

Valence Isomers of Benzene and Their Relationship to Isomers of Isoelectronic P₆

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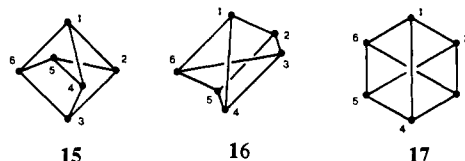
Abstract: We report the results of geometry optimized ab initio SCF MO calculations with 3-21G, 4-31G*, and 6-31G* basis sets for neutral P₆ in forms corresponding to the five valence isomers of benzene, (CH)₆, with which P₆ is valence isoelectronic. At the 6-31G* level benzene, Dewar benzene, benzvalene, prismane, and bicyclopropenyl structures all correspond to real minima on the P₆ energy surface. The order of energies of P₆ structures is quite different from that for the (CH)₆ isomers. For P₆, benzvalene and prismane have low energies and the planar hexagon has the highest. Bond distances are easily classified as single, double, or aromatic. The energy of 2P₆ lies only 30–35 kcal/mol above that of 3P₄ and 60–100 kcal/mol below 6P₂. Energies of the HOMO and the HOMO–LUMO gaps and values of Mulliken net atom populations appear to be normal for these P₆ structures. Calculated energy changes of homodesmotic reactions involving P₆ provide estimates of strain energies for the four nonhexagonal structures. These range from a high (50–55 kcal/mol) for prismane to a low (10–15 kcal/mol) for Dewar benzene. These values are remarkably low compared to strain energies for the same structures of (CH)₆. Using calculated strain energies and resonance energies, we obtain an estimate of 84 kcal/mol for the P=P double bond energy. This is less than twice the energy of an unstrained P–P single bond, 55 kcal/mol. Based on these results, we present a model of benzene isomeric structures ordered in energy by the number of single bonds they contain. Prismane, with nine single bonds, would have the lowest energy, and the Kekulé hexagon would be highest with only three single bonds. The order actually calculated for these structures already includes strain and resonance corrections. Large strain corrections for the (CH)₆ structures raise the energies of those structures, while the resonance energy of the hexagon lowers the energy of benzene. The result is a considerable rearrangement of the basic single bond energy order for (CH)₆. In contrast, the modest resonance energy of planar hexagonal P₆ and the small strain energies of the other structures only slightly perturb the expected bond energy ordering of structural stabilities.

Introduction

Interest in the structure of benzene and its isomers has a history that goes back over 125 years.^{1–4} Figure 1 shows a few of the structural isomers that share the molecular formula C₆H₆. It has been estimated that there are over 200 different possible structures that preserve six tetracoordinate carbon atoms and six hydrogens or other substituents. Benzene itself has long been known to be a planar regular hexagon (1), described as a resonance hybrid of two equivalent Kekulé structures (1'). Benzvalene (2) and Dewar benzene (3) were first prepared in the 1960's.^{5,6} Ladenburg benzene or triangular prismane (4) was synthesized in the 1970's.⁷ Bicyclopropenyl (5) was finally realized only 3 years ago.⁸ The synthetic history of these isomers implies something about their relative stabilities or energies. Structures 1–5 can be described by the formula (CH)₆, each carbon bearing a single hydrogen. Balaban⁹ calls these the *valence isomers*, structures which differ only by the ways in which carbon–carbon single and double bonds connect six CH units. As a counter-example fulvene (6) contains one carbon with no attached hydrogens and one carbon with two hydrogen substituents. According to Balaban's definition, fulvene is simply an isomer, not a valence isomer. This distinction has not been universally followed. All of the isomers 6–14 in Figure 1 have been prepared, some perhaps only in forms which carry stability-enhancing substituents rather than hydrogens.^{10–15}

Isomerization reactions that interconvert several of the structures 1–14 have been observed and rationalized using the principle of conservation of orbital symmetry.^{3,16}

Balaban has enumerated the possible valence isomers of (CH)₆ and found there to be a total of six.⁹ The sixth isomer is chemically unrealistic, but we mention it here because of its topological significance and historical interest. Balaban has called the sixth benzene valence isomer benzmöbiusstripane (15). Visualize it as carbons located at the six corners of an octahedron from which four edge bonds have been deleted and a body-diagonal bond added. Karl and Bauer¹⁷ have suggested a twisted prismane isomer (16) in which two parallel edges on opposite triangles of the prism have been switched to form diagonals across what was formerly a rectangular face of the prism. Numbering shows that 15 and 16 have the same connectivity as the form 17 proposed for benzene



by Claus in the 19th century. Claus benzene has carbons at the corners of a regular hexagon, each carbon connected to its nearest (ortho) neighbors on the perimeter of the hexagon and to the para carbon diametrically across the hexagon. The Claus structure 17 was used by Pauling¹⁸ as the basis for a pre-wave mechanics model of the electronic structure of benzene involving three para

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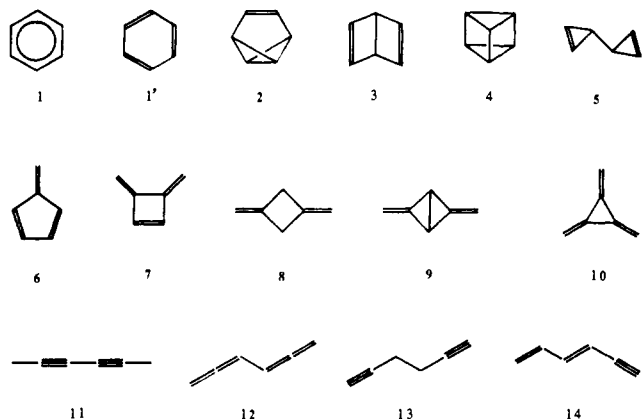
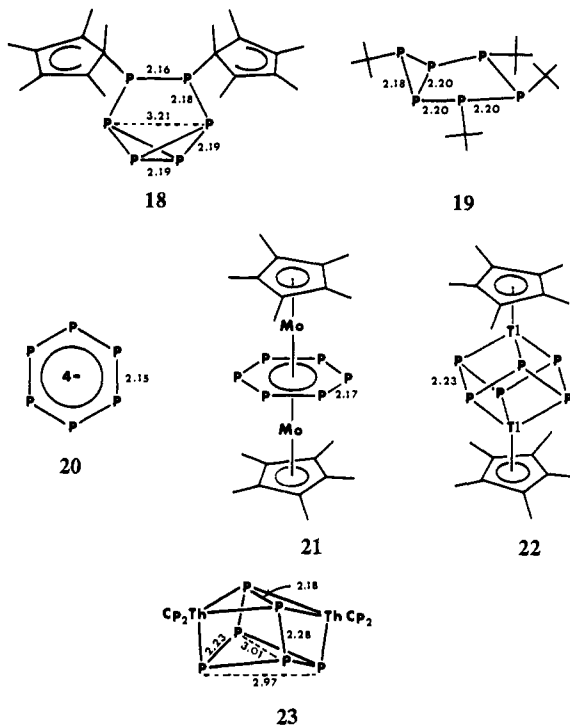


Figure 1. Some isomers of benzene. Structures 1-5 are the valence isomers (CH)₆.

cross-ring Bohr orbits, each describing the motions of an electron pair. The structures 15-17 contain nine C-C bonds, a characteristic of all C₆H₆ isomers.

Because benzene has been pivotal in the development of chemical valence theory, the isoelectronic and, one might have expected, isostructural analogues N₆, Si₆H₆, and P₆ are also of interest. Matrix isolation of N₆ has been claimed¹⁹ and a P₆⁺ peak has been recorded in the mass spectrum of red phosphorus²⁰ although this peak is the smallest of all P_n⁺ observed for n ≤ 10. Despite these observations it is fair to say that the nitrogen, silicon, and phosphorus analogues of benzene are, in fact, unknown.

Although isolated P₆ may be unknown, molecules containing P₆ units have been prepared and characterized by X-ray diffraction. The substituted R₂P₆ (18, R = C₅Me₅) has the structure



of benzvalene with an R group attached at each phosphorus atom of the basket handle or P₂ bridge connecting the wingtips of the P₄ butterfly.^{21,22} The R₄P₆ molecule (19, R = *tert*-butyl) is composed of fused and almost mutually perpendicular 3- and

Table I. Ab Initio Calculated Relative Energies of Isomeric Forms of C₆H₆, N₆, Si₆H₆, and P₆ (kcal/mol)

C ₆ H ₆ ^a	Benzene	Benzvalene	Dewar benzene	Prismane	Bicyclopropenyl
	1	2	3	4	5
Level of theory					
6-31G*/SCF	0	83	86	125	131
6-31G*/MP2	0	75	81	118	126
N ₆ ^b	Benzene	Bicyclopropenyl	Dewar benzene	Benzvalene	Prismane
Level of theory	1	5	3	2	4
4-31G*/SCF	0	43	46	60	139
4-31G*/MP2	0	34	34	41	120
Si ₆ H ₆ ^c	Prismane	Benzene	Benzvalene	Dewar benzene	
Level of theory	5	1	2	3	
3-21G/SCF	0	6.7	13	18	
6-31G/SCF	0	9.5	10	13	
P ₆ ^d	Benzvalene	Prismane	Dewar benzene	Benzene	
Level of theory	2	4	3	1	
Density functional ^d	0	4	3	34	
3-21G/SCF ^e		0	7.6	16	
6-31G*/SCF ^f		0	0.3	1.2	
6-31G(d)/SCF ^f		0	0	24	

^a Reference 32. ^b Reference 38. ^c Reference 40. ^d Reference 46. ^e Reference 43. ^f Reference 45.

5-membered rings bearing substituents.^{23,24} Planar hexagonal P₆⁴⁻ ions (20) exist in the crystals of K₄P₆, Rb₄P₆, and Cs₄P₆.²⁵⁻²⁷ A planar hexagonal P₆ unit also occurs in the middle level of a triple-decker metallocene (21).²⁸ A related structure shows a chair-form P₆ ring as a middle deck connecting two Cp*Ti groups (22).²⁹ In this structure the P₆ ring is said to carry a formal 6- charge. Recently, another P₆ cluster with a formal 4- charge has been prepared in a complex (23) with two Th(Cp)₂ entities.³⁰ This P₆ fragment has a structure related to that of benzvalene (2, 18) but lacking the bond that forms the edge joining the two wings of the benzvalene butterfly. In summary, although neutral P₆ has not been prepared directly from reactions starting with P₄, the many known complexes containing P₆ clusters suggest that isolated or naked P₆ might be formed by oxidation or reduction of P₆ cluster-containing complexes.

Even though structures of N₆, Si₆H₆, and P₆ are not presently available from experimental studies, it is possible to learn something about them by using theoretical methods that have proved to be highly reliable in other applications.³¹ Ab initio molecular orbital (MO) calculations have been reported for C₆H₆,³²⁻³⁷ N₆,^{38,39} Si₆H₆,⁴⁰⁻⁴² and P₆.⁴³⁻⁴⁶ In at least a few of the

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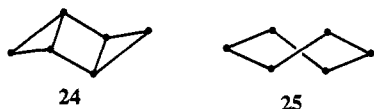
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structural forms represented in Figure 1. In this paper we review the relative energies of these structures, include the results of our own geometry optimized ab initio SCF MO calculations for P_6 in the structural forms of the five valence isomers of benzene, and relate all these results to concepts of aromaticity and strain energy.

Table I contains relative energies of isomeric forms of C_6H_6 , N_6 , Si_6H_6 , and P_6 previously obtained by other investigators from ab initio calculations at various levels of theory. For both C_6H_6 and N_6 the global minimum appears to be the D_{6h} planar hexagon **1**. Saxe and Schaefer³⁹ have made a careful analysis of this form of N_6 using different basis sets. For a basis set of double-zeta quality they found that **1** is an energy maximum or transition state separating but only slightly higher than two equivalent D_{3h} Kekulé forms **1'** which are relative minima but still high above the total energy of $3N_2$. For a double-zeta basis set with polarization functions they found the planar hexagonal D_{6h} form **1** to be a relative minimum for N_6 with Kekulé structures **1'** as transition states, presenting activation barriers of 10 kcal/mol to dissociation of N_6 to $3N_2$. For both C_6H_6 and N_6 the prismane form **4** is a relative minimum on the energy surface but high compared to the planar hexagon and consistent with our notions that prismane structures are highly strained. The bicyclopropenyl structures **5** fall in quite different positions, high in energy for C_6H_6 but rather low for N_6 . The density functional model calculations of Jones and Hohl⁴⁶ for P_6 cover a wide range of structures including two forms, **24** (C_{2h}) and **25** (D_2), that do not correspond to



structural isomers of benzene in that structures of C_6H_6 cannot be drawn that preserve tetracoordinate carbon. Jones and Hohl did not consider the Dewar benzene or cyclopropenyl structures **3** and **5**. Nagase and Ito⁴³ report MO calculations for P_6 in the forms of benzene **1**, Dewar benzene **3**, and prismane **4** but neglected benzvalene **2** and bicyclopropenyl **5**. For Si_6H_6 , Nagase, Kudo, and Aoki⁴⁰ studied structures of benzene, benzvalene, Dewar benzene, and prismane.

The Si_6H_6 and P_6 results differ strikingly from those for C_6H_6 and N_6 . First, the lowest energy calculated thus far for Si_6H_6 is for the prismane structure **3**, and prismane is also among the low energy structures of P_6 . Prismanes are among the high energy structures for C_6H_6 and N_6 . Benzene **1** has the highest energy for P_6 and it is one of the higher energy forms of Si_6H_6 , while this structure appears to be the global minimum for molecular C_6H_6 and N_6 at the highest levels of theory yet attempted. Second, the four structures investigated for Si_6H_6 differ in energy by less than 20 kcal/mol, and the range of energies among P_6 isomers is not much larger. For C_6H_6 and N_6 , however, the range of energies for the same structures is 130 to 140 kcal/mol. These structural and energy differences suggest that resonance stabilization and strain energies, important concepts for the rationalization of structures and relative stabilities of first row elements, must be less significant for elements in the second row and probably lower rows as well.

Calculations

We have carried out geometry optimized ab initio SCF MO calculations for P_6 constrained within the symmetry point group of each of the five valence isomeric structures (**1**–**5**) with the basis sets 3-21G, 4-31G*, and 6-31G* using the GAUSSIAN 82 and 86 program packages.^{47,48} The asterisks (*) indicate that d-type polarization functions were included in these basis sets. We and others before us have found that polarization

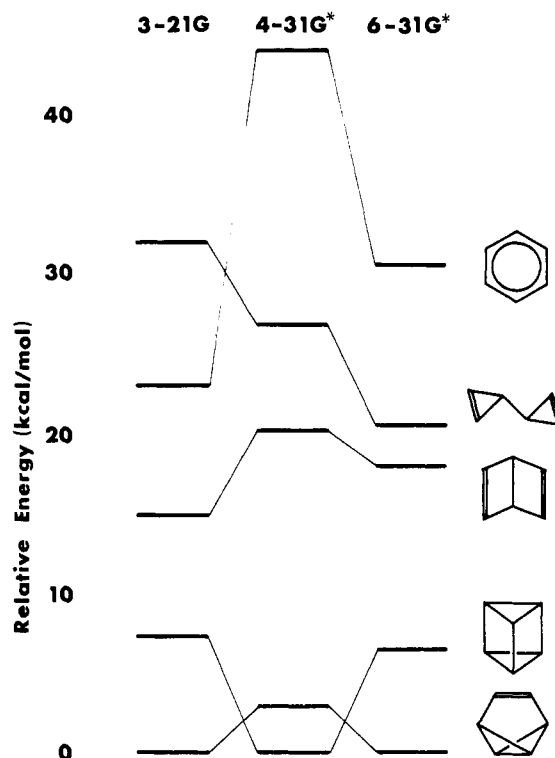


Figure 2. P_6 relative energies for different basis sets.

functions are essential for the realistic expression of structural details in molecules involving second row elements.^{49–52} We have also calculated vibrational frequencies for each structure with 4-31G* and 6-31G* basis sets. Vibrational frequencies that are all real indicate that a particular structure represents a minimum on the energy surface. Imaginary frequencies denote a non-minimum structure. Only the planar hexagon **1** gave imaginary frequencies for the 4-31G* basis set. The other four structures exhibited real minima at the 4-31G* level and all five were real at the 6-31G* level.

Our calculations differ from those of Nagase and Ito in two respects. First, we included benzvalene and bicyclopropenyl structures as well as benzene, Dewar benzene, and prismane. Second, we optimized geometries of all five structures at all levels of basis set. Nagase and Ito calculated the energies of Dewar benzene and prismane P_6 with the 6-31G* basis set but using geometrical parameters determined at the 3-21G level. This explains why their calculated energies for prismane, Dewar benzene, and benzene fall so close together at the 6-31G* level. Our results show that these geometries are far from optimum for the polarized basis sets. In their density functional calculations, Jones and Hohl did not consider Dewar benzene and bicyclopropenyl structures for P_6 . Only benzene and prismane were common to the groups of P_6 structures studied by Nagase and Ito and Jones and Hohl.

It is always possible to appeal to higher levels of theory with the hope that this will improve the reliability of conclusions based on calculated results. We might have considered more extensive basis sets to approach the Hartree–Fock limit more closely or attempted to include the effects of electron correlation by carrying out Moller–Plessett (MP) perturbation or configuration interaction calculations.³¹ Our limited experience with correlation corrections is that unless we also reoptimize geometries at the same level the relative energies turn out to be disappointing. Geometry optimization, even at the 6-31G*/MP2 level, is beyond the capacity of the computing resources available to us. The ultimate level of theory is an ever elusive goal.

Relative Stabilities and Structures

Figure 2 displays the relative energies of the five valence isomeric structures calculated for P_6 . Total energies appear in

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

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Table II. Total Energies (hartrees) and Relative Energies (kcal/mol) of P_6 in the Valence Isomeric Forms of $(CH)_6$

Structure		3-21G/SCF	4-31G*/SCF	6-31G*/SCF	
Benzvalene		E_{tot}	-2033.9602	-2042.2006	-2044.3229
		E_{rel}	0	2.9	0
		ZPVE		0.0111	0.0113
Prismane		E_{tot}	-2033.9488	-2042.2052	-2044.3126
		E_{rel}	7.2	0	6.5
		ZPVE		0.0115	0.0117
Dewar benzene		E_{tot}	-2033.9365	-2042.1730	-2044.2942
		E_{rel}	14.9	20.2	18.0
		ZPVE		0.0109	0.0110
Bicyclopropenyl		E_{tot}	-2033.9091	-2042.1624	-2044.2900
		E_{rel}	32.1	26.9	20.6
		ZPVE		0.0100	0.0101
Benzene		E_{tot}	-2033.9235	-2042.1347	-2044.2739
		E_{rel}	23.0	44.2	30.9
		ZPVE		0.0089	0.0096

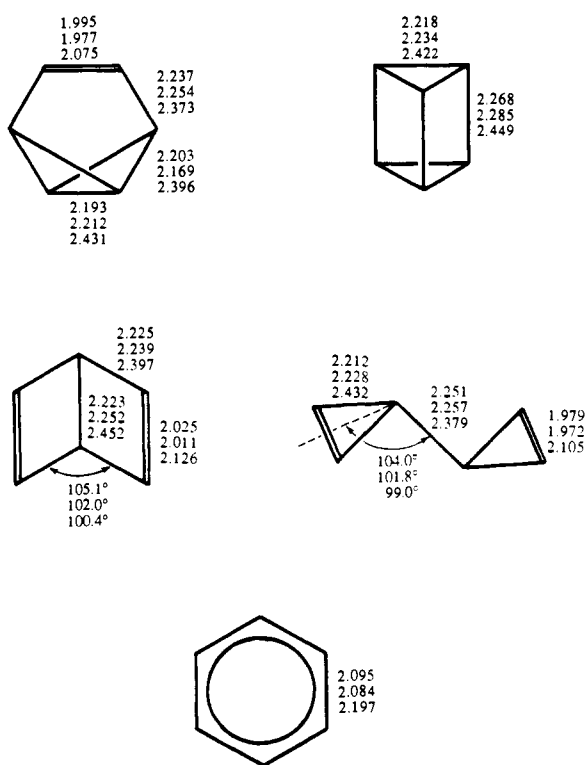
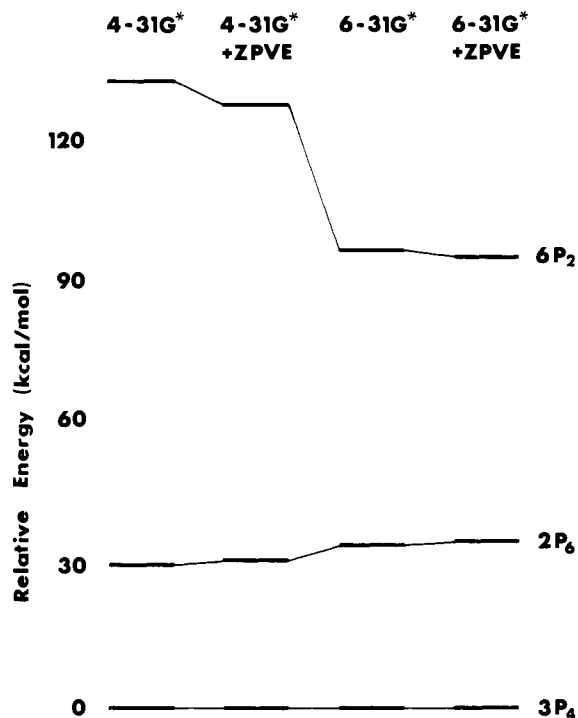
Figure 3. Selected structural parameters for isomeric forms of P_6 . In each stack the uppermost value is the 6-31G* result, intermediate is the 4-31G* result, and the bottom figure is from the 3-21G calculation.

Table II. Despite the intensity of these calculations, results for different basis sets suggest that conclusions are at best qualitative. Of immediate interest is the order of relative energies; benzvalene and prismane structures are the most stable, above them lie Dewar benzene and bicyclopropenyl, and benzene is the highest. At the 6-31G* level the range of relative energies is only a little more than 30 kcal/mol with benzvalene a little more stable than prismane. These results agree with those of the density functional calculations of Jones and Hohl. The order of stabilities for P_6 at the 4-31G*/SCF level is exactly the reverse of that found by Engelke³⁸ for N_6 using exactly the same basis set.

The phosphorus-phosphorus bond distances determined by energy minimizations for the five valence isomeric forms of P_6 at different levels of basis set are shown in Figure 3. For comparison here are typical distances from a survey of experimental structures displaying representative bond types.⁵³

$$P-P = 2.21 \text{ \AA}; P=P = 2.01 \text{ \AA}; P \equiv P = 1.89 \text{ \AA}$$

Figure 4. Relative energies of $6P_2$, $3P_4$, and $2P_6$.

Results from the two polarized basis sets compare quite favorably with each other and with typical experimental distances, the 4-31G* P-P single bonds being generally 0.01 Å longer and P=P double bonds being 0.01–0.02 Å shorter than those from the 6-31G* basis set. The 3-21G results are much too long, typically differing from those of the two polarized sets and from experiment by 0.1 to 0.2 Å. The distances from 6-31G* and 4-31G* basis sets are exactly what one would have expected from analogous structures of $(CH)_6$ valence isomers as established by experiment and ab initio calculations. The 2.084, 2.095 Å distance in P_6 (benzene) is intermediate in length between standard single and double PP bonds but a little on the short side of average. All edges of the P_6 prism are clearly single bonds. The three parallel bonds that join the two triangular ends are longer than the triangular bonds, just as they have been observed to be in $(CH)_6$ prismane itself. In P_6 (benzvalene) the basket handle or bond that ties together the wingtips of the butterfly has the length of a double bond as does the comparable bond in $(CH)_6$ benzvalene, while the other seven bonds are single bonds. P_6 (Dewar benzene) has two parallel-edge P=P double bonds that flank a long P-P bond along the central spine. The same arrangement is observed in $(CH)_6$ Dewar benzene. Finally, in P_6 (bicyclopropenyl) the triangular edges opposite vertices through which the two triangles are connected are P=P double bonds, while the other five bonds are single bonds, as expected for $(CH)_6$ bicyclopropenyl.

Relative Energies of P_2 , P_4 , and P_6

Figure 4 shows the relative energies of $6P_2$, $3P_4$, and $2P_6$. We have included zero point vibrational energies to show their effect. The energy of $2P_6$ lies 60 to 100 kcal/mol below that of $6P_2$ but 30 to 35 kcal/mol above $3P_4$. The fact that P_6^+ is not a prominent peak in the mass spectrum of red phosphorus suggests that the direct assembly of P_6 from P_4 and its fragments is not easy. Whatever it is, the mechanism of rearrangement of $2P_6$ into $3P_4$ is likely to be complicated and have an activation barrier large enough to stabilize $2P_6$. The experimental heat of sublimation of P_4 (s) is 14 kcal/mol. Combining this value with calculated energy differences between P_4 and P_6 gives an estimated heat of formation of P_6 (g) as 31 to 32 kcal/mol.

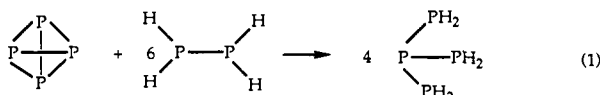
(53) Gimarc, B. M.; Warren, D. S. In *Molecules In Natural Science and Medicine*; Maksic, Z. B., Eckert-Maksic, M., Eds.; Ellis Horwood, Chichester, 1991; p 327.

Table III. Total Energies, Zero-Point Vibrational Energies (hartrees), and Selected Structural Parameters (Å) for P₂, P₄, and Some Phosphines

Molecule		4-31G*	6-31G* or 6-31G**
P ₂	E=	-680.7077	-681.4245
	ZPVE=	0.0022	0.0021
	PP=	1.845	1.859
P ₄ (Td)	E=	-1361.4855	-1362.8999
	ZPVE=	0.0069	0.0070
	PP=	2.190	2.174
P ₂ H ₂ (C _{2h} , trans)	E=	-681.8515	-682.5739
	ZPVE=	0.0191	0.0194
	PP=	1.990	2.004
	PH=	1.414	1.408
	HPP=	95.5°	96.2°
P ₂ H ₂ (C _{2v} , cis)	E=	-681.8450	-682.5683
	ZPVE=	0.0189	0.0191
	PP=	1.995	2.012
	PH=	1.411	1.408
	HPP=	100.6°	101.0°
P ₂ H ₄ (C _{2h} , trans)	E=	-683.0382	-683.7588
	ZPVE=	0.0378	0.0380
	PP=	2.246	2.231
	PH=	1.408	1.405
	HPP=	100.6°	101.0°
P ₂ H ₄ (C ₂ , gauche)	E=	-683.0385	-683.7605
	ZPVE=	0.0380	0.0383
	PP=	2.232	2.214
	PH=	1.405, 1.405	1.403, 1.404
	HPP=	100.6°	101.0°
P ₄ H ₄ (C _{2h} , trans)	E=	-1363.7532	-1365.1852
	ZPVE=	0.0414	0.0418
	PP=	1.990, 2.244	2.005, 2.221
	PH=	1.403, 1.406	1.402, 1.403
	PPP=	101.3°	103.4°
	HPH=	94.3°, 98.6°	95.1°, 100.6°
P ₄ H ₆ (C ₃)	E=	-1364.9387	-1366.3736
	ZPVE=	0.0603	0.0609
	PP=	2.224	2.212
	PH=	1.405, 1.407	1.403, 1.406
	HPH=	101.5°	103.6°
		94.4°	95.8°

Strain Energies of P₄ and P₆

Equation 1 is a homodesmotic reaction involving tetrahedral P₄. Not only are the numbers of bonds of different types the same



on opposite sides of this equation (12 P–P and 24 P–H), but also the bonding around each atom is the same. For example, the left-hand side has four P atoms, each of which is bonded to three other P atoms. Thus there must be four iso-P₄H₆ molecules as product because each of these contains a phosphorus bound to three others. However, the product P₄H₆ molecules introduce 12 P atoms, each bonded to one other P and two hydrogens, requiring 6P₂H₄ molecules as reactants. Since the numbers of different types of bonds are conserved, the energy change from the bond additivity model must be zero. Furthermore, there should be no energy changes due to differences in substitution around each atom. Any energy changes resulting from this reaction must come from the relief of strain in the tetrahedral P₄ molecule on the left-hand side of eq 1. One would anticipate that the relief of strain is exothermic ($\Delta E < 0$). From eq 1 and total energies of P₄, P₂H₄, and P₄H₆ from Table III:






$$\Delta E_1 = 4E(\text{P}_4\text{H}_6) - E(\text{P}_4, \text{tetrahedral}) - 6E(\text{P}_2\text{H}_4) = -24.1 \text{ kcal/mol (4-31G}^*) = -19.7 \text{ kcal/mol (6-31G}^*)$$

The reaction is exothermic as expected and the calculated values, 20–24 kcal/mol, for the strain energy of P₄ overlap the range 24–34 kcal/mol recently estimated for the strain energy using thermochemical and average bond energy data,⁵³ and they bracket the P₄ strain energy of 23 kcal/mol estimated by Pauling and Simonetta 4 decades ago.⁵⁴ Estimates of the strain energy of tetrahedrane, C₄H₄, given by Schulman and Venanzi⁵⁵ (129–137 kcal/mol) and by Nagase⁵⁶ (141 kcal/mol) are five to six times larger than that for tetrahedral P₄. The tetrahedrane has 12 angles of 60°. For P₄ the strain energy would be about 2 kcal/mol per PPP angle of 60° compared to 11 to 12 kcal/mol per CCC angle in tetrahedrane, C₄H₄. The strain energy of cyclopropane, C₃H₆, has been estimated to be 28 kcal/mol or 9 kcal/mol per CCC angle of 60°.⁵⁷

(54) Pauling, L.; Simonetta, M. *J. Chem. Phys.* **1952**, *20*, 29.(55) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.(56) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.(57) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; p 66.**Table IV.** Strain Energies (in kcal/mol) for Valence Isomeric Structures of P₆

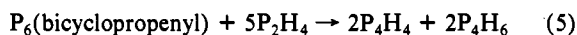
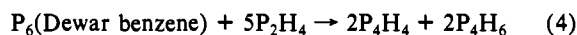
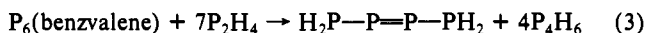
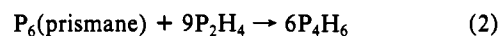
Structure	Strain Energy			
	4-31G*	4-31G*+ZPVE	6-31G*	6-31G*+ZPVE
Prismane	50.7	45.6	52.9	47.5
Benzvalene	23.9	20.5	20.8	17.2
Dewar benzene	11.5	10.1	13.1	11.3
Bicyclopropenyl	18.2	16.2	15.7	13.4

Table V. Relative Energies, Strain Energies, Resonance Energies, and Hypothetical Unstrained Nonresonance Stabilized Energies (kcal/mol) of C₆H₆ and P₆ Valence Isomers at the 6-31G* Level

Structure					
	1	2	3	4	5
C₆H₆					
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
P₆					
Relative energy (A)	30.9	0	18.0	6.5	20.6
Strain energy (+) or resonance energy (-) (B)	-14.9	+20.8	+13.1	+52.9	+15.8
Unstrained or non-resonance stabilized (A-B)	+45.8	-20.8	+4.9	-46.4	+4.8
Renormalized (A-B+49.9)	95.7	25.6	51.3	0	51.2

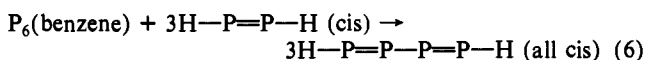
Phosphine, PH₃, is often cited as containing the prototypical unstrained phosphorus atom bound to three equivalent atoms. The HPH angle in phosphine is 93°, far less than the internal tetrahedral angle of 109.5°. This suggests that phosphorus atoms suffer reduction of bond angles from this preferred angle to 60° much more easily than carbon when its bonds are compressed from 109.5° to 60° and rationalizes at least in part the lower strain energy of P₄ compared to tetrahedrane. Experimental structural data on saturated P_nH_m compounds are not plentiful, but our geometry optimized results for iso-P₄H₆ (Table III) show that the central phosphorus in this compound prefers a PPP angle of 101.5° to 103.6°, values that are closer to 109.5° than they are to the HPH angle in phosphine. On the other hand, our calculated HPH angles in P₄H₄ and P₄H₆ fall in the range 94°–96°, close to that in phosphine.

Equations 2–5 are homodesmotic reactions involving four of



the valence isomeric structures of P₆. Notice that one or two P₄H₄ molecules enter on the products sides of eqs 3–5 to carry P=P double bonds from the P₆ isomer reactant. Table IV contains the strain energies calculated as ΔE_2 through ΔE_5 using calculated total energies of P₆, P₂H₄, P₄H₄, and P₄H₆ from Tables II and III. Of the four structures listed in Table IV, P₆(prismane) has the largest strain energy, 50–55 kcal/mol, over twice the size of any of the others, yet considerably less than that for C₆H₆(prismane) for which estimates range from 108 kcal/mol (Greenberg and Liebman⁵⁷), to 145 kcal/mol (Nagase⁵⁶) and 149 kcal/mol (Schulman and Disch⁵²).

In their ab initio study of P₆, Nagase and Ito calculated the resonance energy of planar hexagonal P₆ as the energy change for the homodesmotic reaction:⁴³



With the 6-31G* basis set they obtained a resonance energy for P₆ of 14.9 kcal/mol, comparable to the value of 14.4 kcal/mol for planar hexagonal N₆ but smaller than 24.7 kcal/mol resonance

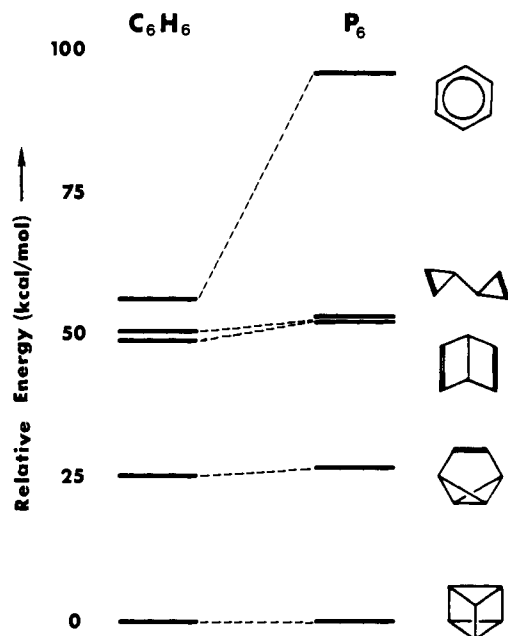


Figure 5. Comparison of hypothetical unstrained or nonresonance stabilized energy orderings of isomeric forms of C_6H_6 and P_6 . Energy differences are those between two single bonds and one double bond: the more double bonds, the higher the energy.

energy for C_6H_6 (benzene) at the same level of theory.

What would be the relative energies of structures 1–5 without the stabilizing effect of resonance or the destabilizing effects of strain? Table V shows relative energies (*A*) of C_6H_6 and P_6 in the forms of the five valence isomers of benzene, the corresponding calculated strain energies or resonance energies (*B*), and their differences (*A* – *B*). Since resonance energy is an unexpected energy lowering, we combine it so that it raises the energy of the nonresonance stabilized result. Strain energy is an unexpected increase in energy, and therefore we subtract it from the relative energy to get an unstrained energy. All results come from ab initio calculations at the 6-31G* level. Relative energies and strain energies for C_6H_6 are those obtained by Schulman and Disch with geometries optimized under MP2 conditions.³² Our results for P_6 were obtained at the SCF level. Resonance energies for C_6H_6 and P_6 were taken from Nagase and Ito.⁴³ The last line of each section, C_6H_6 or P_6 , of Table V contains the renormalized or readjusted energies for unstrained or nonresonance stabilized structures. These results are graphically displayed in Figure 5. The order of energies of unstrained or nonresonance stabilized C_6H_6 and P_6 is the same; prismane is the most stable and the planar hexagon is the least. Furthermore, we can immediately see what gives these structures their energy differences. Two single bonds in prismane have been replaced by a double bond in benzvalene. The energy difference between these two structures is the difference in energy between two single bonds and one double bond. For both carbon and phosphorus, double bond energies are less than twice the single bond energies, giving benzvalene a higher energy than prismane. Using standard values of CC bond energies,⁵⁸

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

a result that is essentially identical with the 25-kcal/mol difference shown in Table V between the energies of C_6H_6 prismane and benzvalene and between those of benzvalene and Dewar benzene and cyclopropenyl. Compounds with P=P double bonds have been prepared only within the last 10 years and experimental values for $D(P=P)$ are not available.^{59–61} Using the unstrained value

for $D(P-P) = 55$ kcal/mol, we can estimate the P=P double bond dissociation energy:

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

Kutzelnigg gives estimates of 48 and 34 kcal/mol for σ - and π -increments, respectively, for PP bonds.⁶² These values combine for a P=P double bond energy of 82 kcal/mol, very close to our result and in agreement with our conclusion that the P=P double bond is weaker than two P–P single bonds. Thus PP multiple bonds are more like those of carbon, where bond energy increments decrease in size as bond multiplicity increases, rather than nitrogen or oxygen for which the increments increase with multiplicity. To complete the comparison $D(P\equiv P) = 125$ kcal/mol.⁵⁸ These conclusions are reinforced by the relative energies of Dewar benzene and bicyclopentenyl. Each has two double bonds, and the essentially equal relative energies of these structures are twice as high as benzvalene is above prismane.

The planar hexagon does not fit quantitatively in either system. For C_6H_6 the hexagon is too low; for P_6 it is too high. One would have expected both to be around 75 kcal/mol above prismane. But the calculated resonance energies were based on regular hexagonal geometry, D_{6h} , not D_{3h} structures that would contain alternant single and double bonds.

The relative energies of these structures are basically determined by differences in single and double bond energies. Considering bond energies only, prismane would have the lowest energy structure because it has the largest number of single bonds; the planar hexagon would have the highest energy because it has the largest number of double bonds. The energy of the hexagon is lowered by resonance stabilization while the energies of the other structures are raised by strain energies. For C_6H_6 , resonance energy is large but strain energies are even larger and they completely reorder the relative stabilities of the structures. For P_6 the resonance energy and strain energies are small and their contributions make only minor adjustments in the basic energy order determined by bond energies. For example, from single and double bond energy differences alone, the energy of P_6 (benzvalene) should be 26 kcal/mol above that of P_6 (prismane). But the prismane total energy is raised by a strain energy of 50 to 55 kcal/mol, while that of P_6 (benzvalene) is raised by only 20 to 25 kcal/mol of strain energy. The net result gives the two structures roughly equivalent total energies with prismane perhaps slightly higher as shown in Figure 2 for the 6-31G* results. The two structures with two double bonds have still smaller strain energies with that for Dewar benzene slightly less than the strain energy for cyclopropenyl. Therefore, the total energy of Dewar benzene falls a little below that of cyclopropenyl. Again, see Figure 2.

Ionization Energy and the HOMO–LUMO Gap

Figure 6 displays the energies of HOMO and LUMO for P_6 in structural forms 1–5 as calculated with the 6-31G* basis set. According to Koopman's theorem, the energy of the HOMO approximates the first ionization potential of the molecule. In practice, orbital energies usually give estimates that are large compared to experimental ionization energies.⁶³ The HOMO energies for P_6 isomeric structures in Figure 6 appear to be rather small compared to ionization potentials of typical molecules. The LUMO is sometimes considered an approximation to the electron affinity. The LUMO levels in Figure 6 are negative with the exception of that for P_6 (prismane) which is barely positive (+0.01 eV). The LUMO for P_6 (benzene) is quite low (–1.5 eV). Indeed, the low-lying LUMO of planar hexagonal P_6 consists of the doubly degenerate e_{2u} pair of π orbitals that must be occupied in the known cluster P_6^{4-} (20). When these MOs are occupied and included in the SCF optimization process, their energy should fall

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(60) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.

(61) Busch, T.; Schoeller, W. W.; Niecke, E.; Nieger, M.; Westerman, H. *Inorg. Chem.* **1989**, *28*, 4334.

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(63) Lowe, J. P. *Quantum Chemistry*; Academic Press: New York, p 321.

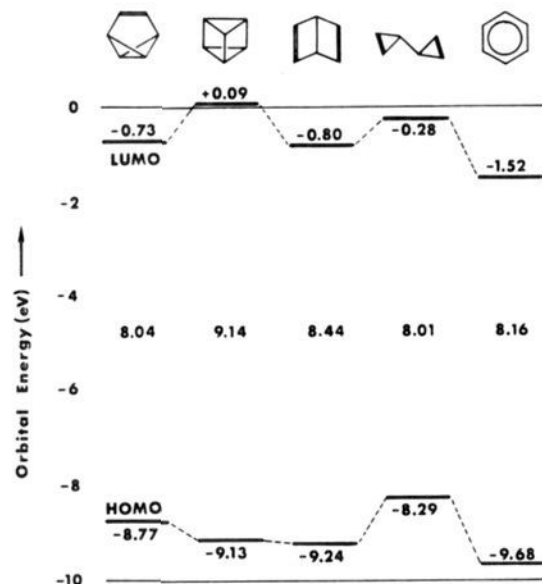


Figure 6. Energies of HOMO and LUMO and the size of the HOMO-LUMO gaps in P_6 isomeric structures as calculated with the 6-31G* basis set.

even lower. Immediately above the doubly degenerate e_{2u} π LUMOs is the singly degenerate completely antibonding π MO b_{2g} . The b_{2g} MO is greatly stabilized by the 3-fold distortion to chair form D_{3d} . Neighboring p AO lobes that are all out-of-phase in b_{2g} (D_{6h}) become in-phase in the resulting a_{1g} (D_{3d}) (26).⁶⁴ If



26

b_{2g} were occupied it would stabilize the chair-form hexagonal ring observed in the formal P_6^{6-} cluster 22. A large HOMO-LUMO gap has long been recognized as being correlated with kinetic and structural stability while a small gap is associated with reactivity.⁶⁵⁻⁷⁰ If the HOMO is too high, the molecule is likely to react by electron donation; if the LUMO is too low the molecule will react by accepting electrons. The HOMO-LUMO gaps (8-9 eV) shown in Figure 6 seem to be adequate for molecular stability.

Charge Distributions

Symmetry requires that all atoms in the planar hexagon and the triangular prism have the same charge density. Benzvalene, Dewar benzene, and bicyclopropenyl lack such high symmetry, and in these structures molecular topology establishes a nonuniform distribution of charges. Figure 7 shows the Mulliken net atom populations for P_6 in these three structural forms as obtained from calculations with 3-21G, 4-31G*, and 6-31G* basis sets. The three sets of results agree at least on the signs of the charges although there are quantitative differences between values from 3-21G and 6-31G*, on the one hand, and 4-31G*, on the other. For the three structures in Figure 7 the charge distributions are remarkably similar. Each has a single pair of three-coordinate sites with negative charge (approximately -0.1 at the 6-31G* level), while the other four sites are positive (+0.05). Adjacent sites with charge of the same sign are electrostatically destabilizing, and molecular symmetry ensures that repulsive adjacent pairs occur in all three structures. But in each structure the number

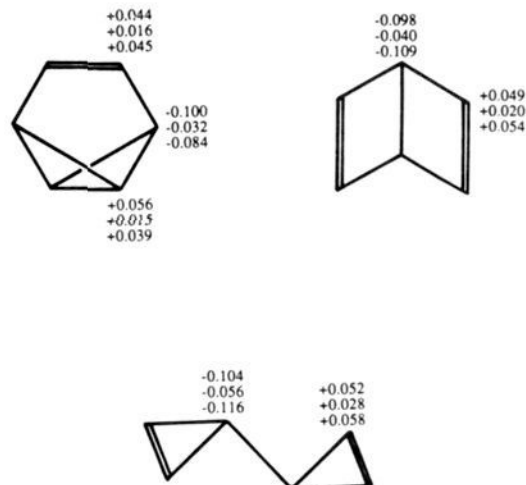


Figure 7. Mulliken net atom populations as calculated for P_6 in benzvalene, Dewar benzene, and bicyclopropenyl structures. In each stack of charges the 6-31G* basis set result appears at the top with 4-31G* and 3-21G values in order below. Symmetry requires zero charges at all sites in the planar hexagon and triangular prism structures.

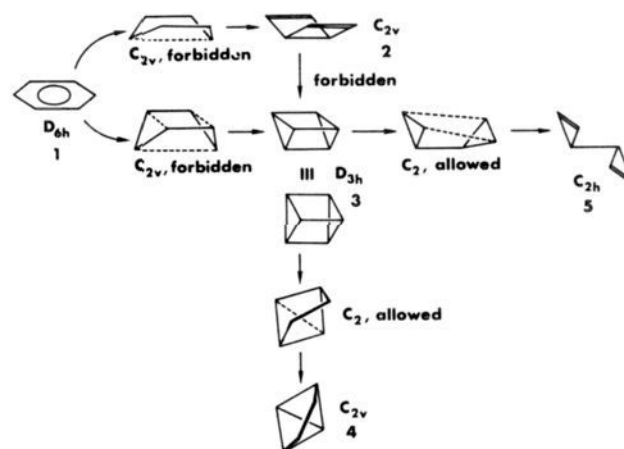


Figure 8. Isomerization processes linking isomers of P_6 . Following the principle of conservation of orbital symmetry, forbidden processes are those that involve HOMO-LUMO crossings.

of pairs of same-sign adjacent atoms is exceeded by the number of pairs of opposite-sign adjacent sites which should be electrostatically stabilizing. The situation is particularly favorable in the benzvalene structure where the larger charged, negative sites are not adjacent, and opposite-sign adjacent pairs outnumber same-sign adjacent pairs 6 to 2. The rule of topological charge stabilization states that more stable species are those in which the electronegativities of heteroatoms match the location of charges established by topology in the isostructural, isoelectronic, but homonuclear analogue.^{71,72} Among the structures in Figure 7 the rule points to a possible heteronuclear benzvalene $C_4H_4N_2$ with nitrogen atoms at the negative sites.

Isomerization Pathways

Nagase and Ito prepared an orbital correlation diagram that showed that isomerizations of P_6 (benzene) to P_6 (Dewar benzene) to P_6 (prismane) are not allowed according to the principle of conservation of orbital symmetry. We also have considered orbital correlations involving these structures as well as those of P_6 (benzalene) and P_6 (bicyclopropenyl), and our findings are summarized in Figure 8. Our conclusions concerning the benzene, Dewar benzene, and prismane isomers are the same as those of Nagase and Ito.⁴³ In addition we find that allowed processes link prismane with both benzvalene and bicyclopropenyl. Our con-

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(72) Gimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1989**, *28*, 2560.

clusions are in accord with experimental observations for the valence isomers of C_6H_6 , in so far as they are known. These processes have been reviewed by Scott and Jones who showed photochemical processes connecting benzene to benzvalene and to Dewar benzene and between Dewar benzene and prismane but a thermal reaction between prismane and benzvalene.³ Bicyclopropenyl has been prepared only recently and its isomerization reactions have not yet been reported.

Conclusions

Geometry optimized ab initio SCF MO calculations for neutral P_6 in various structural forms show that benzvalene and prismane structures have the lowest energies, with Dewar benzene and cyclopropenyl forms lying further above. The planar hexagon or benzene structure has the highest energy of all. Energies of these P_6 structures span a range of only 30 to 45 kcal/mol, compared to 120 to 130 kcal/mol for $(CH)_6$. Calculated vibrational frequencies show that at the highest level of theory attempted here all five forms correspond to real minima on the P_6 energy surface. Optimized bond distances in P_6 structures fall within traditional categories. The triangular prism has all P—P single bonds; the benzvalene form contains one P=P double bond. Dewar benzene and bicyclopropenyl each have two P=P double bonds, and the planar hexagon has six equivalent bonds that could be described as "aromatic" in that they are intermediate in length between single and double bonds.

For the lowest energy P_6 structure, the energy of $2P_6$ is only 30–35 kcal/mol above $3P_4$ and 60–100 kcal/mol below $6P_2$. Energies of the HOMOs and the HOMO–LUMO gap appear to be reasonable. Charge distributions for the less symmetric forms, as determined by Mulliken net atom populations, are equally unremarkable. P_6 clusters bearing hydrocarbon and organometallic substituents have been prepared and characterized.

Calculated energy changes of homodesmotic reactions were used to estimate strain energies for tetrahedral P_4 and the four non-hexagonal valence isomeric P_6 structures. The strain energy of P_4 turns out to be small, 20 kcal/mol, comparable to that of cyclopropane, and far lower than the 140 kcal/mol estimated for tetrahedrane. Strain energies for P_6 structures range from a high (50–55 kcal/mol) for prismane to a low (10–15 kcal/mol) for Dewar benzene. These values are only one-sixth to one-third of

comparable estimates for valence isomeric structures of $(CH)_6$. Adjusting relative energies of the isomers by subtracting out strain energies and adding in resonance energies, we find that the resulting hypothetical structural energies are ordered by the relative energies of single and double bonds. The average P=P double bond is less than twice as strong as the average P—P single bond. Our results give an estimate of 84 kcal/mol as the energy of the average P=P double bond, compared to 55 kcal/mol for the P—P single bond. The prismane structure with nine single bonds should have the lowest energy, while Kekulé benzene or the planar hexagon with three double and three single bonds should be highest. This ordering is altered when strain and resonance energies are included. With a sizable stabilization from resonance, the energy of planar hexagonal $(CH)_6$ is lowered. Energies of all other structures are increased by the effects of ring strain which are large in $(CH)_6$, raising the energies of the other four $(CH)_6$ valence isomers above that of benzene. In P_6 strain energies are small and resonance stabilization of the planar hexagon is modest. These corrections leave the fundamental energy order as determined by bond energies essentially unchanged except to raise the prismane structure to a level comparable to or perhaps a little higher in energy than the benzvalene isomer that contains one P=P double bond. The concepts of ring strain and resonance stabilization, essential in rationalizing the relative stabilities in molecules containing carbon, nitrogen, and oxygen, appear to be much less significant in molecules composed of elements from lower periods.

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Registry No. 1, 71-43-2; 1 (P_6 isomer), 15924-07-9; 2, 659-85-8; 2 (P_6 isomer), 141248-98-8; 3, 5649-95-6; 3 (P_6 isomer), 141248-99-9; 4, 650-42-0; 4 (P_6 isomer), 141249-00-5; 5, 62595-44-2; 5 (P_6 isomer), 141249-01-6; P_2 , 12185-09-0; P_4 , 12185-10-3; P_2H_2 , 41916-72-7; P_2H_4 , 13445-50-6; P_4H_4 , 287-64-9; P_4H_6 , 27208-15-7.