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Theoretical investigation of next neighbour interactions and ring strain in linear and monocyclic phosphanes

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The molecules PH_3, P_2H_4, P_3H_5, P_3H_3, P_4H_4, and P_5H_5 were treated at the SCF level using basis sets of DZP quality. Computed structure constants and energies indicate high stability for P_5-ring systems and small ring strain for P_3- and P_4-ring systems. The computed values for the strain are 28 and 18 kJ/mol for P_3H_3 and P_4H_4, respectively. Neighbouring P atoms with trans-configured lone pairs are favoured in the monocyclic phosphanes considered in this work, as shown by the energy difference of about 10 kJ/mol between trans and cis configured lone pairs, and the shortening of P-P distances by about 2 pm for trans configured P atoms.

Key words: Phosphanes — Structure of phosphanes — Ring strain — Lone pair interactions

1. Introduction

In the past two decades a large number of open-chain, cyclic and polycyclic phosphanes, or rather their derivatives in which the hydrogen atoms are substituted by organyl groups, have been synthesized [1, 2]. The open-chain phosphanes readily polymerize to yellow solids so that only the first members of the homologous series P_nH_{n+2} up to $n=3$ could be isolated as pure compounds. For the mono- and polycyclic phosphanes the P_5-ring structure elements are quite common, indicating high stability for the phosphorous 5-ring systems. In fact,

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the only member of the monocyclic phosphorous hydrides P_nH_n which has been isolated up till now is P_5H_5. Despite the strain expected for 60° bond angles, three membered P_3-rings are frequently found as building structure elements in polycyclic phosphanes; however there are no undisturbed frameworks for such phosphanes with 4-ring structure elements even though no strain should be present in phosphorous 4-ring compounds.

Most of these polyphosphanes were characterized by their ^{31}P-NMR spectra or by mass spectroscopy, and only in a few cases was there the possibility of performing X-ray structure analyses. To get a detailed picture of the molecular and electronic structures of some of the simplest phosphanes we therefore performed *ab initio* calculations for the open-chain phosphanes P_nH_{n+2} up to $n = 3$, and for the cyclic phosphanes P_nH_n up to $n = 5$.

2. Details of computation

All computations were performed at the SCF level of theory with the Karlsruhe version [3] of the Columbus system [4] of programs. Geometry optimizations were carried out by the analytical calculation of the energy gradient together with a quasi-Newton method to find the equilibrium structures [5]. The following contracted Gaussian-type orbital (CGTO) basis sets were employed:

$$\text{P} \quad (11, 7, 1)/[6, 4, 1] \qquad \eta(d) = 0.48$$

$$\text{H} \quad (5, 1)/[3, 1] \qquad \eta(p) = 0.56.$$

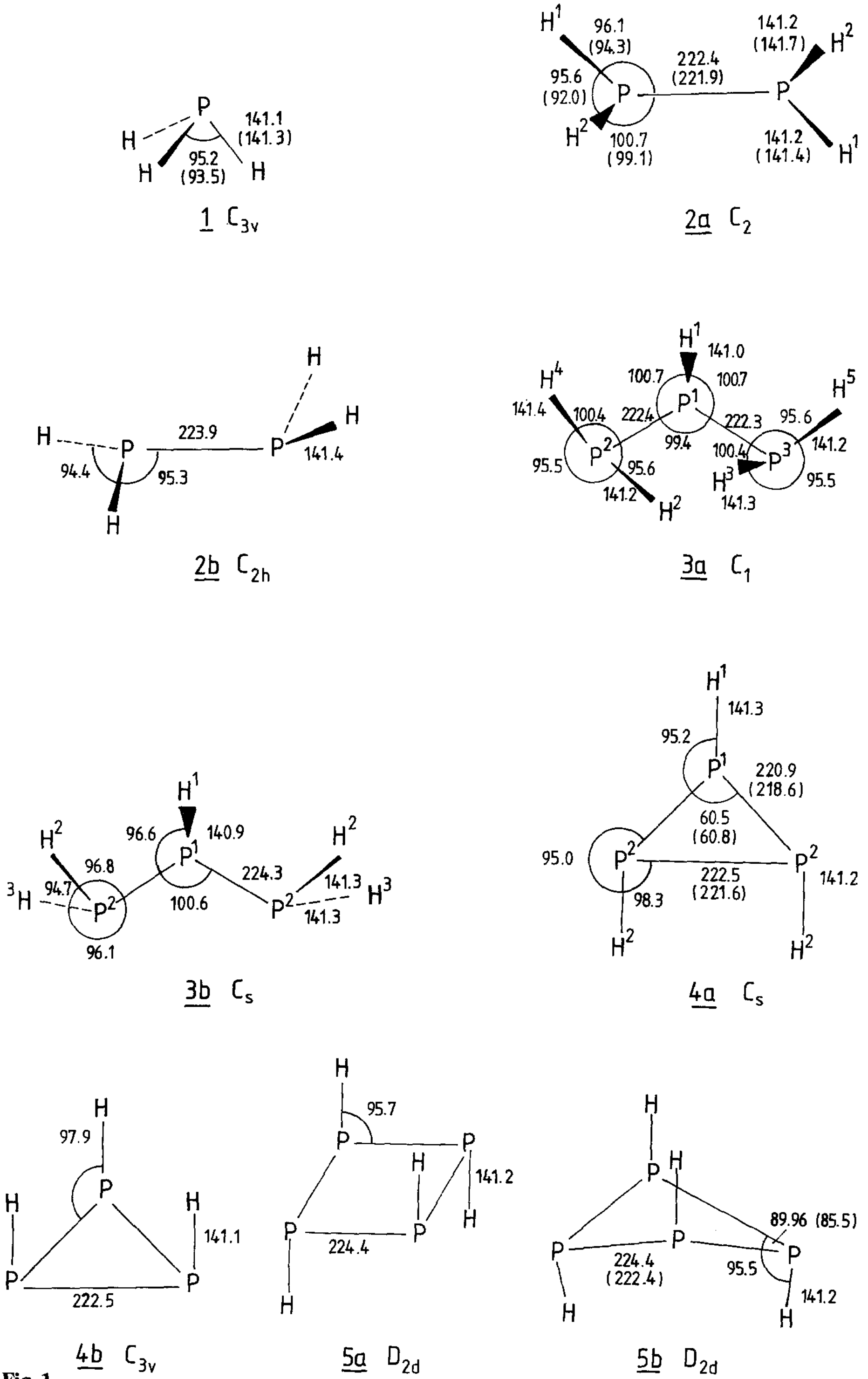
The contraction pattern for the s-type GTOs of P was (521111), and the primitive GTOs were taken from Huzinaga's tables [6]; this basis set is of better than DZP quality and should give molecular and electronic structures close to the SCF limit. The structures obtained were not rigorously verified as minima by force constant calculations. We did not have an analytical second derivatives program at our disposal and corresponding calculations would not have been possible for P_5H_5 with the computers available to us anyway.

3. Equilibrium structure and energetics

The SCF results obtained for the molecular structures are presented in Fig. 1, and the corresponding energies in Table 1.

3.1. *The open-chain phosphanes P_nH_{n+2} with $n = 1, 2, 3$*

The structure constants for PH_3 (*1*) and P_2H_4 (*2a*) can be compared with experimental data [7, 8]. The agreement is excellent: bond lengths differ by less than 1 pm and bond angles are only about 2–3° too large. For the interbond angles we find values around 95–100° in the molecules *1, 2* and *3*. This is expected since bonding in these molecules involves mainly $3p$ orbitals at the phosphorous atoms [9] together with the $1s$ hydrogen orbitals.



1 C_{3v}

2a C_2

2b C_{2h}

3a C_1

3b C_s

4a C_s

4b C_{3v}

5a D_{2d}

5b D_{2d}

Fig. 1

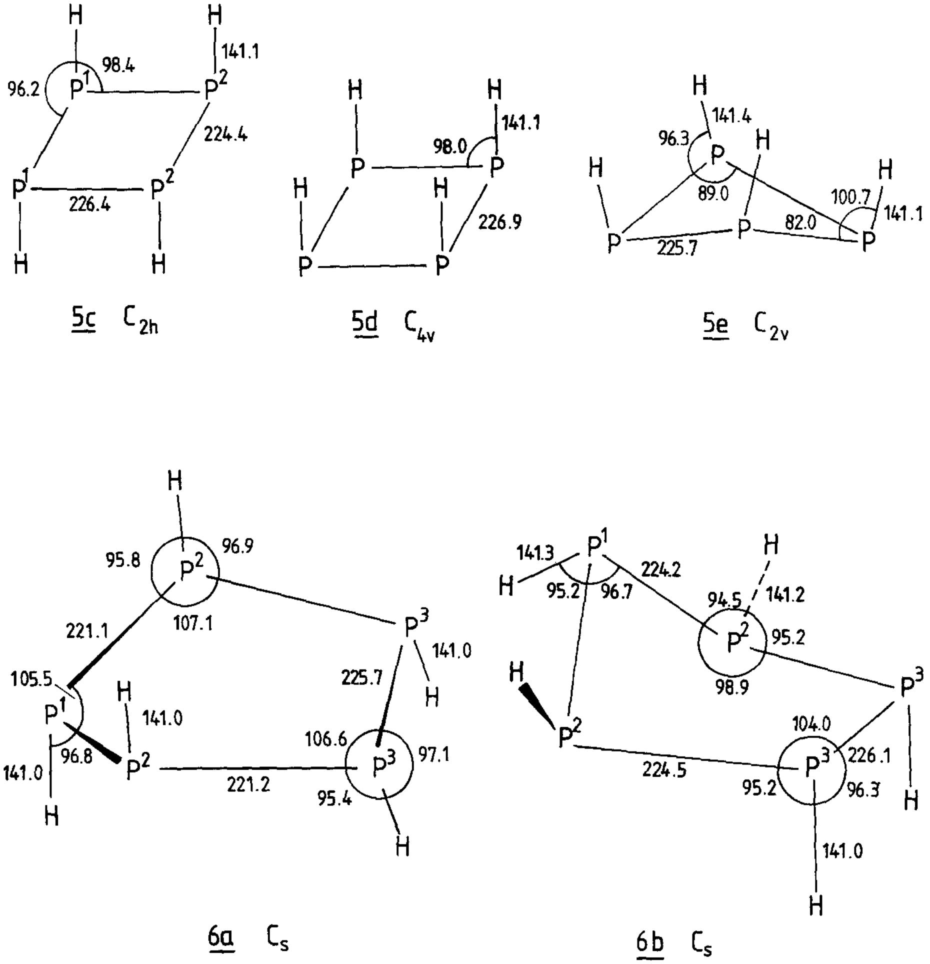


Fig. 1. Structure constants for molecules treated in this work. Distances are given in pm, angles in deg. Experimental structure constants are given in parenthesis. For *4a* and *5b* these are obtained for H replaced by ^{t}Bu [12] and C_6H_{11} [13] respectively

Two local minima were found for the P_2H_4 (*2*) molecule. The most stable of these (*2a* in Fig. 1) shows a gauche configuration for the phosphorous lone pairs with a dihedral angle of 77.7° (exp.: 74.0°, [8]) which is measured from the cis conformation. The secondary minimum (at least in C_{2h} symmetry), *2b* in Fig. 1, is only 2 kJ/mol higher in energy than *2a* and shows a trans configuration for the lone pairs together with a P-P bond distance that is 1.5 pm larger than in *2a*. The relative stability of the gauche and trans isomers is the result of a delicate balance of various effects and may be rationalized on the basis of the "gauche effect" [10] and the hybridization of valence atomic orbitals (AOs) [11].

For P_3H_5, both the unsymmetric structure *3a* and the structure with C_s molecular symmetry, *3b*, were investigated, and the symmetric conformation was found to

Table 1. Computed energies for molecules considered in this work

Molecule[a]	Symmetry	E_{SCF} (a.u.)[b]	ΔE(kJ/mol)[c]
PH_3, *1*	C_{3v}	−342.44397	—
P_2H_4, *2a*	C_2	−683.73804	0
P_2H_4, *2b*	C_{2h}	−683.73715	2.3
P_3H_5, *3a*	C_1	−1025.03154	0
P_3H_5, *3b*	C_S	−1025.02789	9.6
P_3H_3, *4a*	C_S	−1023.86989	0
P_3H_3, *4b*	C_{3v}	−1023.86224	20.1
P_4H_4, *5a*	D_{2d}	−1365.16699	0
P_4H_4, *5b*	D_{2d}	−1365.16703	0.1
P_4H_4, *5c*	C_{2h}	−1365.15732	25.4
P_4H_4, *5d*	C_{4v}	−1365.14607	54.9
P_4H_4, *5e*	C_{2v}	−1365.15289	37.0
P_5H_5, *6a*	C_S	−1706.47944	0
P_5H_5, *6b*	C_S	−1706.46170	46.5

[a] Notation as in Fig. 1 and text
[b] Total electronic energies obtained at the SCF level as described in Sect. 2
[c] Relative stability of isomers of P_nH_m

be 10 kJ/mol higher in energy than the unsymmetric one. The torsional angles for the isomer *3a* are $\measuredangle H^2P^2P^1H^1 = 71.7°$, $\measuredangle H^4P^2P^1H^1 = -25.5°$, $\measuredangle H^3P^3P^1H^1 = -23.9°$, and $\measuredangle H^5P^3P^1H^1 = -72.7°$, while the corresponding angles for the symmetric isomer *3b* are $\measuredangle H^2P^2P^1H^1 = \pm 28.6°$, and $\measuredangle H^3P^2P^1H^1 = \pm 124.1°$. The structure constants of the two PH_2 moieties in *3a* are virtually the same, differing only in hundredths of picometers or degrees. Compared with *3b* the two PH_2 groups in *3a* are rotated by about 100° and −50° respectively, about the P-P axis. Besides the "gauche effect", the relative instability of the isomer *3b* with respect to *3a* may be attributed to a repulsion of the lone pairs on the terminal P^2 atoms, which in turn leads to a 2 pm increase in P-P bond lengths, and a small opening of the PPP-angle.

The nearly negligible energy for the isodesmic reaction

$$2P_2H_4\ (2a) \rightleftharpoons PH_3\ (1) + P_3H_5\ (3a), \qquad \Delta E_{SCF} = 1.5\ \text{kJ/mol} \tag{1}$$

indicates that, just as for the simple alkanes, bond additivity schemes for the open-chain phosphanes can approximately be applied.

3.2. *The cyclic phosphanes P_nH_n with $n = 3, 4, 5$*

The computed structure constants for the ring systems in *4a* and *5a* can be compared with X-ray structure constants for the analogous compounds in which the hydrogen atoms are replaced by $^{t-}$Bu for *4a* [12] and by C_6H_{11} for *5b* [13]. The deviations, especially for the degree of non-planarity for the 4-ring compound, may be caused by the bulky ligands and/or by solid state packing effects.

The most stable configuration of P_3H_3 is shown in Fig. 1 as *4a*, with two P-H bonds lying on one side and the third one on the other side of the P_3-ring.

Therefore two different P-P bond distances are found: one with 220.9 pm between P-atoms in a trans configuration of their P-H bonds, and one with 222.5 pm between P atoms in a cis configuration for their P-H bonds. The secondary minimum, *4b* in Fig. 1, is 20 kJ/mol higher in energy than *4a* and shows an all cis configuration for the P-H bonds; the P-P bond distance of 222.5 pm is the same as in *4a* for the P-P bond between the P atoms with a mutually cis configuration of their P-H bonds.

For P_4H_4 molecular structures with three different arrangements of the P-H bonds were investigated: the all trans isomer, *5a*, the isomer with two trans and two cis configurations for neighbouring P atoms, *5c*, and the all cis isomer, *5d*. Moreover for the isomers *5a* and *5d*, structures with a folded P_4-ring were also taken into account; the results are displayed in Fig. 1 as *5b* and *5e* respectively. For the isomers with a planar P_4-ring system the energetic ordering is as follows: the most stable structure is *5a*, next follows *5c*, which is 25 kJ/mol higher in energy than *5a*, and *5d* is the least stable one, being 55 kJ/mol higher in energy than *5a*. Optimization of the all trans isomer (*5a*) without the restriction of a planar P_4-ring system leads to a minimum with a slightly folded conformation, *5b* - the torsional angle for the P-P bonds is only 2.9° - and virtually no gain in energy when compared with *5a*. The same procedure for the all cis isomer results in a considerably more folded conformation, which is depicted as *5e* in Fig. 1. The lowering in energy compared with *5d* is 37 kJ/mol, the torsional angle for the P-P bonds is 32.4°, and even the P-P bond distances are 1.5 pm shorter than in *5d*.

Concerning the lengths of the P-P bonds in the 4-ring compounds, the same picture emerges as for the 3-ring systems. All distances between neighbouring P atoms with a cis configuration for their P-H bonds are about 2 pm larger than between the trans configured P atoms.

In our treatment of P_5H_5 we have located two minima of the symmetric envelope conformation within C_5 symmetry - *6a* and *6b* in Fig. 1. All efforts to locate a minimum for an asymmetric twisted half chair conformation have been without success. Although the force constant matrix was not evaluated, we believe that *6a* is a minimum, but this is less certain for *6b*, which could be unstable with respect to symmetry lowering distortions. The potential surface is very shallow around *6a*, with very small gradients for some structures, and considerable distortions towards a twisted half chair conformation (C_1 symmetry) being possible with an energy rise of only 10 kJ/mol. Our results therefore do not contradict the fact that solid state $P_5(CF_3)_5$ shows a twisted half chair [14].

Conformations *6a* and *6b* are quite similar since only the P^1H group is flipped. The occurrence of two minima is not unexpected: a planar P_5 ring leads to PPP angles that are too large, and a stabilization can be achieved by moving either towards *6a* or *6b*. The conformation *6a* is 47 kJ/mol lower in energy than *6b* which, in comparison with the ΔE computed for different geometries of other molecules considered in this work, is quite appreciable. There are no obvious reasons for this pronounced energy difference, since both structures have just one unfavourable cis configuration between neighbouring PH bonds.

The more flexible P_5 ring is a more complicated system than the rigid P_3 or P_4 rings, where structure and energetics could easily be rationalized by the cis effect. A consideration of lone pair interactions did not give clues (to us), and since the cis effect is also not relevant we have turned to interactions between non-bonded atoms in an attempt to understand the bond distances and bond angles. The shortest $P \cdots H$ distances are typically 275 pm (±2 pm) in both conformations, and since this is much smaller than the van der Waals distance of 300 pm for $P \cdots H$, the $P \cdots H$ repulsion is certainly important for both the structure and energy. However, since the corresponding distances are very close in *6a* and *6b* this cannot help to rationalize the energy difference.

There is a striking difference between *6a* and *6b*: all corresponding bond distances in *6a* are shorter than in *6b* whereas the corresponding angles in *6a* are larger. With the exception of the special case P_3H_3, *4a*, the shortest computed P–P distances are found in *6a* (221 pm) whereas the PPP angels (105.5°, 107.1° and 106.6°) appear to be extremely large. On the other hand, the P–P distances of 224.2 pm, 224.5 pm and 226.1 pm in *6b* are relatively large, with the second largest P–P distance after P_4H_4, *5d*, which has P–P = 226.5 pm. Further, the conformer *6b* has a relatively short distance between non-bonded P atoms: $P^2 \cdots P^2 = 335$ pm. This is much smaller than the van der Waals distance (360 pm) and other $P \cdots P$ distances in *6a* or *6b*, which all exceed 350 pm (the $P^2 \cdots P^3$ distance in P_3H_5, *3a*, is 339 pm, however). The conformation *6a* is thus characterized by short (strong) P–P bonds, relatively small non-bonded interactions (relatively large $P \cdots P$ distances) but relatively large PPP angles (bond angle strain) whereas *6b* shows quite normal interbond angles, but relatively large P–P bond distances (weak bonds) and small $P \cdots P$ distances. The problem then is: why is there no increase in the PPP angle at P^1 in *6b*, which would increase the $P^2 \cdots P^2$ distance? We have no convincing answer to this question and, frankly, do not know how to tackle it in a simple way. An increase in $P^2P^1P^2$ in *6b* would probably lead to enhanced repulsive interactions between the P^2H groups and the lone pair on P^1. The structures *6a* and *6b* and their relative energy involve a balance of the various effects mentioned above, and these are hard to quantify.

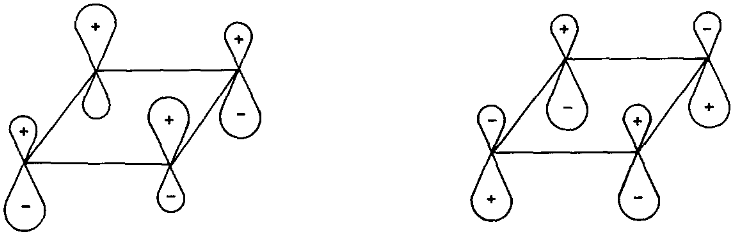
4. Next neighbour interactions

The present results show a consistent pattern for all homocyclic P_3 and P_4 hydrides considered in this work: the P–P distance for neighbouring phosphorous atoms with a cis configuration of their P–H bonds is about 2 pm larger than between P atoms with a trans configuration of their P–H bonds. From the reaction energies of the Eqs. (2), (3) and (4)

$$1/2 P_3H_3\ (4a) \rightleftharpoons 1/2 P_3H_3\ (4b) \qquad \Delta E_{SCF} = 10\ \mathrm{kJ/mol} \tag{2}$$

$$1/2 P_4H_4\ (5a) \rightleftharpoons 1/2 P_4H_4\ (5c) \qquad \Delta E_{SCF} = 13\ \mathrm{kJ/mol} \tag{3}$$

$$1/2 P_4H_4\ (5c) \rightleftharpoons 1/2 P_4H_4\ (5d) \qquad \Delta E_{SCF} = 15\ \mathrm{kJ/mol} \tag{4}$$



$6b_2$ - MO ($5a$) $6b_1$ -MO ($5c$)

Fig. 2. Schematic representation of $6b_2$- and $6b_1$-MOs in *5a* and *5c*, respectively

one gets the energetic difference between these two possible arrangements: for the 3-ring system a value of 10 kJ/mol and for the 4-ring system a somewhat larger value of ≈ 14 kJ/mol. This state of affairs may be rationalized by the repulsion of the lone pairs between neighbouring phosphorous atoms.

The presence of a Pauli-type repulsion is reflected by the relative stabilities of the $6b_2$ molecular orbital (MO) in the all trans isomer *5a*, and the $6b_1$ MO in the all cis isomer *5c*. These two MOs are basically linear combinations of *sp*-hybrid AOs describing the lone pair electrons of phosphorous, as schematically depicted in Fig. 2. In the $6b_1$ MO of *5c* there is a nodal surface passing through the centre of a P-P bond which separates the two *sp*-hybrid AOs of neighbouring phosphorous atoms - a strong indication for lone pair repulsion. The situation is different for *5a*: the $6b_2$ MO shows no repulsion effects between neighbouring *sp*-hybrid AOs for the simple reason of the all trans configuration in *5a*. This view is in fact supported by the orbital energies: $\varepsilon(6b_2) = -13.6$ eV in *5a* and $\varepsilon(6b_1) = -10.1$ eV in *5c*. If Pauli-type lone pair interactions are responsible for the relative stabilities of cis and trans isomers, then the somewhat lower energy difference found for the 3-ring system compared with the 4-ring system (see Eq. (2) above) can be explained: in the 3-ring system the lone pairs are oriented away from each other and therefore show smaller repulsion effects.

5. Strain energies for the P_3- and P_4-ring systems

The widespread occurrence of P_5- and P_3-ring systems in polycyclic phosphanes indicates that these moieties are quite stable. Virtually no strain should be present in P_4-ring systems with 90° bond angles, but such systems are extremely scarce. Using homodesmotic reactions, Eqs. (5)-(7),

$$3P_3H_5\ (3a) \rightleftharpoons 3P_2H_4\ (2a) + P_3H_3\ (4a) \qquad \Delta E_{\mathrm{SCF}} = 28\ \mathrm{kJ/mol} \tag{5}$$

$$4P_3H_5\ (3a) \rightleftharpoons 4P_2H_4\ (2a) + P_4H_4\ (5b) \qquad \Delta E_{\mathrm{SCF}} = 18\ \mathrm{kJ/mol} \tag{6}$$

$$5P_3H_5\ (3a) \rightleftharpoons 5P_2H_4\ (2a) + P_5H_5\ (6a) \qquad \Delta E_{\mathrm{SCF}} = -32\ \mathrm{kJ/mol} \tag{7}$$

one gets an estimate for the ring strain in P_3H_3 (*4a*) of 28 kJ/mol, and of 18 kJ/mol in P_4H_4 (*5b*). Since reactants and products have a closed shell structure and the number and type of bonds remains constant, the reaction energy can be computed with fair accuracy at the SCF level, although a basis set extension (additional *d* and *f* AOs) will certainly lead to a relative stabilization of P_3H_3. The strain in P_3H_3 is in part due to the next neighbour interaction of the cis configured P–P bond of about 10 kJ/mol, as discussed in Sect. 4. The negative reaction energy for Eq. (7) is quite interesting: it indicates that the P_5-ring is considerably more stable than the open-chain phosphanes P_3H_5 (*3a*) and P_2H_4 (*2a*). In the opinion of the authors one may take this result as a firm indication of the instability of open-chain phosphanes P_nH_{n+2} compared with stable ring compounds such as P_5H_5 (*6a*) or P_7H_3 [25].

Recent experimental results [15] for the strain in P_3H_3 and P_4H_4 are obtained relative to P_5H_5 assuming that there is no strain present in the P_5-ring moiety of P_5H_5 (*6a*). From Eqs. (8) and (9)

$$3/5P_5H_5 \ (6a) \rightleftharpoons P_3H_3 \ (4a) \qquad \Delta E_{\mathrm{SCF}} = 47\,(33)\ \mathrm{kJ/mol} \tag{8}$$

$$4/5P_5H_5 \ (6a) \rightleftharpoons P_4H_4 \ (5a) \qquad \Delta E_{\mathrm{SCF}} = 44\,(25)\ \mathrm{kJ/mol} \tag{9}$$

we obtained values comparable with the experimental reaction enthalpies [15], which are given in parentheses in Eqs. (8) and (9).

The experimental as well as the present and previously obtained [24] theoretical results show that the ring strain for P_3H_3 (*4a*) is small, as is not unusual for three-membered ring systems. As examples we mention the P_4 molecule [16], and the relatively small ring strain of cyclopropane (115 kJ/mol), compared with cyclobutane (111 kJ/mol) [17, 18, 21]. Interestingly enough, one finds in P_3H_3 (*4a*) a three-centre shared electron number (SEN) [19] of 0.2 for the P_3-ring moiety, which indicates stabilizing multibonding effects similar to those in P_4 [16].

The slight strain energy of P_4H_4 (*4a*) of 18 kJ/mol may be attributed to the repulsion of parallel P–P bonds [16] which is consistent with the larger P–P bond distance found in *4a* (224.4 pm) compared with the normal single bond length of 221 pm [22].

6. Summary

The five-membered cyclic phosphane P_5H_5 (*6a*) is found to be a molecule with high stability when compared with open-chain phosphanes such as P_2H_4 (*2a*) or P_3H_5 (*3a*). This fact helps to rationalize that thermolysis of diphosphane yields cyclic and polycyclic phosphanes more easily than open-chain compounds.

For the monocyclic 3-, 4- and 5-ring phosphanes considered in this work one finds a nearest neighbour interaction between cis oriented phosphorous lone pairs. The magnitude of this interaction is estimated to be 10 kJ/mol in the 3-ring system and about 14 kJ/mol in the 4-ring systems. This interaction allows one to rationalize the structural features found in the cyclic phosphanes: the P–P bond distances between cis configured P atoms are about 2 pm larger than those between trans configured bonds.

The strain in P_3H_3 (*4a*), 28 kJ/mol, is small, and not unusual for 3-ring systems in general (for example cyclopropane, 115 kJ/mol [17, 18, 21], cyclotrisilane, 160 kJ/mol [21, 23] or the P_4 molecule [16]). That the phosphorous P_3-ring is a relatively stable structure element can also be seen from the short P–P bond length of 220.9 pm between trans configured P atoms, which is of the order of the normal P–P single bond length of 221 pm [22]. However, one does find a non-negligible ring strain energy of 18 kJ/mol for P_4H_4 (*5b*), which may be attributed to parallel P–P bond repulsion. This instability of P_4-ring systems is reflected in larger P–P bond distances, for example 224.4 pm in (*5b*).

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