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Pentagon Stability: Cyclic Delocalization of Lone Pairs through σ Conjugation and Design of Polycyclophosphanes

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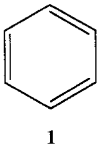
The orbital-phase theory was applied to propose pentagon stability in a well-defined manner. Cyclic delocalization of the lone pair electrons on the five-membered ring atoms through the vicinal σ bonds was shown to be favored by the orbital-phase properties. The pentagon stability was found to be outstanding in saturated phosphorus five-membered rings in the puckered conformation, and was substantiated by the *negative* strain energy of cyclopentaphosphane, P_5H_5 (**3**). The relative increments of the remarkable increase in the strain energies of protonation on the different atoms in the most stable conformers supported the significance of the cyclic delocalization of the lone pairs. Pentagon stability led to the design of three novel polycyclic phosphanes, $P_{12}H_4$ (**18**), $P_{13}H_3$ (**19**), and $P_{14}H_2$ (**20**), with low strain energies due to many puckered pentagon units in them. The low stability of the dodecahedron P_{20} (**22**) was suggested by the high strain energy due to its planar pentagon units. The pentagon stability is less significant in the saturated nitrogen ring molecules due to the greater energy gap between the n and σ* orbitals.

Introduction

Hexagonal structures are thermodynamically preferred in cyclic unsaturated (**1**) and saturated (**2**) hydrocarbons. For planar π-conjugated molecules, benzene (**1**) is the most stabilized by the cyclic electron delocalization, while cyclohexane (**2**) is the most stable due to the lowest strain energy of the saturated ring molecules. In this paper, we applied the orbital-phase theory[1] to predict that the saturated cyclic molecules with lone pairs on the ring atoms, e.g., cyclopentaphosphane (**3**) composed of the group 15 element phosphorus, prefer pentagons. The new concept of pentagonal stability was employed to design some potential polycyclophosphanes, $P_{12}H_4$, $P_{13}H_3$, $P_{14}H_2$, and $P_{15}H_3$ (**18**−**21**), and to discuss the possibility of the existence of the dodecahedral cluster P_{20} (**22**).



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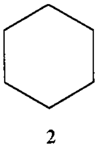

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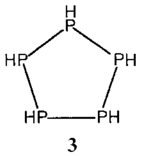

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Results and Discussion

Orbital-Phase Prediction. Electron delocalizations in cyclic conjugated systems involve the cyclic interaction of orbitals. The delocalization is under the control of the orbital-phase property. The continuity−discontinuity of the orbital phase[1] underlies the stabilities of the cyclic conjugated systems, i.e., the Hückel rule for aromaticity and the Woodward−Hoffmann rule for pericyclic reactions. Applications were recently made to the unusually short distance between the silicon atoms in disilaoxiranes and 1,3-cyclodisiloxanes[2] and to the geminal bond participation in organic reactions.[3,4] The finding of cyclic orbital interaction involved even in acyclic conjugation[5] has expanded the application of the orbital-phase theory to acyclic conjugated systems such as the regioselectivities of organic reactions,[6] the abnormally

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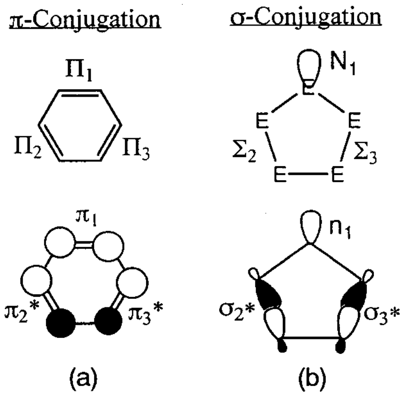


Figure 1. Cyclic orbital interactions in (a) benzene and (b) the saturated pentagon ring.

acute L−M−L angles in ML_2 and ML_3 complexes,[7] the relative stabilities of π-conjugated polyions[8] and diradicals,[10] those of σ-conjugated molecules[11] and diradicals,[12] and the conformational stabilities of the substituted alkenes and alkynes.[13]

In benzene, there is a cyclic interaction of π_1, π_2*, and π_3* orbitals (Figure 1a). The orbital-phase continuity requirement, previously derived from the third-order perturbation energy for the three-system interactions[1] and recently derived from a point of view of electron density,[11] is the simultaneous satisfaction of the following conditions: (1) the electron-donating orbitals are out of phase; (2) the accepting orbitals are in phase; (3) the donating and accepting orbitals are in phase. If the conditions are satisfied or the orbital phase is continuous, the delocalization takes place effectively, and consequently the system is stabilized. The cyclic (π_1, π_2^*, π_3^*) interaction in benzene is favored by the phase continuity.[1] The electron-donating π orbital can be in phase with both of the electron-accepting π^* orbitals in phase with each other, as is required. This suggests that there should be a possible structure of the saturated system similarly stabilized. Replacing one donor orbital, π_1, of benzene with the lone pair orbital n_1, which lies high in energy, and replacing the antibonding π^* orbitals with low-lying σ^* orbitals, we can obtain similar cyclic (n_1, σ_2^*, σ_3^*) orbital interactions of the σ-conjugated five-membered ring (Figure 1b). The delocalization mechanism involving the (n_1, σ_2^*, σ_3^*) interaction was depicted in Figure 2. In the ground configuration, G, the lone pair n_1 and bonding σ_2 and σ_3 orbitals are doubly occupied, and the antibonding σ_2^* and σ_3^* orbitals are empty. The electron in n_1 shifts to the antibonding σ_2^* and σ_3^* orbitals through the interactions of the ground configuration with the transferred configurations, T_1 and T_2, being approximated by the n_1−σ_2^* and n_1−σ_3^* interactions, respectively. The mixing of the transferred configuration gives rise to electron delocalization from the lone pair to the E−E σ bonds. The electron in σ_2^* (σ_3^*) of the transferred configuration T_1 (T_2) further shifts to σ_3^* (σ_2^*), leading to another transferred configuration, T_2 (T_1), via the interaction between T_1 and T_2. The configuration interaction is approximated by the σ_2^*−σ_3^* interaction. It follows that the cyclic (G, T_1, T_2) configuration or the (n_1, σ_2^*, σ_3^*) orbital interactions are involved in the cyclic electron delocalization.

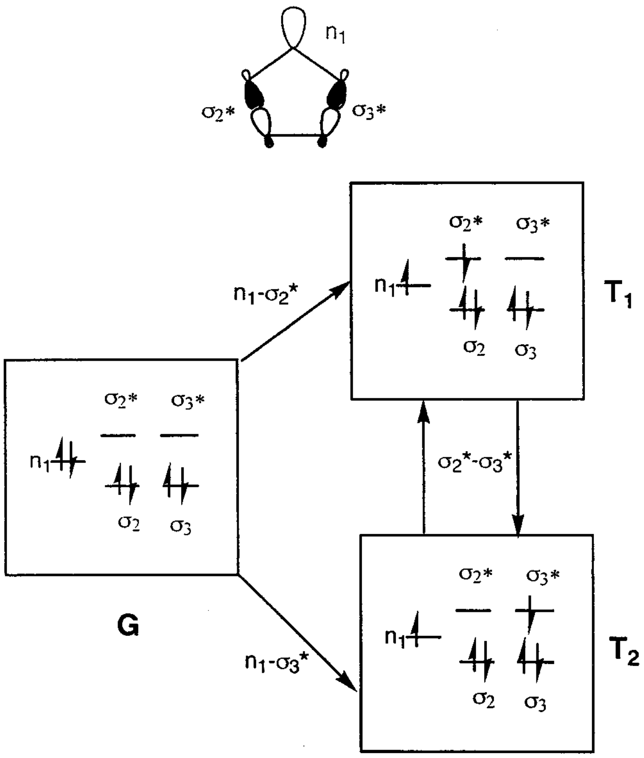
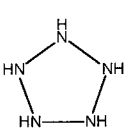


Figure 2. Cyclic electron delocalization mechanism in the pentagon ring.

As shown in Figure 1b, the cyclic (n_1, σ_2^*, σ_3^*) interaction meets the phase continuity requirement: the accepting orbitals σ_2^* and σ_3^* in phase with the donating orbital n_1 can also be in phase with each other at the same time. Thus, the phase continuity suggests a possibility that the cyclic orbital interaction could contribute to the remarkable stability of the pentagons.

Bond Model Analysis. The orbital-phase continuity is not a solely sufficient condition for the effective cyclic delocalization. Delocalization between any adjacent bonds is necessary. This is dependent on the energy gap between the n and σ^* orbitals and on the orbital overlap. We evaluated the bond interactions in the nitrogen and phosphorus pentagons N_5H_5 (**4**) and P_5H_5 (**3**) together with the hexagons N_6H_6 (**6**) and P_6H_6 (**5**) by our bond model method[2−4,10−16] as described below.



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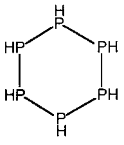

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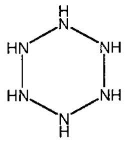

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We previously proposed and applied a bond model to analyze the electronic structures of molecules[2,10−15] and transition states[3,4,16] in terms of *bond interactions*. The single Slater determinant of the Hartree−Fock wave function (Ψ) for the electronic structure of molecules or transition states is expanded into electron configurations:

$$\Psi = C_G\Phi_G + \sum C_T\Phi_T + \sum C_E\Phi_E + ... \qquad (1)$$

where Φ_G, Φ_T, and Φ_E are the ground (G), electron-transferred (T), and locally excited (E) configurations expressed by using *bond orbitals*. The bonding and antibonding orbitals ϕ_i and ϕ_i* of the ith bond are obtained by the diagonalization of the 2 × 2 Fock matrix on the basis of hybrid atomic orbitals χ_{ia} and χ_{ib} on the bonded atoms a and b:[3]

$$\phi_i = c_{ia}\chi_{ia} + c_{ib}\chi_{ib} \qquad (2)$$

$$\phi_i^* = c_{ia}^*\chi_{ia} + c_{ib}^*\chi_{ib} \qquad (3)$$

A set of bond orbitals, i.e., hybrid orbitals, and their coefficients (c_{ia}, c_{ia}*, and so on) give the coefficients of the configurations C_G, C_T, and C_E.[10] This allows one to obtain an optimal set of bond orbitals by maximizing the coefficient of the ground configuration.

The bond interactions are evaluated as the interbond energy between the optimized bond orbitals ϕ_i and ϕ_j, IBE$_{ij}$:[14]

$$\mathrm{IBE}_{ij} = P_{ij}(F_{ij} + H_{ij})$$

where P_{ij}, F_{ij}, and H_{ij} are the elements of the density, Fock, and core Hamiltonian matrixes, respectively.

The geometry optimization of molecules was carried out at the HF/6-31G*, MP2/6-311G**, and B3LYP/6-311G** levels using the Gaussian 98 program.[17] The 6-31G* basis set was used for the analysis of the bond interactions.

The interactions of the lone pair orbital with the vicinal σ and σ* orbitals and the interactions between the vicinal σ* orbitals in the most stable conformers of the five- and six-membered phosphorus and nitrogen rings **3**−**6** are shown in Table 1. The cyclic (n_1, σ_2*, σ_3*) interaction is involved in the cyclic delocalization of the lone pair through σ conjugation, i.e., the electron delocalization between σ_2* and σ_3* ($\sigma_2^* \leftrightarrow \sigma_3^*$) induced by the $n_1 \rightarrow \sigma_2^*$ and $n_1 \rightarrow \sigma_3^*$ delocalizations of lone pair electrons (cf. Figure 2). The total effect of the orbital-phase properties is evaluated by the extent of the delocalization between σ_2* and σ_3*. The IBE value of $\sigma_2^* \leftrightarrow \sigma_3^*$ delocalization in **3** is the largest (−0.013 au), showing the most effective cyclic delocalization in the five-membered phosphorus ring. In the six-membered ring, the σ_2* and σ_3* orbitals are not vicinal to each other, so that the cyclic (n_1,σ_2*,σ_3*) orbital interaction cannot take place efficaciously. This was substantiated by the small IBE value (−0.005 au) of the $\sigma_2^* \leftrightarrow \sigma_3^*$ interaction in **5**. The IBE value is small even between the geminal σ* orbitals (0.001 au) in **5**. The stabilization by the $n_1 \rightarrow \sigma_2^*$ delocalization (−0.135 au) is greater than the destabilization (0.108 au) by the $n_1 \leftrightarrow \sigma_2$ repulsion in the pentagon, while this is not the case with the hexagon. This contrast also supported the cyclic delocalization of the lone pairs being significantly favored by the phase continuity in the pentagon.

Table 1. Interbond Energies (au) in the Five- and Six-Membered Phosphorus and Nitrogen Rings

	IBE (au)		
molecule	$n_1 \rightarrow \sigma_2^*$	$n_1 \leftrightarrow \sigma_2$	$\sigma_2^* \leftrightarrow \sigma_3^*$
3	−0.135	0.108	−0.013
4	−0.189	0.259	−0.003
5	−0.179	0.193	−0.005
6	−0.186	0.367	−0.002

Pentagon stability was also expected for the nitrogen five-membered ring **4** according to orbital-phase continuity (Figure 1b). The intrinsic delocalization of the lone pairs to the vicinal σ_{NN} bonds is a prerequisite to the cyclic delocalization leading to pentagon stability. The delocalizabilities are well-known to increase with a decrease in the energy gap between the orbitals involved in the delocalization and with an increase in the overlap integral. The energy gap (1.484 au) between the n_1 (−0.817 au) and σ_2* (0.667 au) orbitals in N_5H_5 is larger than that (1.351 au) between the orbitals (−1.020 and 0.331 au, respectively) in P_5H_5. The energy gap is less favorable for the $n_1 \rightarrow \sigma_2^*$ delocalization followed by the $\sigma_2^* \leftrightarrow \sigma_3^*$ interaction or the cyclic delocalization in N_5H_5. The overlap (0.093) between the n and σ* orbitals in the nitrogen ring **4** is greater than that (0.063) in the phosphorus ring **3**, favoring the delocalization of the nitrogen lone pair. In fact, the IBE values show that the $n_1 \rightarrow \sigma_2^*$ stabilization (−0.189 au) is smaller than the $n_1 \leftrightarrow \sigma_2$ repulsion (0.259 au) in N_5H_5. This feature is in striking contrast with that of P_5H_5. Thus, the delocalization of the lone pair occurs less effectively in N_5H_5, compared to the $n \leftrightarrow \sigma$ repulsion, due to the larger energy gap, though the overlap is more favorable. The IBE value shows weaker interaction (−0.003 au) between σ_2* and σ_3*, implying less total effect of the orbital-phase continuity and less stability of the nitrogen pentagon.

It is interesting that the electron delocalization from the different lone pair orbitals to the vicinal P−P antibonding orbitals takes place to different extents (Scheme 1). The

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Scheme 1

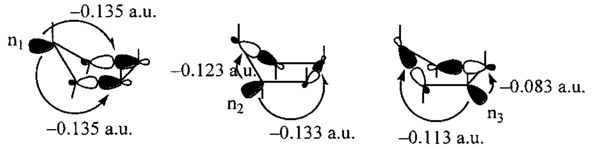


Table 2. Strain Energies (kcal/mol) of Monocyclic Rings

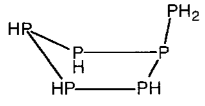
molecule	RHF/6-31G*	B3LYP/6-311G**	MP2/6-311G**
3	−2.53	−3.01	−3.40
4	9.48	15.67	12.51
5	2.89	2.30	1.60
6	6.93	14.76	13.16
8	7.19	6.73	5.95
9	6.36	6.77	5.90
10	2.88	3.30	2.16
11	7.56	6.40	6.72

cyclic (n_1, σ_2*, σ_3*) interaction (Figure 1 and Table 1) is most effective, as shown by the highest IBE value (−0.135 au) of the $n_1 \rightarrow \sigma_2$* interaction. The interactions between n_2 and n_3 and their corresponding vicinal σ* orbitals are weaker (−0.133, −0.123, −0.113, and −0.083 au, in Scheme 1). This suggests that the puckered structure should be important for pentagonal stability.

Strain Energies. Orbital-phase continuity and the small energy gap between n and σ* orbitals give rise to the stabilization by the cyclic delocalization of the lone pairs through the vicinal σ bonds and lower the strain energies of the phosphorus pentagon. We calculated the strain energies (Table 2) according to the homodesmotic reaction (eq 4).[18]

$$(XH)_n + nXH_2XH_2 \rightarrow nXH_2XHXH_2 \qquad (4)$$

The strain energy of **3** was found to be *negative* (−3.01 kcal/mol at B3LYP/6-311G**), in agreement with the results by Schiffer, Ahlrich, and Häser,[19] and by Gimarc and Zhao.[20] The strain energy of **5** is higher (2.30 kcal/mol at B3LYP/6-311G**). Theoretical calculations on the relative stability of **3** were reported by Yoshifuji, Inamoto, and Nagase.[21] The stability of the phosphorus pentagons, cyclopentaphosphanes $(PR)_5$, is in agreement with some experimental observations by Baudler.[22] The parent compound **3** has been isolated and structurally characterized by spectroscopic methods, while **5** is still unknown. Only 1-phosphinocyclopentaphosphane (**7**), a constitutional isomer of **5** with a pentagon unit, has been detected.[22]



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The three- and four-membered rings P_3H_3 and P_4H_4 oligomerize rapidly below room temperature to the five-membered ring P_5H_5 compound. Also the thermolysis of diphosphane, P_2H_4, preferentially gives rise to $(PH)_5$ and polycyclic phosphanes P_nH_m ($m < n$) containing five-membered rings and to much lesser extent to higher homologues of the open-chain phosphanes P_nH_{2n+2}.[22] In addition, the six-membered ring $(PPh)_6$ was observed to be converted into $(PPh)_5$ on warming.[22c]

In contrast with the monocyclic phosphanes, the nitrogen rings $(NH)_5$ and $(NH)_6$ were calculated to have much higher strain energies (Table 2), in agreement with the calculations by Gimarc and Zhao.[20,23] So it is not surprising that none of these nitrogen molecules have been observed yet.[24] The difference in strain energies between $(NH)_5$ and $(NH)_6$ is very small, being only 0.91 kcal/mol at B3LYP/6-311G**. Comparable stain energies were also obtained by Gimarc and Zhao.[20,23] Pentagonal stabilization should also occur in $(NH)_5$, while it is not as effective as that in the phosphorus pentagon. Recent calculations[25] suggest that the five-membered ring is one of the most important factors for the single-bonded nitrogen cluster-type molecules N_x (x = 8−24).

Protonated Cations. The pentagonal stabilization model led to the prediction of a significant increase in strain energy of **3** on protonation, since lone pair for the cyclic delocalization are lost. This was confirmed by the remarkable increase in the strain energies by protonation on the 1-, 2-, and 3-positions of the most stable conformer of **3** ((**8**) 9.74 kcal/mol, (**9**) 9.78 kcal/mol, and (**10**) 6.31 kcal/mol at B3LYP/6-311G** as shown in Figure 3). On the other hand, the increment in the strain energy upon protonation (4.10 kcal/mol at B3LYP/6-311G**) of the six-membered ring $P_6H_7^+$ (**11**) was smaller than those of the five-membered rings **8**−**10**. Similar increases in the strain energies were also provided by the MP2/6-311G** calculations. However, we cannot rule out the possibility that electrostatic repulsion between the positive charges should be responsible for the increase in the strain. We compared the strain energies of the conformers **8**−**10** of **3**, where the electrostatic repulsions are much closer to one another. The increase in the strain on protonation at the 1- and 2-positions (**8** and **9**) is more remarkable than that at the 3-position (**10**). The relative increases were found to be closely related to the delocalizabilities of the n_1, n_2, and n_3 lone pair electrons (Scheme 1). These results imply the significance of lone pair delocalization and the puckered conformation in pentagon stability.

Design of Polycyclophosphanes. The pentagon stability is in agreement with the Baudler rule of the maximum

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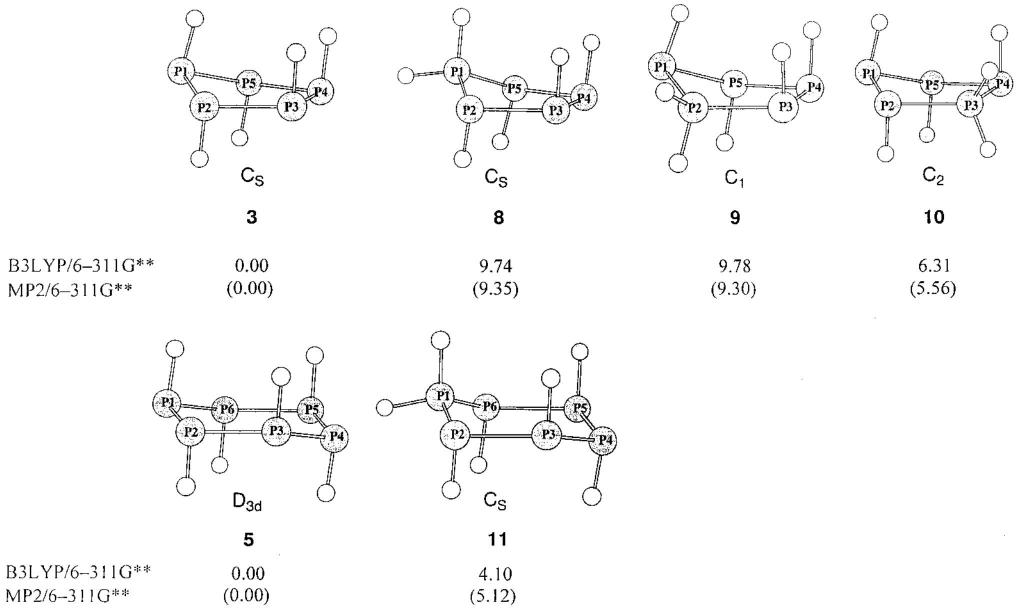

Figure 3. Increase of strain energies (kcal/mol) by protonations relative to those of **3** and **5**.

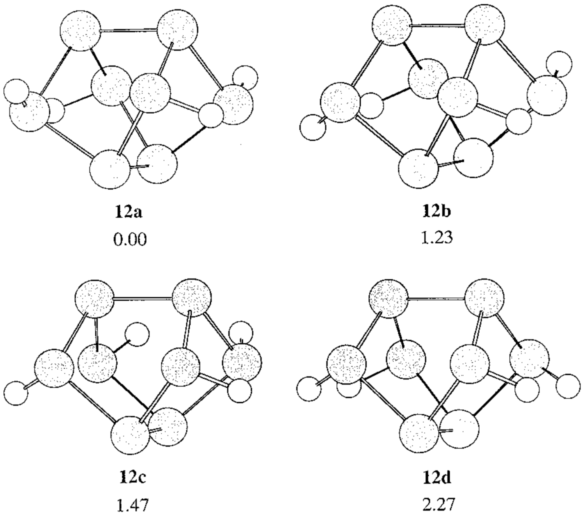

Figure 4. Relative energies (kcal/mol) of conformers of **12** optimized at B3LYP/6-311G**.

number of five-membered ring units.[22] Known polycyclic phosphanes,[22] e.g., “Ufosane” $P_{11}R_3$[26] (the derivatives of **13**) and the $P_{12}R_4$[27] (the derivatives of **14**) substructure of Hittorf’s phosphorus, contain as many pentagonal units as possible. There are many polycyclic phsophanes containing five-membered ring units among those derived from the structured rule by Häser.[28]

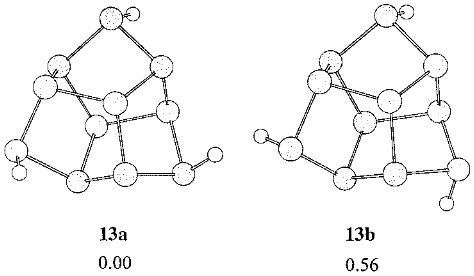

Figure 5. Relative energies (kcal/mol) of conformers of **13** optimized at B3LYP/6-311G**.

Table 3. Strain Energies (kcal/mol) of Polycyclophosphanes Calculated at B3LYP/6-311G**

molecule	strain energy	molecule	strain energy
12	4.01	**19**	0.09
13	−2.19	**20**	1.71
14	−4.35	**21**	12.26
18	3.62	**22**	68.05

We first calculated the strain energies of some known polycyclophosphanes. The smallest cage molecule P_8H_4 (**12**) of high symmetry, composed of pentagon units only, has low strain (4.01 kcal/mol). The relative energies of the conformers (Figure 4) increase with the number of pairs of hydrogen atoms in close proximity. Alkyl derivatives were detected in the mixture of reaction products.[29] The strain energy of $P_{11}H_3$ (**13**) is very low and *negative* (−2.19 kcal/mol at B3LYP/6-311G**; cf. Table 3). The unsymmetrical isomer **13a** was calculated to be slightly (0.56 kcal/mol) more stable than the symmetrical one **13b** (Figure 5), in agreement with the experimental ratio of 3:1 of the two isomers in solution.[22c] Pentacyclo*dodeca*phosphane(4) (**14**) also has a *negative* strain energy of −4.35 kcal/mol at B3LYP/6-311G**. The comparable stabilities of the two stable conformers **14a** and **14b** (Figure 6) account well for the coexistence of these two isomers (ratio **14a**:**14b** = 3:2) in solution.[22c] Häser et al.[30] suggested by the negative values

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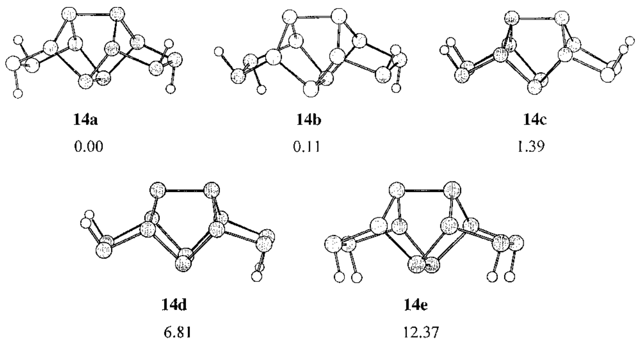
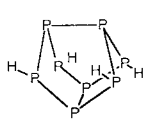


14a 0.00 **14b** 0.11 **14c** 1.39

14d 6.81 **14e** 12.37

Figure 6. Relative energies (kcal/mol) of conformers of **14** optimized at B3LYP/6-311G**.

of $\Delta E_n = E(P_n) - nE(P_4)/4$ that some clusters such as P_{14} (**15**, C_s), P_{16} (**16**, C_{2h}), and P_{18} (**17**, C_{2v}) containing many five-membered rings should be energetically stable relative to P_4, supporting the pentagon stability.



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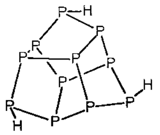

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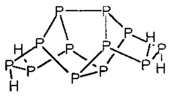

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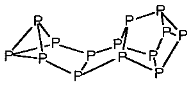

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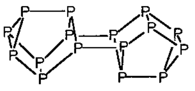

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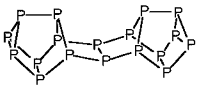

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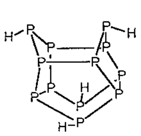
Pentagon stability led to the design of some novel polycyclic molecules, **18**−**21**. The constitutional isomer **18** of the known “rooflike” $P_{12}H_4$ (**14**) has two less five-membered rings, but still has four pentagon units. The strain energy of **18** was calculated to be low (3.62 kcal/mol at B3LYP/6-311G**, Table 3). The low strain energy suggests the possibility of being synthesized in the future, since the strain energy of **18** is smaller than that of the known tetrahedral P_4 molecule (10.15 kcal/mol at B3LYP/6-311G**). The all-exo form (**18a**) is the most stable of all the conformers **18a**−**f** (Figure 7), because all the five-membered rings are puckered in directions favorable to the cyclic delocalizations of the lone pair electrons. The all-endo form (**18f**) isomer is the least stable.



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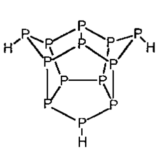

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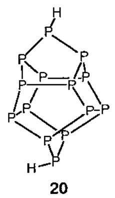

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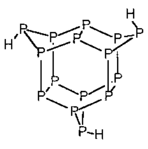

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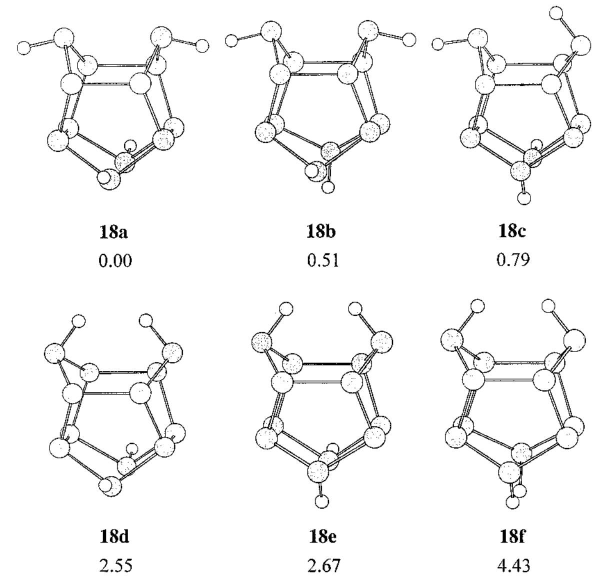
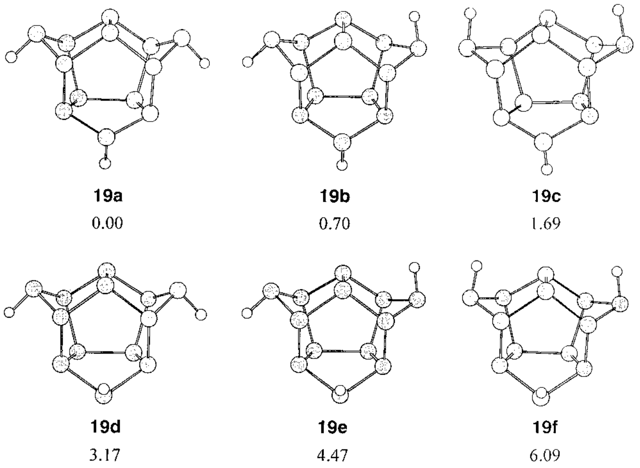


18a 0.00 **18b** 0.51 **18c** 0.79

18d 2.55 **18e** 2.67 **18f** 4.43

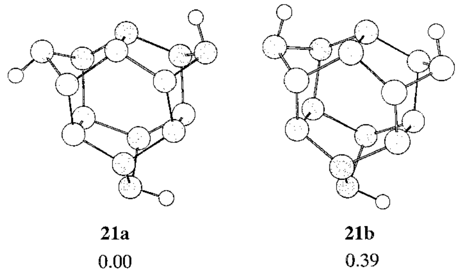
Figure 7. Relative energies (kcal/mol) of conformers of **18** optimized at B3LYP/6-311G**.



19a 0.00 **19b** 0.70 **19c** 1.69

19d 3.17 **19e** 4.47 **19f** 6.09

Figure 8. Relative energies (kcal/mol) of conformers of **19** optimized at B3LYP/6-311G**.



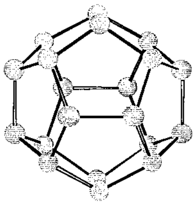
21a 0.00 **21b** 0.39

Figure 9. Relative energies (kcal/mol) of conformers of **21** optimized at B3LYP/6-311G**.

Polycyclophosphanes $P_{13}H_3$ (**19**) and $P_{14}H_2$ (**20**) were calculated to have low strain energies of 0.09 and 1.71 kcal/mol, respectively. These molecules are also recommended as potential targets to be synthesized. There are six stereoisomers, **19a**−**f**, of $P_{13}H_3$ (Figure 8). Each lone pair orbital on the phosphorus bonded to hydrogen is antiperiplanar with the P−P bonds of the five-membered rings in **19a**−**c**, while one of the lone pair orbitals is not antiperiplanar with those of the pentagon but is antiperiplanar with those of the six-membered ring in **19d**−**f**. The stabilities of **19a**−**c** relative to **19d**−**f** demonstrate the prediction that puckering in the direction favorable for the cyclic delocalization of lone pairs is crucial to the pentagon stability.

The polycyclophosphane $P_{15}H_3$ (**21**) is more strained (12.26kcal/mol at B3LYP/6-311G**) than **18**−**20**, while the strain energy is close to that of P_4. The energy difference between the two conformers (Figure 9) is very small (0.39 kcal/mol), as is expected.

The puckered structure of the five-membered ring has been shown to be required for pentagon stability. The pentagons are all planar in the dodecahedral P_{20} (**22**). Thus, the pentagonal stabilization was predicted to occur less effectively. Our calculation did show a very high strain energy of 68.05 kcal/mol (at B3LYP/6-311G**). The strain energy of P_{20} calculated at the HF/6-31G* level (119.3 kcal/mol) is also higher than those of $C_{20}H_{20}$ (43.6 kcal/mol), $Si_{20}H_{20}$ (32.3 kcal/mol), $Ge_{20}H_{20}$ (29.3 kcal/mol), and $Sn_{20}H_{20}$ (21.0 kcal/mol) reported by Nagase et al.[31] Thus, the P_{20} cluster is a less promising target for synthesis, in agreement with the predictions by Häser and co-workers[30] and Hu et al.,[32] although Rulisek et al.[33] and Scherer[34] suggested that the search for P_{20} should not be a search for utopia.



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Conclusions

The orbital-phase theory was applied to propose “pentagon stability”. Cyclic delocalization of the lone pair electrons in the puckered pentagonal ring was shown to stabilize the five-membered phosphorus rings by the cyclic interaction of a lone pair orbital and the vicinal σ^* orbital favored by orbital-phase continuity. The cyclic delocalization is less effective in the nitrogen analogue **4** due to the large energy gap between the n and σ^* orbitals, and in the six-membered rings **5** and **6**. The significance of the cyclic delocalization of the lone pairs in the phosphorus pentagon was substantiated by the *negative* strain energy. Pentagon stability led to the prediction that three novel polycylic phosphanes, **18**−**20**, should be stable enough to be targets of synthesis. The planar structure of the pentagonal units in dodecahedron **22** was suggested to result in high strain and consequently low stability. The puckered five-membered phosphorus ring is an important structural unit for pentagon stability.

Pentagon stability is generally expected for the five-membered ring molecules with the lone pair orbitals on the ring atoms at high energy levels and the antibonding σ^* orbitals of the vicinal bonds at low energy levels. A wide variety of five-membered ring molecules are known in organic and inorganic molecules and in biological systems, and will be synthesized in the future. Pentagon stability will be a useful concept to understand the properties of the known molecules and to design unknown molecules.

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