CHEMISTRY LETTERS, pp. 437 - 440, 1985.

ab initio CALCULATION OF DIPHOSPHENE AND CYCLOPOLYPHOSPHANES

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Total energies and optimized structures were calculated by the ab initio method on the system $(PH)_n$ (n = 2 - 6) and characteristic properties and relative stabilization energies are discussed.

Recently, strong attention has been paid to the compounds with a multiple bond containing higher VA elements in the lower coordination states, because of their unusual chemical and physicochemical properties.

We have been successful in the preparation and characterization of sterically protected diphosphenes such as **1A** and **1B**.[1,2] We reported preliminary results on the ab initio calculation of diphosphene HP=PH (**2**) at the 44-31G* level.[2] The binding energy of the P=P bond for **1C** was estimated as 130 (± 65) kcal/mol from the measurement of resonance Raman spectrum[3] (1 cal = 4.184 J).

Ar-P=P-Ar	Ar-P=P-Mes	Tsi-P=P-Tsi
1A	**1B**	**1C**

Ar = 2,4,6-$Bu^t_3C_6H_2$; Mes = 2,4,6-$Me_3C_6H_2$; Tsi = $(Me_3Si)_3C$.

We have been interested in the fact that not phosphinidene dimers (= diphosphenes) but the cyclopolyphosphanes (3 - 6 membered ring compounds) had so far been isolated as thermally stable compounds depending on the reaction conditions or substituents, when we succeeded in the isolation of the very stable **1A** for the first time.

To shed insight into the situation, we have undertaken the ab initio calculations of the energies and structures of the $(PH)_n$ (n = 2 - 6) systems.[4] The binding energy of the P=P bond for HP=PH is calculated to be 67.4 kcal/mol at the MP3/6-31G**//HF/6-31G* level,[4] which is considerably smaller than the corresponding value of 109.7 kcal/mol for HN=NH. The calculated P=P bond energy might be slightly underestimated comparing with the experimental values for P=O (138 kcal/mol) and P=S (91.5 kcal/mol) in triphenylphosphine oxide and sulfide, respectively.[5]

Figure 1 shows the optimized structures of $(PH)_n$ (n = 2 - 6) obtained at the HF/3-21G level.[4,6] The following points may be noteworthy.

Table 1. Total Energies (E_n) and Relative Stabilization Energies (SE_n) of $(PH)_n$ at the HF/3-21G Level

n	Compound	Total energy E_n / a. u.	Relative stabilization energy SE_n / kcal·mol^{-1}
2	**2**	-679.103098	0.0
3	**3**	-1018.693825	8.2
4	**4**	-1358.280461	11.7
5	**5**	-1697.870865	14.2
6	**6**	-2037.433299	13.0

1) **2** (n=2): Only trans-diphosphene[1] is shown. The cis isomer is 2.5 kcal/mol (3.6 kcal/mol at the CI(S+D+Q)/6-31G*//HF/6-31G* level[4]) less stable than the trans. It is found that there exists a sizable barrier between the isomers.[7]

2) **3** (n=3): Two of the hydrogen atoms are on the same side of the P_3 plane and in the trans position relative to the remaining hydrogen atom in the most stable structure as demonstrated by the X-ray analysis of $(Bu^tP)_3$.[8]

3) **4** (n=4): Four hydrogen atoms are located alternately. The P_4 ring plane is slightly distorted as characterized by the dihedral angle of 170.5° between the three-membered planes $P_1P_2P_4$ and $P_3P_2P_4$. The calculated structure is very similar to the X-ray structure of $(CF_3P)_4$.[9]

4) **5** (n=5): The P_5 plane is in a distorted envelope form in agreement with the X-ray structure for $(PhP)_5$.[10]

5) **6** (n=6): Only the chair form is shown. The X-ray analyses[11,12] demonstrated that $(PhP)_6$ takes chair forms rather than the other forms in a planar, envelope, or boat shape.

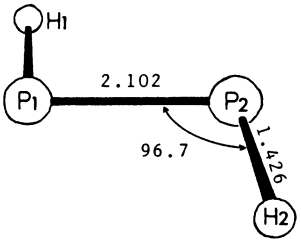
In an attempt to assess the thermodynamic stability of the n-membered ring compounds, the following stabilization energy (SE_n) was defined relative to diphosphene (n = 2), by using the total energy (E_n) of $(PH)_n$.

$$SE_n = -(2E_n - nE_2)/2n$$

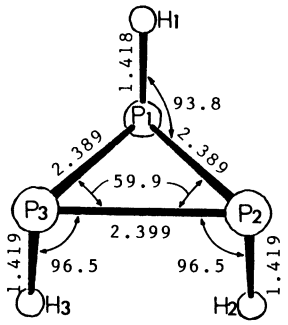
Thus the value of SE_n measures the mean stabilization energy per molar PH of n-membered ring. As Table 1 shows, the calculated SE_n values increase with the increase in "n" (probably due to the release of strain energy), attain a maximum with n = 5, and then tend to decrease gradually (or become constant) with the further progress of ring expansion. This suggests that the formation of cyclopolyphosphanes is more favorable than the formation of diphosphene (n = 2). The advantage of cyclopolymerization over dimerization is also obvious from the large negative values of the calculated disproportionation energies (kcal/mol): -49.2

Table 2. Charge Densities and 3s-Orbital Charges at Phosphorus by ab initio Calculation (3-21G)

Compound	Charge density ($\times 10^{-3}$) at phosphorus atom						3s-Orbital charge at phosphorus atom					
	1	2	3	4	5	6	1	2	3	4	5	6
2	+46	+46					1.893	1.893				
3	+4	+21	+21				1.965	1.968	1.968			
4	-3	-3	-3	-3			1.937	1.937	1.937	1.937		
5	-8	-33	-11	+6	+3		1.916	1.923	1.931	1.926	1.921	
6	+2	+2	+2	+2	+2	+2	1.939	1.939	1.939	1.939	1.939	1.939

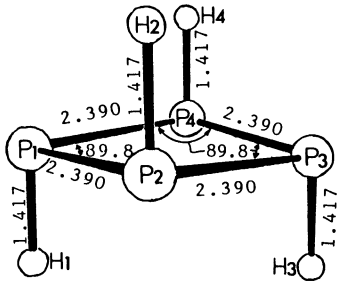


2 (C_{2h})



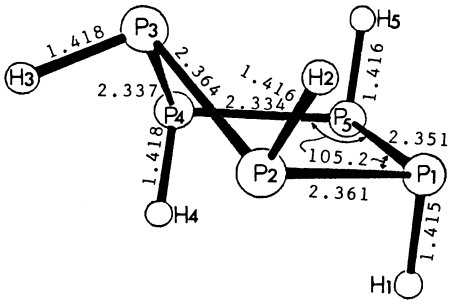
$\angle H_2P_2P_3P_1$=-90.3
$\angle H_1P_1P_3P_2$=-92.2

3 (C_s)



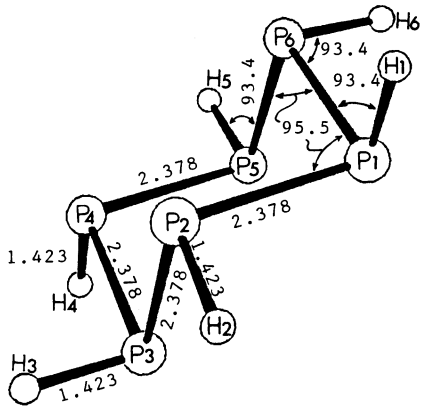
$\angle H_1P_1P_3$=91.1 $\angle H_1P_1P_3H_3$=0.0
$\angle H_2P_2P_4$=91.1 $\angle$H2P2P4H4=0.0

4 (D_{2d})



$\angle P_2P_3P_4$=100.0 $\angle P_3P_2P_1P_5$=-24.3
$\angle P_3P_2P_1$=100.0 $\angle P_2P_1P_5P_4$=- 9.4
$\angle P_3P_4P_5$= 98.0

5 (C_1)



$\angle P_6P_1P_2P_4$= 42.0 $\angle H_6P_6P_1P_2$=177.7
$\angle H_1P_1P_6P_5$=177.7 $\angle P_1P_2P_4P_5$= 0.0

6 (D_{3d})

Fig. 1. Optimized structure of $(PH)_n$ by ab initio calculation (3-21G). Some selected bond lengths, angles, and dihedral angles are shown in Å and degrees.

for $3P_2H_2 \rightarrow 2P_3H_3$, -41.5 for $4P_3H_3 \rightarrow 3P_4H_4$, -50.9 for $5P_4H_4 \rightarrow 4P_5H_5$, and -36.8 for $6P_5H_5 \rightarrow 5P_6H_6$. In other words, steric protection is very important for the isolation of compounds of the type **2**. The reason why the dimer (and not cyclopolyphosphanes) was the only isolated product in our case[1] is not explicable besides the large steric hindrance.

Furthermore, the ^{31}P NMR chemical shift of type **2** compounds, **1A-C**, appear at very low fields, whereas those of all the other cyclopolyphosphanes appear at higher fields. This could be qualitatively explained in terms of the net charge densities and/or 3s-orbital densities at the phosphorus atoms given in Table 2. Further theoretical studies on the $(PH)_n$ systems are extensively in progress in these laboratories.

All calculations were carried out at the Institute for Molecular Science using the GAUSSIAN 80 (WF10-25) program in the IMS Computer Center library program package. We thank Dr. Ken Hirotsu at Osaka City University for his valuable comments. This work was supported in part by the Scientific Research Grant-in-Aids (57540276 and 58840023) from the Ministry of Education, Science and Culture and the Kurata Research Grant from the Kurata Foundation.

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(Received December 20, 1984)