1,2-Diphosphetes with Unusual Structures – A Quantum Chemical Investigation of Bonding Properties[☆]

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According to quantum chemical calculations at an ab initio level parent 1,2-diphosphete is slightly more stable than its corresponding 1,4-diphosphabutadiene structural isomer. The quantum chemical calculations indicate that substituents at phosphorus and to a much less extent at carbon exert strong influences on the equilibrium geometries of 1,2-diphosphete structures: π donors at phosphorus strongly elongate the P–P bond while electronegative substituents at phosphorus increase the interflap angle of the four-membered ring systems, bringing an envelope conformation to the fore. The lengthening of the P–P bond gives rise to a Möbius-type delocalization within the ring moiety.

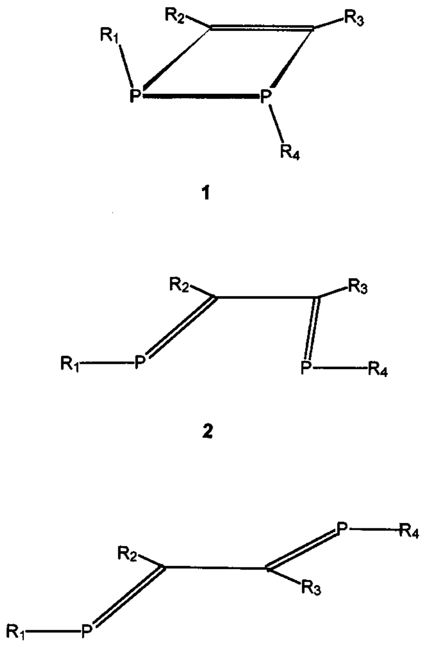
Introduction

Since the first described route for the syntheses of 1,2-diphosphetes **1** by condensation of cyclopolyphosphanes with alkynes[1] a variety of procedures have been reported, involving the [2+2] cycloaddition reaction of diphosphene complexes with alkynes[2], insertion of a phosphenium cation into a three-membered phosphirene ring[3], the reaction of sterically stabilized iminophosphanes with phosphirenes[4], the Zr-to-P metathetical exchange on 1-phospha-2-zirconacyclobutenes[5], and the reaction of butadiynes with terminal phosphanylidene complexes[6]. In addition a variety of other procedures exist[7]. The versatility of 1,2-diphosphetes has been summarized in recent reports[7].

Here we present quantum chemical calculations which reveal that substituents with strong donor capabilities have sizable effects on the P−P bond equilibrium geometries, ranging from usual (P−P = 2.2 A) to strongly stretched (P−P = 2.5 A) bonds. Furthermore, the substituents strongly affect the interflap angle of the four-membered ring system. On this basis we propose 1,2-diphosphetes with noticeable irregular geometries, which are best described by a cyclic delocalized ring system with 4 electrons (Möbius-type aromaticity).

We note that the recent experimental effort in the synthesis of 1,2-diphosphophosphetes has opened a new convenient general access to symmetrically or unsymmetrically substituted species. On the basis of the phosphanylidene complex addition reaction[6], it might be possible to introduce suitable functional groups at the phosphorus atoms. Corresponding precursor phosphanylide complexes have hitherto been reported for the alkoxy[8], alkoxycarbonyl[9], dialkylamino[10], and vinyl[11] substituents. Thus, our quantum chemical predictions should be amenable to experimental verification.

Scheme 1



Methodology

Previous investigations[12] demonstrate that the barriers for valence isomerization as well as the equilibrium geometries of the various stationary points on the electronic hypersurface are strongly sensitive to explicit treatment of electron correlation in the wavefunction. Within this line we have chosen for the present investigations the MP2 level of optimization, conducted by analytically determined gradients[13]. As a basis set we have used a double-ζ basis set

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augmented by polarization functions at the heavy atoms [6-31g(d)][14]. In addition for the anions one set of diffuse s,p functions was added. All details are provided in the discussion. The calculations were performed with the GAUSSIAN-94[15] set of programs.

Results and Discussion

a. Qualitative Considerations

We begin our discussion with an analysis of the electronic hypersurface for the ring-opening reaction of parent **1** (R^1 to R^4 = H) to its valence isomer, the *cis*-diphosphabutadiene **2**. It is valence-isoelectronic to cyclobutene, which undergoes a conrotatory ring opening ($\pi^2 + \sigma^2$) reaction to *cis*-butadiene according to the Woodward-Hoffmann rules[16]. Thus, one expects a similar reaction mode for the case at hand. However, there is an essential difference in bonding between cyclobutene and the 1,2-diphosphete. It becomes apparent by an inspection of bond energies (Table 1).

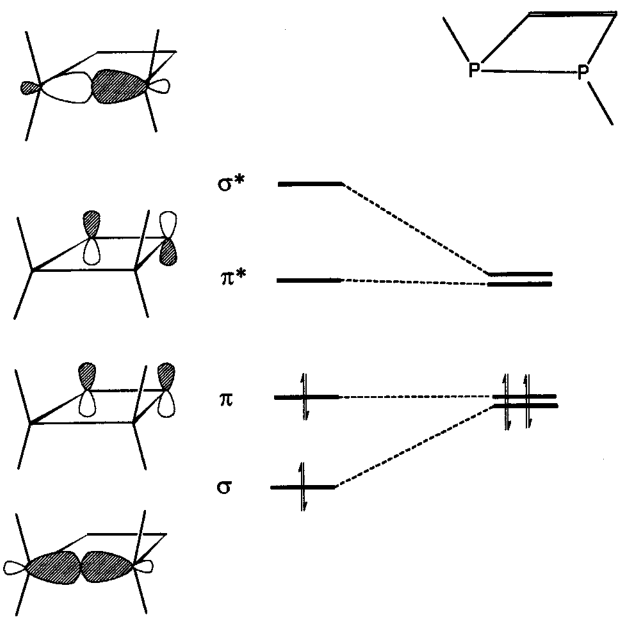
Table 1. Bond energies (in kcal/mol)

Type	*E* [kcal/mol]	Ref.
σ C−C	83	[a]
π C−C	65	[b]
σ P−P	50	[a]
π P−P	34	[b]
σ P−C	71	[c]
π P−C	43	[b]

[a] K. F. Purcell, J. C. Kotz, *Inorganic Chemistry*, Holt-Saunders International Editions, Honkong, **1977**. – [b] M. W. Schmidt, P. N. Truong, M. S. Gordon, *J. Am. Chem. Soc.* **1987**, *109*, 5217; W. W. Schoeller, C. Begemann, U. Tubbesing, J. Strutwolf, *J. Chem. Soc., Faraday Trans. 2* **1997**, *93*, 2957. – [c] Estimated by the Pauling relationship for heteropolar bonds, see: W. W. Schoeller, R. Schneider, *Chem. Ber.* **1997**, *130*, 1013; see Appendix.

A P−P σ bond is essentially weaker than a C−C σ bond. An estimate for the bond energy from (parent) **1** (R^1 to R^4 = H) to **2** results endothermic in $-E_\sigma^{PP} + 2\,E_\pi^{PC} - E_\pi^{CC} = -29$ kcal/mol, with the energy values given in Table 1. This estimate neglects (a) possible ring strain which would be released upon ring opening and (b) rehybridization effects. Since factor (a) is small in phosphorus ring systems[17] it does not contribute significantly to the energy balance. In comparison with, a corresponding energy balance for ring opening in cyclobutene, based on the consideration of bond transformations, results also endothermic ($E_\sigma^{CC} + 2\,E_\pi^{CC} - E_\pi^{CC} = -18$ kcal/mol). However, in cyclobutene the ring strain is large (65 kcal/mol[18]). It has to be added to the energy balance and makes the ring-opening reaction for this case exothermic, in accord with experiment[19] as well as theory[20]. A further consequence of these considerations may be noticed here, schematically shown in Scheme 2.

Scheme 2



In cyclobutene the C−C π (π*) orbitals are higher (lower) in energy than the C−C σ (σ*) orbitals. In (parent) **1** the situation is different. The corresponding orbitals σ and π (σ* and π*) are similar in energy. It is in accord with the result of the quantum chemical calculations (not recorded here). As a consequence of the weaker P −P σ bond (in reference to the C−C σ bond) the energy barrier for an electrocyclic reaction from **1** to **2** should be smaller than in cyclobutene and the P−P σ bond sensitive to donating and/or σ-accepting substitutents attached to the phosphorus atoms. Regarding the ring-opening reaction, experimental investigations on parent **1** are not available, since the structures have to be synthesized with bulky substituents, in order to protect these compounds kinetically.

b. Valence Isomerization of Parent 1 to 2

According to recent quantum chemical calculations[12] the ring opening of the 1,2-diphosphete occurs with an energy barrier of 16.9 kcal/mol, a value comparable with an estimate at an RHF level of quantum chemical sophistication[21]. The energy balance to the *trans*-1,4-diphosphabutadiene **3** is endothermic by 2.9 kcal/mol[12]. The primary product in the ring-opening reaction of **1** is the *cis*-1,4-diphosphabutadiene **2**. It is less stable by 5.1 kcal/mol than its *trans* isomer **3**. It must be noted that the rotational barrier from **2** (C_2 symmetry) to **3** (C_{2h} symmetry) is fairly small[21]. Experimentally only the *trans* isomers are known[22][23] which is the most favoured butadiene structure because of the low-energy barrier for rotation. Overall these investigations indicate that the 1,2-diphosphete is the most stable species, but separated by a relatively small barrier from the butadiene derivatives.

c. Substituent Effects on 1

The conclusion that the P−P σ bond is weaker than a C−C σ bond raises the question about the magnitude of substituent effects on the geometries of 1,2-diphosphetes. To evaluate this aspect in more detail we first performed calculations on a variety of mono-substituted 1,2-diphosphetes, the substituents attached to one phosphorus center.

All geometries were determined at the MP2(fc)/6-31g(d). No symmetry restrictions were imposed in the structural energy optimizations.

Table 2. Relevant structural parameters (bond lengths in Å, bond angles in degrees) in mono-P-substituted 1,2-diphosphetes, at MP2 (fc)/6-31g(d) level, anions calculated at MP2(fc)/6-31+g(d) level

$R^{1[a]}$	P−P	P−C[b]	∠ P−C−C−P	∠ R−P−C−C (∠ H−P−C−C)
H	2.252	1.831	−16.1	110.8 (110.8)
CH_3	2.254	1.859	−15.3	112.5 (111.1)
SiH_3	2.260	1.831	−12.9	107.8 (107.8)
F	2.254	1.801	−25.9	124.2 (120.3)
Cl	2.260	1.827	−22.6	121.6 (116.9)
NH_2	2.291	1.822	−20.5	124.6 (118.0)
PH_2	2.264	1.829	−15.7	118.4 (111.8)
$O^{(-)}$	2.512	1.801	−26.8	131.8 (128.6)
$NH^{(-)}$	3.554	1.741	−20.2	174.1 (172.2)
$NSiH_3^{(-)}$	2.490	1.834	−25.1	131.4 (126.6)
$PH^{(-)}$	2.399	1.817	−16.8	126.4 (117.8)
$PSiH_3^{(-)}$	2.348	1.824	−13.7	127.9 (114.8)

[a] $R^2 = R^3 = R^4 = H$. – [b] P−C bond in vicinity to the the substituent R.

A typical spectrum of substituents at phosphorus were chosen. For the calculations of the anions one set of diffuse s,p functions was added to the heavy atoms.

A sizable lengthening of the P−P bond is already observed to R(P) = NH_2 (P−P = 2.291 A), in reference to the parent compound (R = H; P−P = 2.252 A). It is in conformity with the result of recent experimental findings[24]. An even stronger elongation of the P−P bond results for the substituents which carry a negative charge, $PH^{(-)}$ (2.399 A), $PSiH_3^{(-)}$ (2.348 A). The investigations indicate that π donors strongly elongate the P−P bond. Finally, for R = $NH^{(-)}$ the butadiene structure is already more stable than the diphosphete. Evidently the ring-opening reaction within the latter occurs without an energy barrier. Strong electronegative substituents, e.g., R = F do not exert considerable changes in the P−P bond lengths. Similarly operates a typical electron-accepting substituent, e.g., SiH_3. There is, however, a strong effect on the torsional angle ∠ R−P−C−C and the folding angle ∠ P−C−C−P of the ring moiety. In comparison to the parent compound, **1** (R^1 to R^4 = H), electronegative substituents (e.g., F) tend to increase and electropositive substituents (e.g., SiH_3) to decrease these torsional angles. A plot of both quantities (Figure 1) affirms an approximate relationship between both types of torsional angles (for a related discussion on torsional angles in cyclobutenes, see ref.[25]).

A rationale for the substituent effects can be given in an interaction diagram, as follows. For the case of simplicity we analyze these effects for the case of di-substitution at phosphorus, invoking simple symmetry arguments (Figure 2).

Figure 1. Plot of torsional angles ∠ RPCC vs. ∠ PCCP, for monosubstituted 1,2-diphosphetes (angles in degrees)

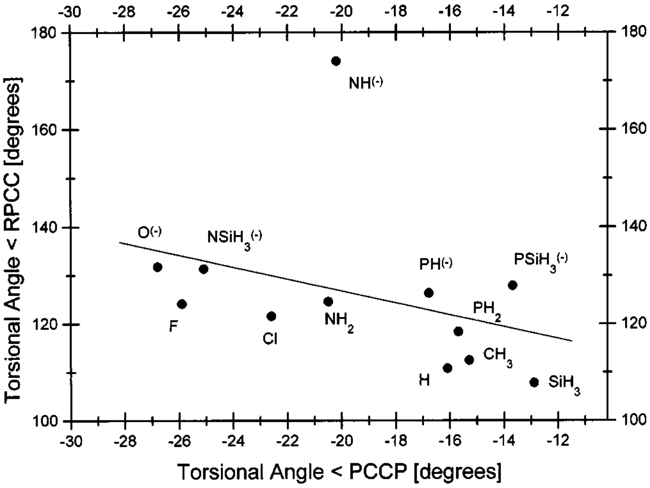
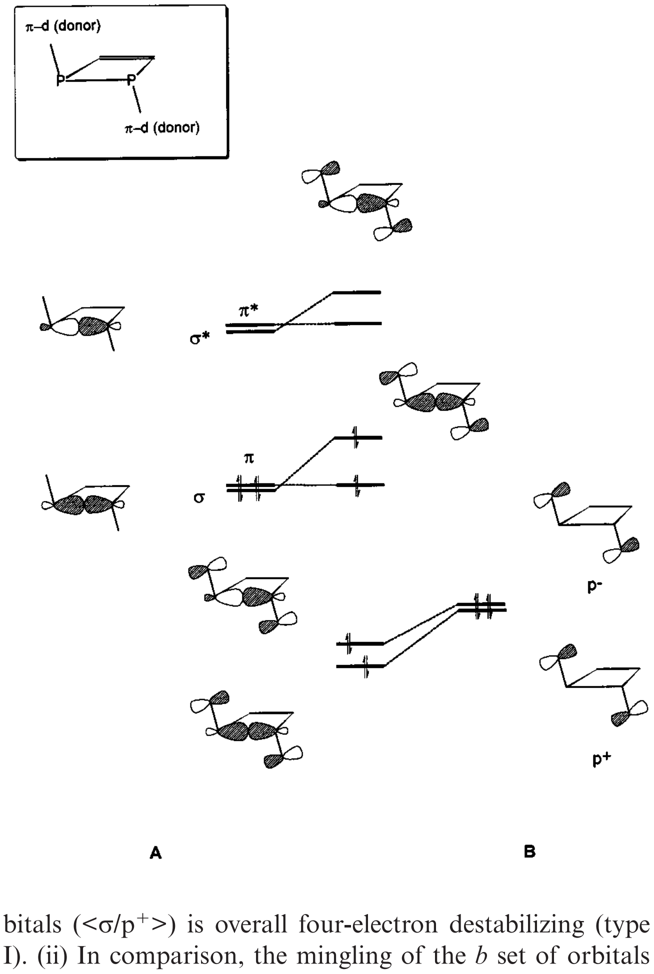


Figure 2. Interaction diagram of two donor p orbitals (**A**) with the σ (σ*) of the P−P bond (**B**)

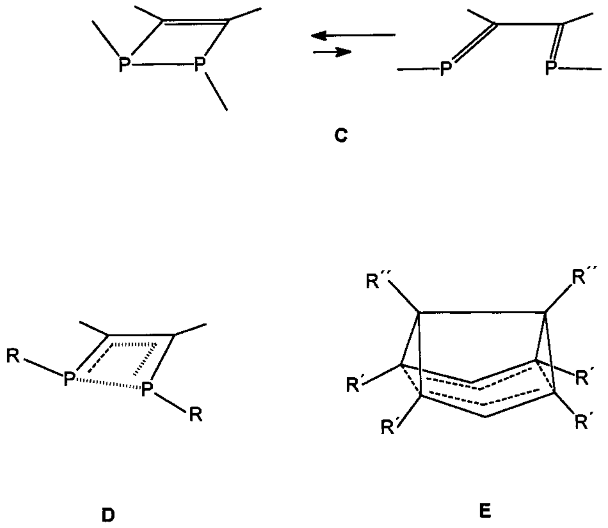


Two π donors at the phosphorus atoms (**B**) form a positive (p^+, *a* within C_2 symmetry) or negative (p^-, *b* within C_2 symmetry) combination of p orbitals, suitable for interaction with the bonding (σ, π) or antibonding (σ*, π*) orbitals of the ring moiety (**A**). Mutual interaction occurs in either of two ways. (i) Interaction among the *a* set of orbitals (<σ/p^+>) is overall four-electron destabilizing (type I). (ii) In comparison, the mingling of the *b* set of orbitals (<σ*/p^->) results in an overall stabilization (type II), since it involves donation of electron density of a doubly occupied orbital (p^- at **B**) into the empty (σ*) orbital (at **A**). With increasing donor capability (lower ionization potential) the stabilizing interaction (type II) comes to the fore. It will cause a weakening of the P−P bond with concomitant lengthening. Alternatively, if the donor p orbitals at R are low in energy, which refers to the case of electronegative substituents (with a high ionization potential, e.g., R = F) the type-II interaction will be weak and the P−P bond length almost unchanged. This tendency is reflected also for the case of the mono-substitution at phosphorus (see Table 2). We note that within this simplified picture the interactions of the donor orbitals (p^+, p^-, at P) with the π (π^*) orbitals are not included in the discussion. To a first order the latter molecular orbitals are not effected, since they are in 1,3-position to the p-set of donor orbitals.

A variety of substituents were also calculated for the cases of di-substitution (a) at phosphorus and/or (b) at the carbon atoms. In contrast to phosphorus substitution, the various carbon-substituted 1,2-diphosphetes do not show considerable changes in the structures. Thus, the unusual bonding properties are only obtained for the case of phosphorus substitution. The di-substitution at phosphorus exerts additive trends on the P−P bond lengths. Corresponding investigations will not be reported here in detail. However, the most important results for the cases (a) and (b) are listed in the Appendix (Table 3).

One important point deserves further discussion. Following our analysis electron-donating substituents weaken the P−P bond. What is its effect on the energy barrier of the conrotatory ring opening reaction? We have examined this aspect in detail for the case of amino di-substitution at the diphosphete **1** ($R^1 = R^4 = NH_2$; $R^2 = R^3 = H$). The energy barrier disappears in fact [at a MP2(fc)/6-31g(d) level, plus additional MP4SDTQ(fc) and zero-point vibrational corrections]. In other words the description of **1** and **2** as two species in equilibrium, **C**, which implies separation by an energy barrier[7], is not valid for the case at hand, i.e., with a strong π-donor substitution at the phosphorus atom(s).

Scheme 3



Consequently, **1** can be considered as a structure with pericyclic electron delocalization. Such a species, **D**, with 4 delocalized electrons may be described as a Möbius aromatic system[26][27].

We note that the discussion presented here is reminescent to the analysis of substituents for the design of a "frozen-in" transition-state geometry in semibullvalene[28][29], **E**. There, a structure with [$\sigma^2 + \pi^2 + \pi^2$] delocalization is promoted for the cases R′ = σ acceptor, R″ = σ donor. It refers to a delocalized Hückel aromatic system. In comparison, our investigations indicate that such a delocalized system may also exist for a Möbius-type arrangement, which involves 4 electrons in pericyclic delocalization [$\sigma^2 + \pi^2$]. This view does, however, imply that the phosphorus lone pairs are not included in the delocalization. It results in unusual structures for the 1,2-diphosphetes. The experimental verification of the concept of 1,2-diphosphete structures with strongly elongated P−P bonds remains, however, a challenge to the experimentalist. In addition, the validity of the presented concept of delocalized Möbius-type structures has to be analyzed for the related cases, such as the mono- and triphosphetes. The bonding situation in the diphosphetes may also be compared with that in the dithietes[33][34]. There, the ring structure (dithiete) and the corresponding open structures (dithioglyoxal) are similar in energy and their mutual energy differences are a balance of delicate substituent effects.

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Appendix

While the case of mono-substitution at phosphorus in the 1,2-diphosphetes was studied at the MP2(fc)/6-31g(d) or for the anions at the MP2(fc)/6-31+g(d) level, for the heterosubstituted cases (at phosphorus and carbon) we employed the less costly 3-21g(d) basis set[30], accounting within the density functional formalism[31][32] [B3LYP/3-21g(d)] for the importance for electron correlation. The results of these investigations are summarized in Table 3.

Table 3. Relevant geometrical parameters (bond lengths in Å, angles in degrees) for disubstituted 1,2-diphosphetes, obtained at B3LYP/3-21g(d) level of sophistication

$R^1 = R^4$	$R^2 = R^3$	P−P	P−C	C−C	∠ P−C−C−P	∠ R−P−C−C
H	H	2.279	1.851	1.346	−11.5	104.4
F	H	2.292	1.805	1.365	−30.3	129.0
Cl	H	2.307	1.822	1.357	−22.9	120.2
CH_3	H	2.276	1.846	1.350	−11.8	109.3
SiH_3	H	2.290	1.850	1.350	−8.0	102.0
PH_2	H	2.297	1.842	1.351	−11.6	113.8
NH_2	H	2.349	1.817	1.360	−20.5	124.8
NH_2	CN	2.338	1.824	1.379	−22.0	126.1
NH_2	NH_2	2.304	1.824	1.471	−17.0	120.3
NH_2	F	2.323	1.823	1.350	−15.1	117.8
Ph	H	2.307	1.838	1.353	−15.0	113.7
CN	H	2.295	1.846	1.347	−15.4	110.3
H	CN	2.269	1.855	1.364	−12.3	105.6
CN	CN	2.289	1.856	1.364	−15.7	110.6
CN	NH_2	2.268	1.839	1.369	−14.5	109.8
F	F	2.282	1.811	1.351	−23.2	120.0

The results, although obtained at a lower level of sophistication, yield similar trends. In addition they indicate that substituents at the carbon position(s) do not exert strong substituent effects at the P−P bond length. As shown for the case of the mono-substitution electronegative substituents at phosphorus tend to increase the folding angle of the four-membered ring. Full details of the obtained equilibrium geometries are available on request.

☆ In memoriam to Professor *M. J. S. Dewar*.

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