Electronic Structure of the 2.4-Diphosphacyclobutane-diyl-1.3 and Substituted Derivatives[§]

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The electronic structure of the 2.4-diphosphacyclobutanediyl-1.3 and its substituted compounds were investigated by various electron-correlated quantum chemical ab initio calculations, at the MCSCF, MP2, and MR−MP2 levels, and compared with the results of RHF level calculations. The structure is in essence a biradical (biradicaloid) species with partial π-delocalization within the ring system. A problem occurs with the description of this species by the MCSCF approach. A limited active configuration space overestimates the biradical nature of the structure. A satisfactory description is given by the MP2 procedure which also takes proper account for the dynamical part of the correlation energy correction to the resulting wave function. A bicyclic structure is more stable than a ring structure. A phosphino-carbene analogous structure is only slightly less stable than the ring structure. A detailed study of the substituent effects indicates that silyl groups at carbon tend to increase considerably the stability of a singlet ground state over a triplet ground state. Bonding within the ring system is discussed in terms of biradical or cyclic delocalized canonical structures.
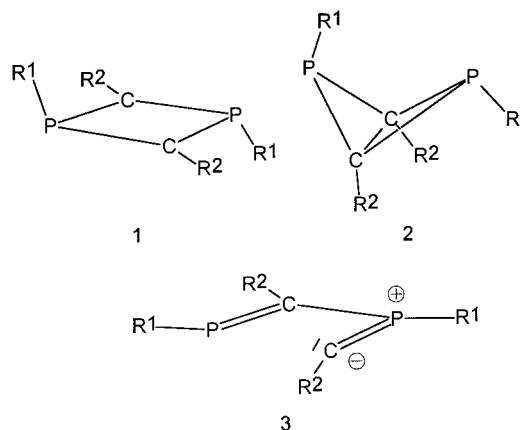
Introduction

Recently the synthesis and structural elucidation of the 2.4-diphosphacyclobutanediyl-1.3, **1** (R^1 = 2.4.6-tri-*tert*-butylphenyl, R^2 = Cl), has been reported[1]. It reveals an unusual structure. The PC bonds are 1.75 Å, and the phosphorus atoms are only weakly pyramidalized. The ring moiety is planar and almost rectangular (< CPC = 87.8°), and overall the molecule adopts C_i symmetry (Scheme 1). These experimental findings are not in accord with the prediction for the structure of the parent compound, **1** ($R^1 = R^2 = H$), based on the results of RHF energy optimized quantum chemical calculations.[2,3] These predict **1** as an unstable species on the electronic hypersurface. It has been stated that **1** is π-delocalized with 6π electrons in the cyclic ring system. Similarly, for the related nitrogen analogue, the 2.4-diaza-cyclobutane-diyl-1.3, a C_s-symmetrical structure has been postulated as a transient species.[4] Again, this prediction is based on the results of quantum chemical RHF calculations. A structural valence isomer of **1** is its bicyclobutane derivative, **2**.[5] A phosphanyl carbene,[6,7] **3**, is a structural isomer of **2** and has been postulated as an intermediate in this reaction. The ring closure reaction of **1** to the 2.4-diphosphabicyclo[1.1.0]butane can also be induced photochemically.[8]
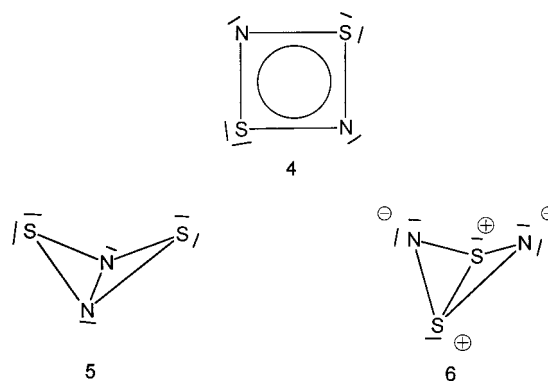
The ring system **1** is valence isoelectronic to the dinitrogen disulfide, **4**, a stable entity with a π-conjugated ring system.[9−11] Various quantum chemical calculations on this system[12−14] indicate that corresponding bicyclic valence isomers, such as **5** or **6**, are higher in energy than the cyclic π-conjugated system (Scheme 2). To this end, we note that parent **1** is valence isoelectronic to bicyclo[1.1.0]butane and its corresponding bond stretched biradical system.[15,16]

In the present publication, we report the result of quantum chemical calculations at various electron-correlated levels

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SCHEME 1

SCHEME 2

(MCSCF, MP2, MR-MP2), to analyze the bonding properties of **1**. Is it a biradical (biradicaloid[17−19]), as emphasized in **1a**, or a 6π-delocalized cyclic species, as described in the limiting structure **1b**? We note here that the description of a biradical is not clear-cut: a recent effort has been given on the basis of the electron density of the unpaired spin,[18,19] and many attempts
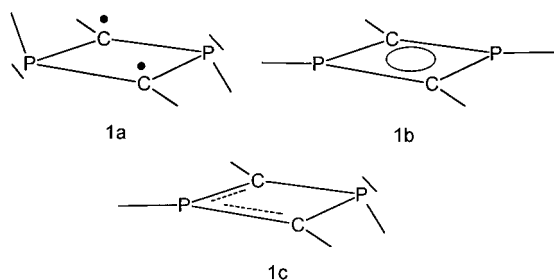
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SCHEME 3

have been made previously to define the nature of a biradical[20,21] (Scheme 3). In view of the fact that the inversion barrier in PH_3 is sizable[22,23] (35.8 kcal/mol, computed at MP4SDTQ(fc)/ 6-31g(d,p)//RHF/6-31g(d,p) level[24]), a planarization at the phosphorus atoms, which is the condition of π-delocalization, seems not profitable. Alternative to the view of **1** as a biradical or a cyclic π-conjugated species is a cyclic bismethylenephosphorane,[25] **1c**. Here, one phosphorus atom is planar, and the other one is pyramidalized. As an overall situation, the phosphorus atoms are between a planar, **1b**, or a pyramidal, **1a**, arrangement. One may note that in bismethylenephosphoranes the phosphorus is only formally pentavalent; in the actual bonding situation, the PC bonds are 1.2-dipolaric in nature.[26,27] Thus, **1c** can be considered as a further limiting structure to a biradical, **1a**, or a cyclic π-conjugated, **1b**, system.

From a quantum chemical viewpoint, the description of a biradical requires an open shell wave function, e.g., of multiconfigurational SCF-type[20] (MCSCF), whereas the cyclic π-conjugated alternative can adequately be described by a closed shell-type wave function (e.g., MP2).

Theoretical Procedure

The results of our investigations are based on quantum chemical calculation at MCSCF,[28] MP2,[29] and MR-MP2[30] level of sophistication. The basis sets for optimization were of double-ζ quality and are augmented at all heavy atoms by a single set of polarization functions. In more detail for the geometry optimization of parent **1** ($R^1 = R^2 = H$) Pople's 6-31g-(d,p) basis set[31] was used. For the parent system, more elaborate basis sets were also probed; details are given in the Discussion. The exploration of substituent effects was done with the less costly 6-31g(d) basis set in which polarization functions are only provided for the heavier main group atoms. All calculations were performed with the program systems *Gaussian-98*[32] and the GAMESS[33] programs. Energy optimization of structures at MP2 level of approximation were performed within the frozen-core approximation. The effects of bulky substituents R^1, R^2 = *tert*-butyl, trimethylsilyl, etc.) were tested at the B3LYP level. The density functional is built with Becke's three-parameter exchange functional[34,35] and the nonlocal correlation functional of Lee, Yang, and Parr.[36]

Results and Discussion

a. Qualitative Considerations. It is informative to begin the discussion with an analysis of the frontier orbitals within the parent system, with the first-order assumption of pyramidalization at the phosphorus atoms and almost planar carbon centers. This is the experimentally observed geometry for **1**. The molecular orbitals are confined to C_i symmetry and the carbon p-orbitals form a *gerade* (a_g) and an *ungerade* (a_u) combination of which the latter compared with the former is slightly lower in energy by transannular overlap. Similarly, the
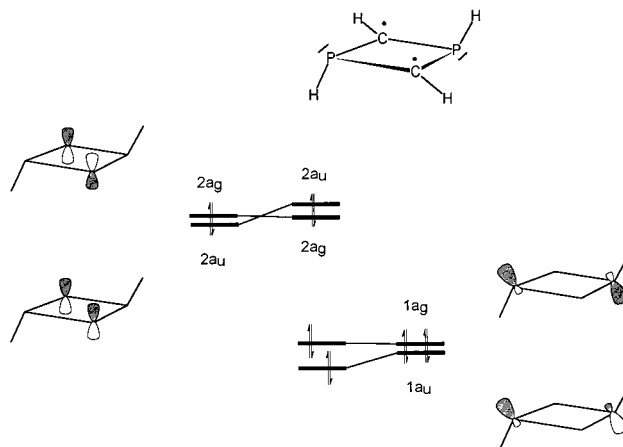

Figure 1. Composition of the frontier orbital system of parent **1** ($R^1 = R^2 = H$).

lone pairs yield corresponding combinations of orbitals (a_g, a_u). The composite orbital system is derived by mutual interaction of both sets of orbitals, of the two nonbonding p-orbitals at the carbon atoms (Figure 1, left) with the lone pairs at the phosphorus atoms (Figure 1, right). The *ungerade* combination of lone pairs interacts with the corresponding combination of nonbonding orbitals at the carbon atoms.

Within C_i symmetry, the two leading configurations are given by eqs 1 and 2.

$$\Psi(^1A_g) = c_1|2a_g2\bar{a}_g\rangle - c_2|2a_u2\bar{a}_u\rangle \qquad (1)$$

$$\Psi(^3A_u) = |2a_g2a_u\rangle + |2\bar{a}_g2\bar{a}_u\rangle \qquad (2)$$

The ^1A_g state, eq 1, refers to the lowest energy singlet.[20] The other, the ^3A_u state, eq 2, is the lowest energy triplet coupled singly excited configuration. According to the given qualitative considerations, the difference in energy between the lowest energy singlet (^1A_g) and triplet (^3A_u) is determined by the magnitude of interaction of the lone-pair orbitals at the phosphorus atoms with the adjacent p-orbitals at the carbon atoms. We note that the qualitative discussion emphasized here is reminiscent of the consideration of through-space versus through-bond interactions of two unpaired electrons in a polymethylene chain.[37,38] A full proof of the presented arguments requires the assumption of C_{2h} symmetry. For this case, the carbon centers would be planar, the p-orbitals are then confined to b_u and b_g, and the lone pairs to a_g and b_u. For symmetry reasons, the b_u orbital (at carbon) is raised in energy by destabilization with the b_u combination of lone pairs (at phosphorus).

Two extreme bonding situations can be recognized in the present discussion: (a) the a_g and the a_u orbitals are degenerate. It is the situation of the biradical structure **1a**: the lowest energy singlet and triplet states are similar in energy ($c_1 \approx c_2$). (b) Alternatively, the overlapping of both sets of orbitals is rather strong, thus placing the a_u orbital considerably above the a_g orbital. This results in the situation $c_1 \gg c_2$ in the CI expansion of the MCSCF wave function for the singlet state, and the singlet ^1A_g would be considerably more stable than the triplet ^3A_u. In terms of limiting structures, this refers to enhanced delocalization of the electrons within the ring system. It has the further consequence that electron density will be distributed from the phosphorus atoms to the neighboring carbons. Consequently, negative charge will be accumulated at the carbon atoms which furthermore induces pyramidalization at these atoms. This aspect
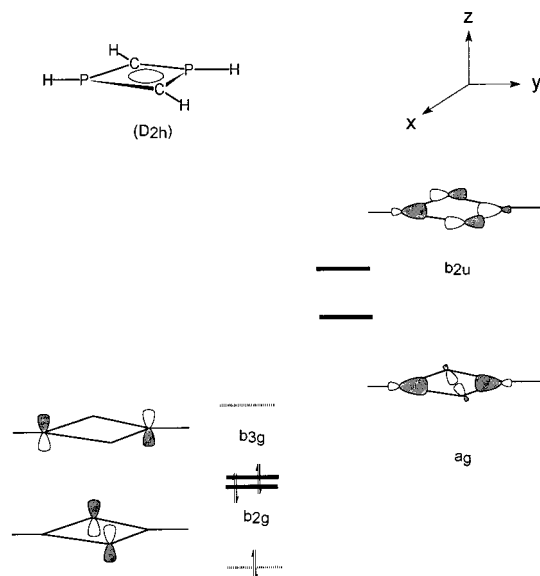
Figure 2. Frontier orbitals of planar **1**: (left) π-orbitals and (right) σ-orbitals (Walsh-type).

of electron density distribution will be discussed in a later section of this publication. For the carbon atoms, anti pyramidalization is preferable, to minimize the anti bonding through-space interactions between the distal atoms (pairs of carbon and of phosphorus).

The present considerations assume that the phosphorus atoms are pyramidalized. This is supported by the experimentally observed structures and the fact that trigonal phosphorus centers possess large inversion barriers. But what happens in the case of full planarization of the overall structure? For this case, the four-membered ring system is confined to D_{2h} symmetry and adopts a cyclic π-conjugated system. The occupied frontier orbitals are constituted by a pairwise anti bonding combination of p-orbitals at the carbon or phosphorus atoms (Figure 2, left). The lower and higher energy π-molecular orbitals are indicated by dotted lines.

In addition to the π-molecular orbitals in the planar four-membered ring system, a set of Walsh-orbitals[39] is present. Of these, the most relevant for the present discussion are given by the a_g and b_{2u} components (Figure 2, right). Due to the fact that the valence s-orbitals in higher main group chemistry are more strongly contracted[40] than the corresponding valence p-orbitals, it follows from the model of orbital nonhybridization[41] that these Walsh-type orbitals of the four-membered ring system are fairly low in energy (e.g., as compared with the corresponding valence orbitals of planar cyclobutane[39b]). Confined to planarity, both sets of molecular orbitals (σ vs π) cannot mingle, since they are orthogonal to each other.

However, upon pyramidalization at the phosphorus atoms, the bonding situation changes, and the set of π-orbitals can now mix with the set of σ-orbitals. The outcome depends on the fact whether anti pyramidalization (C_{2h} symmetry) or syn pyramidalization (C_{2v} symmetry) of the hydrogens at the phosphorus atoms is followed. A third alternative is feasible, the formation of one planar phosphorus center and pyramidalization of the other (**1c**, C_s symmetry); e.g., for anti pyramidalization, the b_{3g} orbital will strongly interact with a_g, by lowering the energy of the former and raising that of the latter. As a consequence of the $\sigma-\pi$ interaction via pyramidalization, the p-orbitals at phosphorus atoms mix in the s-character of the ring orbitals and the latter gain p-character from the π-type orbitals. The mixing of the orbitals will be larger the smaller

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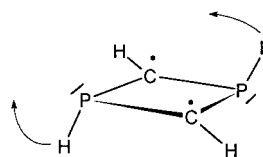
the energy gap is between the frontier π-type orbitals and the lowest energy Walsh-type orbitals in the planar conformation.

The present considerations makes it likely that pyramidalization of one phosphorus atom is strongly coupled with depyramidalization of the other phosphorus center, due to the facile $\sigma-\pi$ interaction, by breaking the planarity of the molecule. Schematically, this is indicated in the following scheme (Scheme 4). This is due to the fact that the loss of p-character in the ring bonds by planarization of one phosphorus center is compensated for by stronger pyramidalization of the other phosphorus center.

As will be shown by the model calculations in section c, the *concerted* pyramidalization versus depyramidalization is an easy, facile process. For the case at hand, this would lead to the bismethylenephosphorane-type structure **1c**, a well-known structural type in phosphorus chemistry.[25]

b. Parent Compound. In carbon chemistry, a π-bond is essentially weaker than a σ-bond, and for the PC bond, both quantities are less in magnitude.[42] This indicates that the description of a biradical structure with higher main group elements within the MCSCF scheme might be more difficult. A large set of π- and σ-orbitals has to be provided in the active orbital space. A full active space of a MCSCF treatment of parent **1** would include all valence electrons and orbitals. Thus this would refer to a CAS(22,20) wave function. Such an attempt is not feasible with the present computer programs. Consequently, we tested simplified models: (1) Model A refers to a CAS(2,2) treatment, and it includes only the configurations determined by the HOMO (a_g) and the LUMO (a_u). (2) A further extension, model B, is given by an additional inclusion of all ring orbitals (four occupied ($2a_g$, $2a_u$) and four unoccupied bond orbitals), resulting in a CAS(10,10) wave function. (3) The most elaborate MCSCF calculation is given by model C, a CAS(14,12) wave function. It differs from model B in further inclusion of the two lone pairs (a_g, a_u) at the phosphorus atoms. Furthermore, the wave functions for the various MCSCF model spaces were subjected to a multireference treatment at MP2 level (MR−MP2). Finally, the results were compared with those obtained from MP2 (for the singlet, ^1A_g) or UMP2 (for the triplet, ^3A_u) calculations.

The equilibrium parameters were obtained under restriction to C_i symmetry and are collected in Figure 3 for the singlet (^1A_g) (left) and the triplet (^3A_u) (right) lowest in energy.

The magnitude of pyramidalization at the phosphorus atoms is determined by the sum of valence angles around these atoms. It indicates whether a biradical, **1a**, or a closed shell structure, **1b**, becomes dominant. For the singlet, the pyramidalization is strong for the models A and B and less pronounced for model C. It is weakest for the MP2 treatment. In other words, with increasing latitude of the MCSCF active orbital space, a planar conformation, **1b**, is pronounced, to the disadvantage of the biradical alternative, **1a**. Nevertheless, model C (CAS(14,12)) is not capable of approaching fully the results of the MP2 calculations. (The latter, however, inevitably assumes a closed-shell structure.) We note here that pyramidalization at the carbon atoms is much less affected by the variability in the MCSCF models. The carbon atoms are only slightly pyramidalized, in agreement with the experimental observations. The effect is
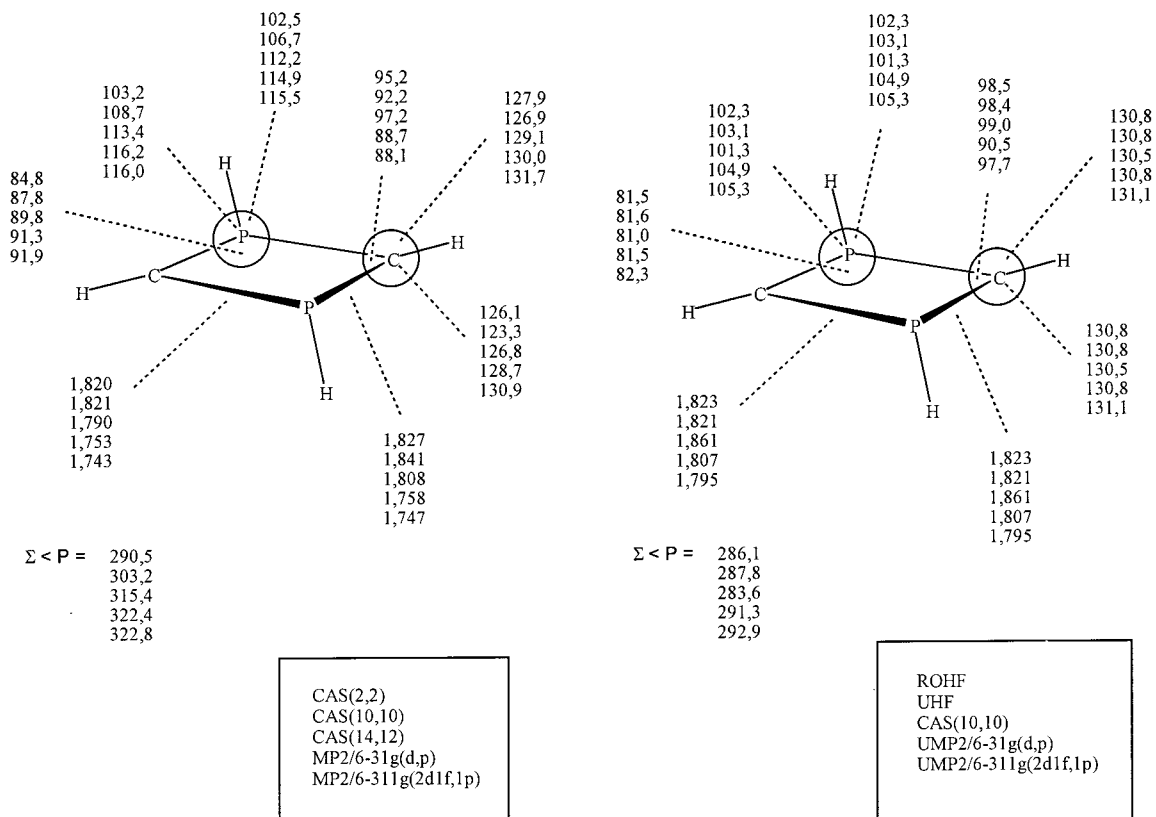
Figure 3 (left structure, singlet ¹Ag):

102,5 / 106,7 / 112,2 / 114,9 / 115,5

95,2 / 92,2 / 97,2 / 88,7 / 88,1

127,9 / 126,9 / 129,1 / 130,0 / 131,7

103,2 / 108,7 / 113,4 / 116,2 / 116,0

84,8 / 87,8 / 89,8 / 91,3 / 91,9

126,1 / 123,3 / 126,8 / 128,7 / 130,9

1,820 / 1,821 / 1,790 / 1,753 / 1,743

1,827 / 1,841 / 1,808 / 1,758 / 1,747

Σ < P = 290,5 / 303,2 / 315,4 / 322,4 / 322,8

CAS(2,2)
CAS(10,10)
CAS(14,12)
MP2/6-31g(d,p)
MP2/6-311g(2d1f,1p)

Figure 3 (right structure, triplet ³Au):

102,3 / 103,1 / 101,3 / 104,9 / 105,3

98,5 / 98,4 / 99,0 / 90,5 / 97,7

130,8 / 130,8 / 130,5 / 130,8 / 131,1

102,3 / 103,1 / 101,3 / 104,9 / 105,3

81,5 / 81,6 / 81,0 / 81,5 / 82,3

130,8 / 130,8 / 130,5 / 130,8 / 131,1

1,823 / 1,821 / 1,861 / 1,807 / 1,795

1,823 / 1,821 / 1,861 / 1,807 / 1,795

Σ < P = 286,1 / 287,8 / 283,6 / 291,3 / 292,9

ROHF
UHF
CAS(10,10)
UMP2/6-31g(d,p)
UMP2/6-311g(2d1f,1p)

Figure 3. Geometry equilibrium parameters (bond lengths in angstroms, bond angles in degrees) of parent **1**, at various levels of sophistication: (left) singlet (^1A_g) and (right) triplet (^3A_u).

TABLE 1: Absolute Energies of the Singlet (^1A_g) and the Triplet (^3A_u) of Parent 1, for Various Models[a]

state	model[b]	MCSCF (SCF)	MR−MP2 (pUMP2)[c]
^1A_g	CAS(2,2)	−759.386 075	−759.849 794
	CAS(10,10)	−759.463 924	−759.850 009
	CAS(14,12)	−759.480 761	−759.862 937
	MP2	−759.863 251	
^3A_u	ROHF	−759.389 063	−759.838 670[d]
	UHF	−759.400 759	−759.843 316
	CAS(10,10)	−759.463 759	−759.843 813
	CAS(14,12)	−759.473 960	−759.853 015
	pUMP2	−759.843 976	

[a] The frozen core approximation was employed throughout. [b] Optimization level. [c] For UHF calculations, spin projected values were taken. [d] The MP2(fc) energy was obtained according to the method of Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130−136.

comparably small, since the overall inversion barriers at these centers are expected to be much smaller than those at the phosphorus atoms (see vide infra). For the triplet, the various calculational models result in almost similar geometries. The phosphorus atoms remain in the triplet more strongly pyramidalized than those in the singlet. In other words, here the structure **1a** prevails. It is also witnessed in larger PC bonds, as compared with the singlet. The structure obtained from the UMP2 calculation is almost identical to that obtained by the ROHF calculation.

It is informative to compare the computed energies at the various levels of sophistication (Table 1). The lowest energy of the triplet (pUMP2) is almost similar to the results from model B plus additional MR-MP2 correction. The situation is more complicated for the singlet. For all chosen MCSCF models, the resulting energies after MR-MP2 corrections are higher; however, the absolute energy (in au) of model C is only slightly

less negative than that resulting from the MP2 optimization. The latter results are the lowest in energy. On the other hand, the MR−MP2 energy for the triplet with model C is lower than the pUMP2 energy.

On the basis of the present data, one is attempt to assign a singlet−triplet energy separation for parent **1**. The sizable changes in energy and structure for the singlet from model A to model C indicates that the ring bonds as well as the phosphorus lone pairs contribute essentially to the amount of electron correlation. A further aspect may be added here. From the present data, very low inversion barriers at the phosphorus atoms are apparent. On the other hand, the description of such features requires the utilization of elaborate basis sets.[43] On this basis, the 6-31g(d,p) basis set seems not fully adequate to balance properly the bonding situation, with a strong flattening of the phosphorus atoms in the singlet, and a weaker flattening of these in the triplet. Thus we have also probed the effect of an improved s,p-basis sets as well as further addition of two sets of d-functions and one f-function on the energy difference in the singlet−triplet separation. The results of these investigations at the various calculational levels are summarized in Table 2. The smallest energy differences between both states are obtained at the MR−MP2 level for models A and B. If we take into consideration that the singlet is not properly described by these models, the values for the singlet must be too high in energy (relative to the triplet) and a small energy difference results. It is also witnessed in the equilibrium geometry of the singlet which is reminiscent of that of the triplet. At the MCSCF level, the best estimate is given by model C. However, it addresses a value (6.2 kcal/mol) which is smaller than obtained at the MP2 treatment (12.1 kcal/mol), with the RHF or UHF wave function. Further inclusion of d- and f-functions were probed for the MP2 treatment; they even enlarge the energy

TABLE 2: Singlet (^1A_g)−Triplet (^3A_u) Energy Separations (in kJ/mol) on Parent 1, at Various Computational Levels

method	ΔE (kcal/mol)[a]
MR−MP2(fc)/CAS(2,2)/6-31g(d,p)	6.9
MR−MP2(fc)/CAS(10,10)/6-31g(d,p)	4.4
MR−MP2(fc)/CAS(14,12)/6-31g(d,p)	6.2
(pU)MP2(fc)/6-31g(d,p)	12.1
(pU)MP2(fc)/6-311g(d,p)	14.6
(pU)MP2(fc)/6-311g(2d,p)	18.1
(pU)MP2(fc)/6-311g(2d1f,1p)	20.4

[a] Without zero-point vibrational energy corrections, the triplets at UMP2 level are energy corrected with spin-projection.

splitting. We may conclude here that at the 6-31g(d,p) basis set level the best result (MR−MP2 for model C) suggest a relative small energy difference between ^1A_g and ^3A_u; on the other hand, the inclusion of further polarization functions increases this value.

Does **1** now possess a pronounced singlet ground state structure? The answer is still not clear, since the present analysis is confined to the experimentally unknown parent compound, **1** with $R^1 = R^2 = H$. In the actual experiment, **1** is substituted by various types of substituents and it is known that electronegative groups at the phosphorus atoms increase sizably their inversion barriers. In other words, they bring a biradical structure to the fore. By this we mean that **1** can behave as a closed-shell species, as indicated in **1b**, or a biradical species, as indicated in **1a**. It is first-order, depending on the substituents attached to the phosphorus atoms. A detailed discussion of substituent effects will be presented in section e.

c. Valence Isomers. The vibrational analysis (within the harmonic approximation, at the MP2/6-31g(d,p) level) reveals for the C_i-symmetrical singlet and triplet states of the parent compound **1** ($R^1 = R^2 = H$) throughout positive eigenvalues.[44] Hence the ^1A_g (^3A_u) states are energy minima on the electronic hypersurface. For the singlet with a planar carbon center (restriction to C_{2h} symmetry), one imaginary vibration (i427 cm^{-1}, b_g) is obtained. It identifies this structure as a first-order saddle point on the electronic hypersurface. The b_g vibration refers to induction of anti pyramidalization at the carbon atoms. However, the tendency for pyramidalization at the carbon atoms is rather small (approx. 1.5 kcal/mol). In addition, we included in our considerations various other conformations of the lowest energy singlet, such as a totally planar geometry, **1b** (D_{2h}), one phosphorus center planar, **1c** (C_s), and a conformation with cis orientation, **1d** (C_{2v}), of the ligands at the phosphorus atoms. These various conformations, although not all stable entities on the singlet surface, yield valuable information on the conformational flexibility of this structure. According to the numerical calculations, the fully planar 6π-system **1b** is highest in energy. In comparison with the planarization of one phosphorus, **1c** is only slightly higher in energy above **1**. While one phosphorus is planar, the other one is strongly pyramidalized (Σ angles at P = 283.3°). In other words, it is more strongly pyramidalized than in parent **1** (Σ angles at P = 322.4°; see Figure 3). It gives support to the qualitative analysis of pyramidalization of one phosphorus with depyramidalization of the other phosphorus. A cis isomer, **1d**, is higher in energy than **1**, but it rearranges without energy barrier to the trans isomer.[45] The various conformations for parent **1**, although not stable entities on the electronic hypersurface of the singlet state, are fairly close in energy. This stresses the importance of further experimental investigations on the conformational aspects of this molecule.

The valence isomers of interest to **1** are the diphosphabicyclobutane, **2**, and the phosphino-carbene, **3**. Other structures of

TABLE 3: Energy Quantities (in kcal/mol) for Various Conformers and Valence Isomers of Parent 1 ($R^1 = R^2 = H$)'

compound (symm)	MP2[a]	MP2/ZPE[b]	MP4[c]	NIMAG[d]
1 (C_i)	0.0	0.0	0.0	0
1b (D_{2h})	39.4	38.0	40.1	3
1c (C_s)	7.1	5.9	6.3	1
1d (C_{2v})	13.5	12.5	11.6	1
2 (C_s)[e]	37.7	35.9	38.7	0
3 (C_1)	21.9	21.0	15.0	0

[a] MP2(fc)/6-31g(d,p). [b] Level a plus zero-point vibrational energy correction. [c] MP4SDTQ(fc)/6-31g(d,p). [d] Number of imaginary frequencies. [e] Endo−exo conformation.
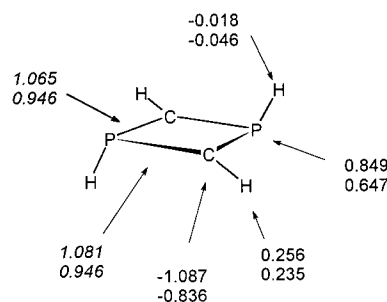
Figure 4. NBO population analysis of the singlet (top) and triplet (bottom) of parent **1**. The Wiberg bond orders are in italics.

the family of valence isomers are the diphosphacyclobutane and the diphosphabutadiene. They have been discussed earlier;[46,47] hence these will not be included in the present considerations. The phosphino-carbene has been postulated as an intermediate in the reaction of **1** to the bicyclobutane valence isomer.[5] The full compilation of the energetic situation of the various structures is given in Table 3. The phosphino-carbene, **3**, is less stable than **1**, and the bicyclobutane, **2**, is considerably more stable. Details of the reaction of **1** to bicyclobutane via the phosphino-carbene route[5] will be presented elsewhere.[48] Importantly, the closed-shell structures, such as **2**, are essentially lower in energy than **1**. This is in strong contrast to S_2N_2, where the corresponding bicyclic structure is remarkably higher in energy than the four-membered ring system.[12]

d. Electron Density Distribution. We have examined the MP2-electron-density distribution within the parent system with various methods, the analyses of (a) the Laplacian of the electron density distribution,[49] the electron localization function (ELF)[50] and the population analysis according to the natural bond orbital scheme (NBO).[51] The essence of bonding is already presented by the NBO analysis. Corresponding values are given in the Figure 4. The values in the bottom lines refer to the triplet state. For both cases, the PC bonds result as single bonds, as determined by the Wiberg bond indices. The singlet possesses slightly stronger PC bonds. There is, however, a difference in the charge densities. In the singlet, the carbon atoms are more negative than in the triplet states. This can be rationalized by assumption of an ylid character, as it is known for the bismethylenephosphoranes.[26] This is in conformity with the fact that for these species a planar environment at the phosphorus is observed and for parent **1** this is easily achieved by flattening of the phosphorus centers.

e. Substituent Effects. In the actual experiment, the diphosphacyclobutane-diyl moiety is always substituted by bulky groups. These exert steric as well as electronic effects on the different states. Thus, it is of interest to have knowledge about these substituent effects. For further analysis, we have first evaluated the relevant electronic states as a function of differently substituted ring systems. For this analysis, the MP2(fc)/
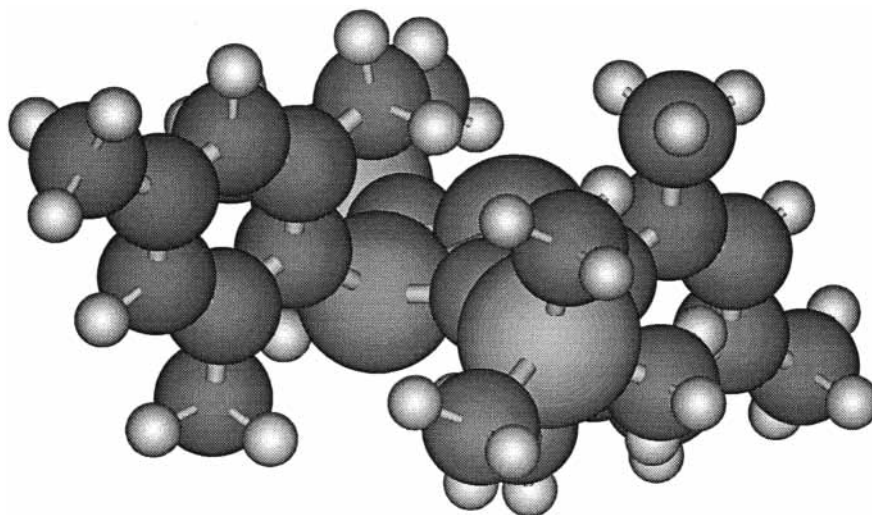
Figure 5. Molden plot of **1** (R^1 = $C_6H_2Me_3$, R^2 = $SiMe_3$).

TABLE 4: Substituent Effects on the Singlet−Triplet Energy Separation (in kcal/mol) and Most Relevant Bonding Parameters for Singlet (bond lengths in Å, bond angles in deg.) of 1

R^1 (P)	R^2 (C)	r (PC)	Σ < $(P)^a$	ΔE^b	ΔE + ZPE^c
H	H	1.753; 1.758	322.4	12.1	11.1
CH_3	H	1.749; 1.753	324.8	16.1	14.9
phenyl	H	1.749; 1.757	325.8	16.2	
SiH_3	H	1.769; 1.775	300.7	22.5	21.1
F	H	1.729; 1.736	327.9	10.1	9.4
H	CH_3	1.765; 1.772	321.1	8.2	7.4
H	SiH_3	1.754; 1.757	323.5	44.1	43.1
NH_2	H	1.829; 1.829	277.0	8.1^d	
NH_2	CH_3	1.833; 1.833	280.8	1.7^d	
NH_2	SiH_3	1.740; 1.761	330.2	61.2	
H	Cl	1.784; 1.794	311.0	5.2	4.8
H	NH_2	1.844; 1.850	284.0	3.7	1.8

^{a} Sum of valence angles at phosphorus. ^{b} Electronic energy (singlet) − electronic energy (triplet), calculated at MP2 (singlet) and pMP2 (triplet) level, 6-31g(d) basis set. ^{c} Zero-point vibrational energy correction added to level b. ^{d} Saddle point; the singlet rearranges without energy barrier to the bicyclobutane structure.

TABLE 5: Sum of Angles at Phosphorus [Σ < P] (in deg.) for Sterically Encumbered Singlet Geometries, Optimized at B3LYP/6-31g(d) Level^a

R^1 (P)	R^2 (C)	Σ < P
H	H	321.4
H	SiH_3	322.4
H	$SiMe_3$	323.1
CH_3	SiH_3	325.7
CH_3	$SiMe_3$	326.2
t-but	$SiMe_3$	328.5
$C(SiH_3)_3$	$SiMe_3$	325.7
CH_3	CH_3	324.7
SiH_3	CH_3	311.4
SiH_3	SiH_3	316.2
$C_6H_2Me_3{}^a$	$SiMe_3$	331.4

^{a} C_i symmetry was imposed. ^{b} 2.4.6-trimethylphenyl ligand.

6-31g(d) level of optimization was chosen. Whenever a vibrational analysis was computationally feasible, it was performed. The results of the investigations, i.e., the energy differences for the relevant states and the most important bonding parameters, are collected in Table 4. For completeness we also have included in the table the value for the parent compound **1** (R^1 = R^2 = H).

The energies for the triplet states refer to spin-projected values.[52] However, in all cases, the spin contamination is fairly small (details of the calculations available on request). The effect of the substituents can be categorized in two groups: (a) σ-donating substituents at the phosphorus (R^1) tend to increase the singlet−triplet energy separation, and σ-attracting substituent (R^1 = F) do the opposite. (b) A sizable substituent effect is exerted at the carbon positions. Silyl groups strongly tend to stabilize a singlet over a triplet state. It is known that these substituents are also prerequisites for the successful synthesis of stable bismethylenephosphoranes.[25] Singlet stabilization appears most strongly pronounced for the substituent combination R^1 = NH_2, R^2 = SiH_3. It must be noted that the singlet states are evaluated within the MP2 approximation. This treatment is quasi-closed shell in nature and does not allow a strong biradical component in the wave function. On this basis, the trends regarding the substituent effects must still be

considered as qualitative, in particular the cases when a triplet state comes to the fore (R^1 = NH_2; R^2 = H, CH_3). Nevertheless, our results are in full accord with the available experimental results on the stability of substituted **1**.

The hitherto investigated structures carry model type substituents which exert only negligible steric hindrance on the various structures. In the actual experiment, however, bulky substituents are required in order to protect the structures kinetically from further reactions. To examine this aspect in more detail, we further performed density functional calculations (B3LYP/6-31g(d)) on a variety of bulky model compounds. The density functional calculations tend to mimic the experiment most closely. The results are collected in Table 5. The replacement of the silyl group by the essentially much more demanding trimethylsilyl substituent, or the replacement of the methyl substituent by the *tert*-butyl group does not essentially alter the sum of angles at the phosphorus atoms; i.e., these atoms are not further flattened by steric effects. However, they may alter the kinetic stabilities of these structures. Corresponding plots of the equilibrium structures in fact evidence that the P_2C_2 ring is strongly encumbered by the sterically strongly demanding substituents. A typical example is shown in a Molden plot[53] for **1** (R^1 = $C_6H_2Me_3$, R^2 = $SiMe_3$) in Figure 5. The central ring system is strongly surrounded by the bulky substituents. Similar considerations also hold true for the other heavily substituted systems **1**.

f. Comparison with S2N2. There is an essential difference between the N_2S_2 systems, **4**−**6**. For this case, the quantum chemical calculations predict that the bicyclic structures will

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be higher in energy[12] than the cyclic congener **4**. In its phosphorus analogue **1**, it is the opposite: the bicyclic structure **2** is essentially more stable than the ring structure **1**.

Why is this so? A rationale for this fact is given by the model of orbital nonhybridization.[41] In this model, the stereochemical activity of an inert s-orbital is analyzed in terms of symmetry considerations for the distortion within a molecular structure. In the cyclic S_2N_2, the sulfur is a higher main group element, thus reluctant toward s,p-hybridization.[40] The sulfur atoms can form "inert" s-orbitals pointing outward the ring, whereas the p-electrons are utilized for ring bonding. For the phosphorus analogue, such a possibility is not given. The phosphorus atoms bear ligands which enforce a trigonal environment.[54] Hence either pyramidalization at the phosphorus atoms or alternatively the easy formation of a phosphino-carbene structure is the consequence. In both cases, the lone-pair orbitals at the phosphorus centers become stereochemically active.

Conclusions

The results of our investigations can be summarized as follows:

(1) The trigonal phosphorus atoms in the 1.3-diphosphacyclobutanediyl-1.3 possess large inversion barriers toward a planar, 4-centered, 6π electron delocalized system. Double inversion at phosphorus is much less likely than single inversion at phosphorus. This is the consequence of the strong mingling of the lone-pair orbitals (at phosphorus) with the ring orbitals of the four-membered ring system. This causes a coupling of pyramidalization at one phosphorus with depyramidalization at the other phosphorus atom. In other words, **1** can easily change its nature from a biradicaloid, **1a**, to a bismethylene–phosphorane-type structure, **1c**. This aspect, predicted by the quantum chemical study, has to be further explored by the experiment.

(2) As a further consequence, the lone pairs at the phosphorus atoms cannot strongly participate in cyclic π-conjugation. The resulting structure possesses a biradicaloid[17] character. By this, we mean that it can behave like a pseudo-closed-shell π-system, **1b**, or a biradical, **1a**. The alternative structure, the bicyclobutane system with formation of transannular CC bonding is easy feasible.

(3) The isoelectronic S_2N_2 system is electronically different, although it is valence isoelectronic. Here, the nonbonding electrons can be placed into orbitals suited in the plane of the ring system to parent **1**. A planar structure is more stable than its bicyclic congeners.

(4) An analysis of the substituent effects in **1** reveals the considerable role of a silyl group at the carbon atoms for singlet stabilization, whereas σ-attracting effects at the phosphorus atoms are in favor of a triplet ground state.

(5) The parent system **1** appears as a structure in which one phosphorus atom can easily flatten. Depyramidalization of one phosphorus is accompanied by pyramidalization of the second phosphorus center. This in fact is an entirely new aspect in phosphorus chemistry. The C_i symmetrical structure can accommodate a C_s symmetrical structure with only a small amount of activation energy. This raises the question of unsymmetrical substitution (different substituents at the two phosphorus centers) in the species **1**. This aspect must await further experimental and theoretical investigations.

Our investigations reveal a biradicaloid character for **1**. It is not a closed-shell species, since a planar 6π-system can be avoided by pyramidalization of the phosphorus centers. The fairly low inversion barriers at the phosphorus atoms are strongly affected by the nature of the substituents, giving credit for

concomitant changes from **1b** to **1a**. The most stable valence isomer is **2**, in accord with the hitherto presented studies at a RHF level of sophistication.[3] On this basis of our investigations, the non-Kekule structure **1** can adequately be described.

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