The Effect of Substituting Phosphorus for a Ring Carbon Atom in the Valence Isomers Cyclobutene, Bicyclobutane, and 1,3-Butadiene. A Quantum-Chemical Investigation

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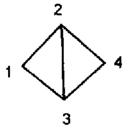
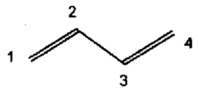
Cyclobutene, bicyclobutane, and 1,3-butadiene are valence isomers within the concept of the Woodward-Hoffman rules. According to thermochemical considerations and in agreement with energy optimized quantum-chemical calculations at the ab initio RHF and MP2/6-31G(d,p) levels bicyclobutane is the least and 1,3-butadiene the most stable valence isomer. Phosphorus substitution exerts a considerable effect on the relative stabilities of the various valence isomers. Bicyclobutanes containing phosphorus atoms in the bridgehead positions are considerably more stable than the other phosphorus-substituted valence isomers. This conclusion was confirmed by an analysis of the natural bond populations.

Since the first reports on the syntheses of bicyclobutane[1−3] (**I**) this compound has been the subject of detailed experimental investigations[4−10]. It is now well established that **I** opens to its valence isomer 1,3-butadiene[4−6] (**II**). The ring-opening reaction of cyclobutene (**III**) is stereochemically controlled[4], in compliance with the orbital symmetry rules[5].



I



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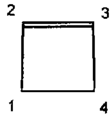
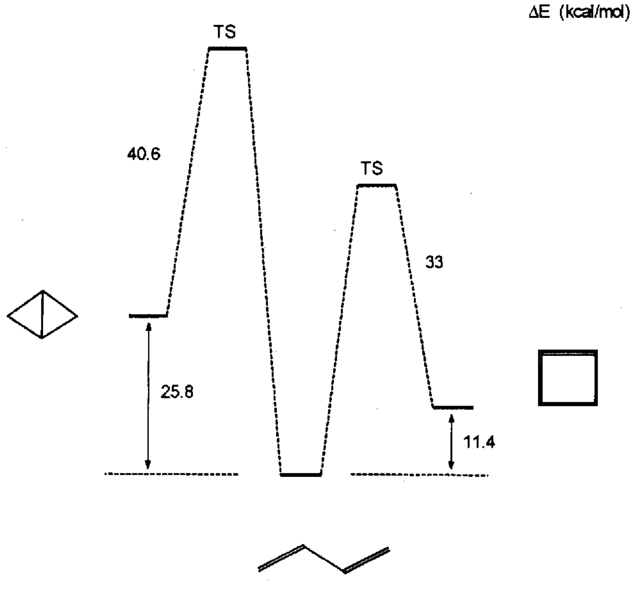


III

The semiempirical quantum-chemical investigations revealed for the isomerization of **I** to **II** a two-step mechanism for the ring opening[6a] while recent ab initio calculations at the MCSCF level[6b] point to a concerted one-step reaction mechanism. On the basis of experimental NMR studies[7] and quantum-chemical investigations[7−10] for **I** a strong p-character to the bridge-head bond was assigned. The 1,3-butadiene is also a valence isomer of cyclobutene (**III**). The latter opens conrotatorily to **II**, i.e. with strict control of orbital symmetry[5,11−20]. The wealth of quantum-chemical investigations[11−20] on these systems as well as thermochemical data[21] suggest that bicyclobutane is the least stable valence isomer while 1,3-butadiene is the most stable compound on the hypersurface of these species. The stability of cyclobutene is intermediate between that of bicyclobutane and 1,3-butadiene. Gase phase kinetical studies revealed an activation energy of 40.6 kcal mol^{-1} for the ring opening of **I** to **II**[22,23]. It is larger than the energy for ring opening of **III** to **II**, 32.9[24,25], 36[26] rsp., kcal mol^{-1} with -11.4 kcal mol^{-1} for the heats of reaction[27]. The energy of the biradicaloid transition state for the ring-opening reaction of **III** was estimated on the basis of experimental studies to 47 kcal mol^{-1}[28]. On this basis the electronic energy hypersurface of **I** to **III** is well characterized by experimental as well as quantum-chemical calculations and can be schematically depicted as follows.



In contrast much less is known about the effect of phosphorus substitution on the structures and stabilities of these valence isomers[29]. Recent investigation showed that 1-phosphabuta-1,3-dienes can be synthesized by HCl elimination of the corresponding alkenylchlorophosphanes[30]. The 2-phosphabuta-1,3-dienes were synthesized so far by various routes[31−33]. A stable 1,3-diphosphabutadiene was first prepared by addition of a trimethylsilyl-substituted phosphaalkene to the phosphaketene[34,35]. A further synthesis of a stable 1,3-diphosphabutadiene is reported in ref.[36] 2,3-Diphosphabutadienes are accessible by the reactions of the phosphaalkenes with hexachloroethane or of diphosphane with pivaloyl chlorides. Furthermore, syntheses of the electron-rich amino-sub-

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stituted diphospha-1,3-butadienes[37,38] as well as a route to 1,4-diphosphabutadienes[39] were reported. Of the trisubstituted butadienes the 1,2,4-triphosphabuta-1,3-diene is known[40]. The 1,2,3-triphosphabuta-1,3-diene has been suggested as an intermediate in the formation of a corresponding bicyclobutane derivative[41,42].

In contrast, much less is known about the existence of phosphorus-substituted bicyclobutanes, triphospha[41,42] and tetraphospha derivatives[43,44,45]. In one case a corresponding zirconium complexes was isolated[46]. A diphosphabicyclobutane derivative has become known recently[47].

In the present publication we evaluate the following aspects on the basis of the corresponding quantum-chemical investigations at the RHF and the MP2/6-31G(d,p) levels: (1) the effect of phosphorus substitution on the bonding properties in the various structural types **I**, **II**, and **III** in general. In more detail it will be shown that (2) 2,3-phosphorus substitution in **II** causes a stability of the corresponding **I** which is higher than that of the other phosphorus-substituted valence isomers and (3) 1,4-substitution in **II** makes the corresponding cyclobutene derivative **III** more stable than corresponding **II**. Hence, for this case also the bicycle **I** is the least stable species on the electronic energy hypersurface.

Methodology

All of the calculations were performed with the GAUSSIAN set of programs[48]. The 6-31G(d,p) basis set[49–50] was used and the energy optimization performed at the RHF and MP2(fc) levels. The structures were subsequently characterized by a vibrational analysis within the harmonic approximation. Corrections for electron correlation were performed with the MP4SDTQ approximation[51,52] by assuming the frozen core (fc) approximation.

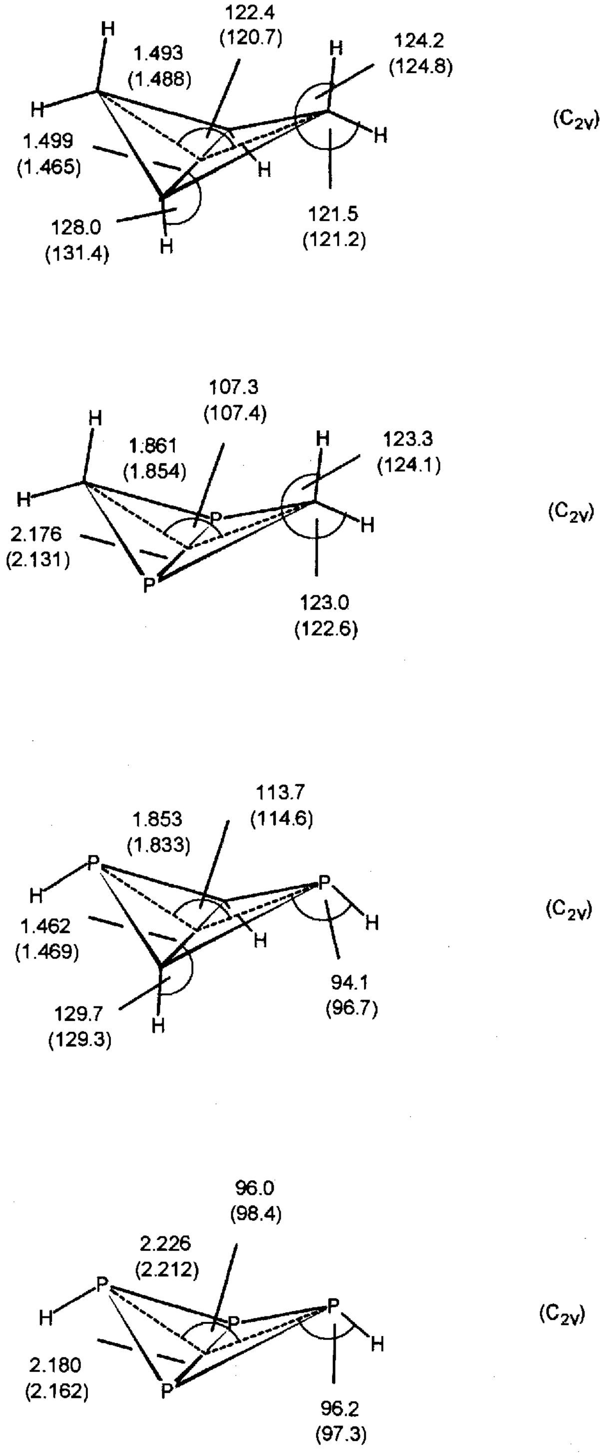
Results and Discussion

a. Geometries and Relative Energies

First, we report on the bonding parameters of the various phosphorus-substituted species. Only disubstituted compounds with a typical substitution pattern of the two phosphorus atoms in the bridgehead or peripheral (as in **I**) position or with the two phosphorus atoms in the 2,3- or 1,4-positions of the 1,3-butadiene were studied. Correspondingly, in the cyclobutenes the phosphorus atoms are located at the double bond or in the single bond positions of the ring systems. The structural parameters (at the heavy atoms) obtained at the RHF and MP2/6-31G(d,p) levels of optimization are compiled in Figures 1 to 3. For comparison, we also included in our considerations the bonding properties of the parent compounds **I**, **II**, and **III**.

Upon optimization of the structures no unusual bonding properties are revealed. The PP distances are within the range of corresponding single bond and/or double bond values[53]. In the 1,4-diphosphorus-substituted cyclobutene the angles at the phosphorus atoms are noticeable smaller than 90 degrees. This is a consequence of the much shorter CC double bond as compared with the PP single bond. The resulting PC double bond value are within the range of the corresponding values obtained for methylenephosphanes[53,54].

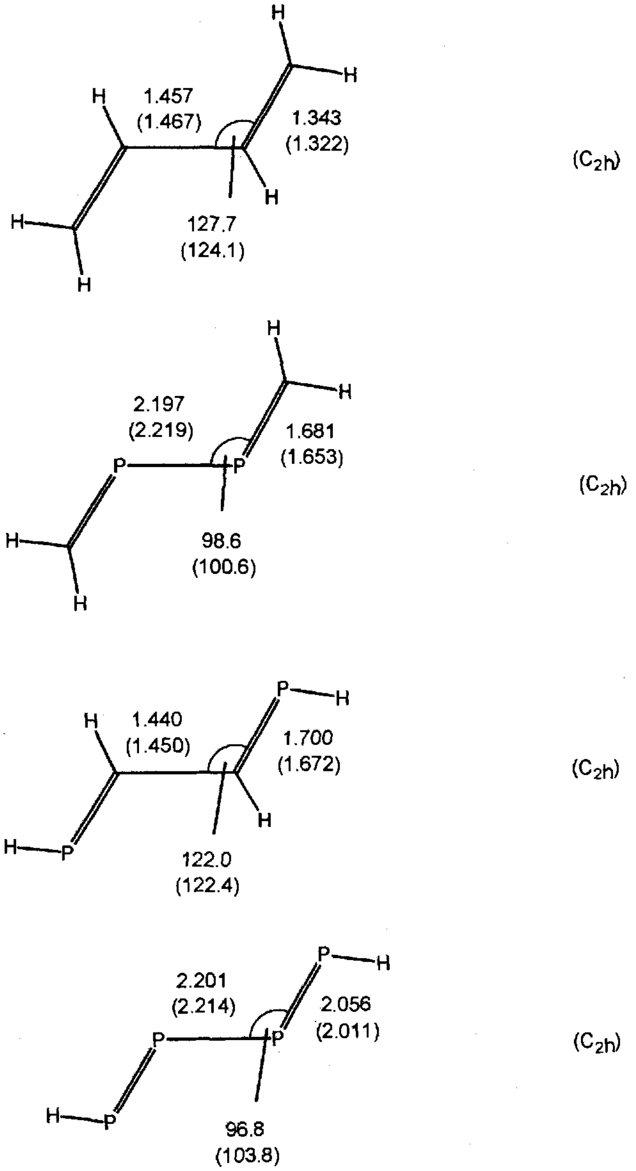
Figure 1. Bonding parameter of (substituted) (I) (bond lengths in Å, bond angles in degrees) between the heavy atoms, at the MP2 (RHF) level of optimization



Of particular interest is the energetic situations of the various substitution patterns resulting from the introduction of phosphorus. The obtained relative energies (in kcal mol^{-1}) are listed in Table 1. The absolute energies (in atomic units) of all investigated species are given in the Appendix.

For the parent case, the family of the C_4H_6 isomers, the bicyclobutane as well as the cyclobutene are less stable than

Figure 2. Bonding parameter of (substituted) (II) (bond lengths in Å, bond angles in degrees) between the heavy atoms, at the MP2 (RHF) level of optimization



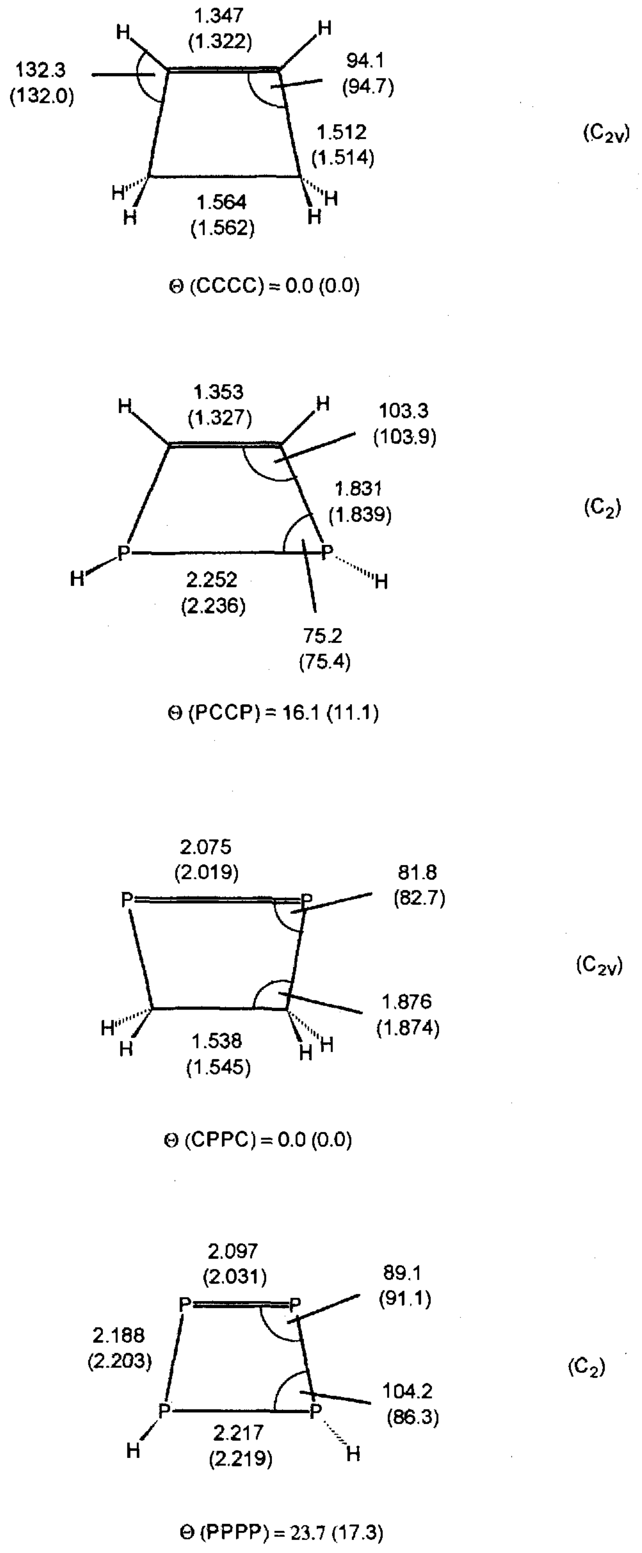
1,3-butadiene. In fact, this is well documented by the facile electrocyclization of **I** to **II**[5]. The ring strain in **I** and in **III** is considerably high as is apparent from thermochemical data[21].

The energy balance between **I**, **II**, and **III** is best understood by thermochemical considerations; e.g., the energy difference between **I** and **III** refers to a transformation of one single bond into one endocyclic π-bond and is given by equation (1),

$$\Delta E(\mathbf{I}\rightarrow\mathbf{III}) = E^{\sigma}_{CC} - E_{ST}(\mathbf{I}) + E_{ST}(\mathbf{III}) - E^{\pi}_{CC} = 88 - 65 + 30 - 65 = -12\,\mathrm{kcal\,mol^{-1}} \quad (1)$$

with E_{ST}(**I**) and E_{ST}(**III**) denote the strain energies[21] of **I** and **III** with the bond energy values summarized in Table 4 (see Appendix). The value obtained from eq. (1) may be compared with −15.4 kcal mol^{-1} resulting from the thermochemical data[21].

Figure 3. Bonding parameter of (substituted) (III) (bond lengths in Å, bond angles in degrees) between the heavy atoms, at the MP2 (RHF) level of optimization



On the other hand, the valence transformation from **II** into **III** is given by equation (2).

$$\Delta E(\mathbf{II}\rightarrow\mathbf{III}) = E^{\pi}_{CC} - E^{\sigma}_{CC} + E_{ST}(\mathbf{III}) = 65 - 88 + 30 = 7\,\mathrm{kcal\,mol^{-1}} \quad (2)$$

Table 1. Relative energies (in kcal mol^{-1}) of various structural isomers

Comp.	RHF[a]	MP2[b]	MP4[c]	MP4/ZPE[d]
I	0.0	0.0	0.0	0.0
II	-30.1	-20.3	-25.2	-26.7
III	-17.2	-12.5	-15.2	-15.4
1,4-P_2-I	0.0	0.0	0.0	0.0
1,4-P_2-II	-13.8	-10.3	-14.9	-15.4
1,4-P_2-III	-25.5	-15.7	-18.1	-18.1
2,3-P_2-I	0.0	0.0	0.0	0.0
2,3-P_2-II	19.2	26.1	20.9	18.7
2,3-P_2-III	3.1	6.9	4.3	4.3
1,2,3,4-P_4-I	0.0	0.0	0.0	0.0
1,2,3,4-P_4-II	27.9	25.2	21.3	20.1
1,2,3,4-P_4-III	10.2	12.3	11.0	10.7

[a] RHF/6-31G(d,p). – [b] MP2(fc)/6-31G(d,p). – [c] MP4SDTQ(fc)/6-31G(d,p)//MP2(fc)/6-31G(d,p). – [d] Level [c] plus zero point energies (unscaled at level [b]).

It suggests that **II** is 7 kcal/mol more stable than **III**, compared with 11 kcal/mol calculated from the difference in heats of formation[21].

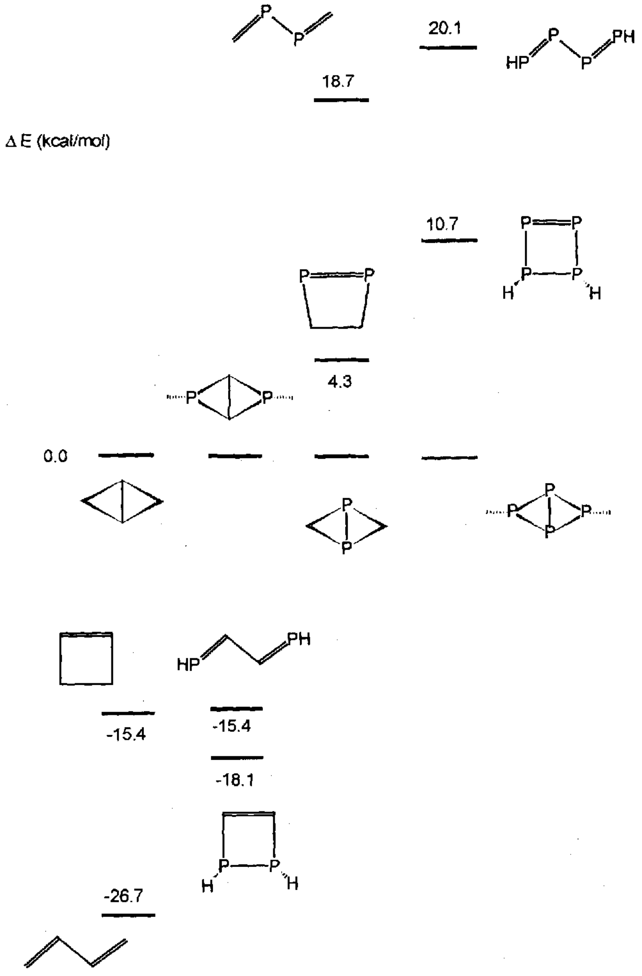
Consider next the perphospha cases. It is known that cyclophosphanes and cyclophosphenes are almost strain-free[55]. On this basis together with the values for bond energies and by neglecting ring strain energies (see Table 4, Appendix) we can establish a similar energy balance, resulting in a reverse order of stabilities. 1,2,3,4-P_4 (**I**) should be most stable, perphospha-(**III**) 27 kcal mol^{-1} higher in energy and perphospha-(**II**) higher in energy (by the same amount) than the former. It should be noted that an accurate balance between the energy difference of the various structural isomers cannot be given on the basis of these estimates, since thermochemical data on phosphorus species were not accurately determined. Nevertheless, these considerations provide relative trends in the order of stabilities.

The overall order of stabilities of the various isomers as the result of the quantum-chemical calculations is depicted as follows, by assuming the best computational level (MP4SDTQ/6-31G(d,p)//MP2/6-31G(d,p) + zero point vibrational energy corrections).

Intermediate cases represent 2,3- and 1,4-diphosphorus-substituted systems. For the former the situation resembles the P_4-substituted compounds and for the latter the carbon compounds. Interestingly, these two classes differ in the relative stabilities of the cyclobutenes with reference to the 1,3-butadienes. Again, this can be rationalized by simple thermochemical considerations. While in the carbon case the driving force of the exothermic ring opening of **III** to **II** is the release of strain energy (30 kcal mol^{-1})[21,55], in the phosphorus case the strain in the four-membered ring is essentially smaller[55]. In addition, a very stable CC π-bond is formed by transformation of 1,4-P_2-(**II**) into 1,4-P_2-(**III**).

b. Population analysis in (I)

With respect to the detailed quantum-chemical investigations of **I** it was of interest to compare bonding in the differently phosphorus-substituted species. For this purpose, we have employed the natural bond analysis (NBO)[56]. Only the most relevant aspects will be discussed here. For the various ring bonds the following compositions of the localized natural bond orbitals were obtained.



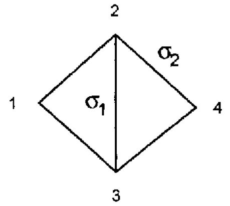


Table 2. Composition of localized natural bond orbitals of bicyclobutanes; coefficients are given according to equations (3a) and (3b)

Comp.	Bond orbital	a (c)	x	y	b (d)	x	y
(I)	σ_1	0.707	8.88	0.02	0.707	8.88	0.02
	σ_2	0.713	2.59	0.01	0.701	3.49	0.01
1,4-P_2-(I)	σ_1	0.707	3.42	0.01	0.707	3.42	0.01
	σ_2	0.794	3.79	0.01	0.607	8.51	0.12
2,3-P_2-(I)	σ_1	0.707	21.50	0.21	0.707	21.50	0.21
	σ_2	0.601	6.85	0.12	0.799	3.68	0.01
1,2,3,4-(I)	σ_1	0.707	11.40	0.16	0.707	11.40	0.16
	σ_2	0.706	9.34	0.14	0.708	9.34	0.14

They are given as linear combinations of local atomic contributions according to:

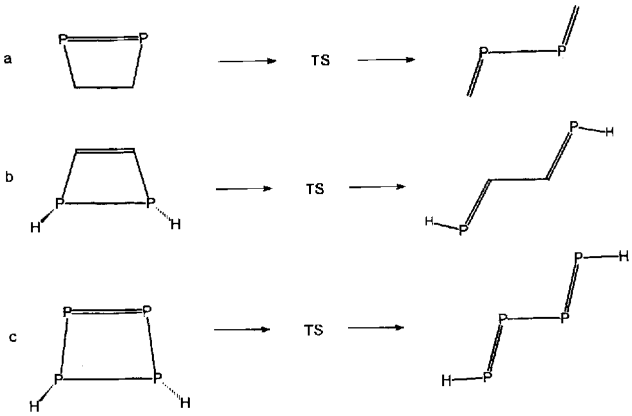
$$\sigma_1 = a\, C_2\,(P_2)\,[sp^x d^y] + b\, C_3\,(P_3)\,[sp^x d^y] \qquad (3a)$$

$$\sigma_2 = c\, C_1\,(P_1)\,[sp^x d^y] + d\, C_2\,(P_2)\,[sp^x d^y] \qquad (3b)$$

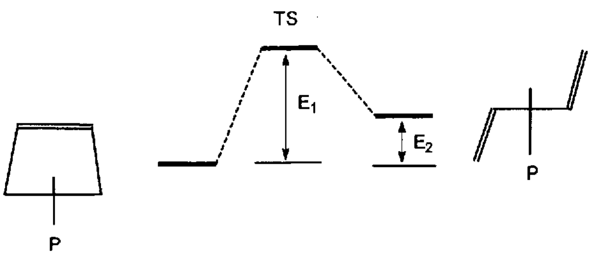
The orbital σ_1 refers to the central bond while σ_2 corresponds to the peripheral bond(s). The coefficients x and y which constitute the corresponding hybrid orbitals are given in Table 2. In accord with the well established picture of bonding in **I** the central bonds possess more p-character than the peripheral bond(s). In comparison, phosphorus substitution in the bridgehead position even increases the p-character of the central bond while phosphorus substitution in the positions 1 and 4 decreases the p-character. A strong p-character of all ring bonds is observed for the perphospha-bicyclobutane, 1,2,3,4-P_4-(**I**). On this basis one expects that phosphorus substitution in the bridgehead positions gives rise to a more effective reduction of the ring strain than phosphorus substitution in the peripheral positions 1 and 4. The increase of the p-character of the ring bonds is concomitant with an increase of the s-character of the phosphorus lone pairs. The p-character of the bridgehead bond reaches a maximum for the case of **I**, substituted with two phosphorus atoms at the bridgehead atoms [2,3-P_2-(**I**)]. It is due to the exert of angle strain of the peripheral CH_2 units which is rather large for a strongly bent three-membered ring unit[21].

c. Energy barriers for ring opening of III to II

For completeness of the electronic hypersurface of the species **I** to **III** we have determined the energy barriers for the corresponding reactions of **III** to **II**. We have evaluate the energy barriers for the following type of reactions (at a MP2 level of optimization).

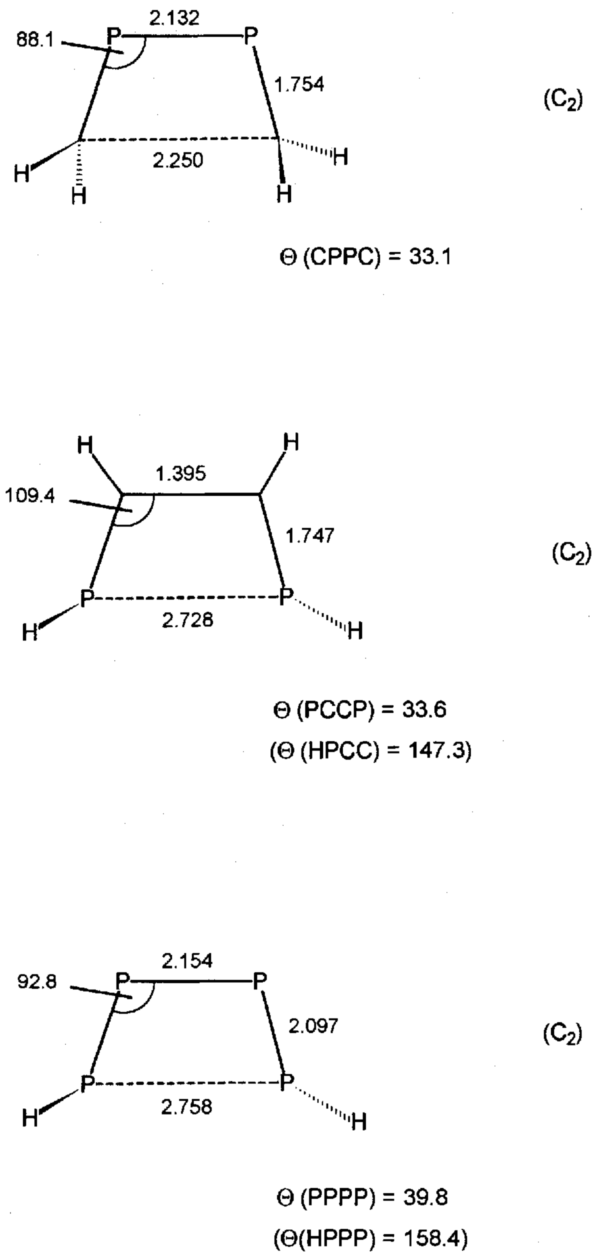


The energy quantities which determine the barrier for the ring opening reactions can be depicted as follows.



E_1 refers to the energy barrier for the ring opening reaction and E_2 is a measure for the energy difference between the cyclobutene (**III**) and the butadiene (**II**) species. The resulting transition state geometries are collected in Figure 4. They reveal partially opened four-membered ring structures in the transition state geometries.

Figure 4. Bonding parameters of transition states (bond lengths in Å, bond angles in degrees) between the heavy atoms, at the MP2 level of optimization



All structures were determined at MP2(fc)/6-31G(d,p) location of the transition state geometries with subsequent MP4SDTQ(fc) and zero point vibrational energy (unscaled) corrections. For diphosphorus-substitution at the double bond [reaction (a)] E_1 results to 39.8 kcal mol^{-1}. This value is comparable to the energy barrier for the ring opening reaction of cyclobutene itself, 33 kcal mol^{-1} obtained from experiment[24,25]. The diphosphorus substitution, as in reaction (b), reduces the activation energy barrier already to 16.9 kcal mol^{-1}, a value which is comparable with previous investigations (MP2/6-31G(d,p)//RHF/6-31G(d,p), 18.0 kcal/mol^{-1}[58]). A similar activation energy barrier for the per-phospha case [reaction (c)] is obtained (16.6 kcal mol^{-1}). Importantly to note, the ring opening reaction of cyclobutene is endothermic for all investigated reactions. In comparison with parent cyclobutene, the ring **III** is less stable than the corresponding 1,3-butadiene (**II**). The resulting values for the reaction energy balance are, reactions (a), (b), and (c): E_2 = 14.4, 2.7, 9.4 kcal mol^{-1} (see Table 1).

Conclusions

In the family of the valence isomers bicyclobutane, cyclobutene, and 1,3-butadiene phosphorus substitution in the bridgehead position strongly favors the bicyclic structure. Furthermore, according to a population analysis, the corresponding bridgehead PP bond in 2,3-P_2-(**I**) possesses a very strong p-character, the largest of all substituted congeners. One question remains still open, the energy barriers for isomerization among the various structures. Such an attempt requires elaborate MCSCF calculations on the transition-state geometries which are being carried out.

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Appendix

All investigated species were characterized by vibrational analysis at the RHF and MP2 levels of approximation, at the corresponding equilibrium geometries. The absolute energies (in aus) of all investigated species are compiled in Table 3.

Table 3. Absolute energies (in au) of structural isomers

Comp.	symmetry	RHF[a]	MP2[b]	MP4[c]	ZPE[d]	v[e]
I	C_{2v}	-154.88241	-155.43852	-155.49048	0.08908	423, A_1
1,4-P_2-I	C_{2v}	-759.41917	-759.91832	-759.98073	0.05269	281, A_1
2,3-P_2-I	C_{2v}	-759.47344	-759.97992	-760.04116	0.05808	387, A_1
1,2,3,4-P_4-I	C_{2v}	-1364.04415	-1364.48170	-1364.54906	0.02386	218, A_1
II	C_{2h}	-154.93032	-155.47093	-155.53505	0.08679	157, A_u
1,4-P_2-II	C_{2h}	-759.44117	-759.93480	-760.00449	0.05191	133, A_u
2,3-P_2-II	C_{2h}	-759.44283	-759.93828	-760.00788	0.05462	40, A_u
1,2,3,4-P_4-II	C_{2h}	-1363.99969	-1364.44150	-1364.51513	0.02204	22, A_u
III	C_{2v}	-154.90978	-155.45839	-155.51898	0.08876	289, A_2
1,4-P_2-III	C_2	-759.45978	-759.94338	-760.00956	0.05261	278, A
2,3-P_2-III	C_{2v}	-759.46855	-759.96892	-760.03433	0.05815	61, A_2
1,2,3,4-P_4-III	C_2	-1364.02789	-1364.46202	-1364.53159	0.02349	189, A

[a] RHF/6-31G(d,p). – [b] MP2(fc)/6-31G(d,p). – [c] MP4SDTQ(fc)/6-31G(d,p)//MP2(fc)/6-31G(d,p). – [d] At MP2(fc)/6-31G(d,p) level (unscaled). – [e] Lowest energy vibration (in cm^{-1}).

Table 4. Energies of bond increments (in kcal mol^{-1}) from ref.[57]

Type	CC	CP[a]	PP
σ	88.0	74.5	61.0
π	65.0	45.0	34.0

[a] $E(CP) = 1/2\,[E\,(CC) + E\,(PP)]$.

The energy balances according to equations (1) and (2) were determined from the literature values listed in Table 4.

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