Relative Energies and Strain Energies of Proposed Structures for P_8

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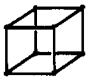
Phosphorus is known to form a wide range of homoatomic clusters. Known examples that contain the P_8 nucleus are the substituted and anionic clusters P_8R_4, P_8R_6, and P_8^{6-}. Although the neutral P_8 naked cluster has never been prepared, there has been theoretical interest in this molecule in recent years. Neutral P_8 would be isoelectronic with $(CH)_8$ hydrocarbons for which at least 13 structural isomers have been prepared. We report the results of geometry optimized ab initio SCF MO calculations with 4-31G* and 6-31G* basis sets for P_8 in the cubane, octabisvalene, and cuneane isomeric forms. These structures are connected by single bonds only and are therefore likely to be the lowest energy forms of P_8. Indeed, calculated bond distances are all consistent with single P–P bonds. At the 4-31G* level all three structures correspond to real minima on the energy surface. The cuneane structure has the lowest energy for both basis sets. At the 6-31G* level the cuneane form of P_8 is only a few kcal/mol higher in energy than $2P_4$. Energy changes for homodesmotic reactions involving P_8 give estimates of strain energies for the three P_8 structures. These range from 45 kcal/mol for cuneane to 76 kcal/mol for cubane, much smaller than the estimated strain energies for $(CH)_8$ in cuneane and cubane forms: 137 and 166 kcal/mol, respectively. Using the strain energy additivity rule, we can decompose the strain energies of the larger cage and polycyclic structures to obtain estimates of strain energies of component monocycles. Applying the additivity rule again, we can estimate strain energies of P_8 structures for which ab initio SCF MO calculations have yet to be done.

Introduction

Phosphorus is known to form homoatomic clusters. Examples include P_4, P_5^-, P_6^{4-}, P_7^{3-}, P_8^{6-}, P_{10}^{6-}, P_{11}^{3-}, and P_{16}^{2-}. Although the neutral P_8 cluster has never been prepared, several investigators have reported ab initio quantum mechanical calculations for this species and found that a proposed cubic structure is a real minimum on the energy surface and not far above the energy of $2P_4$.[1-4] Jones and Hohl have performed density functional calculations to compare cubic and other possible structures for neutral P_8.[5] In this paper we report the results of ab initio SCF MO calculations for three proposed P_8 structures, estimate their strain energies, and relate these results to a simple model for the comparison of a larger variety of structures. Hypothetical P_8 is valence isoelectronic with $(CH)_8$. Therefore, it will be useful to review $(CH)_8$ structures for their comparison with P_8.

The valence isomers of $(CH)_8$ are structures that differ in ways in which eight CH units are linked by CC double and single bonds. These are the structures that are most likely to approximate those of P_8. Balaban has enumerated a total of 20 possible valence isomers of $(CH)_8$.[6] Of these, he counts 5 in which the CH units are connected by 12 C–C single bonds, 5 that contain one double bond and 10 single bonds, 5 that are linked by 2 double bonds and 8 single bonds, 4 with 3 double bonds and 6 single bonds, and 1 isomer (cyclooctatetraene) containing 4 double and 4 single bonds. When $(CH)_8$ isomers were recently reviewed, it was noted that 13 of these isomers have been prepared and a 14th has been implicated as an intermediate in several rearrangements.[7]

Structures **1**–**5** are the valence isomers with 12 single bonds. This set consists of three structures (**1**–**3**) that can be represented by planar graphs and which appear to be chemically realizable for $(CH)_8$. Indeed, cubane (**1**), octabisvalene (**2**), and cuneane (**3**) have all been prepared.[8-10] In this paper we restrict our interest to these three isomeric forms.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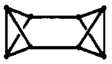
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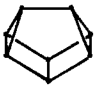
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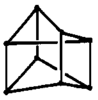
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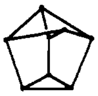
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We have recently demonstrated that the energies of valence isomeric structures are fundamentally ordered by the number of double bonds they contain.[11] For both carbon and phosphorus, the energy of two single bonds is greater than that of a double bond by about 25 kcal/mol. Therefore, the structures with 12 single bonds should have the lowest energy, those with one double bond would be 25 kcal/mol higher, and so on up to the cyclooctatetraene-like structure, which should be 100 kcal/mol higher than the all-single-bond structures. But bond angles in the valence isomeric structures are often severely distorted from preferred valence angles, and this introduces strain energy, a destabilization or energy increase compared to expected levels based on bond additivity alone. The strain energies can significantly modify the energy order of isomeric structures based solely on the number of double bonds. Strain energies of $(CH)_8$ isomers can be very large, as large as 150 kcal/mol and much larger than the 25 kcal/mol spacings between energies of the different classes of valence isomers based on the number of double bonds.

In our study of P_4 and valence isomers of P_6 we found that homoatomic phosphorus clusters have remarkably low strain energies, generally one-third to one-sixth the values of their hydrocarbon analogs. These strain energies make only minor adjustments in the isomer energy order established by the number of double bonds. Compared to the analogous hydrocarbons, we expect P_8 isomers to have small strain energies.

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(1) Trinquier, G.; Malrieu, J.-P.; Daudey, J.-P. *Chem. Phys. Lett.* **1981,** *80,* 552.

(2) Trinquier, G.; Daudey, J.-P.; Komiha, N. *J. Am. Chem. Soc.* **1985,** *107,* 7210.

(3) Ahlrichs, R.; Brode, S.; Ehrhardt, C. *J. Am. Chem. Soc.* **1985,** *107,* 7260.

(4) Schmidt, M. W.; Gordon, M. S. *Inorg. Chem.* **1985,** *25,* 4503.

(5) Jones, R. O.; Hohl, D. *J. Chem. Phys.* **1990,** *92,* 6710.

(6) Balaban, A. T. *Rev. Roum. Chim.* **1966,** *11,* 1097.

(7) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989,** *89,* 1125.

(8) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964,** *86,* 3157.

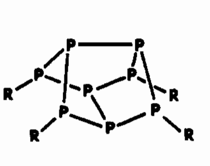
(9) Rücker, C.; Trupp, B. *J. Am. Chem. Soc.* **1988,** *112,* 4828.

(10) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970,** *92,* 6366.

(11) Warren, D. S.; Gimarc, B. M. *J. Am. Chem. Soc.* **1992,** *114,* 5378.

0020-1669/93/1332-1850$04.00/0

Although neutral P_8 has never been prepared, other structures that contain P_8 units have been reported. The mass spectrum of red phosphorus shows a peak for P_8^+, but it is small compared to those for P_7^+, P_5^+, and P_9^+.[12-14] Baudler et al. have prepared the substituted cluster P_8R_4 (R = alkyl).[15] Their ^{31}P-NMR spectra indicate the existence of two isomeric forms, designated α and β (**6**, **7**). These P_8 units would carry a formal charge of 4– and therefore be isoelectronic with P_4S_4 (**8**), which has a structure related to that of the α-isomer of P_8R_4. Dahl and co-workers have prepared a P_8L_4 complex in which the P_8 nucleus of α-isomeric form is complexed with iron carbonyl cyclopentadienyl ligands (**9**).[16] The α-form of the P_8^{4-} unit is similar to the cuneane structure **3** but with two lost bonds presumably replaced by four lone pairs. Baudler and Aktalay have reported P_8R_6 (**10**, R = alkyl), which would contain a formal P_8^{6-} cluster.[17] Finally, Dewalsky and Jeitschko have determined the crystal structure of $WNiP_8$, which contains the ion P_8^{6-} (**11**) with a structure derived from the cube by breaking 3 of the 12 cube edges such that only one of the 3-fold axes of the cube is maintained.[18] The diversity of known P_8 clusters gives hope that neutral P_8 might eventually be made.



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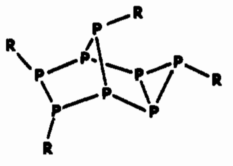

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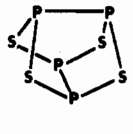

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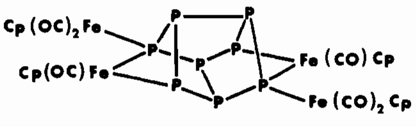

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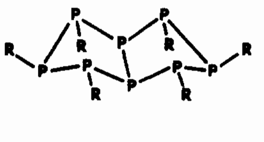

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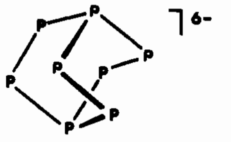

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Calculations

We have carried out geometry-optimized ab initio SCF MO calculations for P_8 constrained within the appropriate symmetry point group for the isomers cubane (**1**, O_h), octabisvalene (**2**, D_{2h}), and cuneane (**3**, C_{2v}). Calculations were performed on FPS and VAX 6000 computers at the University of South Carolina with the Gaussian 82 and 86 program packages and with the basis sets 4-31G* and 6-31G*, where asterisks (*) indicate that d-type polarization functions were included in these basis sets.[19-21] We and others before us have found that polarization functions are essential in order to obtain structural details that compare favorably with experiment for molecules containing atoms of second row elements.[1-4] At the 4-31G* level our calculated vibrational frequencies were all real for each of the three structures **1**–**3**, indicating that they correspond to real minima on the energy surface at this level of approximation. Vibrational frequency calculations with the 6-31G* basis set would have required computing times far beyond the patience of our computational colleagues and the computer center supervisory personnel. Table I contains the total energies and zero point vibrational energy corrections in hartrees and relative energies in kcal/mol for P_8 in structural forms **1**–**3**.

Table I. Total Energies (h), Zero-Point Vibrational Energies (h), and Relative Energies (kcal/mol) of P_8 in Valence Isomeric Forms

structure	*E*	4-31G*	6-31G*
		Cubane, **1**	
	$E_{tot.}$	–2722.9457	–2725.7418
	E_{rel}	18.8	30.8
	ZPVE	0.0164	
		Octabisvalene, **2**	
	$E_{tot.}$	–2722.9347	–2725.7609
	E_{rel}	25.7	18.8
	ZPVE	0.0153	
		Cuneane, **3**	
	$E_{tot.}$	–2722.9757	–2725.7909
	E_{rel}	0	0
	ZPVE	0.0161	

Calculations performed at higher levels of theory should lead to more reliable results. Had we used a more extensive basis set we could have more closely approached the Hartree–Fock limit. By carrying out Moller–Plesset perturbation or configuration interaction calculations, we could have included some of the effects of electron correlation. Allen and co-workers[22] used the 6-31G* basis set for RHF level calculations of strain energies of three- and four-membered cyclosilanes and obtained satisfactory agreement with experiment. To test the effect of correlation corrections on strain energies of phosphorus clusters, we carried out MP2/6-31G** calculations for P_4 and found that the resulting P_4 strain energy was only a few kcal/mol lower than comparable values obtained from RHF/6-31G** results. Details appear in a later section. Our attempts to perform MP2/6-31G* calculations for P_8 required more memory than is available in the computers at our disposal.

Another argument for neglect of correlation corrections here is based on the underlying similarity of isomeric structures **1**–**3**. In each of the three structures all 8 P atoms are 3-coordinate and each is bonded to three other P atoms by single bonds yielding a consistent valence environment for individual P atoms among the three structures. Therefore, differences in correlation energies should be relatively small and should largely cancel when total energies of these isomers are compared. This is basically the same justification we use in a later section for employing homodesmotic reaction energy changes for estimating strain energies. We would expect larger correlation energy differences between isomers that display different bond types.

Relative Stabilities and Structures

At both basis sets the cuneane isomer **3** has the lowest energy for those structures we studied. Relative energies of the cubane and octabisvalene isomers are reversed by the two basis sets. At the 6-31G* level cubane lies above octabisvalene. This ordering of energies, cuneane < octabisvalene < cubane, matches that obtained for these structures by the density functional calculations of Jones and Hohl, whose relative energies (kcal/mol) are cuneane (0), octabisvalene (17.3), and cubane (40.8).[5] Indeed, this is the same order and range of relative energies of the same structures of $(CH)_8$ as predicted by Eaton and co-workers[10] in 1970 and supported more recently by the results of MM2 calculations for the hydrocarbon isomers.[9]

The P–P bond distances determined by energy minimizations for the three isomeric forms of P_8 are shown in Figure 1. For comparison, here is a set of typical bond distances from a survey of experimental structures containing representative bond

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[12] Martin, T. P. *Z. Phys. D* **1986**, *3*, 211.

[13] Kerwin, L. *Can. J. Phys.* **1954**, *32*, 757.

[14] Carette, J.-D.; Kerwin, L. *Can. J. Phys.* **1961**, *39*, 1300.

[15] Baudler, M.; Koll, B.; Adamek, C.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 347.

[16] Barr, M. E.; Adams, B. R.; Weller, R. R.; Dahl, L. E. *J. Am. Chem. Soc.* **1991**, *113*, 3052.

[17] Baudler, M.; Aktalay, Y. *Z. Anorg. Allg. Chem.* **1983**, *496*, 29.

[18] Dawalsky, M. V.; Jeitschko, W. *Acta Chem. Scand.* **1991**, *45*, 828.

[19] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[20] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82. Carnegie-Mellon University, Nov 30, 1984.

[21] Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

[22] Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408.

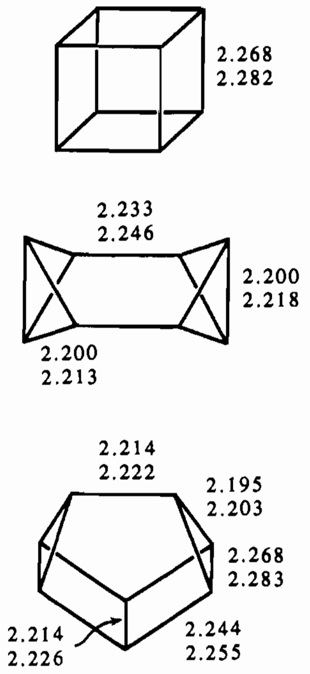


Figure 1. Selected structural parameters for cubane, cuneane, and octabisvalene isomeric forms of P_8. In each stack the upper value is the 6-31G* result and the lower figure is from the 4-31G* calculation.

types:[23]

$$\text{P—P} = 2.21\ \text{Å} \qquad \text{P=P} = 2.01\ \text{Å} \qquad \text{P≡P} = 1.89\ \text{Å}$$

It is clear from Figure 1 that all bonds in the three structures are P–P single bonds as expected. Bond distances at the 4-31G* level are in every instance longer than those from the 6-31G* basis set, the average difference being 0.013 Å. The P–P bond in the cubane structure (2.268 Å, 6-31G*; 2.282 Å, 4-31G*) is notably longer than a standard P–P single bond from P_4 (2.223 Å). The density functional results of Jones and Hohl also show a long P–P distance (2.29 Å) in cubic P_8.[5] The long P–P bond follows a trend observed in $(CH)_8$ cubane where gas-phase electron diffraction experiments[24] and ab initio SCF MO calculations[25] give C–C bonds of 1.575 and 1.570 Å, respectively, compared to 1.534 Å in ethane. In the octabisvalene structure **2**, the P–P bonds that link the two P_4 butterflies are also slightly longer (2.233 Å, 6-31G*; 2.246 Å, 4-31G*) than standard, again in agreement with the longer bond (2.23 Å) from the density functional results.

Relative Energies of P_2, P_4, and P_8

Figure 2 shows the relative energies of $4P_2$, $2P_4$, and P_8 in the isomeric forms considered here both with and without corrections for zero-point vibrational energies. The total energies and zero-point vibrational energies of P_2 and P_4, listed in Table II, are reproduced from our earlier work.[11] Since practical considerations prohibited us from obtaining zero-point vibrational energies for the P_8 isomers at the 6-31G* level, we have corrected 6-31G* total energies with 4-31G* zero-point vibrational energies. Our experience suggests that zero-point vibrational energies as calculated with these two basis sets differ by much less than 1 kcal/mol. Compare results in Table II and in Tables II and III of ref 11. The most notable result of Figure 2 is that at the 4-31G* level the energy of P_8 (cuneane) falls slightly below that of $2P_4$, which is taken as the zero of energy in Figure 2. The density functional results of Jones and Hohl give a similar ordering. This situation is rectified for the higher level 6-31G* basis set for which P_8 (cuneane) lies above $2P_4$ as expected but only by a few kcal/mol. The energy of $4P_2$, for the known P_2 molecule, lies high above all the P_8 isomers. While viewing Figure 2 it is helpful to keep in mind that although the results displayed in that figure are at the limit of what we can hope to accomplish with the computing resources available to us, their value is mainly qualitative.

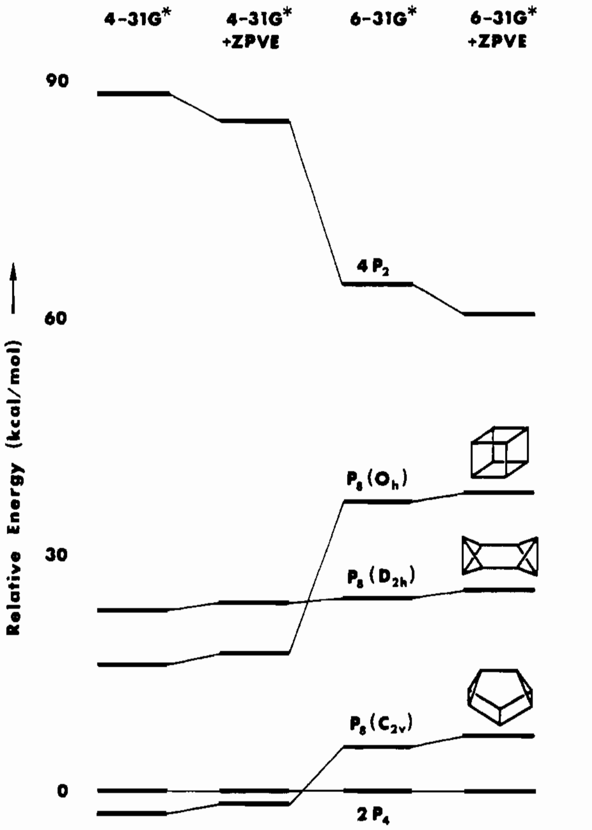


Figure 2. Relative energies of $4P_2$, $2P_4$, and P_8. The zero-point vibrational energy correction applied to the 6-31G* energy for P_8 structures is the value from the 4-31G* calculation.

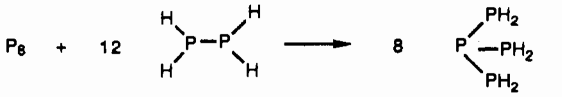
Table II. Total Energies (h) and Zero-Point Vibrational Energies (h) for Useful Molecules[a]

molecule	E	4-31G*	6-31G* or 6-31G**
P_2	$E_{tot.}$	−680.7077	−681.4245
	ZPVE	0.0022	0.0021
$P_4(T_d)$	$E_{tot.}$	−1361.4855	−1362.8999
	ZPVE	0.0069	0.0070
$P_2H_4(C_{2h}$, trans)	$E_{tot.}$	−683.0382	−683.7588
	ZPVE	0.0378	0.0380
$P_2H_4(C_2$, gauche)	$E_{tot.}$	−683.0385	−683.7605
	ZPVE	0.0380	0.0383
$P_4H_6(C_3)$	$E_{tot.}$	−1364.9387	−1366.3736
	ZPVE	0.0603	0.0609

[a] Reference 11.

Strain Energies of P_8 Isomers

Equation 1 is a homodesmotic reaction involving P_8 isomers that contain only P–P single bonds. Homodesmotic reactions

 (1)

$$P_8 + 12\ H_2P{-}PH_2 \longrightarrow 8\ P(PH_2)_3 \qquad (1)$$

conserve the bonding environment around each atom as well as

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(23) Gimarc, B. M.; Warren, D. S. In *Molecules in Natural Science and Medicine*; Maksic, M., Eds.; Ellis Horwood: Chichester, U.K., 1991; p 327.

(24) Almenningen, A.; Jonvik, T.; Martin, H.-D.; Urbanek, T. *J. Mol. Struct.* **1985**, *128*, 239.

(25) Almlöf, J.; Jonvik, T. *Chem. Phys. Lett.* **1982**, *92*, 267.

Table III. Strain Energies (in kcal/mol) for Valence Isomeric Structures of P_8

structure	4-31G*	+ZPVE	6-31G*	+ZPVE[a]
		P_8[b]		
cubane	64.1	58.1	75.8	69.1
octabisvalene	71.0	64.3	63.8	56.4
cuneane	45.3	39.1	45.0	38.1
		P_6[c]		
prismane	50.7	45.6	52.9	47.5
benzvalene	23.9	20.5	20.8	17.2
Dewar benzene	11.5	10.1	13.1	11.3
bicyclopropenyl	18.2	16.2	15.7	13.4
		P_4[c]		
tetrahedral	24.1	20.2	19.7	15.6

[a] Zero-point vibrational energies for P_8 were taken from the 4-31G* calculation and applied to the 6-31G* total energies. [b] This work. [c] Reference 11.

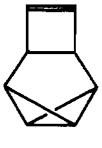
the numbers of P–P and P–H bonds.[26] The bond additivity model would give $\Delta E = 0$ for eq 1. But P_8 structures must be destabilized by ring strain energy that is not otherwise accounted for in the bond additivity model. Therefore, a nonzero, exothermic ΔE would be the strain energy of the P_8 isomer. Table III reports the strain energies ($-\Delta E$) calculated for eq 1 using total energies of P_8 isomers from Table I and total energies for P_2H_4 and P_4H_6 from our earlier work, reproduced in Table II. Again, we used 4-31G* zero-point vibrational energies for P_8 structures to modify total energies from 6-31G* calculations to obtain the right-most column in Table III. As expected the P_8 strain energies are much smaller than those estimated by molecular mechanics for comparable forms of $(CH)_8$: cuneane, 137; octabisvalene, 154; cubane, 166 kcal/mol.[9]

As mentioned above, Allen and co-workers have recently reported results of ab initio SCF MO calculations at the RHF/6-31G* level for three- and four-membered cyclosilanes as well as the molecules H_3SiSiH_3 and $H_3Si(SiH_2)SiH_3$ which are involved in homodesmotic reactions analogous to eq 1.[22] Their calculated strain energies, without correlation corrections, were in satisfactory agreement with experiment. Indeed, one of the justifications for using homodesmotic reactions for calculating energy changes is the expectation that correlation errors should largely cancel in the differences.

To test the effect of electron correlation on the ab initio calculation of strain energies, we carried out geometry-optimized MP2/6-31G* calculations for $P_4(T_d)$ (total energy = −1363.3812 h) and MP2/6-31G** calculations for $P_2H_4(C_2)$ and $P_4H_6(C_3)$ (total energies = −684.0146 h and −1366.8723 h, respectively). Using these energies to calculate the energy change for the appropriate P_4 analog of eq 1 gives a strain energy of 12.8 kcal/mol compared to 19.7 kcal/mol for the RHF/6-31G* result (Table III). Electron correlation corrections at the MP2 level preferentially stabilize the P_4 cluster and lead to lower strain energies. If P_6 and P_8 clusters follow this pattern, then the strain energies at the RHF level are likely to be larger than those obtained by MP2 calculations. Thermochemical data and other considerations have led to P_4 strain energy estimates in the range 24–34 kcal/mol.[23] In all candor, these estimates carry considerable uncertainty. Our estimates from RHF and MP2 calculations, 20 and 13 kcal/mol, respectively, fall outside the small end of this range.

P_8 cuneane has the lowest energy of the three single-bonded structures, but is it more stable than any of the P_8 structures that contain one double bond? If the strain energy of cuneane had turned out to be less than 25 kcal/mol (the energy difference between a pair of single bonds and one double bond), we could have been reasonably certain that the cuneane isomer is the most stable of all P_8 structures. Unfortunately, the cuneane strain energy is about 45 kcal/mol.

The five isomers containing one double bond are **12**–**16**:[6]



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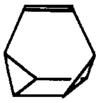

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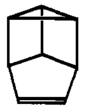

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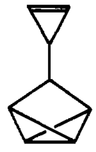

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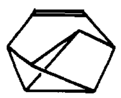

16

We can comfortably eliminate **16** from consideration on the grounds that it is probably not chemically realistic. If any of the remaining structures **12**–**15** has a strain energy of less than 25 kcal/mol, it would have a total energy comparable to that of cuneane **3**. Calculation of total energies of **12**–**15** would be a major project, the subject of a future paper, perhaps. But we can hope to estimate strain energies of the structures **12**–**15** from estimates of monocyclic strain energies and the assumption that strain energies are additive.

Several authors have noted that strain energies of cyclic hydrocarbons are, to a first approximation, additive.[7,27–30] The strain energy of a structure composed of several small rings can be estimated simply by adding up the strain energies of individual rings. Lacking strain energies of small phosphorus rings, we can apply the additivity rule in reverse and decompose the strain energies of some regular polyhedral structures to obtain values for their component small rings and then use the rule again by adding together the strain energies of the monocycles to estimate strain energies of the composite structures **12**–**15**. In the following demonstration we use strain energies for P_n structures calculated at the 6-31G* level without zero-point energy corrections. Our previously calculated strain energy of tetrahedral P_4 is 19.7 kcal/mol (see Table III). Since the tetrahedron has four triangular faces, each triangle can be assumed to have a strain energy of 19.7/4 = 4.9 kcal/mol. This is a small value compared to the 27.5 kcal/mol strain energy in the hydrocarbon cyclopropane, C_3H_6.[29] For P_8 cubane, our calculated strain energy is 75.8 kcal/mol. The cube has six square faces, giving a strain energy of 75.8/6 = 12.6 kcal/mol for each square. Again, this strain energy for the P_4 square is small compared to the value of 26.5 kcal/mol for the square hydrocarbon cyclobutane, C_4H_8.[29] But a more astonishing comparison is that between the small phosphorus rings themselves. The strain energy of the P_4 square is more than twice that of the P_3 triangle. One would have expected the square to have been less strained than the triangle as in hydrocarbon rings. Indeed, Trinquier and co-workers[1] have anticipated an unusually large strain energy for the P_4 square which they describe as resulting from a cis repulsion between parallel P–P bonds. From double-ζ calculations of the energy change for eq 2 and

(2)

using standard values of P–P and P–H bond energies, they obtained an estimate of 11 kcal/mol for the interaction of two parallel P–P bonds. Our comparable value would be half of the P_4 square strain energy or 6.3 kcal/mol.

Now we are ready to combine P_3 and P_4 strain energies to estimate the strain energy of P_6 prismane. This polyhedral structure is composed of three squares and two triangles for a total strain energy of 3 × 12.6 + 2 × 4.9 = 47.8 kcal/mol, a result

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[26] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

[27] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[28] Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

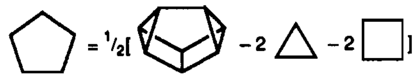
[29] Gasteiger, J.; Dammer, O. *Tetrahedron* **1978**, *34*, 2939.

[30] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

Table IV. Estimates of Strain Energies (kcal/mol) for Phosphorus Monocycles from Decomposition of Polycyclic and Cage Structures

ring	strain energy	ring	strain energy
	4.9		7.8
	12.6		6.5
	4.9		5.5
	22.1		5

that agrees well with the 52.9 kcal/mol value we obtained previously from the energy difference of a homodesmotic reaction.[11] The difference between these two results, ~5 kcal/mol, gives us an estimate of the error inherent in the approximation. In like fashion, we can use the strain energy of P_8 cuneane, as the sum of two triangles, two squares, and two pentagons, to approximate the strain energy of the cyclopentane analog:



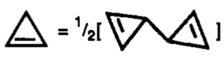
= ½[45.0 − 2 × 4.9 − 2 × 12.6] = 4.9 kcal/mol

Similarly, the strain energy of the boat-shaped hexagon should be a component of that for P_8 octabisvalene:

= ½(63.8 − 4 × 4.9)

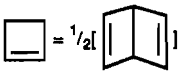
= 22.1 kcal/mol

Double-bond-containing P_6 structures calculated previously can be decomposed to give estimates of monocycles with double bonds.[11] It is clear that the strain energy of the cyclopropene triangle is half that of bicyclopropenyl



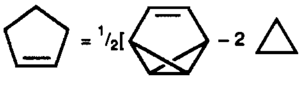
] = ½(15.7) = 7.8 kcal/mol

and the strain energy of the cyclobutene analog should be half of that for P_6 Dewar benzene:



] = ½(13.1) = 6.5 kcal/mol

Finally, the strain energy of the cyclopentene analog is part of that for benzvalene:



] = ½(20.8 − 2 × 4.9)

= 5.5 kcal/mol

Not available from this analysis is an estimate for the cyclohexene analog. We assign a value of 5 kcal/mol to this ring. These results are collected in Table IV. Strain energies for these rings can be calculated directly, just as we have done for the P_8 and P_6 structures, and this project is currently in progress.

The strain energies of the phosphorus monocycles from Table IV can be used to give rough estimates for the P_8 isomers **12–15** with one double bond. Figure 3 shows the effect of adding strain energies to the relative energies of hypothetical unstrained P_8 clusters composed of 12 single bonds compared to those connected by 1 double and 10 single bonds. The unstrained isomers with one double bond start out 25 kcal/mol higher in energy than the unstrained structures connected by single bonds only. The strain energies of the all-single-bond structures are relatively large and even the most stable of these, cuneane (**3**), falls below two of the one-double-bond structures, **12** and **13**, by 5 and 10 kcal/mol, respectively. Therefore, within the limits of our assumptions, **3** and **12** have comparable energies.

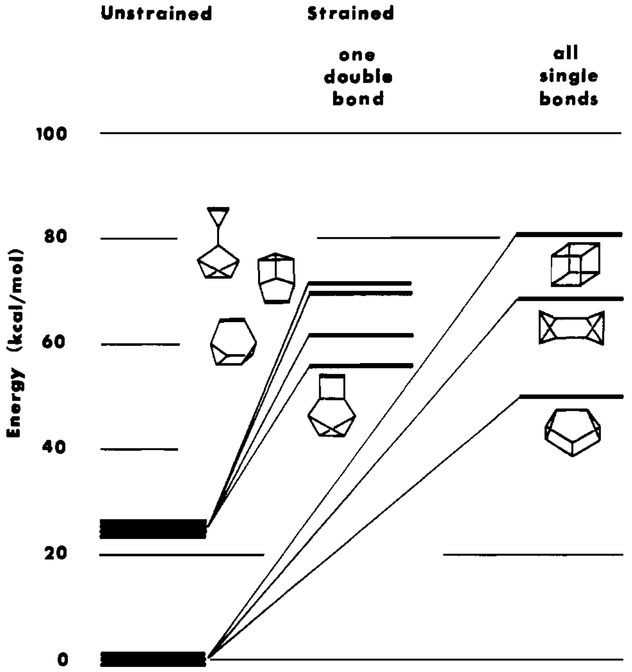
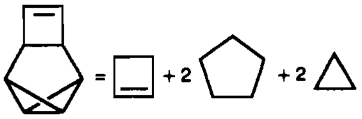
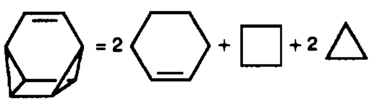


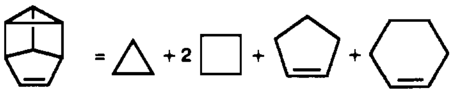
Figure 3. Comparisons of the relative energies of strained and hypothetical unstrained structures for P_8 clusters composed of all single bonds and 1 double and 10 single bonds. The relatively large strain energies of the all-single-bond structures put even the most stable of these, cuneane, into the energy range of the lowest one-double-bond structure.



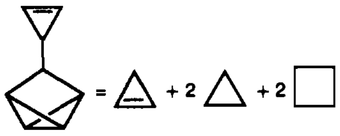
12 = 6.5 + 2(4.9 + 4.9) = 26.3 kcal/mol



13 = 2 × 6 + 12.6 + 2 × 4.9 = 32.35 kcal/mol



14 = 4.9 + 2 × 12.6 + 5.5 = 40.6 kcal/mol



15 = 7.8 + 2 × 4.9 + 2 × 12.6 = 43.0 kcal/mol

To estimate strain energies of **12–15**, we have used the additivity rule twice, once when cluster strain energies were decomposed to give monocyclic strains and again when the small ring strains were recombined to estimate strain energies in a different set of clusters. One could argue that this doubles the possible error in estimated strain energies. Perhaps we should have started from strain energies directly calculated for individual monocycles. On the other hand, strain energies of small rings that compose polycyclic or polyhedral structures should be better approximations to the strain energies of the small rings that constitute other cluster structures. Sets of small ring strain energies obtained from both isolated and polycyclic sources should provide insight here.

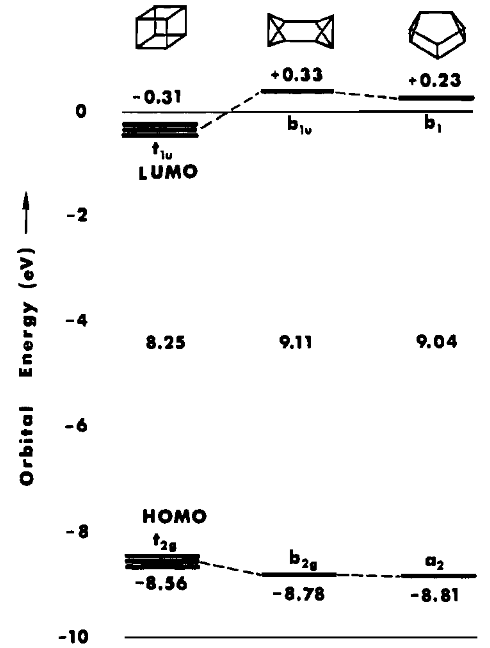


Figure 4. Energies (eV) of HOMO and LUMO and the size of HOMO-LUMO gaps in P_8 isomers as calculated with the 6-31G* basis set.

At least one other attempt has been made to apply the strain energy additivity rule to systems other than hydrocarbons. Allen and co-workers have studied Si_3, Si_2C, SiC_2, and C_3 rings **16**

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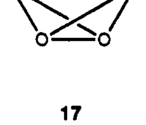

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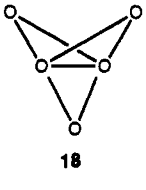
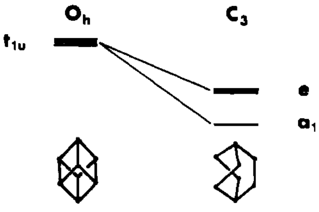


18

fused to form bicyclic **17** and tricyclic (propellane) **18** systems.[22] They found that if the bridgehead atoms are both carbons their calculated strain energies increase linearly with number of rings from **16** to **17** to **18**. In other words, strain energies are approximately additive. On the other hand, if Si atoms occupy both bridgehead sites, strain energy increases from **16** to **17** but with no further increase for **18**. Therefore it may be that strain energy additivity may have only limited applicability.

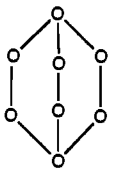
Ionization Energy and Homo-Lumo Gap

Figure 4 displays the energies of HOMO and LUMO for P_8 in isomeric forms **1**-**3** as calculated with the 6-31G* basis set. Koopman's theorem states that the energy of the HOMO approximates the first ionization potential of the molecule.[31] The LUMO is sometimes considered to be an approximation to the electron affinity. A large HOMO-LUMO gap is widely recognized as being related to kinetic and structural stability while a small gap is associated with reactivity.[32-37] Both HOMOs and LUMOs of P_8 structures are generally higher than those of the P_6 isomers previously calculated with the same basis set.[11] However, HOMO-LUMO gaps for P_8 isomers are generally somewhat larger than those for P_6. The P_8 cubane isomer has a negative LUMO, the triply degenerate t_{1u} MO. This orbital could be completely filled with electrons to yield the observed P_8^{6-} ion (**11**). If the P_8^{6-} anion had cubic form, this t_{1u} MO would be completely filled. Loss of three mutually perpendicular but nonadjacent cube edges frees the cube to distort to C_3 symmetry and allows mixing among all t MOs. Lyne and Mingos[38] have discussed the properties of MOs undergoing this O_h to C_3 distortion in order to account for the observed structure of $Te_2Se_6^{2+}$ with which the recently prepared P_8^{6-} (**11**) is isoelectronic and isostructural. Extended Hückel calculations for Se_8^{2+} show that the breaking of the three cube edge bonds produces a significant energy lowering of the a_1 and e MOs of C_3 symmetry that correlate with t_{1u} of the cube:



Lynn and Mingos report calculated charge distributions for Se_8^{2+} in the form of the C_3 distorted cube. Those results show less electron density at the two 3-coordinate sites than at the six 2-coordinate positions. Following the rule of topological charge stabilization,[39] less electronegative Te atoms would prefer to be located at those sites at which charge density is already diminished by topology, as represented by the results for the homoatomic cluster and qualitatively accounting for stoichiometry and site structure of $Te_2Se_6^{2+}$.

The cations S_8^{2+}, Se_8^{2+}, and Te_8^{2+} are isoelectronic but not isostructural with P_8^{6-} and $Te_2Se_6^{2+}$.[40-43] Instead, they have structures that are nonplanar fused 5-membered rings of C_s or C_2 symmetry. Compare the connectivity of $Te_2Se_6^{2+}$ and P_8^{6-} (**19**) with that of S_8^{2+}, Se_8^{2+}, and Te_8^{2+} (**20**). Gillespie and co-workers claim that, compared to the C_3 structure **19**, the fused five-membered ring structure **20** allows for more delocalization of charge and thus offers greater stabilization for homoatomic clusters S_8^{2+}, Se_8^{2+}, and Te_8^{2+}. The same logic should hold for P_8^{6-}, which however takes on another structure.



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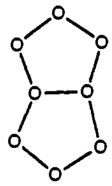

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Isomerization and Dissociation Reactions

Thermal, photochemical, and metal ion-catalyzed rearrangements of $(CH)_8$ have been reviewed by several authors.[7,10,44,45]

The octabisvalene structure consists of a pair of double-linked tetrahedra. The obvious question is whether octabisvalene P_8 could be formed by joining two tetrahedral P_8 units or if octabisvalene P_8, once formed, would dissociate directly into $2P_4$. Figure 5 schematically correlates valence orbitals between $2P_4$-

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(31) Lowe, J. P. *Quantum Chemistry*; Academic Press: New York, p 321.
(32) Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 745.
(33) Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1969**, 240.
(34) Muetterties, E. L.; Beier, B. F. *Bull. Soc. Chim. Belg.* **1975**, *84*, 397.
(35) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423.
(36) Burdett, J. K.; Coddens, B. A. *Inorg. Chem.* **1988**, *27*, 3259.
(37) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5720.
(38) Lyne, P. D.; Mingos, D. M. P. In *Molecules in Natural Science and Medicine*; Maksic, Z. B., Eckert-Maksic, M., Eds.; Ellis Horwood: Chichester, U.K., 1991; p 394.
(39) Gimarc, B. M.; Ott, J. J. *J. Am. Chem. Soc.* **1986**, *105*, 4298.
(40) Collins, M. J.; Gillespie, R. J.; Sawyer, J. F.; *Inorg. Chem.* **1987**, *26*, 1476.
(41) Davis, C. G.; Gillespie, R. J.; Park, J. J.; Passmore, J. *Inorg. Chem.* **1971**, *10*, 2781.
(42) McMullan, R. K.; Prince, D. J.; Corbett, J. D. *Chem. Commun.* **1969**, *1438*; *Inorg. Chem.* **1971**, *10*, 1749.
(43) Beck, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 293.
(44) Balaban, A. T.; Bancin, M. *J. Chem. Educ.* **1984**, *61*, 766.
(45) Qin, X.-Z.; Trifunac, A. D.; Eaton, P. E.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 4565.

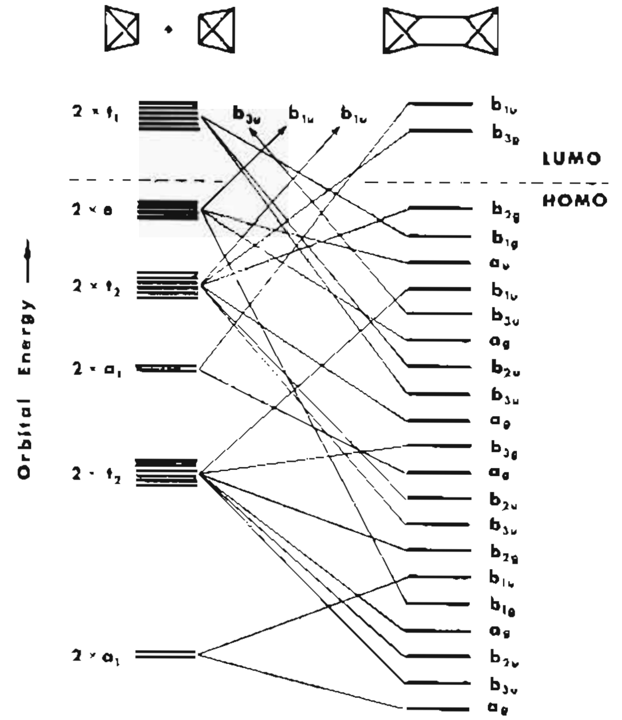
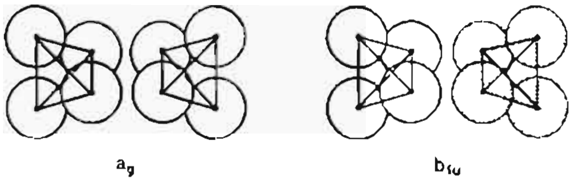


Figure 5. Schematic correlations connecting valence energy levels of two tetrahedral P_4 fragments with valence levels of P_8 octabisvalene.

(T_d) and P_8 (octabisvalene, D_{2h}). Symmetry classifications for both reactants and product are under D_{2h} symmetry. For example, two a_1 MOs of the tetrahedron combine with same phase or opposite phase to form a_g and b_{1u} MOs of octabisvalene. Ordering of valence levels in Figure 5 comes from ab initio calculations. The many HOMO–LUMO crossings in Figure 5 forcefully indicate that this process is symmetry forbidden. A comparable correlation diagram has been proposed relating $(CH)_8$ octabisvalene and two bicyclobutane fragments.[46]



Conclusions

Ab initio SCF MO calculations give the cuneane form (**3**) of P_8 the lowest energy of the three structures studied. With the 6-31G* basis set the cuneane form of P_8 is only a few kcal/mol higher in energy than $2P_4$. With the higher of the two basis sets, octabisvalene and cubane isomers have successively higher energies, the same as the order believed to occur among the three single-bonded forms of $(CH)_8$. Calculated bond distances are all consistent with single P–P bonds for these structures. Strain energies of P_8 isomers, as estimated by calculated energy differences for homodesmotic reactions involving P_8, are small compared to analogous hydrocarbons, as anticipated from previous results for P_4 and P_6. The rule that strain energies are approximately additive was applied twice, first to decompose known strain energies of polycyclic P_4, P_6, and P_8 structures to obtain estimates of strain energies of their component monocycles, and then the strain energies of the monocycles were assembled in different combinations to estimate strain energies of a new set of P_8 isomers. The additivity rule for strain energies gives at least consistent results for P_6 prismane for which it is obvious that contributions for all component small rings have been properly included. Because of the energy difference between two single bonds and one double bond, the P_8 all-single-bond structures **1**–**3** have a 25 kcal/mol stability advantage over the one-double-bond structures **12**–**15**. But strain energy differences could erase this advantage. The estimated strain energy of **12** appears to be 20 kcal/mol less than that of **3**, making these two structures comparable in energy within the limits of the approximations and assumptions on which these results are based.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this research through Grant No. CHE-9012216 to the University of South Carolina. D.S.W. is pleased to acknowledge a U.S. Department of Education graduate fellowship awarded to him through the Department of Chemistry and Biochemistry at the University of South Carolina.

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(46) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.