

## Strain Energies of Inorganic Rings

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Strain energy, an important concept in organic chemistry, can also be applied to inorganic ring systems. Deviations of bond angles and torsional angles from preferred valence values at ring vertices implies a strained structure with increased energy. Strain energy is the energy difference between the energy change for a process as determined by experiment and as determined by a model that does not include strain. In practice, the experimental energy change can be approximated by differences in energies of products and reactants as obtained from *ab initio* SCF MO calculations. The bond additivity model can be used to describe the process that neglects the effects of strain. Strain energies for monocycles  $O_n$  and  $S_n$ ,  $n = 3-8$ , will be compared with those for cycloalkanes. The surprise here is that four-membered rings of sulfur and of oxygen have greater strains than do three-membered rings. Strain energies of polycyclic clusters  $P_4$ ,  $P_6$ ,  $P_8$ ,  $As_4$ , and  $As_6$  are small compared to those of analogous hydrocarbons. The conventional concepts of strain energy, resonance energy, and average bond energy can be combined to rationalize differences in relative energy trends among isomeric structures of  $C_6H_6$ ,  $P_6$  and  $As_6$ . The rule of additivity of ring strain energies, useful in the estimation of polycyclic hydrocarbons, may also be applicable to polycyclic inorganic clusters. The concepts of average bond energies, resonance stabilization, and strain energy and the rules of bond additivity and ring strain energy are useful in understanding properties of inorganic molecules when we know how the inorganic parameters differ from the better known organic values.

### INTRODUCTION

The research we describe in this paper is part of a larger study of the molecular and electronic structures of homoatomic clusters of the representative elements. A homoatomic cluster is a polyatomic molecule or ion, all the atoms of which are alike. The choice of homoatomic clusters of the main group elements might at first appear to be unduly restrictive. In fact, a large collection of these clusters has been prepared and characterized. For example, homoatomic clusters of phosphorus include  $P_4$ ,  $P_5^-$ ,  $P_6^{4-}$ ,  $P_7^3-$ ,  $P_8^{6-}$ ,  $P_{10}^{6-}$ ,  $P_{11}^{3-}$ ,  $P_{16}^{2-}$ . Indeed, the fullerenes, one of the special topics of this sym-

posium, are examples of homoatomic main group clusters. But the clusters we describe here are composed of atoms of the lower periods of the periodic table.

The standard state of phosphorus is white phosphorus,  $P_4$ , the tetrahedral structure of which has been known for 60 years.<sup>1</sup> Figure 1 displays some of the known 6-atom clusters of phosphorus. X-ray diffraction structures are available for all of

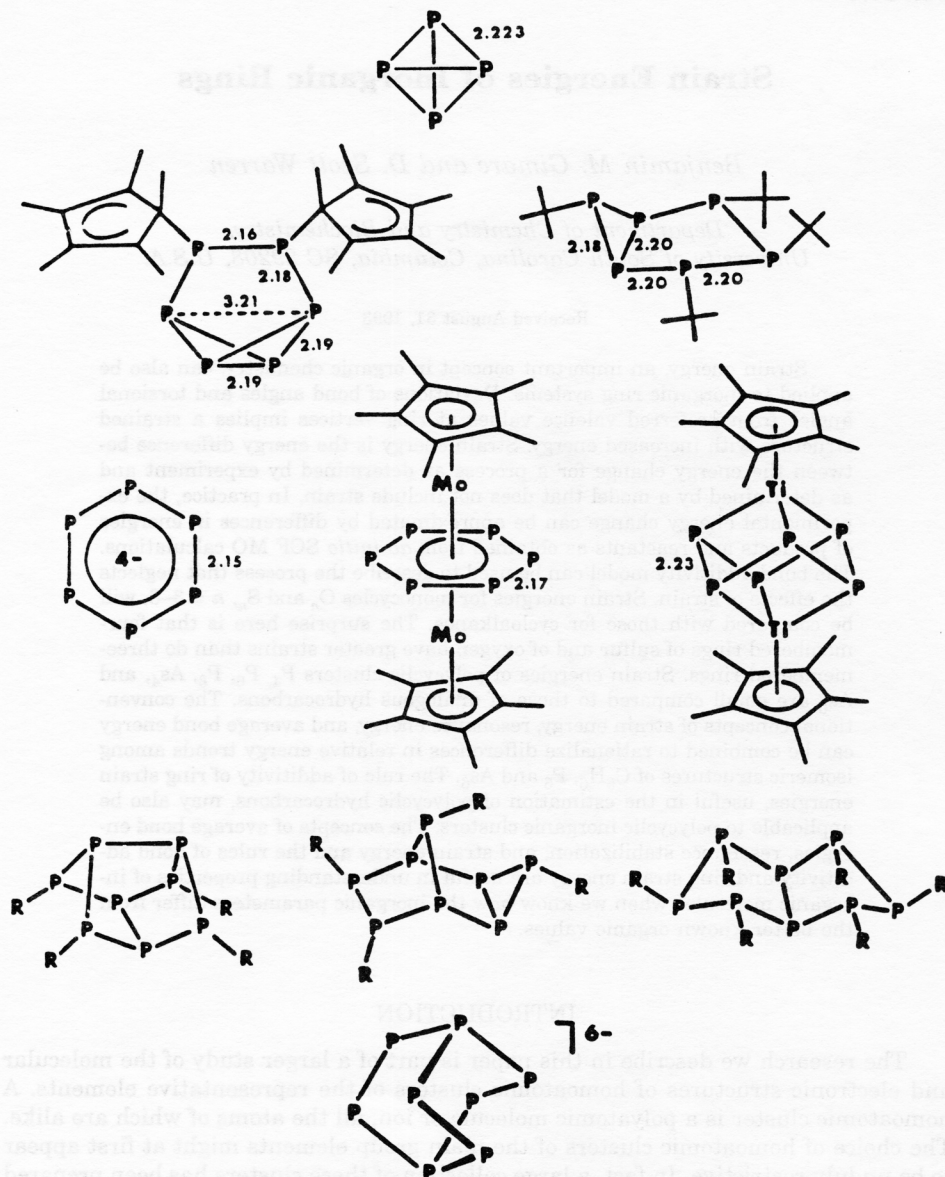
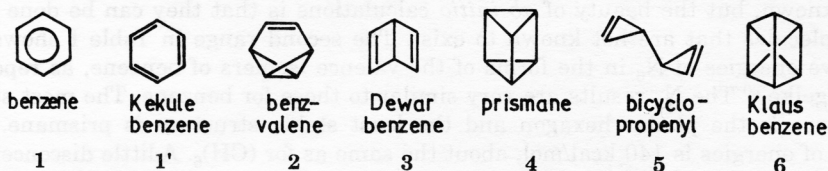


Figure 1. Known 4-, 6-, and 8-atom clusters of phosphorus showing experimentally determined bond distances in Å.

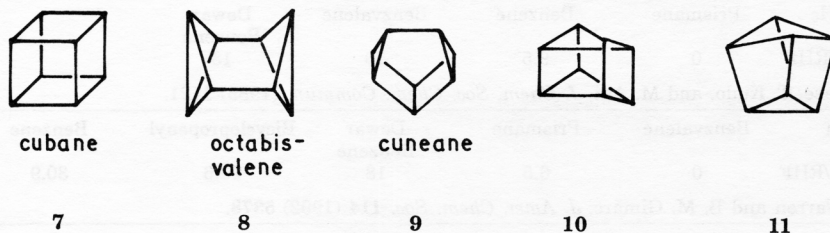
these. The cluster with two cyclopentadienyl substituents can be described as being formally  $P_6^{2-}$ .<sup>2</sup> The one with four *t*-butyl substituents is  $P_6^{4-}$ .<sup>3</sup> The planar hexagonal cluster  $P_6^{4-}$  is known to exist both as isolated units in crystals<sup>4</sup> and as the middle deck of a triple-deck transition metal complex.<sup>5</sup> The Ti complexed  $P_6$  cluster is formally regarded as  $P_6^{6-}$ .<sup>6</sup> Missing from Figure 1 is the unknown naked, neutral cluster  $P_6$ . Also featured in Figure 1 are some  $P_8$  clusters that can be classified as  $P_8^{4-}$ ,<sup>7</sup> and  $P_8^{6-}$ .<sup>8,9</sup> Again, the naked neutral  $P_8$  cluster is unknown.

Even though it has not yet been prepared, we chose to start our study of hexatomic phosphorus clusters with neutral  $P_6$ . One motivation is that  $P_6$  is valence isoelectronic with benzene,  $C_6H_6$ . We argued that the isomeric structures of  $C_6H_6$  should give suggestions of possible structures for  $P_6$ . At the blackboard one afternoon, we tried to draw the isomers of benzene and in about an hour we had written down more than 30 isomeric structures, far too many for us to study with *ab initio* calculations as we had planned. (Much later, we learned that  $C_6H_6$  has 217 possible isomeric structures that satisfy the normal valence rules for carbon and hydrogen.<sup>10</sup>) But we had an inspiration: P should be like CH. Why not study only those structures in which six CH units are connected to each other by single and double bonds? Balaban has enumerated these and found that there are only six such structures, 1–6,



often called the valence isomers of benzene.<sup>11</sup> The problem is even simpler because one of the structures, 6, although it satisfies the valence rules, has a chemically unrealizable structure, so we can ignore it. For pedagogical reasons, we mention Kekulé benzene (1',  $D_{3h}$ ) as well as planar, regular hexagonal benzene (1,  $D_{6h}$ ). The five remaining isomers 1–5 have all been synthesized and characterized. The history of preparation of the five isomers of  $(CH)_6$  follows their relative stabilities. Planar hexagonal benzene has been known since the early 19th century. Benzvalene and Dewar benzene were made in the 1960's.<sup>12,13</sup> Triangular prismane was prepared in 1973.<sup>14</sup> The least stable of the isomers, bicyclopropenyl, was not synthesized until 1989.<sup>15</sup>

Balaban<sup>11</sup> has also shown that there are 20 isomers of  $(CH)_8$  which is valence isoelectronic with  $P_8$ .  $P_8$  structures are barely within the capacity of the computational facilities currently available to us. With the need to limit the structures we would study, we chose to start with the five structures 7–11 that are connected by



single bonds only. Two of these, **10** and **11**, do not appear to be chemically realizable structures, although they satisfy the normal connectivity rules for carbon. Hydrocarbons (CH)<sub>8</sub> corresponding to **7**, **8**, and **9** have all been prepared.<sup>16-18</sup> Therefore, we carried out *ab initio* calculations for P<sub>8</sub> in the forms **7**, **8**, and **9**.

### RELATIVE ENERGIES OF ISOMERS

Schulman and Disch<sup>19</sup> had already reported *ab initio* SCF MO calculations for (CH)<sub>6</sub> in the five valence isomeric forms **1-5** with geometry optimization and employing a split valence shell basis set that included polarization functions. These results, as relative energies in kcal/mol, are displayed in the top range of Table I. Our chemical education has prepared us to understand at a glance the order of these energies. Benzene itself is the most stable isomer because it has a system of six π electrons that are delocalized around the ring to give this structure resonance stabilization. The other structures contain small rings in which bond angles are severely distorted from preferred valence angles so these structures are destabilized by strain. The situation is particularly unfavorable for prismane and bicyclopropenyl. The range of relative energies spans 130 kcal/mol. Isoelectronic with (CH)<sub>6</sub> is N<sub>6</sub>. Of course, N<sub>6</sub> is unknown, but the beauty of *ab initio* calculations is that they can be done even for molecules that are not known to exist. The second range in Table I shows the relative energies of N<sub>6</sub> in the forms of the valence isomers of benzene, as reported by Engelke.<sup>20</sup> The N<sub>6</sub> results are very similar to those for benzene. The most stable structure is the planar hexagon and the least stable structure is prismane. The range of energies is 140 kcal/mol, about the same as for (CH)<sub>6</sub>. A little disconcerting is the result that the bicyclopropenyl isomer, the highest in energy for (CH)<sub>6</sub>, is only about 40 kcal/mol above planar hexagonal N<sub>6</sub>. This ordering can be rationalized from bond energy arguments. For C-C bonds, bond energy does not increase as rapidly

TABLE I  
*Relative Energies of Valence Isomers of Benzene (kcal/mol)*

C <sub>6</sub> H <sub>6</sub>	Benzene	Benzvalene	Dewar Benzene	Prismane	Bicyclopropenyl
6-31G*/RHF	0	83	86	125	131
J. M. Schulman and R. L. Disch, <i>J. Amer. Chem. Soc.</i> <b>107</b> (1985) 5059.					
N <sub>6</sub>	Benzene	Bicyclopropenyl	Dewar Benzene	Benzvalene	Prismane
4-31G*/RHF	0	43	46	60	139
E. Engelke, <i>J. Phys. Chem.</i> <b>93</b> (1989) 5722.					
Si <sub>6</sub> H <sub>6</sub>	Prismane	Benzene	Benzvalene	Dewar Benzene	
6-31G/RHF	0	9.5	10	13	
S. Nagase, T. Kudo, and M. Aki, <i>J. Chem. Soc. Chem. Commun.</i> (1985) 1121.					
P <sub>6</sub>	Benzvalene	Prismane	Dewar Benzene	Bicyclopropenyl	Benzene
6031G*/RHF	0	6.5	18	20.6	30.9
D. S. Warren and B. M. Gimarc, <i>J. Amer. Chem. Soc.</i> <b>114</b> (1992) 5378.					

as bond order. The C=C double bond energy (146 kcal/mol) is less than twice the energy of the C-C single bond (83 kcal/mol). But for nitrogen, the situation is reversed. The N=N double bond energy (100 kcal/mol) is about 2 1/2 times the energy of the N-N single bond (39 kcal/mol). This gives an extra advantage to the two  $N_6$  structures, bicyclopropenyl and Dewar benzene, that contain two N=N double bonds.

Relative energies for  $(SiH)_6$ , calculated by Nagase, Kudo and Aoki<sup>21</sup> and occupying the third range in Table I, are strikingly different from those for  $(CH)_6$  and  $N_6$ . The planar hexagon is no longer the most stable isomer. The prismane structure has a lower energy. Although the bicyclopropenyl structure was not included in these calculations, the energy spread of the four structures studied is only 13 kcal/mol, an order of magnitude smaller than that for  $(CH)_6$ . Finally, the bottom range of Table I shows our relative energies for the  $P_6$  valence isomers.<sup>22</sup> Benzvalene and prismane have low energies. The planar hexagon has the highest. The spread of energies is small, about 30 kcal/mol. Clearly, concepts of chemical valency developed to explain properties of the molecules containing C, N, and O do not seem to apply in the lower rows of the periodic table.

Our calculated relative energies for the three structures we considered for  $P_8$  were: cuneane (**9**, 0), octabisvalene (**8**, 18.8 kcal/mol), and cubane (**7**, 30.8 kcal/mol).<sup>23</sup> This matches the order obtained by Jones and Hohl who performed density functional calculations for  $P_8$  isomers.<sup>24</sup> Indeed, it is same order and range of relative energies for the  $(CH)_8$  isomers predicted by Eaton and coworkers in 1970<sup>18</sup> and supported more recently by MM2 calculations for the hydrocarbon isomers.<sup>17</sup>

A word about our calculations is in order. We used the 6-31G\* basis set for phosphorus (and 6-31G\*\* for hydrogens; see below) and the GAUSSIAN program package to carry out SCF MO calculations at the RHF level.<sup>25</sup> The basis set describes a split valence shell and the first asterisk indicates that a set of d-type polarization functions were included on phosphorus. It is well known that polarization functions are essential in order to obtain correct structural details. The second asterisk means that p-type polarization functions were included for hydrogen atoms. We calculated vibrational frequencies for  $P_4$  and  $P_6$  structures to assure that these structures are real minima on the energy surfaces at the RHF level. Vibrational frequency calculations for the  $P_8$  isomers were beyond the capacity of our computers. Others have shown that when corrections are made to account for part of the effects of electron correlation, total calculated energies change greatly and these changes may even result in the rearrangement of the order of relative energies. Although we were unable to include such corrections in this work, the processes we have adopted in the following section for the calculation of strain energies are expected to be most favorable for the cancellation of correlation and basis set errors.

Among the results of geometry optimized *ab initio* calculations are bond distances. These distances for  $P_4$ ,  $P_6$ , and  $P_8$ , shown in Figure 2, are exactly what one would expect for analogs of the hydrocarbon structures. Any bond which in the hydrocarbon analog would be a single bond turns out to have a P-P distance of around 2.2 Å while those where we would expect a double bond have P=P distances in the neighborhood of 2.0 Å. These values agree well with a survey of experimental P-P single and P=P double bonds.<sup>26</sup> The benzene structure turns out to have a PP distance of 2.09 Å, between single and double bond distances but a little closer to that of a double bond, just as it is in  $(CH)_6$  itself.

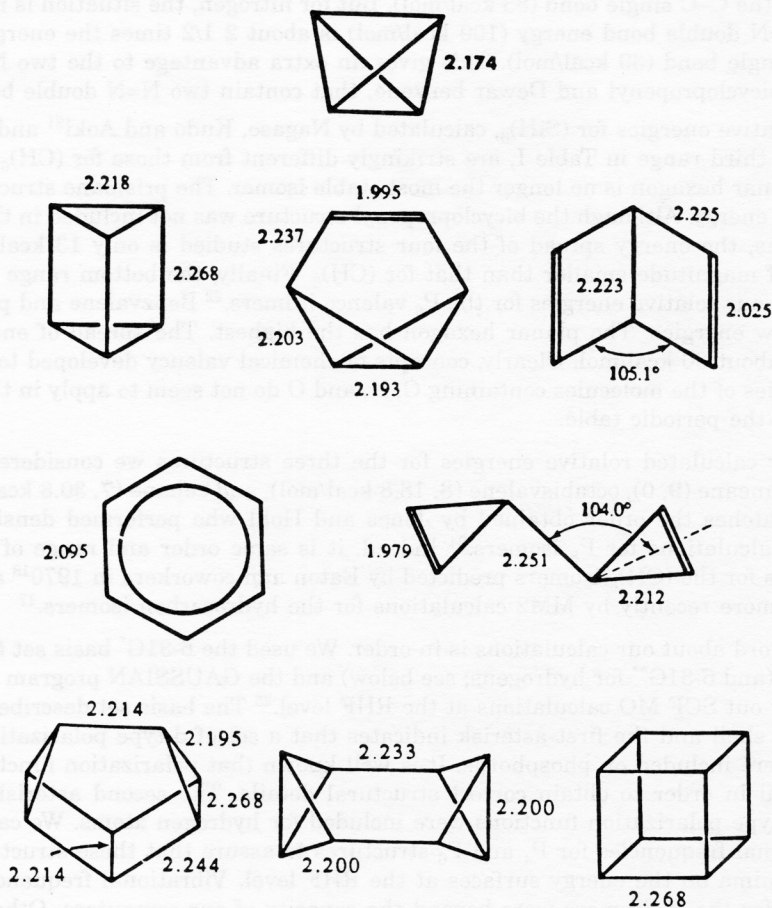
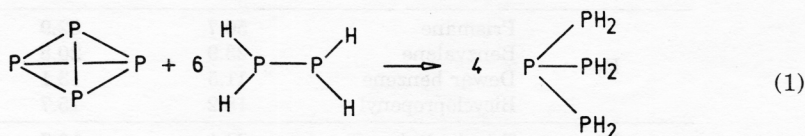


Figure 2. *Ab initio* calculated bond distances (Å) for valence isomeric forms of P<sub>4</sub>, P<sub>6</sub>, and P<sub>8</sub> at the 6-31G\*/RHF level.

### STRAIN ENERGIES

We decided to try to interpret the relative stabilities of phosphorus clusters in terms of strain energies calculated for the various structures. Qualitatively, strain energy is a destabilization caused by the distortion of bond angles from preferred values. Quantitatively, we can relate strain energy to the energy change for a reaction or process that opens a cyclic structure into an acyclic structure. More specifically, strain energy is the energy change as determined by experiment compared to the change as obtained from a model that does not include strain. For our work, we took differences between *ab initio* calculated total energies of products and reactants

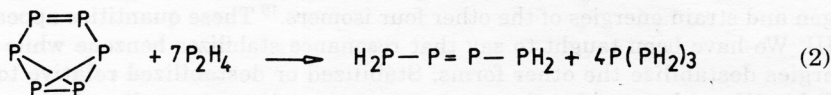
to approximate the experimental energy change of the strain relieving reaction. As the model that does not include strain, we used the bond additivity model from which one can calculate energy changes of reactions from differences of average energies of bonds broken and formed in the reaction. Eq. (1), involving tetrahedral  $P_4$ , serves as an example. Asked to calculate the energy change for this reaction using the bond additivity



model, our freshman chemistry students would give us the answer zero, because the numbers of bonds of different types are the same for reactants and products. The reaction also preserves the valence environment around each atom. Each of the four P atoms in  $P_4$  is bonded to three other P atoms. These appear in the product as the central P in the four  $P(\text{PH}_2)_3$  molecules. In the reactants  $6P_2H_4$  there are  $6 \times 2 = 12$  P atoms, each of which is connected to two hydrogens and one other phosphorus. These end up as  $4 \times 3 = 12$   $-\text{PH}_2$  groups in the product. Reactions such as Eq. (1) that conserve both bond types and valence environment around each atom are called *homodesmotic reactions*<sup>27</sup> and they are known to allow for cancellation of some of the errors of electron correlation and basis set if energy differences are taken among *ab initio* energies of reactants and products.

From the bond additivity model we expect the energy change for Eq. (1) to be zero. But from our chemical experience, we recognize that the tetrahedral  $P_4$  structure is strained and release of strain energy should make Eq. (1) exothermic. Therefore, we take the absolute value of the energy change for Eq. (1) as the strain energy of  $P_4$ . Using *ab initio* calculated geometry optimized total energies for  $P_4$ ,  $P_2H_4$ , and  $P(\text{PH}_2)_3$ , we get 20 to 25 kcal/mol, depending on basis set used, as the strain energy of  $P_4$ . These values fall at the low end of the  $P_4$  strain energy estimates based on thermochemical data and average bond energies.<sup>26</sup> In all candor, the uncertainties associated with the thermochemical data are large.

Homodesmotic reactions analogous to Eq. (1) can be devised to yield strain energies of  $P_6$  and  $P_8$  structures. Eq. (2) is an example of a reaction involving a  $P_6$  valence isomer that contains a double bond. The product  $H_2PP=PPH_2$  is introduced to receive the  $P=P$  double bond



of benzvalene, thereby conserving bond types and preserving atomic valence environments.

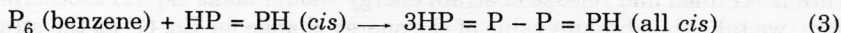
Table II contains strain energies of tetrahedral  $P_4$ , four of the five valence isomers of  $P_6$  (we postpone the benzene isomer for a bit), and the three single-bond connected valence isomers of  $P_8$ .<sup>22,23</sup> The strain energy of tetrahedral  $P_4$ , 20 to 25 kcal/mol, is small compared to that estimated by similar procedures for the isoelec-

TABLE II  
Strain energies (kcal/mol) of phosphorus clusters

	Structure	4-31G*	6-31G*
P <sub>8</sub>	Cubane	64.1	75.8
	Octabisvalene	71.0	63.8
	Cuneane	54.3	45.0
P <sub>6</sub>	Prismane	50.7	52.9
	Benzvalene	23.9	20.8
	Dewar benzene	11.5	13.1
	Bicyclopropenyl	18.2	15.7
P <sub>4</sub>	Tetrahedral	24.1	19.7

tronic hydrocarbon analog, tetrahydrane, 129–141 kcal/mol.<sup>28,29</sup> Tetrahydrane, (CH)<sub>4</sub> has yet to be synthetically realized. Among P<sub>6</sub> isomers prismane has the largest strain energy, 50–55 kcal/mol, but this value is considerably less than estimated for (CH)<sub>6</sub> prismane which range from 108 to 145 to 149 kcal/mol.<sup>19,29,30</sup> Among the three P<sub>8</sub> isomers, cubane has the largest strain energy, 65–75 kcal/mol, again, small compared to (CH)<sub>8</sub> cubane, 166 kcal/mol.<sup>17</sup> The lesson here is that strain energies in phosphorus clusters are very small compared to those of analogous hydrocarbon clusters.

The planar hexagon or benzene form of P<sub>6</sub> can be expected to be stabilized by resonance. Nagase and Ito interpreted the energy change for Eq. (3) as the resonance energy of P<sub>6</sub> benzene.<sup>31</sup>








From geometry optimized total energies with the 6-31G\* basis set, similar to our work, they obtained 14.9 kcal/mol for the resonance energy of P<sub>6</sub> benzene. This is a small value compared to 24.7 kcal/mol calculated by Hess and Schaad<sup>32</sup> as the resonance energy of (CH)<sub>6</sub> benzene, but both of these quantities are modest compared to strain energies. We adopt these values for use in subsequent arguments, but there are other ways to estimate resonance energies and we reserve the right to reexamine the proper evaluation of resonance as part of future work on this problem.

Schulman and Disch reported *ab initio* calculated relative energies of the valence isomers of (CH)<sub>6</sub> benzene along with the resonance energy of the planar hexagon and strain energies of the other four isomers.<sup>19</sup> These quantities appear in Table III. We have been taught to say that resonance stabilizes benzene while strain energies destabilize the other forms. Stabilized or destabilized relative to what? In Table III, we have added the resonance energy of benzene to its relative energy and subtracted strain energies of the other isomers from their relative energies. The isomer with the lowest adjusted energy is now prismane, at –31.4 kcal/mol. We renormalized all the adjusted relative energies by adding 31.4 kcal/mol to all of them, giving prismane zero energy. We call these values hypothetical unstrained nonresonance stabilized energies. Notice that benzvalene is about 25 kcal/mol above prismane. Dewar benzene and bicyclopropane are higher still by another 25 kcal/mol. Benzene is even higher. This order of stabilities can be explained by the



TABLE III

*C<sub>6</sub>H<sub>6</sub> isomers – Hypothetical unstrained nonresonance stabilized energies (kcal/mol)*

Structure					
	1	2	3	4	5
$C_6H_6$					
Relative energy (A)	0	74.8	81.0	117.5	126.4
Strain energy (+) or resonance energy (-) (B)	-24.7	+81.3	+63.6	+148.9	+107.2
Unstrained or non-resonance stabilized (A-B)	+24.7	-6.5	+17.4	-31.4	+19.2
Renormalized (A-B+31.4)	56.1	24.9	48.8	0	50.6

bond additivity model. Prismane, with all single bonds is the most stable. In benzvalene, a C=C double bond has replaced two C-C single bonds. For carbon, it is known that the energy of two single bonds is about 24 kcal/mol greater than that of a double bond:






$$2 D(C-C) - D(C=C) = 2 \times 85 - 146 = 24 \text{ kcal/mol}$$

Dewar benzene and bicyclopropenyl both have two double bonds so we expect their relative energies to be higher by another 24 kcal/mol, again almost exactly what we find. If benzene had three double bonds, we would expect it to be higher by yet another 24 kcal/mol. But the quantitative analogy breaks down; the benzene energy was not calculated for a structure of alternating single and double bonds like Kekule benzene (1'). The benzene nonresonance-stabilized energy is the highest of the five structures.

Table IV makes the same adjustments among relative energies of  $P_6$  isomers and the resulting order of hypothetical unstrained, nonresonance stabilized relative energies turns out to be exactly the same as that for  $(CH)_6$ . If the energy difference

TABLE IV

*P<sub>6</sub> isomers – Hypothetical unstrained nonresonance stabilized energies (kcal/mol)*

Structure					
	1	2	3	4	5
$P_6$					
Relative energy (A)	30.9	0	18.0	6.5	20.6
Strain energy (+) or resonance energy (-) (B)	-14.9	+23.5	+15.0	+56.4	+17.6
Unstrained or non-resonance stabilized (A-B)	+45.8	-23.5	+3.0	-49.9	+3.0
Renormalized (A-B+49.9)	95.7	26.4	52.9	0	52.9

(26 kcal/mol) between structures with different numbers of double bonds is the energy difference between two P-P single bonds and a P=P double bond, then:

$$2 D(\text{P-P}) - D(\text{P=P}) = 26 \text{ kcal/mol};$$

$$2 D(\text{P-P}) - 26 = 2 \times 55 - 26 = 84 \text{ kcal/mol} = D(\text{P=P})$$

Assuming an average value of  $D(\text{P-P}) = 55$  kcal/mole, then the average bond energy of the P=P double bond is 84 kcal/mol. P=P double bonds are known, but no thermochemical data is available to suggest the size of the average P=P energy.

Figure 3 sums up our model. In the center of the diagram are the relative energies of the  $(\text{CH})_6$  and  $\text{P}_6$  valence isomers as based on the bond additivity model. To the left, we see that benzene is indeed stabilized by resonance energy, but the very large strain energies of the other isomers drive their true energies far above that of benzene and spread out the isomer energies across 130 kcal/mol. On the right side of Figure 3, we see that  $\text{P}_6$  benzene is also stabilized by resonance, albeit more modestly than for the hydrocarbon analog. Strain energies of the other  $\text{P}_6$  isomers drive them up toward benzene, but the smaller values compress the true relative energies within a range of 30 kcal/mol.

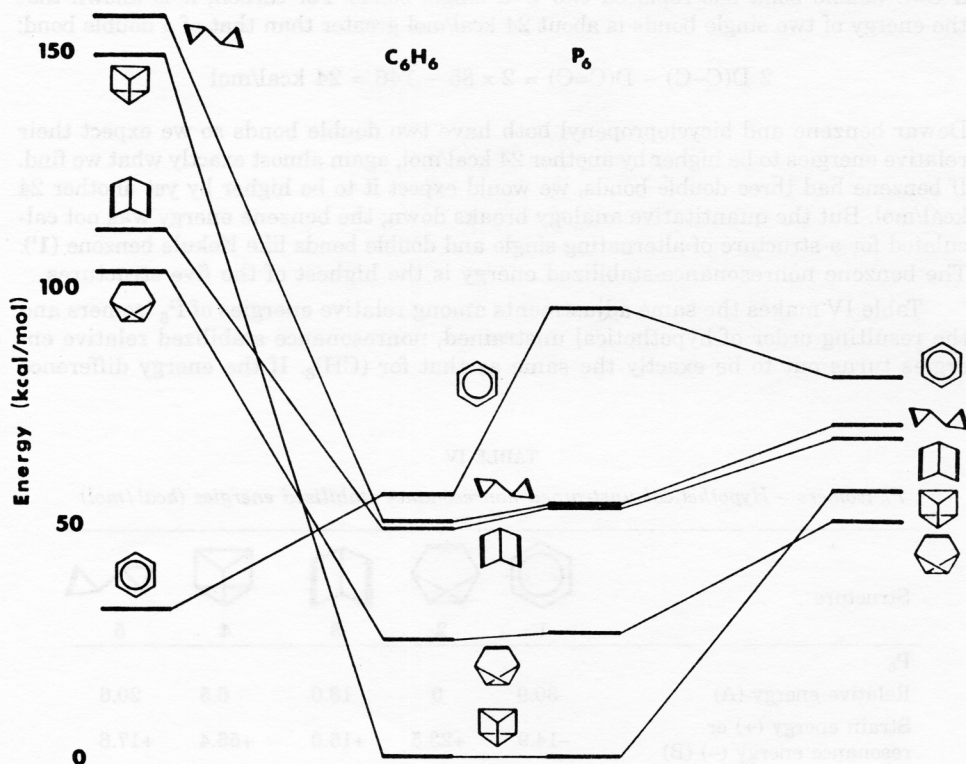


Figure 3. Comparisons of hypothetical unstrained non-resonance stabilized energies and *ab initio* relative energies of  $(\text{CH})_6$  and  $\text{P}_6$  valence isomers.

TABLE V  
Strain energies of arsenic clusters

Structure	Strain Energy (kcal/mol; 752 + P)	
As <sub>6</sub>	Prismane	32.7
	Benzvalene	12.4
	Bicyclopropenyl	7.4
	Dewar Benzene	2.2
As <sub>4</sub>	Tetrahedron	12.6

Recently, we have carried out *ab initio* calculations for tetrahedral As<sub>4</sub> and for As<sub>6</sub> in the forms of the five valence isomers of benzene<sup>33</sup> using the 752 + p basis set of Scuseria.<sup>34</sup> Strain energies of these As clusters, which appear in Table V, are even smaller than those for P<sub>4</sub> and P<sub>6</sub>. Compare the value of 12.6 kcal/mol for As<sub>4</sub> with 19.7 kcal/mol for P<sub>4</sub> and 32.7 kcal/mol for As<sub>6</sub> prismane with 52.9 kcal/mol for P<sub>6</sub> prismane. Adjusting relative energies of the As<sub>6</sub> valence isomers with resonance energies and strain energies as we did for (CH)<sub>6</sub> and P<sub>6</sub> in Tables III and IV, we found the hypothetical nonresonance stabilized unstrained energies of As<sub>6</sub> isomers to follow the same pattern dictated by the bond additivity model as did those for (CH)<sub>6</sub> and P<sub>6</sub>. Energy differences between isomers with different numbers of double bonds give an estimate of the average As=As double bond of 60 kcal/mol, assuming the energy of an average As-As single bond as 43 kcal/mol. As=As double bonds are known, but, as with the case of the P=P bond, no values based on thermochemical data are available.

The benzene and prismane structures each have six equivalent vertices, but the lower symmetry of benzvalene **2**, Dewar benzene **3**, and bicyclopropenyl **5** allows each of these structures to have two or more sets of non-equivalent vertices which may then be expected to have different electron densities. Figure 4 shows *ab initio* calculated Mulliken net atom populations for phosphorus and arsenic structures. In

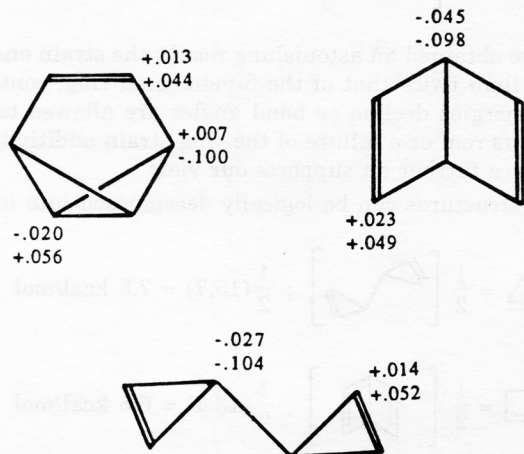


Figure 4. Comparisons of calculated charge densities in P<sub>6</sub> and As<sub>6</sub> isomers. In each stack, the result for As<sub>6</sub> is on top, that for P<sub>6</sub> is on bottom.

the pair of values by each vertex, the arsenic result is on top, phosphorus on bottom. Notice that the arsenic charge densities tend to be smaller than those of phosphorus. One could say there is less localization of charge on arsenic or that the arsenic charges are more diffuse.

As we go from carbon to phosphorus to arsenic, we see weaker bonds and smaller strain energies. These trends are in accord with our expectation of more diffuse valence atomic orbitals as we increase the principal quantum number  $n$  from 2 to 3 to 4. The more diffuse orbitals with higher quantum number also explains the less localized charge densities on arsenic, compared to phosphorus in Figure 4.

### ADDITIVITY OF RING STRAIN ENERGIES

The ring strain additivity rule has been useful in hydrocarbon chemistry.<sup>30,35-38</sup> The rule states that the strain energy of a polycyclic system is approximately the sum of strain energies of the individual component rings. We can attempt to use this rule for our phosphorus clusters by applying it in reverse.<sup>23</sup> Tetrahedral  $P_4$  has four triangular faces. Therefore, the strain energy of a 3-membered phosphorus ring must be  $1/4$  that of  $P_4$  itself:

$$\triangle = \frac{1}{4} \left[ \text{tetrahedron} \right] ; \frac{1}{4} (19.7) = 4.9 \text{ kcal/mol}$$

The cube has six square faces, so the strain energy of a 4-membered phosphorus ring must be  $1/6$  that of  $P_8$  cubane:

$$\square = \frac{1}{6} \left[ \text{cube} \right] ; \frac{1}{6} (75.8) = 12.6 \text{ kcal/mol}$$

Already, we have obtained an astonishing result: the strain energy of the 4-membered ring is more than twice that of the 3-membered ring, contrary to our expectation that strain energies decline as bond angles are allowed to approach normal valence angles. Is this real or a failure of the ring strain additivity rule? We believe it is real and evidence further on supports our view.

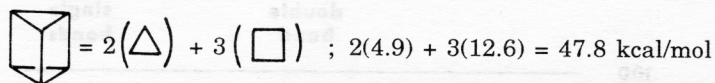
Other isomeric structures can be logically decomposed into individual rings:

$$\triangle = \frac{1}{2} \left[ \text{cyclohexane} \right] ; \frac{1}{2} (15.7) = 7.8 \text{ kcal/mol}$$

$$\square = \frac{1}{2} \left[ \text{cyclohexane} \right] ; \frac{1}{2} (13.1) = 6.5 \text{ kcal/mol}$$

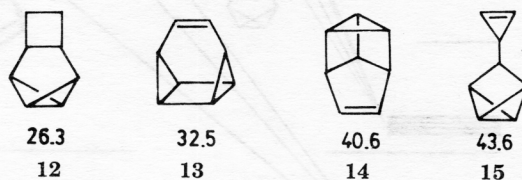
Applying the rule to other structures allows us to compile strain energies of a series of small phosphorus monocycles.

We can test the effectiveness of the strain additivity rule for phosphorus in at least one instance. The strain energy of prismane must be the sum of two triangles and three squares:



Within the accuracy of the rule, this value compares favorably with the 52.9 kcal/mol result we obtained by direct calculation (Table II).

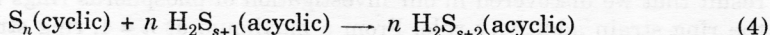
We can use the rule of strain energy additivity to estimate the energies of other  $P_8$  isomers. Structures **12–15** are valence isomers of  $(CH)_8$  that contain one double bond.<sup>11</sup> At the level of the bond additivity rule, the one-double bond structures **12–15** should be 26 kcal/mol higher in energy than the all-single bond structures **7–9**. The structures below include strain energies (kcal/mol) estimated by combining strain energies of the small component rings.



At the level of the bond additivity model the energies of the one-double-bond isomers **12–15** are 26 kcal/mol above those of the all-single-bond isomers **7–9**. Figure 5 shows how these energies are modified when strain energies are added. The strain energies of **12–15** are actually rather small compared to those of **7–9** and therefore the energy of **12** turns out to be only a few kcal/mol higher than that of **7**, a difference that is small compared to inherent limitations of the additivity rule. The direct evaluation of strain energies of other  $P_8$  isomers and more complete evaluation of the ring strain additivity rule are objects of future research.

### RING STRAIN IN SULFUR RINGS

We came to the realization that neither we nor anyone else knew anything about ring strain in inorganic molecules, a particularly glaring deficiency considering what an important concept ring strain is in organic chemistry. In order to study ring strain in simpler systems, we chose to do a systematic investigation of small sulfur rings, some of which are known experimentally.<sup>39–47</sup> Following the work of Zhao and Gimarc<sup>48</sup> on small oxygen rings, we did *ab initio* calculations for products and reactants of Eq. (4) which releases strain in sulfur rings.<sup>49</sup>



The parameter  $s$  changes the properties of the reaction significantly. If  $s = -1$ , the number of bonds, but not bond types, is conserved and the reaction is said to be *isogyric*.<sup>50</sup> If  $s = 0$ , bond types are conserved and the reaction is *isodesmic*.<sup>51</sup> If  $s = +1$ , both bond types and atomic valence environment are conserved and the reaction is *homodesmotic*.<sup>27</sup> For  $s = +2$  bond types and valence environment are conserved and

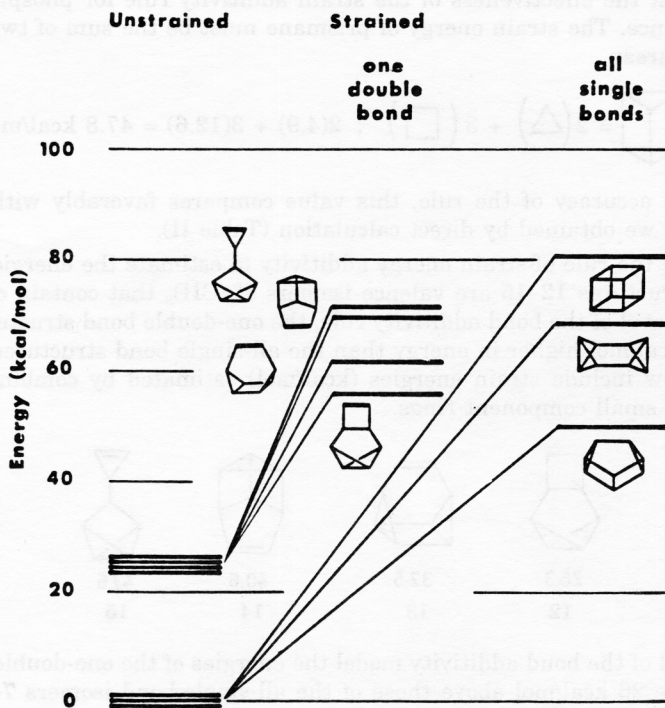


Figure 5. Comparisons of hypothetical or bond additivity ordered energies of isomeric forms of  $(\text{CH})_6$  and  $\text{P}_6$  (center) with unstrained or resonance stabilized structures (edges).

the longer  $\text{HS}_m\text{H}$  chains of reactant and product provide a better approximation of the conformation of a chain related to the  $\text{S}_n$  ring and the reaction is *hyperhomo-**modesmotic*.<sup>32,52</sup> And so on for larger  $s$ . Dixon and Wasserman<sup>53</sup> reported calculations for  $\text{S}_n$ ,  $\text{S}_n = 4-8$  using the valence double  $\zeta$  basis set of McLean and Chandler<sup>54</sup> augmented by a set of d-type polarization functions. We used the same basis set to do calculations for  $\text{S}_3$  and  $\text{HS}_m\text{H}$  chains. Combining results to calculate energy changes for Eq. (4) we obtained strain energies for sulfur rings shown as curve (a) in Figure 6. These results are for frozen-core MP2 calculations for  $s = 2$ . We found that using Eq. (4), strain energies of individual rings approached the same values for  $s \geq 2$  at both RHF and MP2 levels. Notice the maximum ring strain at  $n=4$ , the surprising result that we discovered in our investigation of phosphorus rings by application of the ring strain additivity rule. From a maximum at  $n = 4$ , ring strain energies decline with larger  $n$ , reaching a plateau at  $n = 6$  and  $7$  and a minimum at  $n = 8$ . Similar calculations for  $\text{O}_n$  rings lead to comparable results. This behavior is different from that exhibited by aliphatic hydrocarbon rings  $(\text{CH}_2)_n$ , curve (b), Figure 6, which shows strain energies declining from a maximum of  $n = 3$  to a minimum  $n = 6$ , beyond which they rise again.<sup>30</sup> One aspect of these results is disturbing. The  $\text{S}_4$  strain energy (45 kcal/mol) is larger than the strain energy of any aliphatic hydrocarbon

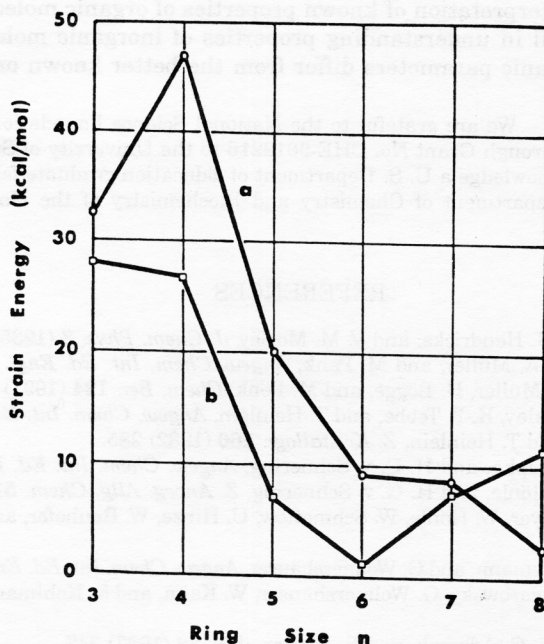


Figure 5. Comparisons of hypothetical or bond additivity ordered energies of isomeric forms of  $(\text{CH})_6$  and  $\text{P}_6$  (center) with unstrained or resonance stabilized structures (edges).

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The concepts of average bond energies, resonance stabilization, and strain energy and the rules of bond additivity and ring strain energy have long been used to give a qualitative interpretation of known properties of organic molecules. They also turn out to be useful in understanding properties of inorganic molecules when we know how the inorganic parameters differ from the better known organic values.

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## SAŽETAK

### Energija napetosti anorganskih prstenova

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Pojam energije napetosti može se primijeniti i u anorganskoj kemiji. Odstupanja kutova među vezama i torzijskih kutova od preferiranih valentnih vrijednosti na vrhovima prstena do- vodi do napregnute strukture s uvećanom energijom. Energija napetosti jest razlika između energijske promjene za proces određene eksperimentom i one koja slijedi iz modela koji ne sadržava napetost. U praksi se eksperimentalne energijske napetosti aproksimiraju razlikama *ab initio* SCF MO energija produkata i reaktanata. Model aditivnosti po vezama može se primijeniti za opis procesa u kojemu su zanemareni učinci napetosti. Energije napetosti prstenova  $O_n$  i  $S_n$ ,  $3 \leq n \leq 8$ , uspoređene su s onima za cikloalkane. Iznenađuje nalaz da četveročlani prsteni smpora i kisika imaju veću napetost od odgovarajućih tročlanih prstenova. Energije napetosti u policikličkim klusterima  $P_4$ ,  $P_6$ ,  $P_8$ ,  $As_4$  i  $As_6$  malene su u usporedbi s analognim ugljikovodicima. Kombinacijom uobičajenih predodžbi o energiji napetosti, o rezonancijskoj energiji i o prosječnoj energiji veze mogu se racionalizirati trendovi u rezlikama relativnih energija među izomerima spojeva  $C_6H_6$ ,  $P_6$  i  $As_6$ . Pravilo aditivnosti eneergija napetosti prstena, koje je korisno pri procjenama policikličkih ugljikovodika, može se primijeniti i na policikličke anorganske klustere. Sve ove, u organskoj kemiji uobičajene predodžbe korisne su i u razumijevanju svojstava anorganskih molekula, ako znamo kako se parametri za anorganske rezlikuju od bol- je poznatih vrijednosti za organske molekule.