state[14] using MP2 calculations. The C$-$P stretching mode of *p*-phenylbisphosphinidene is 546 cm^{-1}, considerably lower than that of phenylphosphinidene (695 cm^{-1}). No vibrational frequencies are found in the range of 1600 to 3100 cm^{-1}, similar to phenylphosphinidene[14] where this range is slightly smaller (1750$-$3000 cm^{-1}).

4. Summary

Para substitution of the triplet phenylphosphinidene C_6H_5-P with a second phosphinidene ligand ($P-C_6H_4-P$) results in an open-shell singlet diradical ground state with a very low, 1.78 kcal/mol, singlet$-$triplet energy separation. A similar small energy gap between the singlet diradical and the triplet state is

TABLE 7: Unscaled Vibrational UB3LYP/6-31+G* Frequencies in cm^{-1} with Intensities (km/mol) in Parentheses for the Pseudo-Singlet Diradical Ground State of *p*-Phenylbisphosphinidene

mode	ν	description	mode	v	description
1	3197 (0.1)	CH stretch	16	982 (0.0)	CH bend (out)
2	3195 (26.2)	CH stretch	17	980 (0.0)	ring-P stretch
3	3179 (0.0)	CH stretch	18	828 (0.0)	CH bend (out)
4	3178 (1.3)	CH stretch	19	816 (42.4)	CH bend (out)
5	1562 (0.0)	C=C ring stretch	20	749 (0.0)	ring bend (in)
6	1488 (3.0)	CH bend (in)	21	707 (0.0)	ring bend (out)
7	1483 (0.0)	CH bend (in)	22	628 (0.0)	ring bend (in)
8	1471 (7.4)	ring stretch + CH bend (in)	23	546 (0.1)	CP stretch
9	1306 (0.0)	CH bend (in)	24	477 (17.2)	ring torsion
10	1293 (0.1)	CH bend (in)	25	390 (0.0)	ring torsion
11	1237 (0.0)	CH bend (in)	26	315 (0.0)	ring-P stretch
12	1126 (0.1)	ring-P stretch + CH bend (in)	27	286 (0.0)	ring-P bend (in)
13	1126 (4.6)	CH bend (in)	28	240 (0.0)	ring torsion
14	1009 (0.4)	CH bend (out)	29	181 (1.6)	ring-P bend (in)
15	986 (0.0)	CH bend (out)	30	81 (0.4)	ring-P bend (out)

also found in *p*-phenylbisnitrene, *p*-phenylbis(chloromethylene), and *p*-phenylbismethylene. With the exception of *p*-phenylbis-(fluoromethylene), the molecules considered in this work form in their ground and lowest triplet state a quinone-like structure. The latter is the least pronounced in *p*-phenylbisphosphinidene, where no clear exocyclic double bond is formed. The reason is that the π_- orbital (the antibonding interaction of the ligand p-orbital with the aryl π-system) is in *p*-phenylbisphosphinidene energetically more favorable than in the other molecules. Consequently the occupation of this orbital is more probable and allows the respective configurations to have larger weights in the wave functions. This highly multiconfigurational character is also responsible for the errors encountered in the DFT calculations on *p*-phenylbisphosphinidene. Although the UHF-based DFT method does not properly describe the open-shell singlet state, but gives an admixture of both singlet and triplet states with the same orbital wave function, it allows us to figure out a qualitative trend of the parameters, in particular in systems having small triplet–singlet energy separations.

In all molecules with a diradical singlet ground state a small singlet–triplet energy gap in the range of 1.3–2.2 kcal/mol has been established by CASPT2 calculations. Remarkably, all molecules have a very large energy gap (>20 kcal/mol) from the ground state to the respective quintet state, except *p*-phenylbisphosphinidene. There the gap amounts to only 11.4 kcal/mol due to the energetically less unfavorable π-orbital which becomes singly occupied in the $^5[\sigma^2\pi^2]$ state.

According to our calculations the closed-shell and the diradical singlet states of *p*-phenylbis(fluoromethylene) should be very close in energy. The CASPT2 calculations, having an inherent tendency to favor the diradical state, predict the singlet diradical to be 1.52 kcal/mol more stable. At the CASSCF-(10,10) level the closed-shell singlet is more stable by only 0.69 kcal/mol, while DFT clearly favors the closed-shell singlet (8.71 kcal/mol). Increasing the basis set in the CASSCF/CASPT2 calculations reduces the relative energy between both singlet states to 0.76 kcal/mol, though the diradical still forms the ground state. Experiment establishes the closed-shell singlet ground-state based on the reactivity pattern and the IR spectra. Nevertheless weak bands in the region typical for the exocyclic double bond are present that lend a further support for our assumption.

A clear relation between the ligand electronegativity and the disturbance of the aromatic ring could be established. The influence on the benzene ring decreases from *p*-phenylbisnitrene via *p*-phenylbismethylene to *p*-phenylbisphosphinidene, in agreement with the diminished electronegativity.

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