Bis(methylene)phosphorane and Related Compounds: Electrocyclization to Ring Systems

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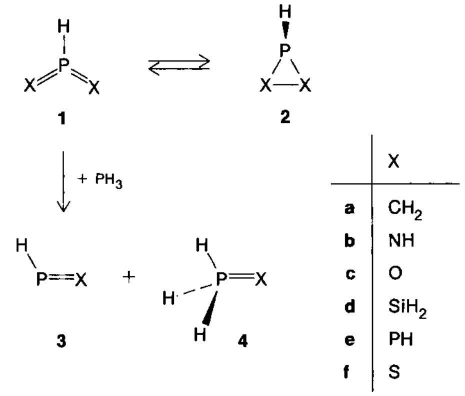
On the bais of ab initio calculations of double-ζ quality at a SCF and MCSCF level, bonding in bis-ylenephosphoranes is compared with the one in phosphoranes. The investigations include the series H_3PX, HPX_2, HPX (X = CH_2, NH, O, SiH_2, PH, S). The bis-ylenephosphorane formation becomes more favorable with increasing electronegativity of X. An extreme case is the electropositive group X = SiH_2. The resulting π-system suffers from the Jahn-Teller distortion, causing reduction from C_{2v} to lower C_2 symmetry in the corresponding bis-ylenephosphorane. Energetically, the corresponding ring systems are more stable than their bis-ylenephoshorane counterparts (for X = CH_2 and PH). The electronic hypersurface of the hitherto unknown bis(phosphinylidene)phosphorane is explored in detail and compared in regard to bonding with its analog bis(methylene)phosphorane. For both cases π-push-pull substitution is important for stabilization of the planar allylic geometry.

Tricoordinated phosphorus systems such as **1** are now well-established[1-5]. Exceptions are **1d** and **1e**, which are hitherto experimentally unknown. The ring isomer to **1e**, cyclotriphosphane (**2e**), is well-established and characterized[6].



	X
a	CH_2
b	NH
c	O
d	SiH_2
e	PH
f	S

Most of the experimental investigations are concerned with syntheses and structural elucidations of bis(methylene)phosphoranes **1a**[1,7]. In fact, the detailed experimental investigations indicate that strong π-electron-accepting groups such as silyl have to be attached to the carbon atoms, in order to stabilize the open form **1a**[8]. Allylic geometries as well as closed-ring structures have been characterized also in detail for the bisiminophosphoranes[2,9].

In the present publication we investigate the following aspects of the bis-ylenephosphorane series, **1**: (i) the ring closure reaction of **1** to its corresponding three-membered ring system **2**; (ii) the stability of **1** towards reaction with PH_3 to the ylenephosphane **3** and the ylenephosphorane **4**. As we have noted earlier[10] the yet unknown **1d** is a special case. It suffers from the Jahn-Teller distortion which causes (a) the formation of a nonplanar allylic system and (b) as a further consequence introduces biradical character within this species. (iii) In detail, we will investigate the structure and electronic properties of **1e**. It will be shown that its verification should be feasible. The quantum-chemical investigation presented in this paper is a comparative study of the whole variety of bis-ylenephosphoranes **1** versus corresponding ring systems **2**. Some aspects of the properties of **1a** have been reported previously[10,11]. All details of the quantum-chemical procedures are given in the theoretical section at the end of this publication.

Results and Discussion

a. Bis(phosphinylidene)phosphorane

In accordance with our previous investigations[11b] planar **1** refers to an allylic system with 4 electrons constituting the π-system. The matter is illustrated for **1a** in Figure 1.

Above and below the set of π-orbitals are corresponding σ (σ*) orbitals. As we have shown in detail previously, the interaction among these orbitals causes a deviation from planarity (C_2 symmetry). It might be strong, as for **1d**[10], or weak, as for **1a**[11b] and is the consequence of a second-order Jahn-Teller interaction. Of importance in these qualitative bonding considerations are two aspects: (a) The coefficient at the terminal positions is larger in magnitude in the orbital π_2 than in π_3. As a consequence the replacement of these positions in **1a** by more electronegative atoms (groups), as in **1b** and to a greater extent in **1c** lowers the former orbital more than the latter. Hence, it will increase the singlet stability of these structures. The opposite holds true for **1d**, when compared with **1a**. The former possesses strong biradical character in contrast to the latter[10]. (b) Alternatively, the allylic systems will gain enormous stability when the terminal atoms are substituted by π-electron-withdrawing substituents, e.g. silyl groups. This has been studied in detail on substituted bis(methylene)phosphoranes, **1a**[8].

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In our investigations we first determined the geometry parameters for **1** by energy optimization of the structures at a SCF level. Only the geometry parameters of **1e** will be reported here in detail, since they offer bonding parameters for hitherto experimentally unknown structures. The parameters are collected in Figure 2.

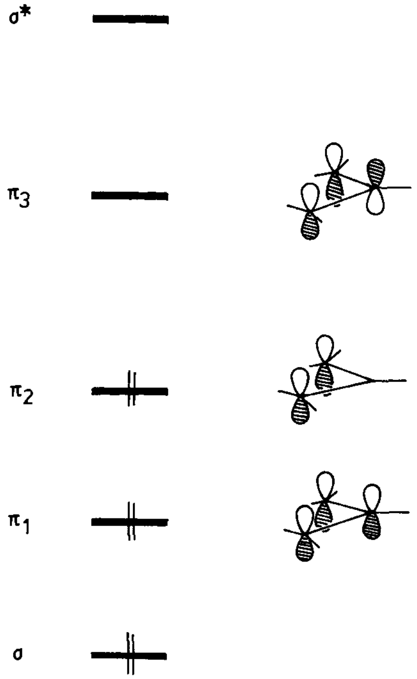

Figure 1. Molecular orbital system of **1a**

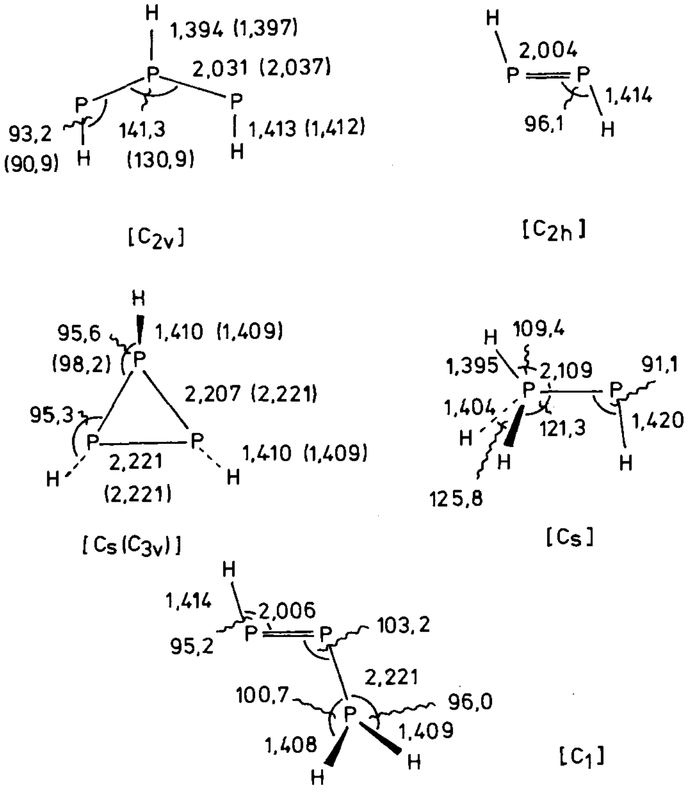

Figure 2. Geometry parameters of **1e**, of its structural isomers and related systems; bond lengths are in Angströms, bond angles in degrees

For completeness, we have included in our considerations the computationally derived structures of diphosphene and of phosphinylidenephosphorane. As it has been found for the bisiminophosphorane[11a] **1b**, its phosphorus analog **1e** can also exist in several conformations, of which only the C_{2v} symmetrical structures are reported here. For **1e** the conformer with a *cis* arrangement of the hydrogens at the terminal phosphorus atoms is slightly more stable than its *trans* conformer (values in parentheses). Simultaneously, the valence angle at the central phosphorus atom is enlarged in the former (141.3°) compared with the latter (130.9°) geometry (see Figure 2, values in parentheses).

For **1e** the theoretical investigations predict a PP bond length between a double bond (ca. 2.03 Å[13]) and a single bond (2.20 Å[14]). The predicted bond length of 2.03 Å is in good agreement with the hitherto reported length PP = 2.05 Å for a (thioxophosphinylidene)phosphorane[5b]. The bonding parameters of the other bis-ylenephosphoranes will not be discussed here. For **1a** and **1b** they are in good agreement with the experimentally reported structures[7], and for **1b** they are also in conformity with a recent theoretical study[12a]. **1e** (C_{2v}, hydrogens *cis*) is more stable than **1e** (C_{2v}, hydrogens *trans*) by 4.5 kcal/mol at a SCF/CEPA-1 level. A geometry in which one hydrogen is *cis* and the other *trans* is intermediate in stability, 2.1 kcal/mol less stable than **1e** (*cis,cis*). The bonding situation may be compared with **1b** which result 10.1 kcal/mol energy difference (for the C_{2v} symmetrical structures) in favor of the *cis* geometry. In other words there the *cis* effect is much stronger pronounced (compared with **1e**). The isomer phosphinodiphosphene prefers a *trans* conformation, in which the phosphino substituent is oriented such as to enforce π-overlap with the PP-π-bond (see Figure 2). This isomer is 21.7 kcal/mol more stable than **1e** (*cis*). One may compare the situation with bonding in **1a**. There the corresponding methylenephosphane isomer is more stable than **1a** by 50 kcal/mol at a SCF/MP2 level[12c].

One aspect must be further discussed here. The bis-ylenephosphoranes possess planar structures. How large is the pyramidalization force at the central phosphorus atom? In order to elucidate this aspect, we performed for all the species under consideration a vibrational analysis within the harmonic approximation. The resulting wave numbers [cm^{-1}] for the corresponding pyramidalization vibration are: **1a** 390.2; **1b** (*cis*) 544.5; **1b** (*trans*) 610.7; **1c** 730.9; **1e** (*cis*) 270.4; **1e** (*trans*) 331.3; **1f** 564.2. The data indicate an increasing tendency for planarity with increasing electronegativity of the ligands at the central atom. In other words **1c** has less tendency for pyramidalization at the central atom than **1a**. On this basis **1e** possesses the most floppy π-system in the bis-ylenephosphorane series. This trend is just opposite to the effect of substituents on the inversion barrier in phosphines. There the inversion barrier increases with increasing electronegativity of the ligands[15]. Electronegative ligands in the structural type **1** also tend to withdraw the electron density from the central phosphorus atom. On this basis the pyramidalization force is diminished.

For further investigation of the stabilities of the species **1** we also have calculated the vertical singlet-triplet energy separations. The results are summarized in Table 1.

Table 1. Vertical singlet-triplet energy separations [kcal/mol] for **1**

X	ΔE	c_0[a]	c_1[a]
CH_2	66.8[b]	0.982	−0.187
NH (*cis*)	101.1	0.986	−0.169
O	130.7	0.990	−0.138
PH (*cis*)	37.5	0.958	−0.286
S	60.3	0.980	−0.197
SiH_2	18.9[b]	0.903	−0.429

[a] Coefficients of 2X2 MCSCF wave function. — [b] Values taken from ref.[10].

Except **1d**, which has to be described as a biradical structure and to less extent also **1e**, all other species possess definite singlet ground states. This is also in accord with the large ground state contribution in the MCSCF wave function (see Table 1). The vertical singlet-triplet energy separations parallel the previously discussed pyramidalization vibrations for 1.

b. Phosphiranes

Next we will discuss our results on the ring systems **2**. They have been studied by assuming C_s symmetry, in a *trans* or *cis* conformation of the hydrogens. Only the geometries of the ring structures for **2e** will be reported here. As noted before some of the ring systems are known. The structure of a derivative of **2b** has been reported[9]. **2a** opens conrotatorily in a thermally induced retroelectrocyclic reaction[16]. This is to be expected since the isovalence electronic aziridines are known to undergo conrotatory electrocyclization as well[17].

We are now able to compare the energy differences of open **1** and closed **2** structures (Table 2).

Table 2. Energy differences [kcal/mol] between open (**1**) and closed (**2**) structures

X	ΔE	ΔE (SCF/CEPA-1)
CH_2	−47.2	−46.8
NH (*cis*)	21.2	19.7
O	85.0	79.6
SiH_2	−58.1	−42.2
PH (*cis*)	−36.3	−27.9
S	6.8	9.0

A negative (positive) value in the energy balance indicates exothermicity (endothermicity) for the ring opening. The chosen conformations of the three-membered ring systems **2** are slightly more stable in their *trans* conformations, although the energy differences are small ($\leqslant 2$ kcal/mol). The tendencies are also retained at the correlation corrected level. The bisylenephosphorane **1** with electronegative atoms (groups) in the terminal positions (O, NH, S) are more stable than their corresponding ring structures. These cases may be compared with X = CH_2, SiH_2, PH which are considerably more stable as ring systems. Further investigations with semiempirical methods[11b] evidence that in **1a** electron-withdrawing substituents at the terminal carbons considerably stabilize **1a** over **2a**. In other words, the existence of **1a** as a stable entity on the electronic hypersurface is due to substituent effects which stabilize the negative charge at the terminal positions in **1a**. This is in full accord with experiment.

Since the bis(phosphinylidene)phosphorane **1e** is still an open target for experimentalists we have explored the electronic hypersurface of it in more detail. It includes the evaluation of a more detailed elaboration of the ring closure process. Table 3 collects various SCF-optimized points of the hypersurface for the ring closure reaction of **1e**. It appears as an energy minimum and is separated by a sizable energy barrier to ring closure to **2e**. The well is a consequence of the allylic π-conjugation in **1e** which has to be set off before ring closure occurs.

Table 3. Various points on the electronic hypersurface for ring closure reaction of **1e** (*cis*)

PPP [°]	ΔE (SCF)	ΔE (SCF/MR-ACPF)
141.3 (**1e**)	0.0	0.0
110	21.1	17.9
108	24.0	20.4
106	27.0	22.8
104	29.3	19.9
103	29.1	17.3
102	28.2	15.7
100	25.8	13.8
59.8 (**2e**)	−36.3	

The picture of bonding for **1e** will be completed by a Mulliken population analysis in its *cis* conformation. For convenience, we have also included the corresponding data for **1a** (in parentheses) (Figure 3).

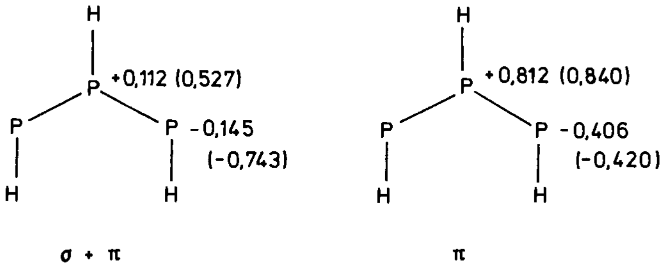

Figure 3. Mulliken population analysis for **1e** (*cis*) and **1a** (in parentheses)

Both species reveal similar features: in the π-space electron density is withdrawn from the central phosphorus atom and shifted to the terminal atoms (groups). The effect is stronger in **1a** than in **1e**. This indicates that the mechanism which stabilizes **1e** should be similar. It requires further withdrawal of electron density from the central phosphorus atom. In more detail a π-donating group (e.g. an amino substituent) should be attached to the central atom and electron-accepting substituents to the peripheral phosphido groups. Hence, there should be no essential difference in bonding between **1a** and **1e**. The only difference is the weaker allylic bond in the latter compared with the former system.

c. Ylenephosphoranes

In the last section we will compare bis-ylenephosphoranes **1** with ylenephosphoranes **4**. For this purpose, we have employed the reaction of **1** with PH_3 to **3** and **4**. It yields information on the tetracoordination of phosphorus in **4**, in comparison to tricoordination, as in a **1**. The corresponding energy balances have been obtained at a SCF and SCF/CEPA-1 level. They are collected in Table 4.

Table 4. Energy balances [kcal/mol] for reaction **1** + PH_3

X	ΔE (SCF)	ΔE (SCF/CEPA-1)
CH_2	9.7	10.1
NH[a]	23.8	24.8
O	24.5	26.5
SiH_2	−13.7	−1.0
PH[a]	9.2	15.4
S	13.2	17.2

[a] Energy difference between **1** (*cis*) and **2** (*trans*) conformation.

Again negative (positive) values for ΔE refer to exothermic (endothermic) reactions. Except for the case **1d** the energy balances are endothermic. The stability of the bis-ylenephosphoranes **1** in comparison with their mono-ylenephosphoranes **4**, i.e. increases with increasing electronegativity of X.

Some of the phosphoranes have been structurally evaluated previously by other authors[18]. The reported results agree with the one obtained here. In addition, some of the systems **3** have been discussed previosuly[19], again the results are in accord with ours.

The present data also allow an analysis of changes in structural parameters, especially of bond lengths in **1**, **3** and **4**. Hitherto such a gathering of information has not been possible since in most cases the basis sets of the various quantum-chemical studies are not strictly comparable. Concomitant changes in PX bond lengths are collected in Table 5.

According to the calculations, the PX bonds in **3**, **4** and **1** are similar in lengths. They shorten slightly in the bis-ylenephosphorane formation with electronegative ligands X (NH < O). On the other hand, **4** (X = SiH_2) possesses an equilibrium PSi bond (2.417 Å) which is even slightly longer than the corresponding single bond (ca. 2.254 Å[10]). The fact that the bond distance decreases with increasing difference in electronegativity of the constituting atoms is also evidenced by the well-known series ($CH_3F > CH_2F_2 \gg CF_4$), with the average CF bond energy[20] increasing in the same order.

Table 5. Relevant PX bond lengths [Å] in **1**, **3** and **4**; first entry absolute values, second entry relative changes (in per cent) with respect to **3**

X	**3**	**4**	**1**
CH_2	1.654	1.670 (+1.0)	1.636 (−1.1)
NH	1.556	1.548 (−0.5)	1.521 (−2.2)
O	1.462	1.418 (−3.0)	1.435 (−1.8)
SiH_2	2.057	2.417 (+17.5)	2.164 (+5.2)
PH	2.004	2.109 (+5.2)	2.031 (+1.3)
S	1.913	1.945 (+1.7)	1.892 (−1.1)

Conclusion

The present report is concerned with the following aspects in phosphorus chemistry:

(i) a detailed investigation of the bis-ylenephosphoranes **1** with X = CH_2, NH, O, SiH_2, PH, S. Besides the case X = SiH_2 and to less extent X = PH, all species are predicted as closed shell species on the electronic hypersurface. The latter species suffers from the Jahn-Teller distortion of the geometry which causes a C_2 symmetrical allyl system with biradical character. The resulting PSi bond length is intermediate between a double bond and a single bond. For all other species **1** the resulting allylic π-bonds are similar in lengths to the corresponding real double-bonded systems **3**.

(ii) The electrocyclic ring closure reaction of **1** to its corresponding three-membered ring systems is exothermic for X = CH_2, SiH_2 and PH. In the other cases (X = O, NH, S) **1** is more stable than **2**, due to the stabilization of **1** by electronegative ligands incorporated in the allylic system.

(iii) The monoylene formation of **4** from **1** by corresponding group transfer reactions to PH_3 is endothermic in case X is more electronegative than phosphorus (O, S, NH). For **1e** compared with **1a** the calculations predict similar bonding properties. Hence, it should be feasible to experimental verification. Nevertheless, the calculations also reveal a relatively small energy barrier to ring closure to **2e**. Further π-push-pull substitution will in fact be of energetic advantage of **1e** compared with its ring isomer **2e**.

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Theoretical Procedure

All the quantum-chemical calculations were carried out at an ab initio double-ζ level including polarization functions at the heavy atoms. The corresponding basis sets were constructed from Huzinaga[21]-type functions as follows:

C, N, O, (9,5) in the contraction [5,4X1/3,2X1]; P, S, (11,7) in the contraction [5,6X1/4,3X1]; H (4) [3,1]. One set of polarization functions was added to the heavy atoms, ζ_d(C,N,O,P,S) = 0.8; 0.95; 1.25; 0.5; 0.55.

Corrections for electron correlation were performed according to the CEPA-1 method[22a] at the SCF geometries. For the determination of singlet-triplet energy separations the SCF determined ground state geometries were taken; for the singlet energies MR-ACPF[22b] calculations were performed, given a 2X2 MCSCF[22c] calculation between HOMO and LUMO as reference, the triplet energies were determined from corresponding ACPF calculations with the RHF solution of the triplet state. For the evaluation of energy points near the transition state geometries (optimization at SCF level) also the 2X2 MCSCF wave function served as reference for the MR-ACPF calculations. All energy minima were identified by overall an positive force constant from a corresponding vibrational analysis (within the harmonic approximation). All calculations at a SCF level were performed with the TURBOMOLE program systems[23] while the correlation calculations were carried out with the MOLPRO program systems[24]. Full details of all geometries and frequencies within the harmonic approximation are available on request.

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