

Ab Initio Conformational Study of the P₆ Potential Surface: Evidence for a Low-Lying One-Electron-Bonded Isomer

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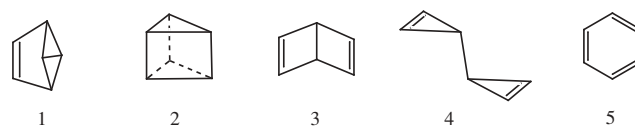
ABSTRACT: The low-lying isomers of the P₆ species are investigated at various levels of calculations, ranging from MP2/6-31G(d) to CCSD(T) in triple-zeta basis set involving polarization functions up to f. In addition to the five possible normal-valent isomers, which obey the octet rules, several other conformations are found to be stationary points on the potential energy surface. Among the five normal-valent isomers, the benzvalene structure is found to be the most stable one, in agreement with former studies. The benzene-like D_{6h} planar hexagon is the least stable one, lying 32.3 kcal/mol over benzvalene, and spontaneously distorts to a less symmetrical, nonplanar six-membered ring. Above the benzvalene structure, and lying, respectively, 5.8 and 15.8 kcal/mol higher, the two lowest lying isomers are the prismane and the chair-like forms. This latter conformation, which does not obey the octet rule, exhibits two one-electron P–P hemibonds and can be considered as a generic model for a new category of heterobenzene analogs, among which is the recently discovered dimer of diphosphirenyl radical. © 2007 Wiley Periodicals, Inc. *Heteroatom Chem* 18:129–134, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20324

INTRODUCTION

Hexaphosphabenzene, the formal analog of benzene obtained by replacement of each CH unit by an iso-

electronic phosphorus atom, was first synthesized in 1985 by Scherer et al. [1], as part of the triple-decker sandwich complex [{(η⁵-Me₅C₅)Mo}₂(μ,η⁶-P₆)]. The crystal structure analysis of this compound revealed planar P₆ ring with equalized P–P bond lengths. However, it soon became evident that the cyclic form was not the sole, and not the lowest, isomer of the isolated P₆ cluster.

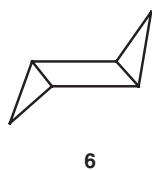
If one excepts some chemically unrealistic arrangements, there are five possible valence isomers (1–5) that comply with the octet rule. By analogy with the benzene valence isomers, these will be referred to in what follows as benzvalene (1), prismane (2), Dewar (3), bicyclopropenyl (4), and benzene (5) structures.



Soon after the synthesis of P₆ as a complex ligand, some early ab initio calculations [2,3] showed that isolated cyclic hexaphosphabenzene should be stable, unlike the isoelectronic N₆ cluster, against dissociation to three diatomic fragments, and proposed the benzvalene and prismane forms as alternative low-lying structures. These two latter structures were subsequently found to be significantly more stable than the benzene form, by some 30 kcal/mol, by Jones and Hohl [4] who applied a Car–Parrinello technique [5] coupled to a density functional of local spin density (LSD) type. One

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unexpected outcome of this computational study was the finding of a curious structure **6**, which does not obey normal valency rules, lying only 13.6 kcal/mol over the global minimum **1**. The Car–Parrinello investigations were completed [6] with the inclusion the Dewar (**3**) and bicyclopropenyl (**4**) structures, which were found to lie 15.0 and 29.3 kcal/mol over benzvalene (**1**), leading to the order of stability: **1** < **2** < **3** < **4** < **5**. Somewhat surprisingly, structure **6** was not considered in subsequent computational studies.



The first ab initio computational study that investigated the five valence isomers (**1–5**) at a consistent level of theory was that of Warren and Gimarc [7]. At the Hartree–Fock/6-31G* level, the results for structures **1**, **2**, and **5** confirmed the Car–Parrinello calculations of Jones et al. [4,6], whereas the agreement was poorer for structures **3** and **4**. The cyclic isomer **5** was characterized as a true minimum in 6-31G* basis set, but was found to lie much higher in relative energy and to display one imaginary frequency in 4-31G* basis set, thus showing clearly the basis set dependency of ab initio calculations for P₆. Subsequent calculations by Gimarc and Zhao, still in 6-31G* basis set, showed that electron correlation effects are also important, since the prismane structure **2** was found to lie 22 kcal/mol above benzvalene at the MP2 level [8], versus only 6 kcal/mol at the Hartree–Fock level.

Further, ab initio calculations focused on the relative energies of the prismane and benzvalene isomers, and definitely established the benzvalene form as the global minimum for isolated P₆. These studies, performed at the MP2, CCSD(T) or gradient-corrected density functionals, showed once again that both basis set and level of correlation are important for yielding reliable relative energies of phosphorus clusters [9–11].

On the experimental side, Schwarz and Jutzi achieved a major breakthrough in 1999 with the detection of neutral P₆ in the gas phase by neutralization and reionization (NR) mass spectrometry [12]. As the Cp₂P₆ and CpP₆⁺ precursors display a hexaphosphabenzvalene skeleton stabilized by cyclopentadienyl ligand(s), the same structure was assumed to be that of the observed isolated P₆ molecule. It is noteworthy that other low-lying structures were found to be secondary local minima on

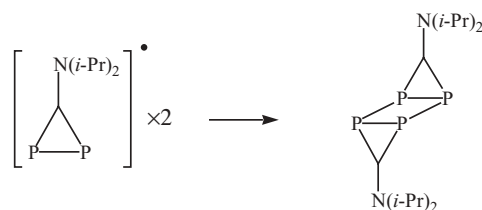
the CpP₆⁺ potential surface in computations using the density functional theory (DFT) [13].

Another fascinating experiment, indirectly related to the structure of P₆, was the isolation of a tetraphosphabenzene valence isomer displaying a one-electron P–P hemibond [14]. This species, which results from the dimerization of the diphosphirenyl radical (Scheme 1), bears strong analogy with the P₆ isomer **6** above, which suggests that the latter could also involve P–P one-electron hemibonds. Other P–P bonds of this type have recently been observed in a bis(phosphinine) [15]. It therefore appears that structure **6** of P₆ deserves investigation, as being the prototype of various possible phosphabenzenes and other complexes involving phosphorus clusters.

The above-mentioned computational and experimental results show that the P₆ cluster is stable, both as an isolated species and as a constituent of organic or organometallic complexes. They also show that several low-lying structures span a rather small range of energy, unlike the C₆H₆ analog [7]. What is still missing, however, is a consistent study of the five valence isomers (**1–5**) at a modern level of computation. One motivation for the present work is to provide these missing data, which we feel to be important on account of the apparent ability of the P₆ unit to get involved in complexes under several isomeric forms. Another aim of this study is to perform an in-depth investigation, both quantitative and qualitative, of structure **6**, which has been unduly neglected in most previous computational studies. Lastly, the status of the planar P₆ ring as a minimum or transition state, and its possible distortions off the plane, will also be examined.

THEORETICAL METHODS

All calculations have been done with the Gaussian 03 series of programs [16]. The geometry optimizations have been performed at two levels of theory. The first level used the Møller–Plesset many-body perturbation theory at second order (MP2), in the frozen-core approximation, with the 6-31G(d) basis set, which



SCHEME 1 Dimerization of the diphosphirenyl radical (from Canac et al. [14]).

TABLE 1 Relative Energies, in kcal/mol, of the P₆ Isomers at Various Computational Levels

	1	2	3	4	5	6	7	8	9	Ref.
HF/6-31G(d)	0	6.5	18.0	20.6	30.9					7
DFT-LSD	0	3.9	15.0	29.3	33.7	13.6		27.0		4,6
MP2/6-31G(d) ^{a,b}	0	21.7	21.5	19.7	23.9*	13.6	21.2*	20.9	33.3*	This work
CCSD(T)/6-31G(d) ^a	0	17.5	23.6	18.2	23.7	21.4	21.8	21.8	39.6	This work
MP2/cc-pVTZ ^c	0	7.6	15.6	22.9	33.5	3.6	28.8	28.2	30.0	This work
CCSD(T)/cc-pVTZ ^c	0	5.8	22.8	21.4	32.3	15.8	29.6	29.5	40.1	This work

^aGeometries optimized at the MP2 level in 6-31G(d) basis set.

^bAn asterisk denotes a stationary point that has one or more imaginary frequencies and is therefore not a minimum on the potential surface.

^cGeometries optimized at the MP2 level in cc-pVTZ basis set.

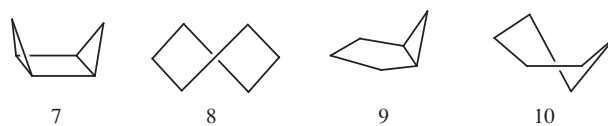
Hartree–Fock calculations of Warren and Gimarc [7]: the benzvalene structure **1** is the absolute minimum on the potential energy surface, whereas the highest structure is the benzene form **5**, the other structures lying in between and spanning a rather small energy range. On the other hand, the energy of the prismane structure **2** is significantly upshifted by electron correlation, lying 21.7 kcal/mol above **1** at the MP2 level, versus 6.5 kcal/mol at the Hartree–Fock level.

Going to the much more accurate CCSD(T) level, in the same basis set, does not significantly modify the MP2 picture. More important are the basis set effects. At the MP2 level, when increasing the size of the basis set from the modest 6-31G(d) basis set to the relatively sophisticated cc-pVTZ, which is of triple-zeta quality and involves polarization functions up to f, the prismane structure **2** drops drastically in energy whereas the aromatic structure **5** goes up in energy. Once again, the CCSD(T) level, in the same basis set, confirms the MP2 relative energies. The basis set dependency of the relative energies can be understood if one assumes that strained conformations require flexible basis sets to be adequately described, and that poor basis sets exaggerate strain energies. According to Gimarc's calculations, **5** is not strained, **1**, **3**, and **4** have moderate strain energies ranging from 13 to 21 kcal/mol, and **2** has a much larger strain energy, 53 kcal/mol. As a consequence, lowering the strain energies by increasing the basis set size results in a lowering of all structures relative to **5**, and in a further lowering of the prismane structure **2** relative to **1**, **3**, and **4**.

Other Isomers

One common feature of our ab initio calculations and the earlier DFT–LSD calculations of Jones and Hohl [4] is the finding that the D_{6h} structure **5** is a stationary point, but not a minimum on the potential surface. Consequently, one may expect the planar regular hexagon to distort to less symmetrical but more stable structures. In accord, we have

investigated five types of distorted six-membered rings. Structure **6** is the chair conformation, analogous to the dimer of the diphosphirenyl radical in Scheme 1, and **7** is its “boat” analog. The other isomers are the twist (**8**), sofa (**9**), and half-chair (**10**) conformations.



At the MP2/6-31G(d) level, no stationary point for the half-chair geometry (**10**) could be found on the potential surface. The geometries for the other structures, **6–9**, are displayed in Fig. 2.

Although the isomers **6** and **8** are true minima, the other two, **7** and **9**, are characterized as transition states at this level. Structure **7**, first considered in the initial guess geometry as the “boat” counterpart of **6**, turns out to be very different with a wide P4–P2–P5 angle (see Fig. 2), and rather looks like a distorted aromatic ring, like **8**. Besides,

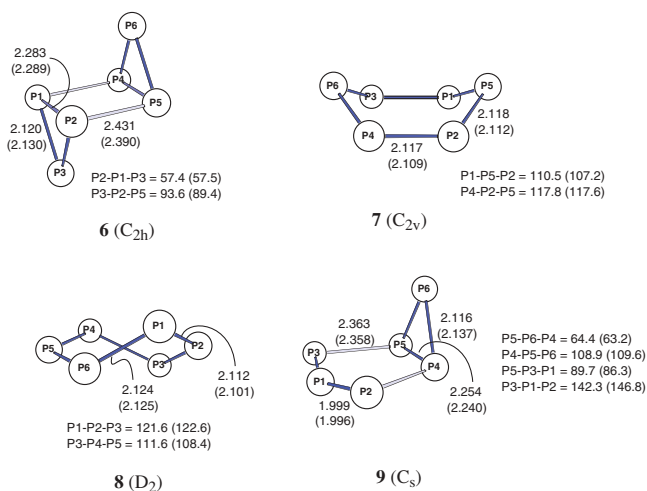


FIGURE 2 Some selected geometrical data for the isomers **6–9** of P₆, as optimized at the MP2 level in 6-31G(d) basis set. Bond lengths are in angstroms, and angles are in degrees. Data optimized in cc-pVTZ basis set are indicated in parentheses.

both structures have P–P bond lengths in the range 2.11–2.12 Å, intermediate between typical single and double P–P bonds. These two structures are in fact very similar, and one can consider **8** as a symmetry-broken analog of **7**. It is therefore expected that both **7** and **8** have a significant aromatic character and that **8**, which is characterized as a true minimum, is the P₆ conformation that is the closest analog of benzene at the MP2/6-31G(d) level.

The bond lengths of the isomer **6** are particularly insightful (Fig. 2). Three clear-cut categories of bond lengths are found: (i) the P1–P2 and P4–P5 bond lengths of 2.283 Å are typical single bonds; (ii) the remaining bond lengths of each three-membered rings, 2.12 Å, suggest partial double bonds with a bond order of 1.5; (iii) lastly, the long P1–P4 and P2–P5 bond lengths (2.431 Å) suggest a bond order smaller than unity and could reveal the presence of one-electron bonds.

The energies of structures **6–9** relative to the lowest structure **1** are displayed in Table 1. At the MP2/6-31G(d) level, the rather exotic structure **6** appears as a low-lying isomer, 13.6 kcal/mol above **1**, whereas the distorted six-membered rings **7** and **8** are slightly lower than the planar aromatic hexagon **5**, as expected since this latter structure is not a minimum. Increasing the level of theory from MP2 to CCSD(T) has the effect of upshifting the energy of **6** relative to **1**, while the other isomers remain stable, indicating that **6** is particularly sensitive to electron correlation effects. However, reoptimizing the geometries of structures **1** and **6** at the CCSD(T) level leads to negligible changes in the CCSD(T) absolute energies, 0.2 and 0.4 kcal/mol for **1** and **6**, respectively. On the other hand, increasing the basis set lowers the energy of **6** (compare entries 3 and 5 of Table 1) relative to the other isomers. Thus, increasing the level of correlation and increasing the basis set have opposite effects for structure **6**, so that the MP2/6-31G(d) calculated relative energy is expected to be realistic for this structure. Indeed, structure **6** is found to lie 15.8 kcal/mol above **1** at our best level of calculation, in good agreement with the MP2/6-31G(d) level and with the early DFT–LSD calculation of Jones and Hohl [4].

Structures **7** and **8** remain extremely close in energy at all computational levels, indicating the great fluxionality of the six-membered ring conformation of P₆.

A FRAGMENT ORBITAL ANALYSIS OF BONDING IN STRUCTURE **6**

On account of its two long P1–P4 and P2–P5 bond lengths, structure **6** can be viewed as two triphospha-

cyclopropenyl radicals held together by two weak bonds. A qualitative analysis of the bonding scheme of this molecule will therefore be performed in terms of fragment orbitals, by considering **6** as the product of the recombination of two triangular P₃ units.

The fragment orbitals and the qualitative interaction diagram, restricted to the π molecular orbitals of the P₃ fragments, are displayed in Fig. 3. Note that the two highest lying orbitals of each fragment, 2b₁ and 1a₂, should be degenerate if the three-membered rings had the shape of equilateral triangles. However, the P1–P2 bond length being longer than P1–P3 and P2–P3 (with identical distortions in the other P₃ fragment) lifts the degeneracy in the way indicated in Fig. 3, lowering the 1a₂ orbital with respect to 2b₁.

As the two P₃ fragments are brought together from infinite separation to bonding distances, the two 1b₁ fragment orbitals form one bonding and one antibonding combinations, Ψ_1 and Ψ_2 , which are both doubly occupied. On the other hand, only the bonding combination (Ψ_3) of the 1a₂ orbitals is occupied. These orbital occupancies can be used to characterize various types of bonds that hold phosphorus atoms together in structure **6**.

Let us first consider the interfragment bonds, P1–P4 and P2–P5. As the Ψ_1 and Ψ_2 orbitals are alternatively bonding and antibonding, the only contribution to interfragment bonding arises from Ψ_3 . As this interaction brings two bonding electrons for two linkages, each linkage can be considered as displaying a one-electron bond (also called hemibond), hence the rather long bonding distance of 2.431 Å. Similar hemibonds (P–P = 2.427 Å) have been recently experimentally characterized in an analogous P₄ rectangular moiety [20].

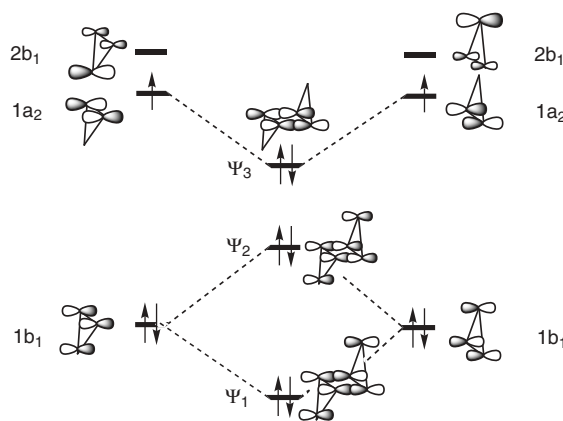
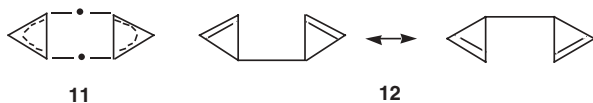


FIGURE 3 Schematic diagram showing the construction of the highest occupied molecular orbitals of the isomer **6** of P₆ from the interaction of two triangular P₃ radicals.

The analysis of the intrafragment linkages follows the same lines. Focusing on the left fragment alone, and on the P1–P3 and P2–P3 linkages, one may notice that the $1b_1$ and $1a_2$ fragment orbitals are topologically equivalent to the π orbitals of allyl radical. Therefore, the P1–P3 and P2–P3 linkages have a bond order of 1.5 and can be considered as partial double bonds, in agreement with the bond lengths of 2.120 Å. All in all, structure **6** can be represented by the bonding scheme **11**, which emphasizes the one-electron character of the interfragment bonds, or by the resonating scheme **12**.



CONCLUSION

Ten low-lying isomers of the P_6 clusters have been investigated at increasing levels of the *ab initio* molecular orbital theory. Both basis set effects and electron correlation effects have a very significant influence on the relative energies; however, these two effects act in opposite directions, so that our highest computational level, CCSD(T) in cc-pVTZ basis set, yield relative energies that are very close to former calculations at the Hartree–Fock/6-31G(d) level, for the five normal-valent isomers. In agreement with this latter study, benzvalene is the most stable conformer, the six-membered ring is the highest normal-valent isomer, and the prismane, Dewar, and bicyclopentenyl forms lie in-between. On the other hand, the six-membered ring is found, in the present study, to lose its planarity and to distort to a less symmetrical and quite fluxional twisted structure.

Among the low-lying structures, the chair-like conformation **6**, previously discovered by Jones et al., lies only 15.8 kcal/mol above benzvalene, although it does not obey normal valence rules. A fragment orbital diagram shows that this species clearly displays two linkages that are of the one-electron hemibond type. The present study thus shows that the one-electron option is to be considered in clusters involving phosphorus atoms and support similar interpretations in recent experimental works [14,15,21]. As such, the chair-like conformation **6** can be considered as a generic model for a new category of heterobenzene analogs.

REFERENCES

[1] Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew Chem Int Ed Engl* 1985, 24, 351.

- [2] Nagase, S.; Ito, K. *Chem Phys Lett* 1986, 126, 43.
 [3] Nguyen, M. T.; Hegarty, A. F. *J Chem Soc Chem Commun* 1986, 383.
 [4] Jones, R. O.; Hohl, D. *J Chem Phys* 1990, 92, 6710.
 [5] Car, R.; Parrinello, M. *Phys Rev Lett* 1985, 55, 2471.
 [6] Jones, R. O.; Seifert, G. *J Chem Phys* 1992, 96, 7564.
 [7] Warren, D. S.; Gimarc, B. M. *J Am Chem Soc* 1992, 114, 5378.
 [8] Gimarc, B. M.; Zhao, M. *Coord Chem Rev* 1997, 158, 385.
 [9] Häser, M.; Schneider, U.; Alhrlachs, R. *J Am Chem Soc* 1992, 114, 9551.
 [10] Ballone, P.; Jones, R. O. *J Chem Phys* 1994, 100, 4941.
 [11] Häser, M.; Treutler, O. *J Chem Phys* 1995, 102, 3703.
 [12] Schröder, D.; Schwarz, H.; Wulf, M.; Sievers, H.; Jutzi, P.; Reiher, M. *Angew Chem Int Ed* 1999, 38, 3513.
 [13] Reiher, M.; Schröder, D. *Chem Eur J* 2002, 8, 5501.
 [14] Canac, Y.; Bourissou, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Science* 1998, 279, 2080.
 [15] Choua, S.; Dutan, C.; Cataldo, L.; Berclaz, T.; Geoffroy, M.; Mézailles, N.; Moores, A.; Ricard, L.; Le Floch, P. *Chem Eur J* 2004, 10, 4080.
 [16] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision A.1*, Gaussian, Inc.: Pittsburgh, PA, 2003.
 [17] (a) Woon, D. E.; Dunning, T. H., Jr. *J Chem Phys* 1993, 98, 1358; (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J Chem Phys* 1992, 96, 6796; (c) Dunning, T. H., Jr. *J Chem Phys* 1989, 90, 1007.
 [18] (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem Phys Lett* 1989, 157, 479; (b) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *J Chem Phys Lett* 1990, 165, 513.
 [19] Schleyer, P. von R.; Jiao, H.; Hommes, N. van E.; Malkin, V. G.; Malkina, O. L. *J Am Chem Soc* 1997, 119, 12669.
 [20] Kato, T.; Gornitzka, H.; Schoeller, W. W.; Baceiredo, A.; Bertrand, G. *Angew. Chem Int Ed* 2005, 44, 5497.
 [21] Grützmacher, H.; Breher, F. *Angew Chem Int Ed* 2002, 41, 4006.