

## ELECTRONIC STRUCTURE OF THE 1,3-DIPHOSPHETANE

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The equilibrium structures of *cis*- and *trans*-1,3-diphosphetane were evaluated at the RHF/6–31 g\*\* level of optimization, with MP2 electron correlation correction. Both structures are puckered, the *trans* isomer being slightly lower in energy than the *cis* isomer. The inversion barrier in 1,3-diphosphetane is lower in energy than in phosphetane.

### 1. INTRODUCTION

The self-addition of phosphalkene, **I**, to form the diphosphetane is an important type of reaction.<sup>1–5</sup> The reaction proceeds predominantly by head-to-tail combination to the 1,3-diphosphetane, **II** (Scheme 1). It is initiated by light or elevated temperatures. It has been discussed that in solution there might be partial or complete dissociation, forming monomers.<sup>2,3,6–8</sup> The tendency for dimerization increases with decreasing volume of the substituents at phosphorus<sup>2,9–15</sup> and/or at the methylene C-atom.<sup>16,17</sup>

Although in most cases 1,3-diphosphetanes, **II**, have been observed in the self-dimerization of phosphalkenes, 1,2-diphosphetanes, **III**, have also been obtained.<sup>18,19</sup> A qualitative rationale for the head-to-tail versus tail to tail (or head-to-head) dimerization has been given on the basis of frontier orbital considerations.<sup>20</sup> Alkyl substituents and  $\pi$ -donor substituents at the carbon (e.g. OSiMe<sub>3</sub>) of the PC double bond generate a HOMO with a greater coefficient at phosphorus (in comparison with parent phosphalkene).

Consequently, the first link in the [2 + 2] dimerization occurs between the two P positions of higher  $\pi$ -electron density leading to the 1,2-diphosphetanes.

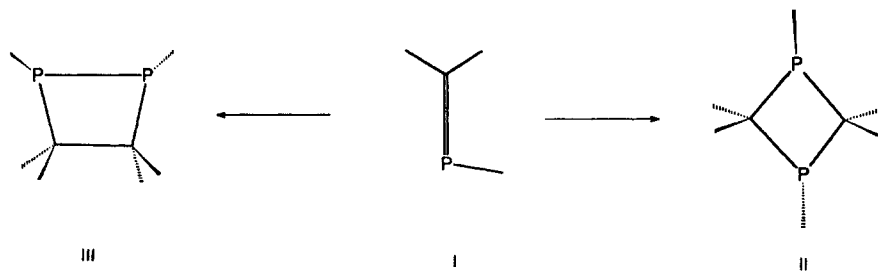
In this paper, we evaluate the bonding properties of the parent 1,3-diphosphetane, **II**, the most common product in the self-addition process of phosphalkenes. In detail, we analyse (a) the equilibrium structures, (b) the inversion barriers at phosphorus and (c) the ring strain in **II**, utilizing corresponding homodesmotic reactions. Computational details are given in the Appendix.

### RESULTS AND DISCUSSION

#### Structures

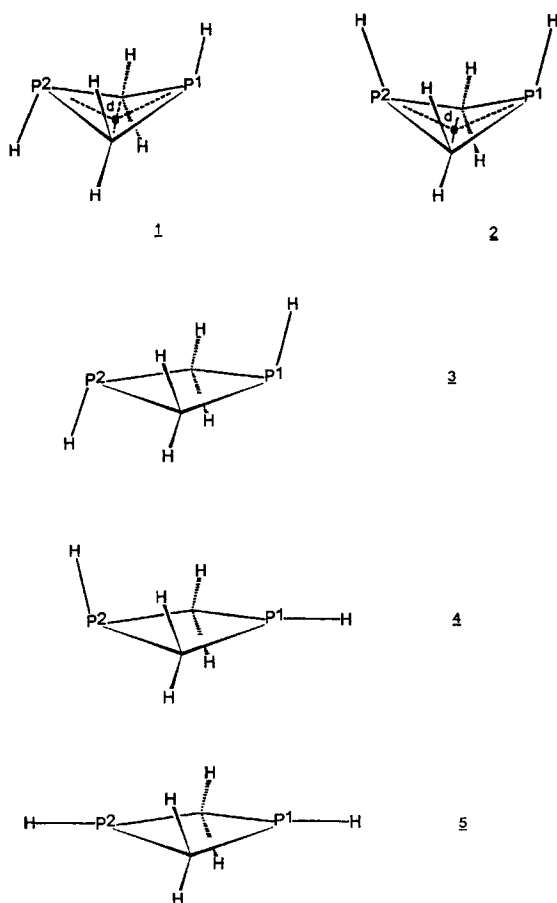
For parent **II** (all substituents at the ring atoms are hydrogens), we obtained upon geometry optimization at the RHF/6–31 g\*\* level the stationary points shown in Scheme 2.

The absolute energies of all the compounds investi-



Scheme 1

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Scheme 2

gated are given in Table 1 and the most important geometrical parameters are summarized in Table 2.

In **1** the hydrogens are in *trans* and in **2** in *cis* positions relative to each other. These geometries are the only energy minima on the electronic hypersurface, as revealed by the corresponding vibrational analyses. In both geometries the four-membered ring is slightly folded, so that the lone pair orbitals at the phosphorus atoms point maximally away from each other. On this basis, the repulsion between the lone pair orbitals is minimized. A structure with a planar ring moiety ( $C_{2h}$  geometry), **3**, possesses one imaginary vibration ( $i91\text{ cm}^{-1}$ ,  $b_{3u}$ ). It is only slightly higher in energy ( $4.9\text{ kJ mol}^{-1}$  at the MP2 level plus zero point energy correction, see Table 1) than the puckered structure **1**. The PC bonds in all the compounds investigated refer to single bond values;<sup>21</sup> the PCP angles are larger than the CPC angles. This is a consequence of the larger valence angle strain at carbon compared with phosphorus.<sup>22</sup>

Of further interest are the transition state structures for the inversion at the phosphorus center(s), **4** and **5**. In the former the ring moiety is planar; the CP(1)C angle is decreased while the adjacent PCP angles are shrunk. This is due to enhanced angle strain at the trigonal planar phosphorus atom. In addition, the PC bonds at the phosphorus are elongated ( $1.896\text{ \AA}$ ). The structure **4** with only one planar phosphorus centre possesses one imaginary frequency ( $i975$ ,  $a$ ). Hence it is a transition state structure. In comparison, in **5** two phosphorus centres are planar. This structure possesses two imaginary frequencies ( $i1123$ ,  $b_{2g}$ ;  $i1038$ ,  $b_{1u}$ ) which refer to a *trans* ( $b_{2g}$ ) or a *cis* ( $b_{1u}$ ) movement of the hydrogens at P to **1** or **2**. Hence **5** is not a transition state for the inversion process.

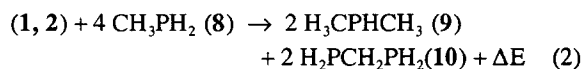
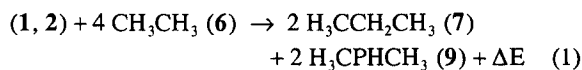
### Inversion barriers

The energies of all the species investigated were evaluated at (a) the RHF/6-31  $g^{**}$  level and with (b) additional electron correlation correction at the MP2 level (MP2/6-31  $g^{**}$ /RHF/6-31  $g^{**}$ ) and further zero-point energy corrections. Absolute (in atomic units) and relative energies (in  $\text{kJ mol}^{-1}$ ) of all species under investigation are given in Table 1. The structure **1** is lowest in energy, with **2** slightly above. Together with values for related systems, the energy barriers for inversion are given in Table 3.

For the nitrogen cases the inversion barriers are considerable lower in energy than for the phosphorus structures. Interestingly, the inversion barrier for 1,3-diphosphetane [ $162.1\text{ kJ mol}^{-1}$  (Ref. 27)] is lower than for phosphetane ( $178.5\text{ kJ mol}^{-1}$ ). In other words, the presence of the second phosphorus centre makes the inversion process more facile.

### Ring strain energies

Ring strain-energies were evaluated by means of corresponding homodesmotic reactions.<sup>28,29</sup> For the molecules studied, the selection of proper reactions is not unique. Hence we chose two different routes for the evaluation of strain energies:



For 6-9 the equilibrium geometries have been reported previously, utilizing a basis set without polarization functions at the hydrogens (6-31  $g^*$ ).<sup>30</sup> For these species we repeated the optimization of structures, using the better basis set (6-31  $g^{**}$ ). Our geometries are in accord with the findings of the previous workers. Hence the resulting geometries for 6-9 will not be

Table 1. Absolute (au) and relative energies (kJ mol<sup>-1</sup>)

Compound	RHF <sup>a</sup>	MP2 <sup>b</sup>	ZPE <sup>c</sup>	$\nu(\text{cm}^{-1})^d$
1	-760.649378 0.0 <sup>e</sup>	-761.154564 0.0	-761.074974 0.0	1263, <i>a'</i>
2	-760.649159 0.6	-761.153892 1.8	-761.074295 1.8	145, <i>a</i> <sub>1</sub>
3	-760.648587 2.1	-761.152500 5.4	-761.073104 4.9	191, <i>b</i> <sub>u</sub>
4	-760.581326 178.6	-761.092007 164.2	-761.013218 162.1	i975, <i>a'</i>
5	-760.501377 388.5	-761.017324 360.3	-760.939716 355.1	i1123 <i>b</i> <sub>2g</sub> ; i1038, <i>b</i> <sub>1u</sub>
6	-79.238235	-79.543355	-79.464143	328, <i>a</i> <sub>1u</sub>
7	-118.276159	-118.725275	-118.615433	234, <i>a</i> <sub>2</sub>
8	-381.495435	-381.763685	-381.705494	244, <i>a''</i>
9	-420.538214	-420.951473	-420.862036	193, <i>a'</i>
10	-722.787023	-723.164156	-723.096266	120, <i>a''</i>

<sup>a</sup> RHF/6-31 g<sup>\*\*</sup>.<sup>b</sup> MP2(fc)/6-31 g<sup>\*\*</sup>//RHF/6-31 g<sup>\*\*</sup>.<sup>c</sup> Level (b) plus zero-point energy correction (harmonic approximation at RHF level, unscaled).<sup>d</sup> Energy lowest vibration(s).<sup>e</sup> Second entry, relative energies in kJ mol<sup>-1</sup>.

Table 2. Geometry data for stationary points on the potential energy surface

Compound	Symmetry	Geometry data
1	<i>C</i> <sub>s</sub>	P <sup>1</sup> C = 1.879, P <sup>2</sup> C = 1.871 <P <sup>2</sup> CP <sup>2</sup> = 92.6, <CP <sup>1</sup> C = 84.2, <CP <sup>2</sup> C = 84.6, <HP <sup>1</sup> d = 99.3, <H <sup>2</sup> P <sup>2</sup> d = 105.8, <P <sup>1</sup> dP <sup>2</sup> = 154.7
2	<i>C</i> <sub>s</sub>	PC = 1.877 <PCP = 94.4, <CPC = 84.2, <HPd = 99.3, <PdP = 163.0
3	<i>C</i> <sub>2h</sub>	PC = 1.878 <PCP = 94.0, <CPC = 96.0, <HPd = 102.0, <PdP = 180.0
4	<i>C</i> <sub>s</sub>	P <sup>1</sup> C = 1.832, P <sup>2</sup> C = 1.896 <CP <sup>1</sup> C = 88.5, <CP <sup>1</sup> C = 93.6, <CP <sup>2</sup> C = 89.5, <H <sup>1</sup> P <sup>1</sup> d = 180.0, <H <sup>2</sup> P <sup>2</sup> d = 100.4, <P <sup>1</sup> dP <sup>2</sup> = 179.2
5	<i>D</i> <sub>2h</sub>	PC = 1.855 <P <sup>1</sup> CP <sup>2</sup> = 84.4, <CP <sup>1</sup> C = 95.6, <H <sup>1</sup> P <sup>1</sup> d = 180.0, <H <sup>2</sup> P <sup>2</sup> d = 180.0, <P <sup>1</sup> dP <sup>2</sup> = 180.0

<sup>a</sup> Bond lengths in Å, angles in degreesTable 3. Inversion barriers<sup>-1</sup>

Structure	$\Delta E$ (kJ mol <sup>-1</sup> )	Ref.
Dimethylamine	18.4	23
Azirine	72.1	24
Azetidine	74.9	25
Phosphine	149.0 <sup>a</sup>	26
Methylphosphine	152.8 <sup>a</sup>	26
Dimethylphosphine	160.1 <sup>b</sup>	27
Phosphirane	285.8 <sup>b</sup>	27
Phosphetane	178.5 <sup>b</sup>	27
1,3-Diphosphetane (one P)	162.1 <sup>c</sup>	This work
(two P)	355.1 <sup>c</sup>	This work

<sup>a</sup> MP3/6-31 g<sup>\*</sup>//RHF/3-21 g<sup>\*</sup>.<sup>b</sup> MP2/6-31 g<sup>\*</sup>//RHF/6-31 g<sup>\*</sup> + ZPE correction (at RHF level).<sup>c</sup> MP2/6-31 g<sup>\*\*</sup>//RHF/6-31 g<sup>\*\*</sup> + ZPE correction (at RHF level).

Table 4. Energies (kJ mol<sup>-1</sup>) for reactions (1) and (2)

Reaction	Structure	RHF <sup>a</sup>	MP2 <sup>b</sup>	ZPE <sup>c</sup>
(1)	1	70.0	68.7	63.2
	2	69.4	67.0	61.4
(2)	1	51.3	59.4	53.4
	2	50.8	57.6	51.6

<sup>a</sup> RHF/6-31 g<sup>\*\*</sup>.<sup>b</sup> MP2(fc)/6-31 g<sup>\*\*</sup>//RHF/6-31 g<sup>\*\*</sup>.<sup>c</sup> Level (b) plus zero-point energy correction (computed at RHF approximation).

recorded. The strain energies thus calculated are given in Table 4.

Reaction (2) seems more appropriate for the estimation of strain, since in diphosphinomethane (10) as well as in diphosphetane (1, 2), one methylene carbon is surrounded by two phosphino groups. On the basis of both reactions (1) and (2), the ring strain in 1 (2) is lower in energy than in phosphetane [74.9 kJ mol<sup>-1</sup> (Ref. 27)]. In other words, the introduction of the second phosphorus atom into the four-membered ring system lowers the ring strain.

### CONCLUSIONS

The results of our investigations can be summarized as follows. 1,3-Diphosphetane adopts a puckered ring structure. The most stable geometry has the hydrogens in *trans* positions to each other. The introduction of a second phosphorus in the four-membered ring moiety further lowers the ring strain: cyclobutane 110.9 kJ mol<sup>-1</sup> (Ref. 22), phosphetane 74.9 kJ mol<sup>-1</sup> (Ref. 27), 1,3-diphosphetane 51.6 kJ mol<sup>-1</sup> [reaction (2)]. The ring strain energy is drastically reduced to 15.1 kJ mol<sup>-1</sup> in cyclotetraphosphane.<sup>31</sup> In fact, the introduction of phosphorus into small ring systems reduces their strain, a classical deduction by Pauling and Simonetta.<sup>32</sup> At the same time, the energy barrier for inversion at phosphorus is also slightly lower in 1,3-diphosphetane than in phosphetane.

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## APPENDIX

All of the quantum chemical calculations were carried out with the Gaussian 92 set of programs.<sup>33</sup> For the RHF calculations the 6-31 g\*\* basis set<sup>34</sup> was used. It is of double- $\zeta$  quality and contains polarization functions at all atoms. The MP2 electron correlation corrections<sup>35</sup> were computed within the frozen core approximation. All energy optimizations were performed with analytically determined nuclear coordinate gradients. The vibrational analyses were carried out within the harmonic approximation.