

o-, *m*-, and *p*-Diphosphabenzenes and Their P₂(C–H)₄ Valence Isomers. An Ab Initio Theoretical Study

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Abstract: The 24 valence isomers of diphosphinine, P₂(C–H)₄, have been investigated at an electron-correlated ab initio level and by density functional theory. In analogy with benzene, the three planar forms exhibit full aromaticity and are the most stable isomers on the potential surface. The next isomers, by order of stabilities, are the diphosphabenzvalenes, the Dewar diphosphabenzenes, the prismanes, and the diphosphabicyclopropenyls. They are distinctly less stable than the planar isomers, and their relative energies range from 23 all the way to 93 kcal/mol above the absolute minimum. Among the planar isomers, the most stable one is the (ortho) 1,2-diphosphabenzene, in apparent contradiction with the fact that this species has not been synthesized yet. Some lines of thought to resolve this apparent dilemma are proposed, and the relative reactivities of planar isomers are discussed in terms of their different diradical character. Strain energies are calculated for the nonplanar isomers and compared to those of the isomers of C₆H₆ and P₆. Tentative extrapolations to tri-, tetra-, and pentaphosphinines are proposed.

Introduction

The carbon–phosphorus analogy is a powerful concept in heterochemistry, more useful in fact than the carbon–silicon analogy, although the latter atoms belong to the same column of the periodic table.¹ The reactivity² and conjugative ability^{3,4} of the λ³-P=C bond have been shown to be quantitatively similar to those of the C=C bond. The analogy is general and applies, among others, to aromatic systems, leading to the family of phosphinines by replacement of one or several C–H entities by P atoms in a benzene ring. Phosphinines have been discovered by Märkl⁵ in 1966, opening the way to an active chemistry that has been reviewed by the same author.⁶ While monophosphinines are well-known and display an aromatic stability that is just slightly less than that of benzene,⁷ diphosphinines have been much less studied and present some intriguing features.

Assuming the hexagonal planar conformations to be the most stable, three isomers of diphosphinine (**1–3** in Figure 1) can be a priori anticipated to be observable. Indeed, 1,3-diphosphinines (**2**) are rather stable and have been prepared in the coordination sphere of iron.^{8,9} On the other hand, only one 1,4-

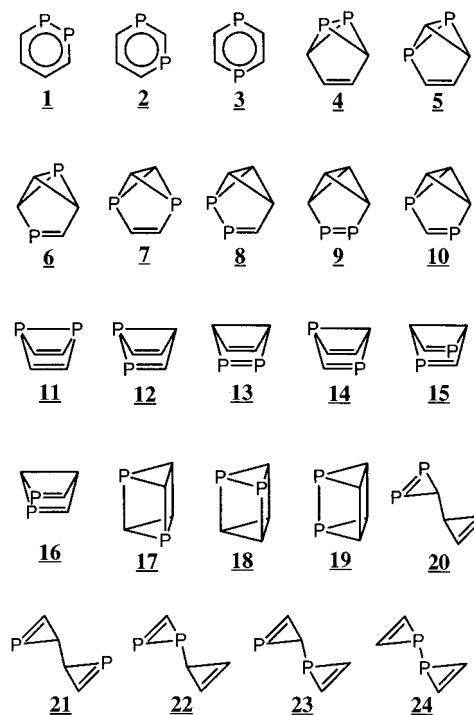


Figure 1. 24 valence isomers of diphosphinine.

diphosphinine (**3**) is known, bearing four CF₃ substituents.¹⁰ This species is rather unstable and may react with CCl₄¹¹ or sulfur,¹² or photoisomerize.¹³ Last, and somewhat surprisingly, 1,2-diphosphinines (**1**) are unknown, leading to the widespread feeling that this isomer might be unstable.

These contrasted features of the chemistry of diphosphinines

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raise a number of questions: (i) Why does one not observe 1,2-diphosphinine? (ii) Why is 1,4-diphosphinine so reactive? (iii) What is the order of stabilities of the three planar isomers of diphosphinine? (iv) Are there other accessible valence isomers, similar to the various isomers of benzene or P_6 ?

In the case of benzene, if one excepts some chemically unrealistic isomers that are only of topological interest,^{14,15} there exist five possible valence isomers that can be described by the formula $(C-H)_6$. All of them have been synthesized,¹⁶ although they have widely different stabilities. According to ab initio calculations,¹⁷ the benzvalene and Dewar benzene lie some 75–80 kcal/mol above the planar regular hexagon, and the prismane and the bicyclopentenyl still lie some 45 kcal/mol higher. On the other hand, the analogous isomers of P_6 span a much smaller interval of relative energies, about 30 kcal/mol,¹⁷ and follow a very different order of stabilities, the planar aromatic isomer being the least stable one! This clearly indicates that any endeavor to predict the order of stabilities of the various isomers of diphosphinine by qualitative considerations is hopeless.

Due to lower symmetry, the valence isomers that fit the formula $P_2(C-H)_4$ are more numerous than those of benzene or P_6 and amount to 24 different structures, which can be decomposed into three planar diphosphabenzene (**1–3**), seven diphosphabenzvalenes (**4–10**), six Dewar diphosphabenzene (**11–16**), three prismanes (**17–19**), and five diphosphabicyclopentenyls (**20–24**), as displayed in Figure 1. In the rest of this paper, the presentation and discussion of the computational results will be organized according to this classification. The aim of this paper is to try to answer the questions that have been raised above, by means of a theoretical investigation of the $P_2(C-H)_4$ potential energy surface, by assessing the geometrical features and the relative stabilities of all the 24 possible isomers of diphosphinine.

Theoretical Methods

All calculations have been performed with the GAUSSIAN-94 series of programs.¹⁸ In what follows, the various sets of basis functions that have been used are named after their GAUSSIAN-94 acronym: 6-31G**, 6-311G**, 6-311G(2df,p), cc-pVDZ, and cc-pVTZ.

All basis sets involve polarization functions on P, C, and H atoms. The 6-311G** has the same polarization functions as 6-31G** and is in principle a basis set of valence triple- ζ type. However, it should be mentioned that the standard basis set that is so referred to in GAUSSIAN-94 is indeed made of 6-311G basis functions for first row atoms¹⁹ but uses the McLean–Chandler (12s,9p) \rightarrow (621111,42111)

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basis set for second-row atoms.²⁰ The 6-311G(2df,p) basis set is just an extension of the latter one, with a split- ζ set of d functions and an additional set of f functions for the first-row atoms and beyond.

The two remaining basis sets are the so-called “correlation-consistent” basis sets of Dunning.²¹ These basis sets have a high reputation and are known to yield nearly as much correlation energy as the very elaborate atomic natural orbital (ANO) basis sets. The cc-pVDZ basis set is of double- ζ type, with a (d,p) set of polarization functions, just like 6-31G**. The cc-pVTZ is a triple- ζ basis set, with a (2df) set of polarization functions on carbon and phosphorus and a (2pd) set on the hydrogens. This latter basis set will be taken as a reference in the present study.

Beyond the Hartree–Fock level, the computational methods that include electron correlation are of two different types. The first type is the Møller–Plesset many-body perturbation theory, that will be used at second order (MP2) and fourth order (MP4SDTQ, or MP4 for short), this latter level using the frozen-core approximation. The second type of method is more sophisticated and uses the coupled-cluster theory²² at two levels: CCSD, which includes single and double excitations, and CCSD(T), which treats, in addition, the triple excitations in a perturbative way.

Last, the density functional theory has also been used, in its popular B3LYP version,²³ which uses a three-parameter mixture of gradient corrected correlation functional with Becke exchange²⁴ and exact Hartree–Fock exchange.

As all of the methods that have been used in this work are of single-reference-determinant type, we have found it useful to check that the major Slater determinant in a multideterminant wave function is indeed largely predominant in the wave functions for problem at hand. Thus, an MCSCF calculation of complete-active-space type (CASSCF) has been performed for each of the planar isomers (**1–3**), in 6-31G** basis set, with an active space involving the full π electronic system. As a result, the major Slater determinants have coefficients of 0.919, 0.917, and 0.916, respectively, for **1**, **2**, and **3**, close to the coefficient 0.936 that is found in benzene and close enough to unity to make multireference methods unnecessary.

After some computational tests aimed at establishing its reliability (vide infra), the MP2/6-31G** computational level will be used for all geometry optimizations for the post-Hartree–Fock calculations and at the B3LYP/6-31G** level for B3LYP calculations.

Results for the Planar Isomers

Among the 24 possible isomers of diphosphinine, the planar ones have a special status. They are presumably the most stable ones, since only isomers of this type have been synthesized to date, and their order of stability is an open question in the chemistry of phosphorus. For these reasons, these isomers have been studied at several levels of calculation, covering a wide spectrum of sophistication, and using more and more complete basis sets. The results of these test calculations have then been used to choose a basis set and a level of calculation that combine reasonable accuracy and cost efficiency, to be employed for the remaining 21 isomers.

The consistency of the different basis sets has been examined first. Table 1 reports the geometries and energies of the three planar isomers, using five different basis sets ranging from various types of Pople’s basis sets to Dunning’s double- and triple- ζ correlation-consistent basis sets. All geometries and energies are determined at the MP2 level. It first appears that

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Table 1. Geometries and Energies of the Planar Isomers of Diphosphinine (MP2 Level) (distances in Å, angles in deg)

basis set	6-31G**	cc-pVDZ	6-311G**	6-311G-(2df,p)	cc-pVTZ
1,2-Diphosphabenzene (1)					
PP	2.111	2.130	2.112	2.110	2.112
PC	1.745	1.757	1.742	1.738	1.743
CC ^a	1.392	1.402	1.395	1.388	1.389
CC ^b	1.400	1.409	1.402	1.394	1.397
CPP	105.0	105.0	105.0	105.0	105.0
PCC	129.6	129.4	129.7	129.4	129.4
CCC	125.4	125.6	125.3	125.6	125.6
E(HF) ^c	-835.22386	-836.26221	-836.28708	-836.31285	-836.33114
E(MP2) ^c	-835.97283	-836.02159	-836.06874	-836.21833	-836.25525
E(HF) ^d	0	0	0	0	0
E(MP2) ^d	0	0	0	0	0
1,3-Diphosphabenzene (2)					
PC ^e	1.738	1.750	1.734	1.729	1.734
CC ^f	1.741	1.753	1.738	1.734	1.738
PC	1.395	1.405	1.398	1.391	1.393
CPC	102.7	102.6	102.7	102.9	102.8
PCC	128.5	128.5	128.5	128.4	128.4
CCC	125.8	125.8	125.6	125.7	125.8
PCP	131.8	131.9	132.0	131.5	131.6
E(HF) ^d	7.5	10.1	4.2	5.6	8.0
E(MP2) ^d	5.4	7.9	0.3	4.9	6.8
1,4-Diphosphabenzene (3)					
PC	1.744	1.756	1.741	1.737	1.741
CC	1.391	1.401	1.395	1.387	1.389
CPC	102.1	102.1	102.0	102.4	102.3
PCC	128.9	129.0	129.0	128.8	128.9
E(HF) ^d	9.4	11.9	6.7	8.1	10.2
E(MP2) ^d	7.7	10.3	3.3	8.0	9.7

^a Adjacent to the P–P bond P. ^b In front of the P–P bond. ^c Absolute energies in hartrees. ^d Relative energies in kcal/mol. ^e Inside the PCP subunit. ^f Outside the PCP subunit.

Table 2. Standard Bond Lengths (Å) and Bond Strengths (kcal/mol) for the C–C, P–C, and P–P Single and Double Bonds

	bond lengths ^a	bond strengths ^b
	Single Bonds	
C–C	1.54	80
C–P	1.86	64
P–P	2.22	48
	Double Bonds	
C=C	1.34	145
C=P	1.67	107
P=P	2.01	82

^a From ref 25. ^b For single bonds, see ref 26. Recent values for the single → double bond energy increments are taken from ref 27a.

the geometries are remarkably insensitive to the quality of the basis set. The optimized angles are practically unchanged along each row of the table. As for the bond lengths, all basis sets yield very similar results except perhaps cc-pVDZ, which yields slightly longer bond lengths, but the discrepancy with other basis sets never exceeds 0.02 Å.

In the three isomers, all C–C bond lengths are very close to the value 1.40 Å, which typifies the benzene ring, indicating the absence of any phenomenon of bond fixation (preference of one Kekulé structure over the other) and that resonance fully takes place in planar diphosphinines. In line with this argument, the P–P and P–C bond lengths of the three isomers (about 2.11 and 1.73–1.74 Å, respectively) lie between the accepted values for the corresponding single and double bonds (see Table 2), 2.22 vs 2.01 Å for the P–P bond and 1.86 vs 1.67 Å for P–C.²⁵

Using the MP2-optimized geometries, the different basis sets are also compared in Table 1 for their ability to estimate the relative stabilities of the 1,2, 1,3, and 1,4 isomers. It is seen that the two largest basis sets, 6-311G(2df,p) and cc-pVTZ, yield results in good agreement with each other, putting the 1,3 isomer

below the 1,4 one by 3 kcal/mol at the MP2 level, and above the 1,2 isomer by 5–7 kcal/mol. Interestingly, very similar relative stabilities are calculated at the Hartree–Fock level, indicating that electron correlation has a rather minor effect in this respect. As for the smaller basis sets, the results they offer are generally in good agreement with those of the best basis sets, with the exception of the 6-311G** basis set that finds the 1,3 isomer to be nearly as stable (only 0.3 kcal/mol higher) as the 1,2 one at the MP2 level, at variance with all other basis sets at both the MP2 and HF levels. A possible explanation for the apparent inadequacy of 6-311G** for the diphosphabenzenes might lie in the way this basis set is constructed in GAUSSIAN 94: as a mixture of true 6-311G functions for carbon and hydrogen with functions of a different source for phosphorus. In fact, while the contraction schemes (see Theoretical Methods) are of valence triple- ζ type for carbon, they look more as quadruple- ζ for phosphorus, leading to imbalance in the description of both atoms. In these conditions, it is quite possible that the 1,2 isomer and the two other planar isomers, whose types of bonds are different, are not described in a balanced way. This inadequacy is damped in the bigger 6-311G(2df,p) basis set, a natural consequence of the larger number of basis functions. On the other hand, the 6-31G** basis set appears to be the one whose results best compare, at both the MP2 and HF levels, to those of 6-311G(2df,p) and cc-pVTZ.

Using geometries optimized at the MP2/6-31G** level, the order of stabilities of the three planar isomers has been calculated at several levels of calculation of increasing sophistication, ranging from Hartree–Fock all the way to CCSD(T), the latter level being usually considered as yielding results close to the full configuration interaction limit. The results, displayed in Table 3, confirm that electron correlation effects, though not negligible, have a rather weak effect on the relative energies which do not differ much from HF to MP2. Moreover, the various levels of post-Hartree–Fock calculations are in astonishingly good agreement with each other. The MP2 and MP4 results are practically the same, showing an excellent convergence of the Møller–Plesset series. Going to the more sophisticated coupled-cluster level still yields the same relative energies within a few tenths of a kilocalorie per mole, and the inclusion of the triple excitations at the CCSD(T) level, which has been found to be important in other instances, proves to have a negligible effect for the problem at hand. All in all, the MP2 results are in excellent agreement with higher levels, showing that more elaborate treatments of electron correlation are insignificant as far as *differences* between absolute energies are considered.

On the other hand, the B3LYP results (calculated with B3LYP-optimized geometries) slightly depart from the previous ones and more or less reproduce the HF tendencies. Judging from comparison with the CCSD(T) which is generally considered as the reference, it may be concluded that DFT theory is less appropriate for the problem at hand than classical post-Hartree–Fock levels.

In light of the above computational tests, it is clear that a good compromise between accuracy and cost efficiency is the calculation of molecular energies at the MP2 level in 6-31G** basis set, using geometries optimized at the same level. This is

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Table 3. Energies of the Ortho (**1**), Meta (**2**), and Para (**3**) Planar Isomers, at Various Computational Levels Using the 6-31G** Basis Set^a

	absolute energies (au) ^b			relative energies (kcal/mol) ^c		
	1,2 (ortho)	1,3 (meta)	1,4 (para)	1,2 (ortho)	1,3 (meta)	1,4 (para)
HF	-835.223 86	-835.211 86	-835.208 85	0	7.5	9.4
MP2	-835.972 83	-835.964 28	-835.960 55	0	5.4	7.7
MP4(SDTQ)	-836.054 52	-836.045 94	-836.042 83	0	5.4	7.3
CCSD	-836.011 34	-836.002 04	-835.999 24	0	5.8	7.6
CCSD(T)	-836.051 91	-836.043 00	-836.040 16	0	5.6	7.4
B3LYP ^d	-837.526 77	-837.512 77	-837.510 07	0	8.8	10.5

^a The geometries are optimized at the MP2/6-31G** level, unless otherwise specified. ^b Absolute energies in hartrees. ^c Relative energies in kcal/mol. ^d Geometry optimized at the B3LYP/6-31G** level.

the type of computation that will be used throughout the rest of this study. For comparison purposes, the results of B3LYP calculations, in the same basis set, will also be indicated.

Results for the Nonplanar Isomers

Three factors can make the stabilities of the nonplanar isomers different from those of the planar ones: (i) lack of resonance energy, (ii) different types (σ/π) of bonds, leading to different sums of bond strengths, and (iii) strain. Knowledge of the first two factors and of calculated relative energies allows an interesting quantity, strain energy, to be estimated for each isomer.

Resonance energies can be easily estimated for structures **2** and **3**, which both have degenerate Kekulé structures (unlike structure **1**). Values of 25 and 16 kcal/mol have been estimated¹⁷ for benzene and P₆, respectively, using homodesmotic thermodynamic cycles, leading to an interpolated value of 22 kcal/mol for **2** and **3**. Either of these two structures is therefore a good reference for an unstrained isomer of known resonance energy, to be used for calculation of strain energies in **4–24**. As for the second factor, the sum of bond strengths (D_i), it can be estimated for each isomer by using a set of standard bond strengths^{26,27} as displayed in Table 2. Knowing these parameters, the strain energy $S(\mathbf{x})$ of an isomer \mathbf{x} can be estimated by assuming that the exothermicity of the conversion of \mathbf{x} to **3** (taking **3** as the above-mentioned reference isomer) is the balance of loss of resonance energy (22 kcal/mol), change of bond strengths ($D_i \rightarrow D_j$), and relief of strain energy:

$$E(\mathbf{x}) - E(\mathbf{3}) = 22 - \sum D_i(\mathbf{x}) + \sum D_j(\mathbf{3}) + S(\mathbf{x}) \quad (1)$$

As the sum of bond strengths for each Kekulé structure of the planar isomer **3** amounts to 567 kcal/mol (see Table 2), a definition of strain energy can be given for each nonplanar structure, in kcal/mol:

$$S(\mathbf{x}) = E(\mathbf{x}) - E(\mathbf{3}) + \sum D_i(\mathbf{x}) - 589 \quad (2)$$

Those values, as well as calculated energies $E(\mathbf{x})$ (relative to **1**) and sum of bond strengths $D_i(\mathbf{x})$, are displayed in Table 4. It is clear that taking **2** instead of **3** as the reference unstrained isomer would have led to nearly similar strain energies, within 2 kcal/mol. It should however be noted that our calculation of strain energies is based on the near-constancy of bond strengths in the different molecules, a condition that is certainly far from being accurately satisfied. Therefore, the calculated strain energies that are displayed in Table 4 are not to be considered as more than rough estimations.

Table 4. Relative Energies, Sum of Standard Bond Strengths, and Strain Energies for the Nonplanar Isomers of Diphosphinine, as Calculated at the MP2/6-31G**//MP2/6-31G** Level^a

isomer	relative energy ^b	sum of bond strengths	strain energy
Diphosphabenzvalenes			
4	23.1 (31.4)	609	35 (41)
5	26.9 (33.5)	609	39 (43)
6	34.6 (45.6)	603	41 (49)
7	38.5 (46.5)	609	51 (56)
8	42.6 (49.5)	603	49 (53)
9	43.3 (52.1)	610	57 (63)
10	45.2 (55.4)	603	52 (59)
Dewar Diphosphabenzenes			
11	44.8 (44.9)	594	42 (39)
12	45.2 (48.1)	588	37 (37)
13	46.6 (50.7)	595	45 (46)
14	47.0 (52.0)	588	38 (41)
15	51.1 (58.2)	582	36 (41)
16	52.4 (60.8)	582	38 (43)
Prismanes			
17	61.5 (68.5)	624	89 (93)
18	62.6 (69.9)	624	90 (94)
19	65.4 (69.8)	624	93 (94)
Bicyclodiphosphapropenyls			
20	70.2 (84.2)	595	69 (80)
21	75.4 (84.2)	582	61 (67)
22	84.6 (87.8)	588	76 (76)
23	85.0 (89.4)	588	76 (78)
24	92.8 (89.0)	594	90 (84)

^a All quantities are in kcal/mol. Values calculated at the B3LYP/6-31G**//B3LYP/6-31G** level are indicated in parentheses. ^b The reference energy is that of the planar isomer **1**.

Diphosphabenzvalenes. The geometries of the seven possible forms of diphosphabenzvalene (**4–10**) are displayed in Figure 2. The bond lengths are, roughly speaking, consistent with standard values for single and double C–C, P–C, and P–P bonds, with positive as well as negative deviations.

At the MP2 level, all diphosphabenzvalene isomers are less stable than the planar forms, making the P₂(C–H)₄ species closer to C₆H₆ than to P₆. However, while benzvalene lies as much as 73 kcal/mol above benzene,²⁸ the corresponding difference is much reduced in diphosphinines as the most stable diphosphabenzvalene (**4**) lies only 15 kcal/mol above the least stable planar form, 1,4-diphosphabenzene. The various isomers span a rather wide range of stabilities, from 23 to 45 kcal/mol above the absolute minimum on the P₂(C–H)₄ potential surface. The reason clearly arises from the strain energies which are widely different from one structure to the other. As intuition suggests, phosphorus appears to be less sensitive than carbon to angular strain that affects the atoms lying in bridging position (i.e., on the axis of the butterfly). As a consequence, the most stable and less strained structure (**4**) is the one that has two

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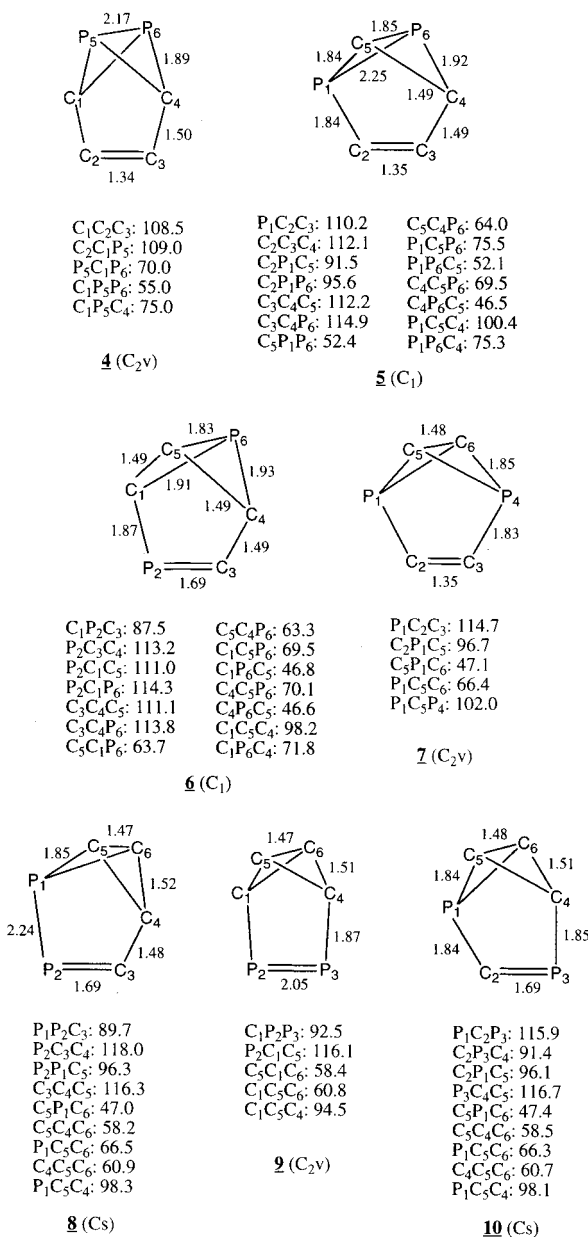


Figure 2. Geometric parameters of diphosphabenzvalenes. Distances are in angstroms and angles in degrees.

phosphorus atoms in bridging positions, vs only one for the two structures that are next in stability (**5** and **6**), and none for the least stable structures (**7**–**10**). On the other hand, the sums of bond strengths are roughly the same in the various isomers (from 603 to 610 kcal/mol) and play a minor role in the order of stabilities.

The B3LYP relative energies, also displayed in Table 4, are on the whole rather similar to the MP2 ones. The whole set of diphosphabenzvalene energies is shifted upward, by some 10 kcal/mol, relative to the MP2 level. However, the order of stabilities is the same, and within the diphosphabenzvalene family, the relative energies are also the same, within 3 kcal/mol.

Dewar Diphosphabenzenes. The geometries of Dewar diphosphabenzenes are displayed in Figure 3. Once again, the bond lengths are reasonably close to standard values for formal single and double bonds. Some interatomic angles are rather small, however less than in diphosphabenzvalenes, leading to strain energies that are, on the whole, smaller than in the

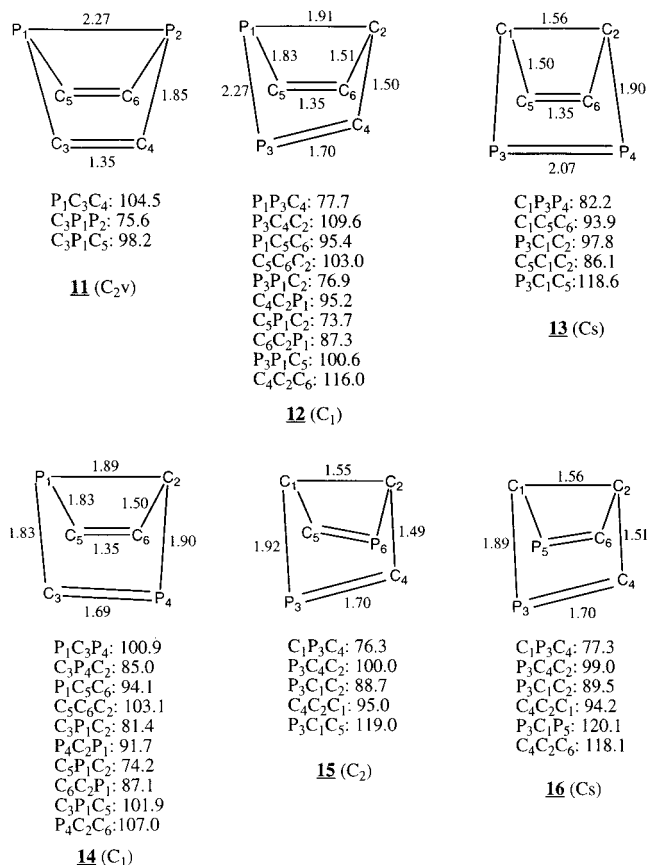


Figure 3. Geometric parameters of Dewar diphosphabenzenes. Distances are in angstroms and angles in degrees.

previous case, and less scattered. As a consequence, the family of Dewar diphosphabenzenes displays a spectrum of stabilities in which the organizing quantity appears to be the sum of bond strengths (in the range 582–595 kcal/mol) rather than strain energies. In accord, the most stable structures (**11**–**14**) are those displaying at least one C–C double bond (which is stronger than either P–P or P–C double bonds) while **15** and **16** are higher although their strain energies are rather small.

As in the preceding case, the MP2 and B3LYP results display exactly the same order of stabilities for the six Dewar structures, the B3LYP relative energies being consistently upshifted relative to MP2. At this latter level, all Dewar structures but one are less stable than the highest lying diphosphabenzvalene and span a relatively small range of relative energies (45–52 kcal/mol above the most stable planar isomer at the MP2 level). On the other hand, much more overlap between the relative energies of the two families of isomers is found at the B3LYP level.

Prismanes. As a whole, the three prismanes (**17**–**19**) lie some 10 kcal/mol above the least stable Dewar diphosphabenzene (MP2 level). More or less fortuitously, the sums of bond strengths are exactly the same in the three isomers. All atoms lie on a sharp corner (see Figure 4) and are subject to angular strain whatever the isomer that is considered, so that the strain energies are also about the same. As a consequence, all prismanes have rather similar relative energies, 62–65 kcal/mol above 1,2-diphosphabenzene at the MP2 level and 69–70 kcal/mol at the B3LYP level.

Bicyclodiphosphapropenyls. The five bicyclodiphosphapropenyl structures (**20**–**24**), constituted of two subunits of cyclopropenyl type that are linked by a single bond (Figure 4), still lie distinctly higher in energy and constitute the least stable category of diphosphinine isomers. The structures display two

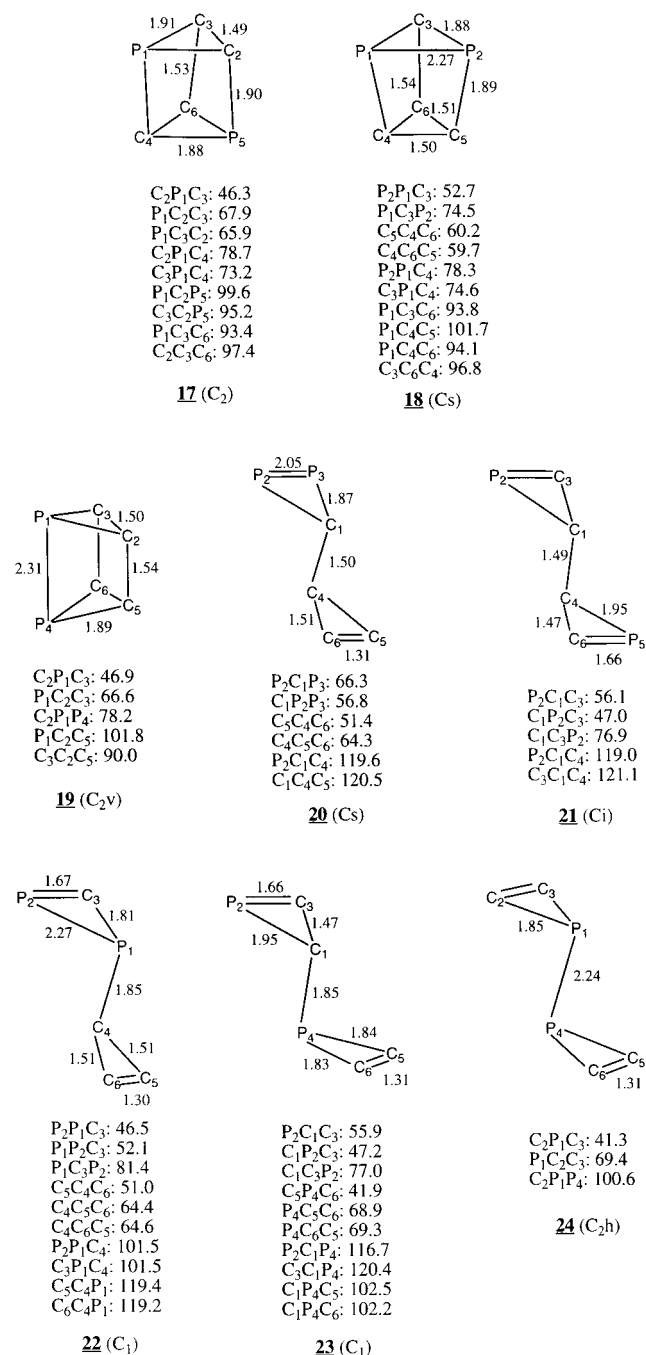


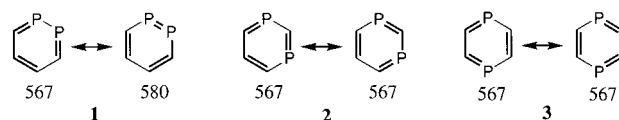
Figure 4. Geometric parameters of prismanes and diphosphabicyclopropyls. Distances are in angstroms and angles in degrees.

double bonds, but each of them is the site of such an angular strain that the stability rules, which are valid for benzvalene and Dewar structures, are inverted: a structure is now more stable if a phosphorus rather than a carbon is involved in a π bond. This principle rationalizes the wide range (23 kcal/mol) of relative energies that comes out from the MP2 calculations: structures **20** and **21**, with two unsaturated phosphorus atoms, are the most stable, followed by **22** and **23**, which have only one unsaturated phosphorus, followed by **24** that has none. On the other hand, the range of relative energies is found to be much narrower at the B3LYP level, yet the order of stabilities is practically unchanged.

Discussion

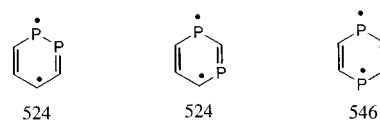
Planar Isomers. The planar diphosphabenzenes (**1–3**) constitutes the lowest lying family of isomers on the $P_2(C-H)_4$

potential surface, a consequence of their aromaticity due to the resonance energy associated with conjugation within the π system. At all computational levels, the ortho isomer (**1**) is found to be the most stable, while the meta (**2**) and para (**3**) isomers are rather close together in energy and both lie a few kcal/mol above **1**. This computational finding, which contrasts with the absence of the ortho isomer among the diphosphinines that have been synthesized to date, is in fact quite reasonable and can be interpreted in terms of bond strengths and resonance energies. According to the data displayed in Table 2, the various Kekulé structures of **1–3** have the sums of bond strengths indicated as follows:



It is seen that all Kekulé structures have the same energies in **2** and **3**. Assuming the resonance energy to be the same (22 kcal/mol) in both systems, the para and meta isomers are predicted to have about the same relative energies, in agreement with computations. As for the ortho isomer **1**, one of its Kekulé structures has the same energy as those of **2** and **3**, while the other is more stable by 13 kcal/mol. With these data in hand, the energy of **1** relative to **2** or **3** can be deduced by reasoning in the framework of the 2×2 configuration interaction that mixes the two Kekulé structures.²⁹ The picture that arises from this simple estimation is that of two degenerate structures, **2** and **3**, higher than **1** by 7.4 kcal/mol,²⁹ in good agreement with the computational results.

Another intriguing experimental fact that remains to be explained is the reactivity of the para isomer **3**, suggestive of some diradical character. A good indication of this latter property for a molecule is its singlet–triplet energy gap: the smaller the gap, the larger the diradical character in the singlet ground state. In accord, the singlet–triplet gap has been calculated for the three planar isomers, at the restricted-open-shell MP2 level. As a result, the gaps amount to 73.4, 74.3, and 66.3 kcal/mol for **1**, **2**, and **3**, respectively, showing a larger diradical character for the para isomer than for the other two. Once again, this computational result can be understood in terms of relative stabilities of Kekulé structures. Using the standard bond strengths of Table 2, the relative energies of the various diradical structures can be estimated and compared. The lowest diradical structure is indicated below for each isomer, showing that the lowest diradical structure among all possibilities is indeed found in 1,4-diphosphabenzene (**3**), with the odd electrons located on the phosphorus atoms.



Nonplanar Isomers. Distinctly higher than the aromatic isomers **1–3**, the nonplanar isomers exhibit a rather continuous spectrum of relative energies from 23 to 93 kcal/mol above the absolute minimum. As a rough general rule, the order of stabilities within a given family is determined more by the strain energies than by the sum of bond strengths which remain roughly constant. Accordingly, both diphosphabenzvalenes and bicyclic diphosphapropenyls span a large range of energies because the strain energies vary widely within both of these families, while the reverse is true in Dewar diphosphabenzene

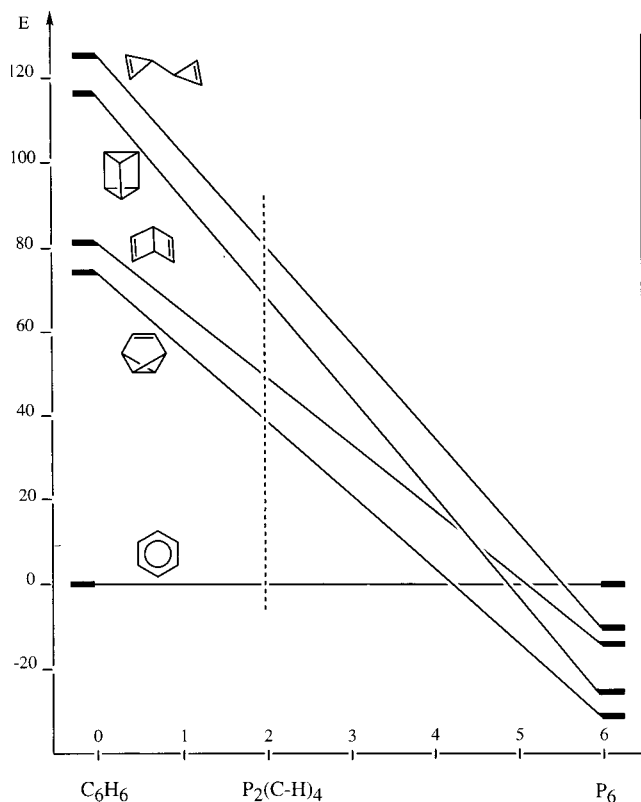


Figure 5. Correlated energy levels of the valence isomers of C_6H_6 and P_6 . The number of phosphorus atoms in the $P_n(C-H)_{6-n}$ phosphinine is indicated on the abscissa. Energies are reported in ordinate, in kcal/mol.

and especially in prismanes. On the other hand, both factors compete to determine the relative orders of the various families. Thus, the very high lying prismanes have the strongest bonds (624 kcal/mol), but also the highest strain energies.

Comparison with C_6H_6 and P_6 . How do diphosphinines find their place between C_6H_6 and P_6 ? These molecules can first be compared from the standpoint of strain energies. Using homodesmotic cycles, Warren and Gimarc¹⁷ have calculated some strain energies of 81, 64, 149, and 107 kcal/mol for the benzvalene, Dewar, prismane, and bicyclopentenyl isomers of benzene, respectively, and 21, 13, 53, and 16 kcal/mol for their P_6 analogues. It can be seen that the corresponding strain energies of diphosphinines (36–53, 37–43, 90–94, and 62–91 kcal/mol at the MP2 level) nicely fit between the C_6H_6 and P_6 limits. This suggests that the mean relative energies of each family of $P_2(C-H)_4$ isomers might be roughly estimated by linear interpolation, as is done in Figure 5. By drawing straight lines between the energy levels of the corresponding C_6H_6 and P_6 isomers, it is possible to guess the relative energies of the same isomers in any $P_n(C-H)_{6-n}$ phosphinine. For diphosphinines, this leads to a set of mean relative energies of 40, 50, 71, and 81 kcal/mol for diphosphabenzvalenes (4–10), Dewar diphosphabenzenes (11–17), prismanes (18–20), and diphosphabicyclopentenyls (20–24), respectively, to be compared with the MP2 values 23–45, 45–52, 62–65, and 70–93 kcal/mol.

(29) The mixing of two Kekulé structures of unequal energies (say 0 and Δ) coupled by a resonance integral β corresponds to the diagonalization of the general 2×2 CI matrix whose diagonal elements are 0 and Δ and the off-diagonal is β . Taking the highest Kekulé structure of **1** as the reference of energy 0, Δ takes the value -13 kcal/mol in **1** and 0 in **2** and **3**. The β integral, which can be assumed to be the same for **1–3**, is given by the resonance energy in **2** or **3**, 22 kcal/mol. Performing the 2×2 CI in the zero-differential-overlap approximation leads to a ground-state energy of -29.4 kcal/mol for **1** vs -22 kcal/mol for **2** or **3**.

The agreement is encouraging and suggests that similar interpolations might be tempted to predict the relative energies of other phosphinines. Following this reasoning, one may speculate that the planar aromatic isomers are still the lowest ones in triphosphinines $P_3(C-H)_3$ and that the crossing between planar and benzvalene-type isomers should occur near tetrphosphinine $P_4(C-H)_2$.³⁰

Conclusion

The 24 possible valence isomers of $P_2(C-H)_4$ have been investigated at the electron-correlated ab initio theoretical level. Far beyond computational uncertainties, it emerges from this study that the three planar isomers (**1–3**) are distinctly more stable than the others. Next in stability come the diphosphabenzvalenes (**7–10**) and the Dewar diphosphabenzenes (**11–16**), followed by the prismanes (**17–19**) and the diphosphabicyclopentenyls (**20–24**). The various families of isomers have distinct ranges of stabilities, which practically do not overlap at the MP2 level, while diphosphabenzvalenes and Dewar diphosphabenzenes are somewhat more imbricate at the B3LYP level. The most detailed computations have been carried out for the three lowest structures (**1–3**) on the potential energy surface, using a variety of basis sets and computational levels. Each of these planar isomers is fully aromatic, as can be judged from the calculated bond lengths which are intermediate between single- and double-bond standard values and exclude any possibility of bond fixation. This and the fact that the relative energies of the various families of isomers follow the same order as in C_6H_6 suggest that diphosphinines bear a close resemblance to benzene, a feature that can be anticipated to hold in triphosphinines, but probably not in tetra- or pentaphosphinines.

Some comparisons between our computational results and the available experimental data are in order. First, the 1,4 planar isomer (**3**) has been shown to display more diradical character than the other two, which may explain its high and spontaneous reactivity. Second, all calculations, whatever the basis sets or computational method that is used, as well as semiquantitative considerations based on standard bond strengths and resonance energies, point to the conclusion that the ortho isomer, 1,2-diphosphabenzene (**1**), is the most stable among the three planar isomers. This finding contrasts with the utter absence of experimental observation for this isomer, leading some workers in the field to suppose that it is unstable or less stable than the other two. This latter supposition is definitely ruled out by the present study, which suggests that the reason the 1,3 or 1,4 isomers are preferentially formed might rather lie in the synthetic methods that are used to generate diphosphinines. Indeed, 1,3 isomers (**2**) are always formed by ring expansion of four-membered rings in which the phosphorus atoms are already in the 1,3 position,^{8,9} while the 1,4 isomer (**3**) is obtained either from an 1,4-bicyclooctatriene¹⁰ or a dichloro-1,4-diphosphabicycloheptadiene,¹¹ two compounds in which the phosphorus atoms are right at the outset in the 1,4 position. Thus, it is our feeling that the synthetic methods that have been used to date favor the formation of 1,3 or 1,4 isomers and that the preparation of various derivatives of the 1,2 isomer should be feasible. It is hoped that the present study will stimulate further efforts to prepare such isomers by using new synthetic methods.

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(30) Calculations of the valence isomers of tri-, tetra-, and pentaphosphinines are in progress.