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Theoretical Studies on Inorganic Ring Systems. Tetraphosphabicyclobutane, Cyclotriphosphane, and White Phosphorus: Ring Strain and Hybridization

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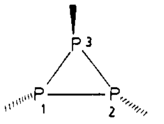
The electronic nature of white phosphorus, cyclotriphosphane, and tetraphosphabicyclobutane is investigated by ab initio calculations at a double-ζ level and with inclusion of electron correlation. The photoelectron spectrum of the last compound is reported as well, the assignment of the bands being based on the results of the ab initio calculations. The analysis of localized orbitals reveals that in tetraphosphabicyclobutane the central bond has almost the same p character as the peripheral bonds. The bonding situation is similar to that in cyclotriphosphane but rather different from that in cyclopropane. In contrast to bicyclobutane, tetraphosphabicyclobutane and cyclotriphosphane are almost free of ring strain, as proven by corresponding isodesmic reactions.

Introduction

Since Baeyer[1] first studied deviations of carbon from tetrahedral valency, the electronic structure of strained ring hydrocarbons has been the subject of increasing interest.[2] Early attention focused on cyclopropane, as well documented in the classical contributions of Walsh,[3] Coulson and Moffitt,[4] and Förster.[5] A later milestone in the understanding of the electronic nature of strained hydrocarbons is the detection of through-bond vs. through-space interaction.[6]



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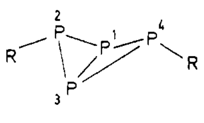

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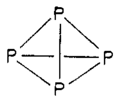

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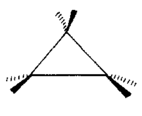

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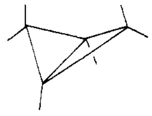

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The chemistry of inorganic ring systems is very different from that of carbon-hydrogen ring compounds. Their bonding properties are not well understood, although a large amount of experimental data has been collected in recent reviews.[7] It is the purpose of this paper to deal with the electronic structure of a number of phosphorus ring compounds.[8] The following points will be discussed in detail: (a) interpretation of the photoelectron spectrum of **2** (R = $N(SiMe_3)_2$) by means of ab initio calculations on **2** (R = H) and some of its derivatives (R = CH_3, NH_2); (b) Mulliken population analyses of **1**-**3** in terms of localized orbitals and a comparison with the strain-free compounds phosphine and diphosphine; (c) ring strain in **1**-**3** as obtained from studies of isodesmic reactions. The results obtained will be compared with the findings for analogous carbon-hydrogen systems, i.e. cyclopropane (**4**) and bicyclobutane (**5**).

Theoretical Procedure

Our analysis of the bonding in **1**-**3** is based on the results of ab initio SCF calculations. A few selected calculations were also performed with inclusion of electron correlation using the PNO-CI and CEPA schemes.[9,10] The following basis sets were used for the ab initio calculations.

Table I. Energies of the Highest Molecular Orbitals of Parent **2** (R = H) Obtained with the Various Basis Sets[a]

HOMO	energy, eV[b]		
i	basis I	basis II	basis III
0	5.61 (a_1)	8.96 (a_1)	8.91 (a_1)
1	6.24 (b_1)	9.64 (b_1)	9.58 (b_1)
2	7.51 (a_2)	10.90 (a_2)	10.83 (a_2)
3	7.84 (b_2)	11.01 (b_2)	10.96 (b_2)
4	7.93 (a_1)	11.51 (a_1)	11.46 (a_1)
5	9.80 (b_2)	12.67 (b_2)	12.61 (b_2)
6	12.50 (a_1)	15.31 (a_1)	15.26 (a_1)

[a] Symmetry designations (in parentheses) are according to C_{2v}. [b] Negative energies.

(1) Basis I refers to a minimal GTO basis set for first- and second-row elements as developed by Pople et al.[11]

(2) Basis II consists of Gaussian lobe functions.[12] It is of double-ζ quality, supplemented by polarization functions at phosphorus (DZ+P) and constructed from the following Huzinaga[13] bases:

C (7,3) in the contraction (4,3×1/2,1)
N (8,4) in the contraction (5,3×1/3,1)
P (10,6,1) in the contraction (5,5×1/4,2×1/1); $\zeta_d = 0.5$
H (4) in the contraction (3,1)

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(1) Baeyer, A. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269.

(2) Greenberg, A.; Liebman, J. F. *Strained Molecules*: Academic: New York, 1978. Liebman, J. F.: Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. See also: Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814.

(3) Walsh, A. D. *Trans. Faraday Soc.* **1946**, *42*, 56; **1947**, *43*, 60, 158; *Discuss. Faraday Soc.* **1947**, *No. 2*, 18. See also: Bent, H. A. *Chem. Rev.* **1961**, *61*, 275. Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907. Günther, H. *Tetrahedron Lett.* **1970**, 5173.

(4) Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1. See also: Bernett, W. A. *J. Chem. Educ.* **1967**, *44*, 17.

(5) Förster, Th. *Z. Phys. Chem., Abt. B* **1939**, *43*, 58.

(6) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. Klessinger, M. *Elektronenstruktur organischer Moleküle*; Verlag Chemie: Weinheim, 1982.

(7) (a) Baudler, M. *Angew. Chem.* **1982**, *94*, 520; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492. (b) Roesky, H. W. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 239. (c) Keat, R. *Top. Curr. Chem.* **1982**, *102*, 89.

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(9) Ahlrichs, R.; Lischka, H.; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *62*, 1225.

(10) Meyer, W. *Int. J. Quantum Chem.* **1971**, *S5*, 341; *J. Chem. Phys.* **1973**, *58*, 1017.

(11) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(12) The computer program used is described by: Ahlrichs, R. *Theor. Chim. Acta* **1974**, *33*, 157. See also ref 9.

(13) Huzinaga, S. "Approximate Atomic Functions II"; Technical Report; The University of Alberta, 1971.

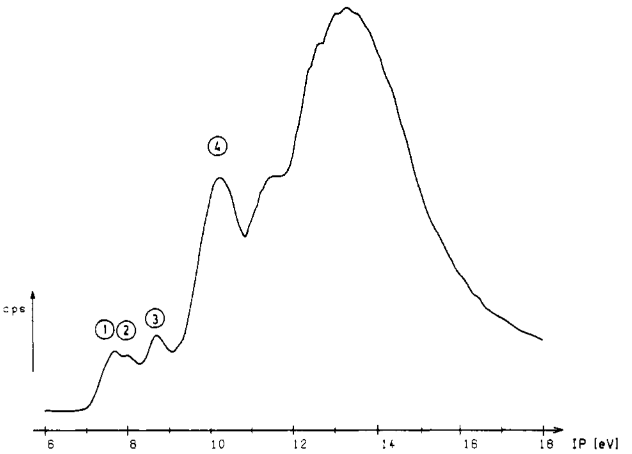


Figure 1. The He I photoelectron spectrum of **2** (R = $N(SiMe_3)_2$ (perpendicular)).

(3) Basis III consists of Gaussian lobe functions. The contraction scheme is

C as basis II
N as basis II
P (10,6,1) in the contraction (4,6×1/3,3×1/1); $\zeta_d = 0.5$
H (4,1) in the contraction (3,1/1); $\zeta_p = 0.65$

Here the phosphorus atom is described by almost triple zeta (TZ) quality. Calculations of electron correlation were performed with basis II.

The interpretation of the results, in particular the Mulliken population analysis, is based on localized orbitals that were obtained from the ab initio SCF calculations by using the Boys criterion.[14]

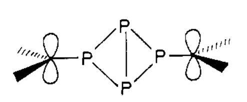
Experimental Section

Tetraphosphabicyclobutane **2** (R = $N(SiMe_3)_2$) was prepared according to the reported procedure.[15] The photoelectron spectrum was recorded with a UPG 200 spectrometer (Leybold-Heraeus) with He I excitation (21.21 eV). The calibration of the energy scale was performed with an Ar–Xe mixture. The accuracy of measurement is ±0.05 eV for the bands.

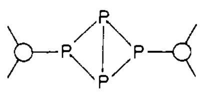
Photoelectron Spectrum of 2

The photoelectron spectrum of **2** (R = $N(SiMe_3)_2$) is presented in Figure 1. The four ionization bands lowest in energy appear at ① 7.72, ② 8.04, ③ 8.78, and ④ 10.42 eV. Hence the first two bands are close in energy while the higher ones are well separated from the first two. The assignment of the bands will now be performed with the ab initio calculations on **2**. The orbital energies obtained for parent **2** (R = H) are displayed in Table I, and those for its derivatives (R = CH_3, NH_2), in Table II.

It must be noted that the calculations are based on the geometries of the experimental X-ray study[15] of substituted **2**. The two amino groups are exo with respect to the ring moiety, and the lone pairs at the amino groups take up a perpendicular position.



bisected



perpendicular

From the computational view perpendicular as well as bisected orientations of the lone pairs of the exo-standing amino groups have been studied (see Table II).

Table II. Energies of the Highest Molecular Orbitals of the Derivatives (R = NH_2, CH_3) of **2**, at the Basis II Level

HOMO	energy, eV[a]		
i	NH_2 (perpendicular)	NH_2 (bisected)	CH_3
0	8.58 (a_1)	8.68 (a_2)	8.69 (a_1)
1	8.78 (b_2)	8.96 (a_1)	9.38 (b_1)
2	9.35 (b_1)	9.02 (b_1)	10.06 (a_2)
3	10.40 (a_2)	10.76 (b_2)	10.23 (b_1)
4	10.93 (a_1)	11.23 (a_1)	11.27 (a_1)
5	12.30 (a_1)	12.17 (b_1)	11.72 (b_2)
6	12.88 (b_2)	13.32 (a_2)	14.13 (a_1)

[a] Negative energies.

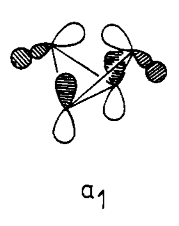
Table III. Total Mulliken Populations between Bonds and at Atoms (Effective Charges) for (A) Parent **2** (R = H) and (B) Its Derivatives (R = NH_2, CH_3), Obtained at the Basis II Level

atoms	overlap pop.	atom	charge
	(A) Parent		
P(1)P(3)	0.366	P(1)	−0.049
P(1)P(2)	0.454	P(2)	−0.026
P(2)H	0.609	H	0.075
P(2)P(4)	−0.267		
	(B) Derivatives		
P(1)P(3)	0.384[a]	P(1)	−0.040
	0.250[b]		−0.083
	0.344[c]		−0.041
P(1)P(2)	0.466	P(2)	0.258
	0.495		0.289
	0.477		0.082
P(2)R	0.442	R	−0.691
	0.492		−0.675
	0.546		−0.525
P(2)P(4)	−0.207		
	−0.211		
	−0.247		

[a] Perpendicular/perpendicular orientation of NH_2 groups; *E*(SCF) = −1473.563 136 au. [b] Bisected/bisected NH_2 groups; *E*(SCF) = −1473.572 534 au. [c] CH_3 (di)substitution at P(2) and P(4).

The calculations show that the orbital energies at the minimal basis set level (basis I) are too low compared with the DZ (basis II) or TZ (basis III) level.[16] However, the ordering of symmetry orbitals is already correctly reproduced at the basis I level. The improvement of the basis set at phosphorus beyond DZ+P (basis III vs. basis II) only slightly influences the orbital energies.

According to Tables I and II, the first two bands, ① and ②, correspond to ionizations from the a_1 and b_2 orbitals (within C_{2v} symmetry[8]). For parent **2** (R = H) the energy lowest a_1 orbital is as follows:



It possesses considerable π character at the central bond P(1)P(3).[8] The interpretation of the photoelectron spectrum of the derivative of **2** (R = $N(SiMe_3)_2$) in Figure 1 is more difficult. In the four bands ① to ④ (probably ④ consists of two bands due to the closely spaced orbitals *i* = 3, 4 of Table II) the valence orbitals of the frame (P_4H_2) strongly mix with the valence orbitals of the amino group. Therefore one cannot assign these bands unequivocally to certain types of (localized) orbitals such as P lone pairs, P–P bonds, etc. Some additional calculations on HP_4N-

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(15) Niecke, E.; Rüger, R.; Krebs, B. *Angew. Chem.* **1982**, *94*, 553; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 544. Riedel, R.; Hausen, H.-D.; Fluck, E. *Angew. Chem.* **1985**, *97*, 1050; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1056. The bonding parameters used are as follows: (a) bond lengths (in Å), P(1)P(3) = 2.200, P(1)P(2) = 2.200, PH = 1.420; (b) bond angles (in deg), [P(1)P(2)P(3)] = [P(1)P(4)P(3)] = 95.6, HP(2)d [bisecting the bond axis P(1)P(3)] = 100. For the derivatives of **2** (R = NH_2, CH_3) the following parameters (Å or deg) were chosen: PN = 1.720, NH = 0.90, HNH = 120; PC = 1.840, CH = 1.090, HCH = 109.5 (tetrahedral).

(16) The SCF calculations with basis I (minimal basis set) yield orbital energies that are too low by approximately 2.5 eV for R = NH_2 (see also Table I).

Table IV. Hybridization of Localized Molecular Orbitals (LMO's) for **1**–**3**, Phosphine, and Diphosphine, Computed at the Basis II Level (s Part Always Normalized to 1)

molecule	bond	hybridizn[a]	atom	hybridizn[a]
PH_3	PH	$sp^{3.26}d^{0.19}$	P	$sp^{0.88}d^{0.00}$
P_2H_4[b]	PP	$sp^{3.45}d^{0.14}$	P	$sp^{0.88}d^{0.00}$
	PH	$sp^{3.26}d^{0.20}$		
P_3H_3	P(1)P(2)	$sp^{4.20}d^{0.16}$	P(1)	$sp^{0.70}d^{0.00}$
	P(1)P(3)	$sp^{4.21}d^{0.15}$–$sp^{4.15}d^{0.15}$	P(3)	$sp^{0.69}d^{0.00}$
	P(1)H	$sp^{2.96}d^{0.17}$		
	P(3)H	$sp^{3.02}d^{0.18}$		
P_4H_2	P(1)P(3)	$sp^{5.19}d^{0.19}$	P(1)	$sp^{0.52}d^{0.00}$
	P(1)P(2)	$sp^{3.85}d^{0.15}$–$sp^{4.15}d^{0.16}$	P(2)	$sp^{0.69}d^{0.00}$
	P(2)H	$sp^{3.06}d^{0.18}$		
P_4	P(1)P(2)	$sp^{4.85}d^{0.17}$	P(1)	$sp^{0.44}d^{0.00}$

[a] In the case of a bond between two nonequivalent P atoms the hybridizations at the two atoms are given in consecutive order of the atoms. [b] Trans conformation.

$(SiH_3)_2$ show that the energies of the highest orbitals which belong to the SiH_3 substituent(s) are in the range of 12–14 eV. Hence, the bands ① to ④ of **2** (R = $N(SiMe_3)_2$) are entirely due to the PN frame while the orbitals of the $SiMe_3$ substituents contribute to the broad maximum around 13.5 eV.

Population Analysis

The Mulliken population analyses at one basis set level (basis II) are collected in Table III. Accordingly, methyl groups attached to the peripheral phosphorus atoms exert only minor effects on the bonding properties. The populations between bonds and at the atoms are only slightly changed. In comparison the effect of the amino groups is large, such as to strengthen (perpendicular) or weaken (bisected orientation of the lone pairs at the amino groups with respect to the ring moiety) the central bond P(1)P(3). This is in agreement with the predictions of recent investigations.[8]

For further analysis of the bonding properties of parent **2** (R = H) and related compounds, we have employed a localized orbital description. Hybridization of phosphine,[17] diphosphine,[18] cyclotriphosphane,[19] and white phosphorus[20] are collected in Table IV. The localized orbitals are listed for all nonequivalent nuclei and bonds.

Some general trends are obvious. In the strained structures **1**–**3**, the P–P bonds acquire more p character, which leaves for the lone-pair orbitals (at phosphorus) more s character (in comparison with phosphine and diphosphine). In all cases the contributions from the d orbitals are minor. In other words, they contribute to bonding as polarization functions[21] rather than being involved in hybridization. The highest p character is found at the central bond P(1)P(3) in **2**; a hybridization such as $sp^{5.19}d^{0.19}$ corresponds to 81% p character for this bond. The peripheral bonds P(1)P(2) have a hybridization of $sp^{4.00}d^{0.15}$ (average of the two hybridizations at the two nonequivalent P atoms adjacent to this bond), i.e. a p character of 78%. This is very close to the P–P bonds in **1**. Thus, the central bond in **2** differs from the peripheral bonds and comes closer to the P–P bonds in P_4 (80% p character). However, in bicyclobutane the central bond is almost a pure p bond ($sp^{24.3}$, i.e. 96% p character[22a] while the peripheral bonds have more s character ($sp^{4.0}$). Thus, all P–P bonds are rather similar and the bonding situations in **1** and **2** are essentially identical.[23]

For completeness we included in our considerations white phosphorus **3**. A corresponding localization procedure yields P–P bonds that possess more p character than the corresponding ones in **1** and are intermediate between the central and peripheral P–P bond(s) in **2**.

In **2** (R = H) the hybrid orbitals between P(1) and P(3) form a bond bent by 12°, as compared with 10.2° in **1** (bond P(1)(P(2)). On this basis one suspects that the ring strain in **2** is not much different from that in **1**. Similar considerations, which will not be recorded here, apply to the other ring bonds in **1** and **2** and agree with the expectation from the hybridizations.

Estimation of Ring Strain

We have seen that the localized orbital picture is different from the theoretical[22,24] and experimental[25] findings on the nature of the strained bonds in carbon–hydrogen chemistry; structures **1**–**3** reveal much less bent bond character. We will now try to obtain a quantitative estimate for the ring strain in **1**–**3**. Table V summarizes the energies of **1**–**3**, phosphine, and diphosphine at various levels of sophistication. Using isodesmic reactions,[26] an estimate of ring strain can then be provided by the reactions

$$P_3H_3 + 3PH_3 \rightarrow 3P_2H_4 \tag{1}$$

$$P_4H_2 + P_2H_4 \rightarrow 2P_3H_3 \tag{2}$$

and a combination of eq 1 and 2

$$P_4H_2 + 6PH_3 \rightarrow 5P_2H_4 \tag{3}$$

Equations 1 and 3 present a measure of ring strain for **1** and **2**, since they compare cyclic with acyclic analogues. On the other hand eq 2 refers to the heat of isomerization of the bicyclic to the monocyclic structure. Corresponding reactions for **3** are given by eq 4 and 5.

$$P_4 + 8PH_3 \rightarrow 6P_2H_4 \tag{4}$$

$$P_4 + 2PH_3 \rightarrow 2P_3H_3 \tag{5}$$

The heats of reactions thus obtained are summarized in Table VI. Negative values correspond to exothermic and positive values to endothermic reaction energies. Within the minimal basis set (basis I) the ring strain in **1** is rather large and comparable to that in cyclopropane. It must be emphasized, however, that minimal basis set calculations do not yield reliable energies for structures with second-row elements. Basis sets of at least DZ+P quality (basis II and basis III) should be used for the calculations

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(17) The geometrical parameters of PH_3 were chosen according to: Ahlrichs, R.; Keil, F.; Lischka, H.; Kutzelnigg, W.; Staemmler, V. *J. Chem. Phys.* **1975**, *63*, 455.

(18) For previous calculations on this structure see: Ahlrichs, R.; Heinzmann, R.; Zirz, C. *Theor. Chim. Acta* **1976**, *43*, 29. See also: Cowley, A. H.; Mitchell, D. J.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224. Albrand, J. P.; Faucher, H.; Gagnaire, D.; Robert, J. B. *Chem. Phys. Lett.* **1976**, *38*, 521. The geometrical parameters were chosen according to Ahlrichs et al.; trans conformation was assumed.

(19) The structural parameters were chosen according to: Hahn, J.; Baudler, M.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 797. Baudler, M. *Pure Appl. Chem.* **1980**, *52*, 755. In detail the geometrical parameters (bond lengths in Å; bond angles in deg) are as follows: PP = 2.200, PH = 1.420, HP(1)P(2) = 96.9, HP(1)P(3) = 95.1, HP(3)P(1) = HP(3)P(2) = 95.0.

(20) PP = 2.21 Å: Maxwell, L. R.; Hendricks, S. B.; Mosley, V. M. *J. Chem. Phys.* **1935**, *3*, 699. For the photoelectron spectrum of P_4 see: Brundle, C. R.; Keubler, N. A.; Robin, M. B.; Basch, H. *Inorg. Chem.* **1972**, *11*, 20.

(21) See also: Kutzelnigg, W. *Einführung in die Theoretische Chemie*; Verlag Chemie: Weinheim, 1978; Vol. 2.

(22) (a) Newton, M. D.; Schulmann, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767. Schulmann, J. M.; Fisanick, G. J. *J. Am. Chem. Soc.* **1970**, *92*, 6653. (b) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739. Kollmar, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 2617.

(23) It is known that the nuclear spin–spin coupling constants are proportional to the s content of a bond. Such relationships are well established for carbon–hydrogen compounds (e.g.: Pople, J. A.; McIver, J. W., Jr.; Ostlund, N. S. *J. Chem. Phys.* **1968**, *49*, 2965). On the basis of our theoretical findings the PP coupling constants of the central bonds should be comparable in value with those of the peripheral bonds.

(24) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419.

(25) An estimate of strain energies in cyclopropane, bicyclobutane, and related compounds may be found in: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley Interscience: New York, 1976.

(26) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, *1036*. George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

Table V. Molecular Energies (au) for Phosphine, Diphosphine, Cyclotriphosphane, Bicyclotetraphosphabutane, and White Phosphorus

molecule	SCF basis I	SCF basis II	SCF basis III	CEPA[a] basis II
PH_3	−338.633 584	−342.329 881	−342.395 822	−342.460 262
P_2H_4	−676.139 677	−683.519 150	−683.639 200	−683.764 640
P_3H_3	−1012.470 416	−1023.558 623	−1023.721 543	−1023.914 225
P_4H_2	−1348.803 032	−1363.598 780	−1363.805 397	−1364.065 898
P_4		−1362.467 413	−1362.663 541	−1362.928 746

[a] Correlation is included only for the valence electrons (i.e. localized P–P bond, P–H bond, and P lone-pair electrons).

Table VI. Heats of Reactions (kcal/mol) for (1)–(5) Obtained at Various Levels of Sophistication

reacn	SCF basis I	SCF basis II	SCF basis III	CEPA basis II
1	−30.0	−5.8	−5.4	0.7
2	1.1	0.4	0.9	1.3
3	−58.9	−11.1	−9.8	2.7
4		−5.3	−3.2	14.4
5		6.2	7.6	13.1

of the isodesmic reactions, such as eq 1–5.

At the SCF level, reactions 1, 3, and 4 are slightly exothermic, which indicates that there is a certain but small ring strain in cyclic structures **1**–**3**. Inclusion of electron correlation favors the tighter structures;[27] the ring structures are more stabilized such that reactions 1 and 3 become thermoneutral while reaction 4 is even endothermic. At the SCF level, isodesmic reactions 1 and 3 may be compared with their well-known carbon–hydrogen analogues, which are exothermic by ≈30 kcal/mol (reaction 1[22,24,26] with different basis sets) and ≈70 kcal/mol (reaction 3,[22] STO 4-31G bases), respectively. Electron correlation reduces these values by ≈7 kcal/mol,[22] as can be seen by comparing the SCF results with experimental strain energies.[25] In tetrahedrane, the strain energy is as high as ≈135 kcal/mol.[22b] Thus we conclude that, in contrast to those in the highly strained carbon ring systems, the strain energies in **1**–**3** are very small or even zero.

Isomerization reactions 2 and 5, on the other hand, are slightly endothermic at all levels of sophistication. [It should be noted that the inclusion of d functions is compulsory,[28] basis II without d AO's yields −23.4 kcal/mol (SCF) and 5.9 kcal/mol (CEPA) for reaction 4.]

The endothermicity of reaction 4, after inclusion of correlation effects, seems to contradict the textbook knowledge that P_4 has a strain energy of about 20 kcal/mol, which is why white phosphorus is less stable than red phosphorus.[29] But one should be careful in identifying the ring strain in P_4 with the reaction energy of reaction 4, which is only true if the PH bond energies in PH_3 and P_2H_4 are identical. Since as many as 24 P–H bonds enter eq 4, a small change in the P–H bond energy makes estimates of the ring strain based on (4) unreliable. The existent thermochemical data are also not accurate enough. Possibly, the study of homodesmic reactions instead of the isodesmic ones (1)–(5) would yield slightly more reliable estimates of strain energies.[26] However the structural parameters of triphosphane are not known and since our study is based on experimental geometries, we have to restrict our considerations to isodesmic reactions. However, our conclusions that ring strain in the cyclic phosphorus compounds is low or negligible will not be affected by this restriction. The relative stabilities of P, P_2, P_4, and P_8 have been studied by several authors recently.[28]

Conclusions

The results of our investigations can be summarized as follows: (1) The photoelectron spectrum of the first derivative of **2** with R = $N(SiMe_3)_2$ is reported. It shows two closely spaced bands at low ionization energies. The first corresponds to an a_1 orbital (within C_{2v} symmetry) that possesses considerable π character at the central bond P(1)P(3). (2) Cyclotriphosphane, tetraphosphabicyclobutane, and white phosphorus reveal unusual low ring strain energies. These conclusions are reached by the calculations of corresponding isodesmic reactions of their strained structures to their acyclic analogues. The inclusion of electron correlation favors the tighter structures, and the rings become more stable than their open-chain analogues. (3) These conclusions are in accordance with population analyses of localized orbitals of the P–P bonds in **1**–**3**. In parent **2** (R = H) the central bond P(1)P(3) possesses p character similar to that of the peripheral P–P bonds. This contrasts with the case of bicyclobutane, in which the central bond possesses a higher degree of p character (sp^{24}). The hybridizations of all P–P bonds in **1**–**3** are almost the same; the lone pairs at the phophorus atoms acquire predominant s character. We note that recent theoretical investigations[28] on the condensed-ring systems white phosphorus (**3**) and perphosphacubane evidence a larger stability of the three-membered-ring system compared to the four-membered-ring system. Finally, our findings are in strong contrast to recent theoretical results for silicon ring systems;[30] there the ring strain is rather large.

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