Structures, energetics and vibrational spectra of the valence isomers of phosphinine. An ab initio and DFT study

3 AUTHORS, INCLUDING:

Tandabany C. Dinadayalane
Clark Atlanta University
66 PUBLICATIONS   1,155 CITATIONS

SEE PROFILE

G Narahari Sastry
Indian Institute of Chemical Technology
262 PUBLICATIONS   5,262 CITATIONS

SEE PROFILE

Structures, energetics and vibrational spectra of the valence isomers of phosphinine. An ab initio and DFT study

U. Deva Priyakumar, T.C. Dinadayalane, G. Narahari Sastry *

Department of Chemistry, Pondicherry University, R. Venkatraman Nagar, Kalapet, Pondicherry 605 014, India

Received 19 September 2000; in final form 4 January 2001

Abstract

The structures and energetics of nine valence isomers of phosphinine, $(CH)_5P$, have been investigated by ab initio (HF, MP2 and CCSD(T)) and hybrid density functional (B3LYP) methods. The relative stability ordering of the $(CH)_5P$ isomers is similar to those of $(CH)_6$. Strain energies are evaluated for all the non-planar isomers based on the sum of standard bond strengths, taking the planar resonance stabilized isomer, phosphinine as the reference. Lower magnitudes of the frequencies corresponding to the first few normal modes compared to their benzene isomers account for smoother isomerization reactions among them. © 2001 Published by Elsevier Science B.V.
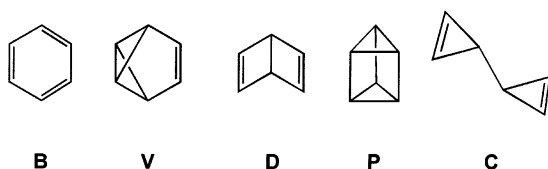
1. Introduction

Among more than 200 possible isomers of benzene, the five classical valence isomers, Benzene (**B**), Benzvalene (**V**), Dewar Benzene (**D**), Prismane (**P**) and bi-Cyclopropenyl (**C**) are predominantly interesting (Scheme 1). After the successful synthesis of these valence isomers, they have become subjects of various theoretical studies [1–4]. Replacement of one or more methine groups in the six-membered ring by an isoelectronic group opened up the exciting field of heteroaromatics [5–11]. Recent calculations predicted that phosphinine as well as di- and triphosphabenzenes are almost as aromatic as benzene based on geometric, energetic and magnetic criteria [8]. The classical valence isomers of $(CH)_5P$, where one of the methine groups is replaced by the isoelectronic P

(considering only the valence electrons), gives rise to nine possible isomers: one benzene (**B1P**), three benzvalenes (**V1P**, **V2P**, and **V3P**), two Dewar benzenes (**D1P** and **D2P**), one prismane (**P1P**) and two bicyclopropenyls (**C1P** and **C2P**) and these structures form an interesting class of compounds (Scheme 2). The synthesis of many of these valence isomers of phosphinine was achieved by ingenious isomerization reactions carried out by Regitz and co-workers starting from Dewar phosphinine [12,13]. Interestingly, these valence isomers of phosphinine exhibit novel modes of binding to transition metal fragments [5,14]. With this background, it is surprising to note that while the di-, tri-, tetra- and pentaphosphabenzene, P_6 and their valence isomers continue to draw theoretical attention, computational studies on valence isomers of phosphinine are conspicuously missing [6,8,15–17]. Proper description of molecular and electronic structures is essential to understand and appreciate the relationships among isoelectronic species. This Letter, to our knowledge, is the first systematic
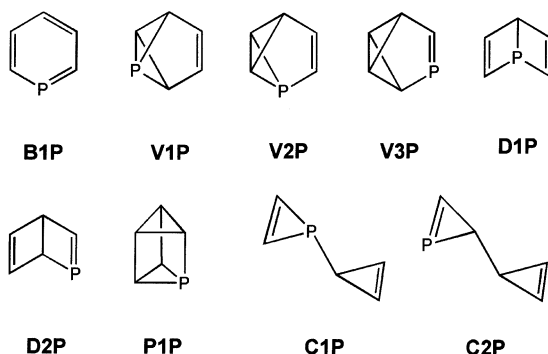
---

* Corresponding author. Fax: +91-413-655-211.

  E-mail address: gnsastry@yahoo.com (G. Narahari Sastry).

Scheme 1. The valence isomers of benzene: Benzene (**B**), Benzvalene (**V**), Dewar benzene (**D**), Prismane (**P**) and Bicyclopropenyl (**C**).

Scheme 2. The nine valence isomers of phosphinine, $(CH)_5P$, considered in this study.

attempt to study the valence isomers of phosphinine at quantitatively reliable levels of theory and is aimed at understanding the structure, energetics and vibrational frequencies based on the standard electron-correlated ab initio and DFT calculations. Examination of the equilibrium geometries, relative stabilities and harmonic frequencies of all nine valence isomers of $(CH)_5P$ provides a clear idea of its potential energy surface.

2. Computational details

The geometries of all the structures are fully optimized within the symmetry constraints initially at HF/6-31G* level [18]. Further refinement of geometries is done at B3LYP and MP2 levels with the 6-31G* basis set. Geometry optimizations are carried out also using the 6-31G** basis set at MP2 level to assess the effect of adding a set of polarization functions on the peripheral hydrogens. The MP2/6-31G* and MP2/6-31G** geometries are virtually identical indicating that the 6-31G* basis

set is adequate in giving proper equilibrium geometries. The nature of the stationary points is characterized by frequency calculations at HF and B3LYP [19,20] levels, which yielded all real frequencies for all the structures, indicating that all the valence isomers considered in the study are local minima. Based on the better agreement between MP2 and CCSD(T) energetics compared to those of HF and B3LYP as well as observations from previous calculations, MP2/6-31G* is the best choice for obtaining equilibrium geometries. Therefore, single point calculations are done at CCSD(T)/6-31G* level on MP2 geometries. Previous studies on related systems show that the major Slater determinant in a multi-determinant wave function is largely predominant and employing multi-reference methods is unnecessary to tackle such problems [6]. The couple cluster method, which is known to yield quantitative results for chemical problems that are not severely multi-reference in nature, is expected to yield quantitatively reliable energetics. To test the adequacy of the basis set used in giving correct energetics, MP2 single point calculations are done with the 6-311+G** basis set, which is of triple ζ-quality with added polarization and diffuse functions on main group elements and on hydrogens. The enthalpy and zero point energy corrections for obtaining the best estimates are taken from the vibrational data at B3LYP level. All the calculations are done using GAUSSIAN 94 suite of programs [21]. The B3LYP/6-31G* frequencies are scaled with a factor of 0.98 [22,23].

3. Results and discussion

The optimized skeletal parameters obtained at MP2/6-31G* level are given in Fig. 1. The geometry of phosphinine is in good agreement with previous calculations [10]. While HF method consistently underestimates bond lengths for well-known reasons [18], the variations are smaller between B3LYP and MP2 levels. Marginal and consistent overestimation of bond lengths by B3LYP level is observed compared to MP2, and the bond angles are virtually identical. The change of basis set at MP2 level from 6-31G* to 6-31G**

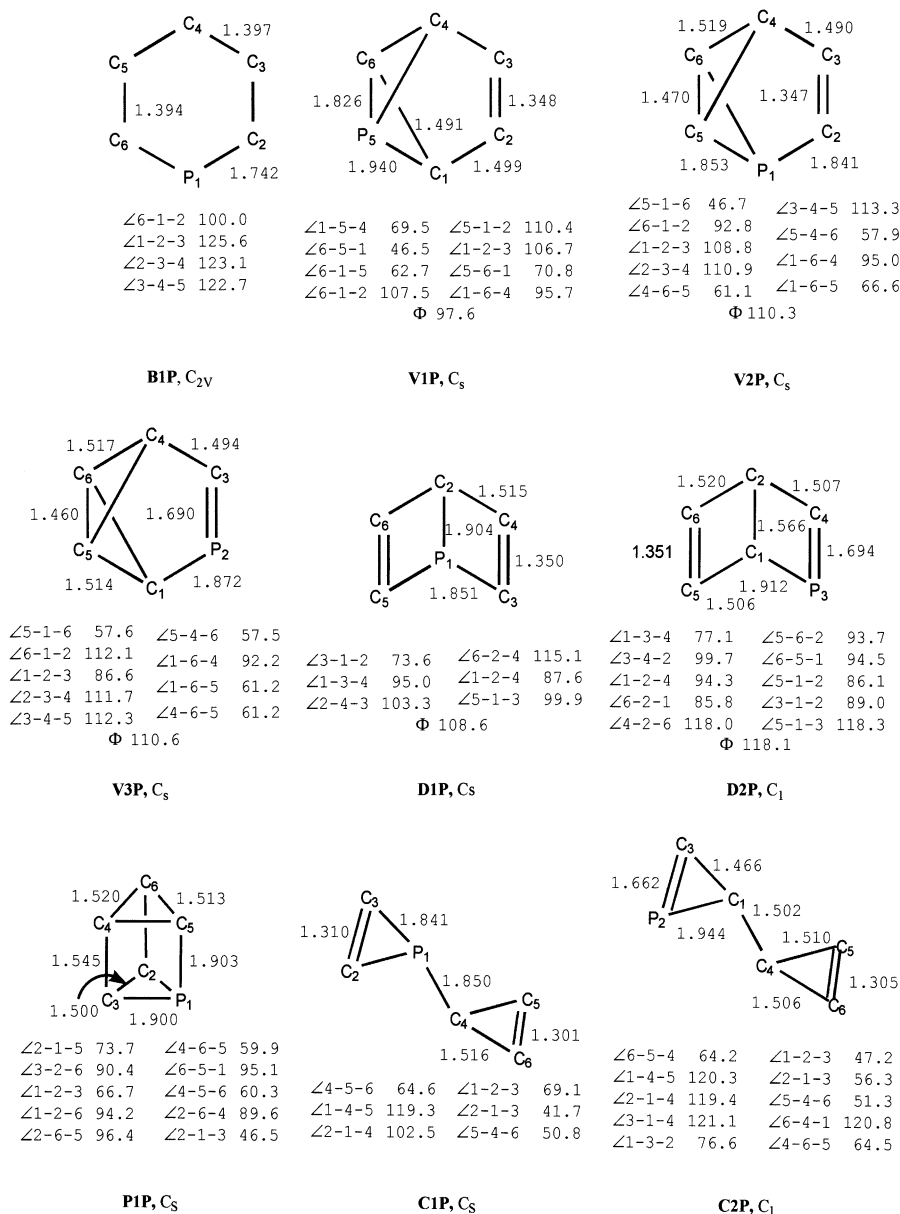Fig. 1. Selected geometric parameters of the valence isomers of phosphinine obtained at MP2/6-31G* level. Bond lengths are in Å and angles are in degrees. Φ is angle between the two planes formed by the three-membered rings in the bicyclobutane moiety in benzvalene and the four-membered rings in Dewar benzene isomers.

did not give any noticeable changes. The total energies at various levels of theory, along with zero point energy correction and enthalpy corrections (at 298 K) at B3LYP level are listed in Table 1. Table 2 gives the relative energies at various levels

of theory, along with the sum of standard bond strengths and the strain energies for each of the isomers. A quick look at the table clearly reveals that HF and B3LYP methods overestimate the stability of the planar isomer. MP2 method is in

Table 1
The total energies of the valence isomers of phosphinine at various levels of theory. Zero point corrections and enthalpy corrections are given at B3LYP/6-31G* level only. All values are given in Hartrees

Structure	HF/ 6-31G*	B3LYP/ 6-31G*	MP2/ 6-31G*	MP2/ 6-31G**	MP2/ 6-311+G**[a]	CCSD(T)/ 6-31G*[a]	ZPE[b]	Enthalpy Correction[b, c]
B1P	−532.95481	−534.87799	−533.69541	−533.73541	−533.82970	−533.77075	0.08463	0.09040
V1P	−532.87000	−534.79740	−533.62522	−533.66546	−533.76296	−533.69868	0.08320	0.08887
V2P	−532.86423	−534.78640	−533.61216	−533.65255	−533.74963	−533.68677	0.08223	0.08786
V3P	−532.84395	−534.77026	−533.59976	−533.64015	−533.73558	−533.67330	0.08266	0.08820
D1P	−532.86064	−534.78304	−533.60230	−533.64262	−533.74006	−533.68202	0.08199	0.08794
D2P	−532.84287	−534.77007	−533.59400	−533.63410	−533.73048	−533.67303	0.08250	0.08835
P1P	−532.80531	−534.73208	−533.55610	−533.59674	−533.69342	−533.63103	0.08263	0.08799
C1P	−532.78236	−534.70564	−533.52278	−533.56268	−533.66162	−533.60212	0.07724	0.08479
C2P	−532.78367	−534.71498	−533.53870	−533.57890	−533.67535	−533.61554	0.07930	0.08641

[a] Single point calculations on MP2/6-31G* geometries.
[b] ZPE and enthalpy corrections are obtained at B3LYP/6-31G* level.
[c] Enthalpy correction is obtained at 298 K.

Table 2
The relative energies for all the valence isomers of phosphinine at various levels of theory. The cumulative bond strengths and the strain energies (using Eq. (1)) are also given. All values are in kcal mol^{-1}

Structure	HF/ 6-31G*	B3LYP/ 6-31G*	MP2/ 6-31G*	MP2/ 6-31G**	MP2/ 6-311+G**[a]	CCSD(T)/ 6-31G*[a]	Best estimate[b]	Sum of bond strengths[c]	Strain energy
B1P	0.0	0.0	0.0	0.0	0.0	0.0	0.0	621	[d]
V1P	53.2	50.6	44.0	43.9	41.9	45.2	42.0	657	54.5
V2P	56.8	57.5	52.2	52.0	50.3	52.7	49.1	657	61.6
V3P	69.6	67.6	60.0	59.8	59.1	61.2	58.8	651	65.3
D1P	59.1	59.6	58.4	58.2	56.3	55.7	52.0	642	49.5
D2P	70.3	67.7	63.6	63.6	62.3	61.3	58.7	636	50.2
P1P	93.8	91.6	87.4	87.0	85.5	87.7	84.3	672	111.8
C1P	108.2	108.2	108.3	108.4	105.5	105.8	99.4	642	96.9
C2P	107.4	102.3	98.3	98.2	96.9	97.4	93.4	636	84.9

[a] Single point calculations on MP2/6-31G* geometries.
[b] Best estimate is obtained from Eq. (1) for all the structures.
[c] The bond strengths of C—C, C=C, C—P and C=P are 80, 145, 64 and 107 kcal mol^{-1}, respectively. (Taken from [24,25]).
[d] Phosphinine, **B1P**, is taken as the reference structure.

better quantitative agreement with CCSD(T) method compared to HF or B3LYP. The best estimate is obtained for all the valence isomers considered in this study, using Eq. (1).

$$\Delta E = \Delta E_{\text{CCSD(T)}}$$
$$+ \Delta E_{(\text{MP2/6-311+G**}-\text{MP2/6-31G*})} + \Delta H \quad (1)$$

ΔH is the enthalpy correction factor obtained by B3LYP/6-31G* method. The discussion of energetics from now on will be based on the best estimates unless otherwise specified. The strategy adopted to evaluate the strain energies of non-planar isomers is borrowed from [6]. Taking

Warren and Gimarc's resonance energies, obtained from homodesmic equations, of 25 and 16 kcal/mol for benzene and P_6, an interpolated value of 23.5 is obtained for phosphinine [15]. The resonance energy (23.5 kcal/mol) thus obtained is added to 621 kcal/mol, obtained by taking the sum of bond strengths for the Kekule form of phosphinine and the strain energies are evaluated by the following equation:

$$S(\mathbf{X}) = E(\mathbf{X}) - E(\mathbf{B1P}) + \sum BS_i(\mathbf{X}) - 644.5 \quad (2)$$

Here $S(\mathbf{X})$ is defined as the strain energy, $E(\mathbf{X}) - E(\mathbf{B1P})$ as the relative energy of isomer $\mathbf{X}$

with respect to **B1P** and $\sum BS_i(\mathbf{X})$ is obtained by summing the standard bond strengths [24,25].

However, in this approach identical bond strengths are assumed for a given type of bond in different molecules and to that end the calculated strain energies are only some approximate estimates. Hiberty et al. have predicted, based on the correlation of relative energies of $(CH)_6$ and P_6 valence isomers, that all the mono skeletally substituted isomers follow the same trend as that of benzene [6]. Although this is true to a great extent, the Dewar benzene isomer, **D1P**, is lower in energy than a Benzvalene isomer, **V3P**, consistently at all levels of theory. The relative energies of **D2P** and **V3P** are almost identical, which is again not in strict agreement with the prediction. However, the

relative stabilities of the rest of the isomers are similar to their benzene isomers.

The relative stabilities of the positional isomers are controlled by many factors. **V3P**, which contains P atom at the sp^2 centre, is obviously less stable compared to **V1P** and **V2P**. The 5 (or 6) centre is constrained to have smaller bond angles compared to 1 (or 4) centres in **V1P** and **V2P**, and naturally P which has a smaller natural angle brings in less strain in **V1P** when compared to **V2P**. The higher stability of **D1P** over **D2P** may be traced to the placement of P on an unfavourable sp^2 centre in **D2P**. In contrast, **C2P**, which has P on an sp^2 centre, is surprisingly more stable than **C1P**, despite the fact that the sum of the bond strengths is higher than that in **C1P**. This difference

Table 3
The B3LYP/6-31G* harmonic frequencies (cm^{-1}) of the valence isomers of phosphinine scaled uniformly with a factor of 0.98

Structure	Harmonic frequencies (cm^{-1})
B1P(C_{2v})	296.9 (B$_1$), 351.2 (A$_2$), 459.6 (A$_1$), 536.1 (B$_2$), 615.1 (B$_1$), 701.4 (B$_1$), 750.4 (A$_1$), 769.1 (B$_2$), 822.0 (A$_2$), 902.1 (B$_1$), 909.3 (A$_1$), 972.4 (A$_2$), 999.6 (B$_1$), 1002.8 (A$_1$), 1103.2 (B$_2$), 1195.4 (B$_2$), 1196.3 (A$_1$), 1298.7 (B$_2$) , 1416.2 (A$_1$), 1423.5 (B$_2$), 1547.6 (B$_2$), 1583.1 (A$_1$), 3093.0 (A$_1$), 3097.3 (B$_2$), 3113.9 (A$_1$), 3116.4 (B$_2$), 3133.3 (A$_1$)
V1P (C_s)	363.4 (A′), 395.0 (A″), 438.0 (A′), 574.3 (A″), 674.4 (A′), 691.1 (A′), 789.5 (A′), 798.1 (A″), 859.7 (A′), 871.4 (A″), 879.2 (A″), 905.3 (A″), 935.9 (A′), 975.1 (A′), 998.2 (A″), 1045.0 (A′), 1109.1 (A′), 1214.0 (A″), 1252.6 (A″), 1324.8 (A′), 1324.8 (A″), 1601.5 (A′), 3120.6 (A′), 3140.5 (A″), 3142.2 (A′), 3171.5 (A″), 3194.3 (A′)
V2P(C_s)	406.9 (A″), 470.6 (A″), 538.8 (A′), 580.0 (A′), 590.1 (A″), 644.7 (A′), 676.4 (A″), 770.8 (A′), 771.1 (A″), 792.6 (A′), 872.9 (A′), 907.4 (A″), 948.5 (A″), 980.4 (A′), 1057.5 (A″), 1063.0 (A′), 1101.6 (A′), 1107.5 (A″), 1181.5 (A′), 1285.4 (A′), 1364.0 (A′), 1585.6 (A′), 3095.1 (A′), 3128.7 (A′), 3132.6 (A″), 3145.3 (A′), 3174.7 (A′)
V3P(C_s)	365.3 (A″), 475.3 (A″), 495.0 (A′), 650.6 (A′), 682.7 (A′), 692.3 (A″), 751.7 (A′), 769.7 (A″), 795.6 (A″), 868.3 (A′), 908.1 (A″), 916.8 (A′), 931.2 (A′), 990.4 (A″), 1004.6 (A′), 1114.9 (A″), 1118.8 (A″), 1169.4 (A′), 1196.9 (A′), 1250.8 (A′), 1269.8 (A′), 1409.0 (A′), 3115.9 (A′), 3123.1 (A′), 3157.0 (A″), 3162.6 (A′), 3173.7 (A′)
D1P(C_s)	322.2 (A″), 331.5 (A′), 398.2 (A′), 565.2 (A″), 614.2 (A′), 657.8 (A′), 664.9 (A″), 751.8 (A″), 764.3 (A′), 794.6 (A′), 905.4 (A′), 925.8 (A″), 953.7 (A′), 976.9 (A″), 1015.7 (A′), 1051.0 (A″), 1099.4 (A′), 1212.0 (A″), 1257.9 (A″), 1268.1 (A′), 1560.6 (A″), 1593.5 (A′), 3064.9 (A′), 3088.8 (A″), 3092.8 (A′), 3168.7 (A″), 3169.8 (A′)
D2P(C_1)	253.6 (A), 328.6 (A), 418.5 (A), 511.7 (A), 706.0 (A), 747.1 (A), 803.4 (A), 852.3 (A), 858.2 (A), 888.4 (A), 931.5 (A), 944.2 (A), 966.3 (A), 992.6 (A), 1038.6 (A), 1103.1 (A), 1148.0 (A), 1164.1 (A), 1203.4 (A), 1254.0 (A), 1281.7 (A), 1591.4 (A), 3009.6 (A), 3054.5 (A), 3135.2 (A), 3138.4 (A), 3165.0 (A)
P1P(C_s)	454.7 (A″), 514.2 (A′), 569.8 (A′), 641.4 (A″), 689.3 (A′), 735.8 (A″), 768.8 (A′), 801.9 (A″), 846.1 (A′), 867.3 (A″), 917.1 (A′), 920.3 (A″), 931.5 (A′), 977.0 (A′), 993.8 (A″), 1014.9 (A″), 1042.1 (A′), 1176.5 (A″), 1190.4 (A′), 1218.4 (A′), 1249.1 (A″), 1319.9 (A′), 3128.7 (A″), 3137.2 (A′), 3140.5 (A″), 3145.3 (A′), 3154.8 (A′)
C1P(C_s)	54.6 (A″), 187.8 (A′), 192.3 (A″), 322.4 (A′), 385.2 (A″), 565.5 (A′), 605.7 (A′), 623.2 (A″), 688.4 (A′), 736.2 (A′), 757.8 (A″), 832.7 (A″), 865.7 (A″), 902.3 (A′), 918.2 (A′), 1000.1 (A″), 1004.5 (A″), 1034.2 (A″), 1123.9 (A′), 1273.9 (A′), 1642.3 (A′), 1714.6 (A′), 2966.6 (A′), 3167.4 (A″), 3204.1 (A′), 3204.9 (A″), 3250.3 (A′)
C2P(C_1)	63.8 (A), 179.0 (A), 277.4 (A), 332.9 (A), 460.3 (A), 567.2 (A), 611.7 (A), 677.3 (A), 785.3 (A), 842.3 (A), 897.0 (A), 917.8 (A), 954.6 (A), 1014.3 (A), 1016.3 (A), 1057.2 (A), 1103.0 (A), 1161.0 (A), 1193.0 (A), 1289.3 (A), 1396.8 (A), 1703.3 (A), 2994.9 (A), 3025.9 (A), 3157.9 (A), 3193.5 (A), 3237 (A)

between **C1P** and **C2P**, which is marginal at HF level, becomes very significant at all correlated levels. All the benzvalene isomers are highly strained compared to their Dewar benzene counterparts, which is consistent with the situation in pristine system, where the strain energies on Dewar benzene and benzvalene are 63.6 and 81.3 kcal/mol, respectively.

All the vibrational frequencies are given in Table 3. The first two vibrational frequencies of phosphinine, **B1P**, are the out-of-plane modes and are much lower in magnitude compared to the degenerate mode in benzene. This observation is consistent with previous theoretical and experimental results. The first few vibrational frequencies of all the valence isomers of phosphinine are lower in magnitude compared to their benzene counterparts, indicating easier skeletal reorganizations, facilitating the viability of isomerization reactions among them compared to their benzene counterparts. Detailed exploration of all the isomerization paths among the valence isomers of phosphinine is currently under progress in our laboratory.

4. Conclusions

The present study explores the potential energy surface of $(CH)_5P$ valence isomers and identifies all the local minima. The relative energy ordering of various classes of positional isomers follows trends similar to those of benzene and not as in P_6. The reduction in energy gap between the most stable and least stable isomers, lower strain energies and smaller magnitude of vibrational frequencies for the skeletal reorganizations compared to the benzene analogue, account for smoother skeletal rearrangements among the classical valence isomers of $(CH)_5P$.

Acknowledgements

References

[1] J.M. Schulman, R.L. Disch, J. Am. Chem. Soc. 107 (1985) 5059.
[2] Z. Li, D.W. Rogers, F.J. McLafferty, M. Mandziuk, A.V. Podosenin, J. Phys. Chem. A 103 (1999) 426.
[3] Y.-S. Cheung, C.-K. Wong, W.-K. Li, J. Mol. Struc. (THEOCHEM) 17–24 (1998) 454.
[4] M.D. Newton, J.M. Schulman, M.M. Manus, J. Am. Chem. Soc. 96 (1974) 17.
[5] G. Markl, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorous Chemistry, Thieme, Stuttgart, Germany, 1990, p. 220.
[6] L. Colombet, F. Volatron, P. Maitre, P.C. Hiberty, J. Am. Chem. Soc. 121 (1999) 4215.
[7] U.D. Priyakumar, G.N. Sastry, J. Am. Chem. Soc. 122 (2000) 11173.
[8] M. Hoffmann, P.v.R. Schleyer, M. Regitz, Eur. J. Org. Chem. (1999) 3291.
[9] A.R. Barron, A.H. Cowley, Angew. Chem. Int. Ed. Engl. 26 (1987) 907.
[10] V. Jonas, G. Frenking, Chem. Phys. Lett. 210 (1993) 211.
[11] G. Frison, A. Sevin, N. Avarvari, F. Mathey, P.L. Floch, J. Org. Chem. 64 (1999) 5524.
[12] J. Fink, W. Rosch, U.-J. Vogelbacher, M. Regitz, Angew. Chem. Int. Ed. Engl. 25 (1986) 280.
[13] K. Blatter, W. Rosch, U.-J. Vogelbacher, J. Fink, M. Regitz, Angew. Chem. Int. Ed. Engl. 26 (1987) 85.
[14] J. Simon, U. Bergstraber, M. Regitz, Chem. Commun. (1998) 867.
[15] D.S. Warren, B.M. Gimarc, J. Am. Chem. Soc. 114 (1992) 5378.
[16] S. Nagase, K. Ito, Chem. Phys. Lett. 126 (1986) 43.
[17] M.T. Nguyen, A.F. Hegarty, J. Chem. Soc. Chem. Commun. (1986) 383.
[18] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab initio Molecular Orbital Theory, Wiley, New York, 1986.
[19] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[20] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[21] M.J. Frisch, et al., GAUSSIAN 94, Gaussian Inc., Pittsburgh, PA, 1995.
[22] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.
[23] M.A. Palafox, Int. J. Quant. Chem. 77 (2000) 661.
[24] W. Kutzelnigg, Angew. Chem. Int. Ed. Engl. 23 (1984) 272.
[25] M.W. Schmidt, P.N. Truong, M.S. Gordon, J. Am. Chem. Soc. 109 (1987) 5217.