710 *Inorg. Chem.* **1994,** *33,* 710–715

Valence Isomers of Benzene and Their Relationship to the Isoelectronic Isomers of As_6

D. Scott Warren, Benjamin M. Gimarc,* and Ming Zhao

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

Received May 7, 1993®

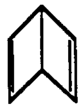
We report the results of geometry-optimized *ab initio* SCF–MO calculations for As_6 in structural forms corresponding to the five valence isomers of benzene, C_6H_6, with which As_6 is valence-isoelectronic. We used Scuseria's 752+P polarized basis set for arsenic. The resulting energy ordering of As_6 isomeric structures is very similar to what we found previously for P_6 isomers but quite different from that known for the C_6H_6 valence isomers. For As_6, as for P_6, prismane and benzvalene structures have the lowest energies while the planar hexagon (benzene) has the highest. The range of energies of the five structures is small, around 45 kcal/mol, somewhat larger than for the P_6 isomers but far smaller than for C_6H_6. Calculated bond distances are easily identified with experimental examples of AsAs single, double, and aromatic bonds. The energy of $2As_6$ lies only 30 kcal/mol above that of $3As_4$. Calculated energy changes of homodesmotic reactions involving As_4 and As_6 give estimates of strain energies and resonance energies. The strain energies range from 2 kcal/mol for Dewar benzene to 33 kcal/mol for prismane. These are uniformly lower than comparable calculated strain energies of P_6 isomers and much lower than strain energies of the valence isomers of C_6H_6. Our estimate of the resonance energy of planar hexagonal As_6 is 17.6 kcal/mol, somewhat larger than that for the same structure for P_6 and smaller than the calculated resonance energy of benzene, C_6H_6. Using calculated strain and resonance energies for As_6 isomers, we obtain an estimate of 60 kcal/mol for the As=As double bond energy. As with carbon and phosphorus, the homoatomic double bond is weaker than two homoatomic single bonds, and it is this result that establishes the basic energy ordering of As_6 isomers. Calculated charge densities for As_6 isomers are uniformly smaller than those for comparable P_6 structures. Weaker bonds, smaller strain energies, and lower charge densities are properties that are consistent with the fact that valence AO's of larger principal quantum number are more diffuse.

Introduction

Numerous homoatomic arsenic clusters have been observed, including As_4, As_5^-, As_6^+, and As_6^{4-}.[1-4] Other larger clusters are also known.[5-8] These arsenic clusters are isoelectronic with phosphorus analogs and generally share the same geometry. P_4 and As_4 are tetrahedral,[1,9] P_5^- and As_5^- are both planar pentagons[2,10] although As_5^- is severely distorted from the D_{5h} symmetry, and P_6^{4-} and As_6^{4-} are both planar hexagons[4,11] found associated with metals in sandwich complexes. Mass spectroscopy reveals the existence of As_6^+. The abundance of As_6^+ is only about 10^{-5} that of As_4^+.[3] We recently compared *ab initio* calculations of the P_6 valence isomers of benzene with their hydrocarbon analogs.[12,13] The five valence isomeric structures of C_6H_6 are benzene (or planar hexagon) (**1**), benzvalene (**2**), Dewar benzene (**3**), triangular prismane (**4**), and bicyclopropenyl (**5**).[14] They share the property that six CH groups are connected to each other by single and double CC bonds. P and As atoms should more closely resemble these CH units rather than C or CH_2 units that occur in other C_6H_6 isomers. Here, the trend of strain energies and bond energies of homoatomic clusters in the form of the valence isomers of benzene is further explored with respect to the corresponding arsenic clusters.

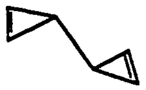
1

2



3

4



5

Experimental AsAs Bond Distances

Table 1 lists some typical arsenic–arsenic bond distances. The As—As single bond ranges from 2.44 to 2.475 Å.[1,15] The As=As double bond ranges from 2.224 to 2.244 Å.[16] The As≡As triple

---

[®] Abstract published in *Advance ACS Abstracts,* January 1, 1994.

(1) As_4: Maxwell, L. R.; Hendricks, S. B.; Mosley, V. M. *J. Chem. Phys.* **1935,** *3,* 699 (elec diff). Morino, Y.; Ukaji, T.; Ito, T. *Bull. Chem. Soc. Jpn* **1966,** *39,* 64 (elec diff).

(2) As_5^-: DiMaio, A.-J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1987,** 404.

(3) As_6^+: Kane, J. S.; Reynolds, J. H. *J. Chem. Phys.* **1956,** *25,* 342 (mass spec).

(4) As_6^{4-}: Schnering, H. G. v. *Angew. Chem., Int. Ed. Engl.* **1981,** *20,* 33. Roziere, J.; Seigneurin, A.; Belin, C.; Michalowicz, A. *Inorg. Chem.* **1985,** *24,* 3710 (EXAFS). Scherer, O. J.; Sitzmann, H.; Wolmershausen, G. *Angew. Chem., Int.* Ed. Engl. **1989,** *28,* 212 (X-ray).

(5) As_7^{3-}: Schmettow, W.; Schnering, H. G. v. *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 857 (X-ray).

(6) As_8: Kane, J. S.; Reynolds, J. H. *J. Chem. Phys.* **1956,** *25,* 342 (mass spec).

(7) As_8^{10-}: Deller, K.; Eisenmann, B. *Z. Naturforsch.* **1976,** *B31,* 1023 (X-ray).

(8) As_{11}^{3-}: Belin, C. H. E. *J. Am. Chem. Soc.* **1980,** *102,* 6036 (X-ray).

(9) P_4: Maxwell, L. R.; Hendricks, S. B.; Mosley, V. M. *J. Chem. Phys.* **1935,** *3,* 699 (elec diff).

(10) P_5^-: Baudler, M.; Duster, D.; Ouzounis, D. *Z. Anorg. Allg. Chem.* **1987,** *544,* 87.

(11) P_6^{4-}: Schmettow, W.; Lipka, A.; Schnering, H. G. v. *Angew. Chem., Int. Ed. Engl.* **1974,** *13,* 5 (X-ray). Abicht, H.-P.; Honle, W.; Schnering, H. G. v. *Z. Anorg. Allg. Chem.* **1984,** *519,* 7 (X-ray).

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

(13) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1985,** *107,* 5059.

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

(15) Eisenmann, B.; Jager, J.; Zagler, R. *Z. Kristallogr.* **1991,** *197,* 259. Eisenmann, B.; Zagler, R. *Z. Kristallogr.* **1991,** *197,* 261.

(16) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1984,** *34,* 1.

0020-1669/94/1333-0710$04.50/0

Table 1. Experimental Bond Data for AsAs Bonds

bond type	length, Å	compd
As—As	2.44	As_4[a]
	2.475–2.481	$K_4As_2Te_4$[b]
As=As	2.224–2.244	RAs=AsR′[c]
As≡As	2.103	As_2[d]
As—H	1.519	AsH_3[e]

bond type	bond enthalpy, kcal/mol at 25 °C	compd
As—As	43	As_4[f]
As≡As	91.3	As_2[g]

[a] Reference 1. [b] Reference 15. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 19. [g] Reference 20.

bond in As_2 is 2.103 Å.[17] Experimental As—H bond distances in AsH_3 are 1.519 Å.[18] Experimentally determined bond enthalpies are also available and are shown in Table 1. The arsenic triple bond in As_2 has a bond enthalpy of 91.3 kcal/mol, and that of the As—As single bond is estimated at 43 kcal/mol.[19,20] There is no available experimental bond enthalpy for the As=As double bond.

Calculations

The following *ab initio* calculations were performed using the Gaussian 90 program[21] on an IBM RS/6000 at the University of South Carolina. We used Scuseria's 752+P basis set for arsenic.[22] The 752+P basis set consists of 14 primitive s, 11 primitive p, and 5 primitive d-type Gaussians contracted into 7s, 5p, and 2d Gaussians. The basis set also includes a diffuse d-type Gaussian for polarization. The polarization functions are necessary in order to obtain reasonable bond distances and relative energies for the elements of the lower periods.[24-26] The 6-311G** basis set supplied with Gaussian 90 was used for the hydrogen atoms. Geometries were optimized under symmetry constraints as noted in the text. Only singlet-state restricted Hartree–Fock calculations were performed. We calculated vibrational frequencies for the five valence isomeric structures **1**–**5**. For structures **2**–**5**, all calculated frequencies are positive, indicating that these isomers correspond to real minima on the RHF/752+P energy surface. The planar regular hexagon **1** turned out to have one doubly degenerate negative frequency, revealing that **1** is a transition state and not a relative minimum at this level of theory. Because of the importance of the hexagonal shape in chemistry (it is a relative minimum on energy surfaces calculated for C_6H_6,[27] N_6,[28] and P_6[12]), we have used the symmetry-constrained (D_{6h}) total energy to provide comparisons of relative isomer energies and resonance energies. Perhaps the most significant point concerning the regular hexagonal structure is that it has the highest energy of the five valence isomeric forms for both As_6 and P_6 and not the lowest as it does for C_6H_6 and N_6.

Relative Stabilities and Structures

Table 2 shows the total and relative energies of the five valence isomeric structures calculated for As_6. The relative energies are compared to the results from P_6 in Figure 1. The energy ordering is qualitatively similar to that of P_6 with the exception that prismane is lower in energy than the benzvalene structure for As_6. The energy difference between the As_6 prismane and benzvalene structures is not great (about 6 kcal/mol). The range of relative energies (46 kcal/mol) for As_6 isomers is somewhat greater than the range of relative energies for P_6 (35 kcal/mol at 6-31G*) but much less than the range for C_6H_6 (126 kcal/mol at 6-31G*).

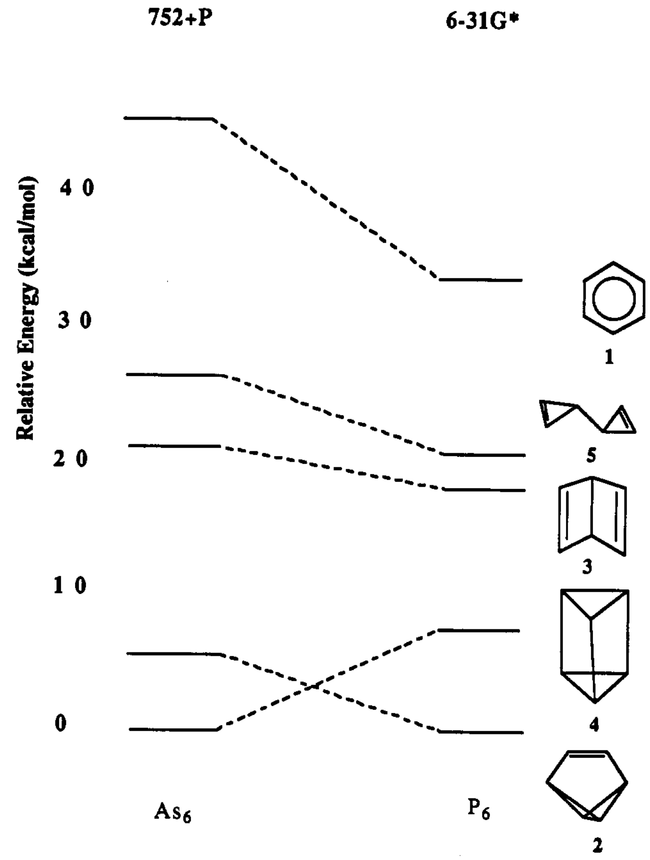


Figure 1. As_6 and P_6 relative energies for basis sets shown.

Table 2. Total and Relative Energies among the Five As_6 Valence Isomers of Benzene

structure	no.	tot. energy, hartrees	rel energy, kcal/mol
prismane	4	−13 404.172 309 6	0
benzvalene	2	−13 404.163 331	5.6
Dewar benzene	3	−13 404.138 355 2	21.3
bicyclopropenyl	5	−13 404.130 180 5	26.4
planar hexagon	1	−13 404.099 655 7	45.6

The optimized bond distances for As_6, As_4, and As_2 are shown in Figure 2. The calculated As—As single bond in tetrahedral As_4 (2.432 Å) is in excellent agreement with the gas-phase electron diffraction value of 2.435 ± 0.004 Å.[1] In As_6 prismane, the calculated As—As rectangular edge bond is long compared to average As—As single bonds (2.507 Å from these calculations; experimental averages in other compounds range from 2.44 to 2.47 Å) following a trend noted in C_6H_6 and P_6.[12,27] The triangular edge bonds calculated for As_6 prismane (2.466 Å) fall within the range of experimental averages. For As=As double bonds, calculated values of 2.217 Å in both HAs=AsH and HAs=As—As=AsH, 2.219 Å in H_2As—As=As—AsH_2, 2.200 Å in benzvalene, 2.203 Å in bicyclopropenyl, and 2.237 Å in Dewar benzene compare with experimental averages of 2.224–2.244 Å in substituted RAs=AsR′. The conjugated bond in planar hexagonal As_6 is 2.307 Å, between average distances for single and double bonds. It is of some note that this distance is less than the values of 2.35 and 2.37 Å found experimentally for planar hexagonal As_6^{4-}.[4] The As≡As triple bond in As_2 presents the

---

(17) As_2: Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand, Reinhold: New York, 1979.

(18) AsH_3: Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Structure Data on Free Polyatomic Molecules*; Landolt-Bornstein, New Series Group II; Springer-Verlag: Berlin, 1976; Vol. 7.

(19) Sanderson, R. T. *Chemical Bonds and Bond Energy*, 2nd ed.; Academic Press: New York, 1976; p 51.

(20) Kordis, J.; Gingerich, K. A. *J. Chem. Eng. Data* **1973**, *18*, 135.

(21) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *GAUSSIAN 90*, Revision J.; Gaussian Inc.: Pittsburgh, PA, 1990.

(22) Scuseria, G. E. *J. Chem. Phys.* **1990**, *92*, 6722.

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

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

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

(26) Schmidt, M. W.; Gordon, M. S. *Inorg. Chem.* **1985**, *24*, 4503.

(27) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 5059.

(28) Engelke, R. *J. Phys. Chem.* **1989**, *93*, 5722.

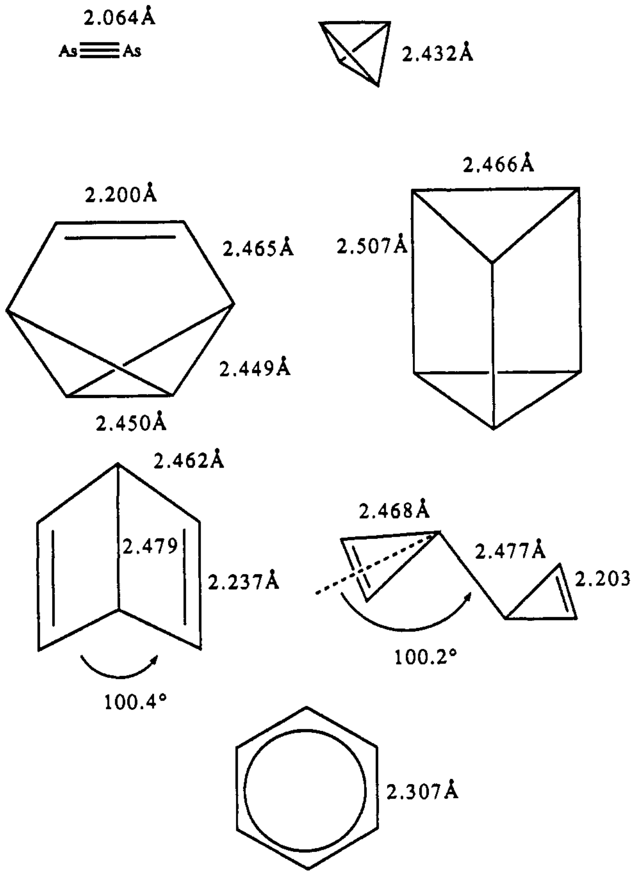


Figure 2. Selected structural parameters for isomeric forms of As_6 using the 752+P basis set. Bond lengths are in angstroms, and bond angles are in degrees.

least favorable comparison between calculation and experiment. Our calculated result, 2.064 Å, is considerably shorter than the spectroscopic value, 2.103 Å.[17] The direction and size of this error are consistent with what we found for the P≡P triple bond, 1.859 Å with the 6-31G* basis set compared to 1.894 Å from experiment.

Arsines

Geometry-optimized parameters for a few arsines are shown in Table 3. While As_2H_2 and As_2H_4 are known,[29,30] they readily break down and experimental structures are not available for comparison. Calculated As—H bond distances listed in Table 3 for a series of arsenic compounds range from 1.505 to 1.510 Å, somewhat shorter than the experimental distance of 1.519 Å in AsH_3.[18]

The AsAsAs angle in $As(AsH_2)_3$ is 99.7° from the 752+P calculations, somewhat smaller than the PPP angle in $P(PH_2)_3$ of 103.6° from 6-31G** calculations that we reported previously. This parallels a decline in HAsH angles of 94.3 and 94.5° in As_4H_6 and As_4H_4, respectively, compared with HPH angles of 95.8 and 96.1° in P_4H_6 and P_4H_4. The same trend is observed in HAsH and HPH angles from spectroscopic determinations of structures of AsH_3 (92.0°)[31] and PH_3 (93.3°).[32]

Table 3. Total Energies (hartrees) and Selected Structural Parameters (Å and deg) for As_2, As_4, and Some Arsines

molecule		752+P
As_2	*E*	−4468.026 858 6
	AsAs	2.064
As_4 (T_d)	*E*	−8936.129 480 4
	AsAs	2.432
As_2H_2 (C_{2h}, trans)	*E*	−4469.173 202 1
	AsAs	2.217
	AsH	1.510
	HAsAs	94.6
As_2H_2 (C_{2v}, cis)	*E*	−4469.168 811 4
	AsAs	2.225
	AsH	1.507
	HAsAs	99.0
As_2H_4 (C_2, gauche)	*E*	−4470.349 214 9
	AsAs	2.457
	HAs	1.504, 1.505
As_4H_2 (C_2, cis)	*E*	−8937.197 152 5
	AsAs	2.217, 2.483
	HAs	1.507
	HAsAs	115.2
	AsAsAs	102.0
As_4H_4 (C_2, trans)	*E*	−8938.382 770 1
	AsAs	2.462, 2.219
	AsH	1.505, 1.506
	AsAsAs	107.9
	AsAsH	93.3, 95.9
	HAsH	94.5
As_4H_6 (C_3)	*E*	−8939.561 211 2
	AsAs	2.455
	AsH	1.507
	AsAsAs	99.7
	HAsH	94.3

Table 4. Comparison of Relative Energies of $2B_6$, $3B_4$, and $6B_2$ Units for B = As, P

	rel energy, kcal/mol	
	As (752+P)	P (6-31G*)
three tetraatomic units	0	0
two hexaatomic units	+27.5 (benzvalene)	33.9 (prismane)
six diatomic units	+142.6	95.8

Relative Energies of As_2, As_4, and As_6

The relative energies of $6As_2$, $3As_4$, and $2As_6$ are compared to previous results for phosphorus in Table 4. Although the hazards of comparisons of relative energies obtained from limited basis sets and without corrections for electron correlation are appreciated,[29,33,34] the two sets of results are qualitatively similar. For both arsenic and phosphorus, the two hexaatomic units (benzvalene was taken for As_6, prismane for P_6) lie ~30 kcal/mol above the energy of three tetraatomic units while that of six diatomic units is far above. The high energy of the diatomic units can be rationalized by the bond additivity model; P≡P and As≡As triple bonds are much weaker than 3 times the average energies of their respective single bonds.

Strain Energies of As_4 and As_6

We have previously employed homodesmotic reactions which preserve bond type and immediate bond environment to ascertain strain energies in homoatomic clusters.[12,35] Equation 1 shows the homodesmotic reaction for As_4. The AsAsAs bond angles in As_4 are severely distorted from expected valence angles and therefore we expect As_4 to be destabilized by strain. Each arsenic atom in As_4 has an immediate environment of three single bonds to other arsenic atoms. In As_4H_6, the central arsenic atom is

---

(29) As_2H_2: Omstead, T. R.; Annapragada, A. V.; Jensen, K. F. *Appl. Phys. Lett.* **1990**, *57*, 2543.

(30) As_2H_4: Jolly, W. L.; Anderson, L. B.; Beltrami, R. T. *J. Am. Chem. Soc.* **1957**, *79*, 2443.

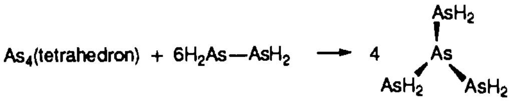
(31) PH_3: Helms, D. A.; Gordy, W. *J. Mol. Spectrosc.* **1977**, *66*, 206. McRae, G. A.; Gerry, M. C. L.; Cohen, E. A. *J. Mol. Spectrosc.* **1986**, *116*, 58.

(32) AsH_3: Helminger, P.; Beeson, E. L., Jr.; Gordy, W. *Phys. Rev.* **1971**, *43*, 122. Olson, W. B.; Maki, A. G.; Sams, R. L. *J. Mol. Spectrosc.* **1975**, *55*, 252. Helms, D. A.; Gordy, W. *J. Mol. Spectrosc.* **1978**, *69*, 473. Carlotti, M.; DiLonardo, G.; Fusina, L. *J. Mol. Spectrosc.* **1983**, *102*, 310.

(33) Raghavachari, K. *J. Chem. Phys.* **1986**, *84*, 5672.

(34) Raghavachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191.

(35) Gimarc, B. M.; Warren, D. S. *Inorg. Chem.* **1993**, *32*, 1850.



$$\mathrm{As_4(tetrahedron)} + 6\mathrm{H_2As{-}AsH_2} \rightarrow 4\ \mathrm{As(AsH_2)_3} \qquad (1)$$

bonded through single bonds to three other arsenic atoms. Each arsenic atom in As_2H_4 is bonded to two hydrogens and one arsenic atom, and a similar arrangement holds for each terminal arsenic in the As_4H_6 product. A central assumption of this model is that the AsAsAs bond angle in As_4H_6 is not strained and any deviation from that angle shows up as strain energy. Since the numbers of different types of bonds are conserved, the energy change from the bond additivity model must be zero. The relief of strain energy is expected to be exothermic ($\Delta E < 0$). From eq 1 and energies in Table 3

$$\Delta E = 4E(\mathrm{As_4H_6}) - E(\mathrm{As_4}, T_d) - 6E(\mathrm{As_2H_4}) = -12.6\ \mathrm{kcal/mol}$$

There are no experimental data to compare with this result, but this strain energy is slightly lower than comparable estimates for strain energy in P_4 (20 kcal/mol calculated, 20–34 kcal/mol experimental).[36,37] The expected trend of lower strain energies with respect to bond angle distortions is borne out here. Equations 2–5 are homodesmotic reactions involving four of the As_6 isomers.

$$\mathrm{As_6(prismane)} + 9\mathrm{As_2H_4} \rightarrow 6\mathrm{As_4H_6} \qquad (2)$$

$$\mathrm{As_6(benzvalene)} + 7\mathrm{As_2H_4} \rightarrow \mathrm{H_2As{-}As{=}As{-}AsH_2} + 4\mathrm{As_4H_6} \qquad (3)$$

$$\mathrm{As_6(Dewar\ benzene)} + 5\mathrm{As_2H_4} \rightarrow 2\mathrm{As_4H_4} + 2\mathrm{As_4H_6} \qquad (4)$$

$$\mathrm{As_6(bicyclopropenyl)} + 5\mathrm{As_2H_4} \rightarrow 2\mathrm{As_4H_4} + 2\mathrm{As_4H_6} \qquad (5)$$

Equation 6 is the arsenic analog to Nagase and Ito's equation[38] used for the calculation of the resonance stabilization energy of

$$\mathrm{As_6(benzene)} + 3\mathrm{H{-}As{=}As{-}H(cis)} \rightarrow 3\mathrm{H{-}As{=}As{-}As{=}As{-}H(all\ cis)} \qquad (6)$$

planar hexagonal P_6. Table 5 contains the strain or resonance energies calculated for the As_6 valence isomers of benzene along with the calculated results for P_6, As_4, and P_4. Our results show that eqs 2–5 are exothermic, indicating that strain is a destabilizing effect. The calculated negative energy changes for these reactions are reported in Table 5 as positive strain energies. Equation 6 turns out to be endothermic, indicating that planar hexagonal As_6 is stabilized by resonance. The calculated positive energy change for eq 6 is reported as a negative strain (or resonance) energy. Qualitatively the trends are similar although the arsnic clusters show much lower strain energies. Strain energies for the arsenic clusters are nearly half of the phosphorus values, with Dewar benzene standing out as having almost no strain at all. Interestingly, the resonance stabilization energy is slightly larger for the As_6 planar hexagon (17.4 kcal/mol) than for the P_6 planar hexagon (14.9 kcal/mol).

Table 5. Strain/Resonance Energies for Valence-Isomeric Structures of As_6 and P_6 and Tetrahedral As_4 and P_4

structure	strain/resonance energy, kcal/mol As (752+P)[a]	 P (6-31G*)[b]
prismane	32.7	52.9
benzvalene	12.4	20.8
Dewar benzene	2.2	13.1
bicyclopropenyl	7.4	15.7
benzene	−17.4	−14.9
tetrahedron	12.6	19.7

[a] This work. [b] Reference 12.

The relative energies of the As_6 valence isomers of benzene without strain destabilization or resonance stabilization are shown in Table 6. The differences in energies among the structures are now only the differences between having two single bonds or one double bond in the structure. The difference between the all-single-bonded prismane and the one-double-bonded benzvalene is found to be 26 kcal/mol, identical to the value found for P_6 and close to the value of 25 kcal/mol found for C_6H_6. The difference between the benzvalene and Dewar benzene/bicyclopropenyl structures is again just the difference between two single bonds and one double bond, i.e. 26 kcal/mol. The planar hexagon structure does not fit the pattern; but, this structure is not truly made of three single and three double bonds. The relative energy of the unstrained As_6 planar hexagon (96 kcal/mol) is the same as that for the P_6 planar hexagon. The above results can be used with the experimental bond dissociation energy for the As—As single bond to obtain an estimate of 60 kcal/mol for the bond dissociation energy of an As═As double bond:

$$2D(\mathrm{As{-}As}) - D(\mathrm{As{=}As}) = 26$$

$$D(\mathrm{As{=}As}) = 2D(\mathrm{As{-}As}) - 26 = 2 \times 43 - 26 = 60\ \mathrm{kcal/mol}$$

Table 7 compares the bond dissociation energies of HC—CH, N—N, P—P, and As—As. The bond dissociation energies of the P═P and As═As double bonds are from our calculations. The other numbers are experimental values. The expected trends are observed, with the arsenic bonds being less stable than the phosphorus bonds. Phosphorus and arsenic are similar to carbon in that the double bond energy is less than twice the energy of the single bond. Nitrogen's single bond energy is so small that two single bonds are not favored over one double bond.[39] In an excellent review of chemical bonding in higher main-group elements, Kutzelnigg gives estimates for P═P and As═As double bonds.[40] His value of 82 kcal/mol for P═P is essentially identical to our 84 kcal/mol result. However, for arsenic, Kutzelnigg proposes 42 and 29 kcal/mol as σ- and π-increments, respectively, for AsAs bonds. For the As═As double bond, the increments sum to 71 kcal/mol, uncomfortably larger than our estimate of 60 kcal/mol for As═As. Comparing energy differences between single, double, and triple bonds among PP bonds and AsAs bonds (Table 7), we feel that our 60 kcal/mol result for As═As more closely matches the position of P═P between single and triple bonds, while Kutzelnigg's 71 kcal/mol estimate for As═As seems to be too large.

Figure 3 compares the energies of the As_6 structures as calculated directly with those of the hypothetical structures that are not destabilized by strain or stabilized by resonance. The relative energies of the hypothetical unstrained or non-resonance-stabilized structures are basically established by the bond additivity model, with higher energies given to structures with larger numbers of double bonds. The prismane structure, with the relatively large strain energy of 32.7 kcal/mol, is elevated to an energy comparable to that of benzvalene, which, at the hypothetical level, is 26 kcal/mol higher than that of prismane. Resonance stabilization lowers the energy of the planar hexagon, but not enough to put it within the range of the other structures. Introduction of resonance and strain energies to the hypothetical structures compresses their energies from a spread of almost 100

---

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

(37) Pauling, L.; Simonetta, M. *J. Chem. Phys.* **1952**, *20*, 29.

(38) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43.

(39) Foner, S. N.; Hudson, R. L. *J. Chem. Phys.* **1978**, *68*, 3162.

(40) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(41) Zimmerman, J. A.; Bach, S. B. H.; Watson, C. H.; and Eyler, J. R. *J. Phys. Chem.* **1991**, *95*, 98.

Table 6. Relative Energies, Strain Energies, Resonance Energies, and Hypothetical Unstrained Non-Resonance-Stabilized Energies (kcal/mol) for As_6 and Comparisons with C_6H_6 and P_6 (6-31G* Energies)

	 1	 2	 3	 4	 5
	As_6				
rel energy (A)	45.6	5.6	21.3	0	26.4
strain or resonance energy (B)	−17.4	+12.4	+2.2	+32.7	+7.4
unstrained or non-resonance-stabilized energy ($A - B$)	+63.0	−6.8	+19.1	−32.7	+19.0
renormalized energy ($A - B + 32.7$)	+95.7	+25.9	+51.8	0	+51.7
	P_6				
	95.7	25.6	51.3	0	51.2
	C_6H_6				
	56.1	24.9	48.8	0	50.6

Table 7. Comparison of Bond Dissociation Energies[a]

bond type	bond energy, kcal/mol carbon	nitrogen	phosphorus	arsenic
single	85	38	55	43
double	146	128	84[b]	60[c]
triple	200	226	125	91

[a] Reference 35, except as noted. [b] Reference 12. [c] This work.

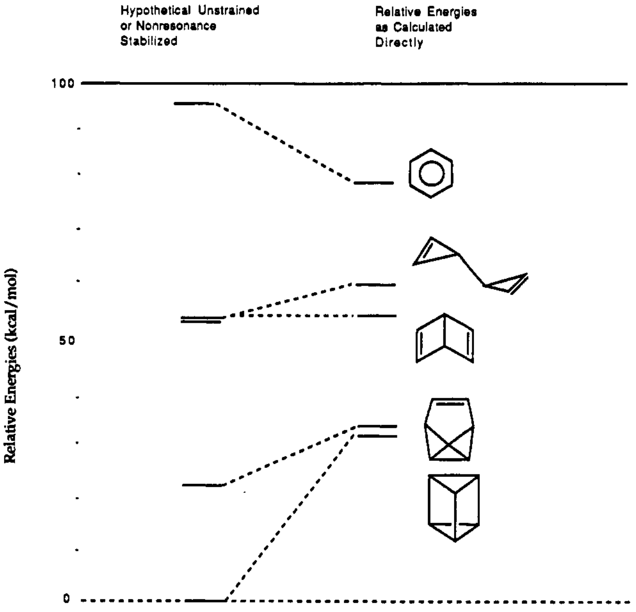


Figure 3. Relative energies of As_6 structures as calculated directly compared with energies of hypothetical structures relieved of calculated strain energies or deprived of resonance energy.

kcal/mol to a range of around 45 kcal/mol. The range of energies among As_6 isomers is larger than that among comparable P_6 isomers because of lower strain energies for the arsenic molecules.

In earlier work on P_8 clusters, we used the ring strain additivity rule, known to operate approximately in the chemistry of hydrocarbons,[42–45] to decompose the strain energies of polycyclic clusters into energies of individual rings.[35] Here we apply the additivity rule to arsenic clusters. The calculated strain energy of tetrahedral As_4 is 12.6 kcal/mol. Since the tetrahedron has four triangular faces, the strain energy of each triangular face must be 12.6/4 = 3.2 kcal/mol. The trigonal prism **4** consists of three square faces and two triangular faces. If As_6 prismane has a strain energy of 32.7 kcal/mol, the strain energy of a square As ring can be approximated by

$\square = \frac{1}{3}\Big[$  $-2\ (\triangle)\Big] = \frac{1}{3}\Big[32.7-2(3.2)\Big] = 8.8$ kcal/mol

Thus, the strain energy of a four-membered As ring is significantly larger than that of the three-membered ring. This result is contrary to what one would expect on opening bond angles from 60 to 90°, but it is in accord with what we found for P_3 and P_4, for which strain energies are estimated to be 4.9 and 12.6 kcal/mol, respectively.[35] In further studies of inorganic rings, we found that the four-membered rings O_4 and S_4 have larger strain energies than do the smaller O_3 and S_3 rings.[46,47]

Ionization Energy and HOMO-LUMO Gap

Figure 4 shows the energies of the HOMO and LUMO for the As_6 valence isomers of benzene as calculated with the 752+P basis set. The energy of the HOMO approximates the ionization potential of the molecule according to Koopmans' theorem. While there are no experimental values to compare with those calculated for the As_6 molecules, there are experimental values for As_4 and As_2.[41] These values are compared in Table 8, along with previous results for P_4 and P_2 (with the 6-31G* basis set). Except for those for As_2, the calculated results follow the trend that calculated values are usually larger than experimental values for ionization potentials.

Charge Distributions

Mulliken net atom populations as calculated are shown in Figure 5. Symmetry requires that all atoms in the planar hexagon and the triangular prism have the same charge density. The As_6 results uniformly show less charge separation than the P_6 results. The benzvalene results even show a reversal for arsenic, placing the positively charged sites adjacent to each other.

The hardness in a chemical system can be approximated by[48–50]

$$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2$$

Table 9 contains the calculated hardness values for the P_6 and As_6 valence isomers of benzene.[51] For all structures, the phosphorus systems are chemically harder than the arsenic systems. Just how basis set dependent these trends are has not been explored. However, these trends match the expected periodic relationship between phosphorus and arsenic. Arsenic with more diffuse, higher energy, valence atomic orbitals has less tendency than phosphorus to attract electron density in a bonding situation.

---

(42) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125.
(43) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.
(44) Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.
(45) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.
(46) Zhao, M.; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4023.
(47) Warren, D. S.; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4031.
(48) Pearson, R. G. *J. Mol. Struct. (THEOCHEM)* **1992**, *255*, 261.
(49) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283.
(50) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1992**, *131*, 1854.
(51) Warren, D. S.; Gimarc, B. M. *Int. J. Quantum Chem.*, in press.

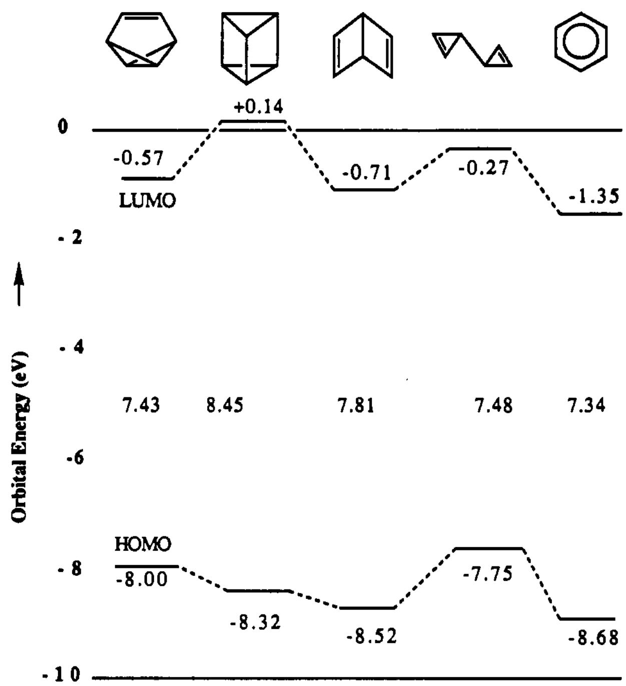


Figure 4. HOMO and LUMO energies and the size of the HOMO–LUMO gaps in As_6 isomeric structures as calculated with the 752+P basis set.

Table 8. Experimental and Calculated (6-31G*) Ionization Potentials for P_2 and P_4 and for As_2 and As_4 (752+P)

structure	ionization potential, eV	
	exptl[a]	calcd (ϵ_{HOMO})
P_2	10.6	9.84
P_4 (T_d)	9.23–9.28	9.93
As_2	9.89	9.38
As_4 (T_d)	8.63	8.92

[a] Reference 40.

This is revealed throughout this comparison by weaker bonds, less strain energy, and lower charge separation for the arsenic valence isomers of benzene compared with their phosphorus counterparts.

Conclusion

Geometry-optimized ab initio SCF–MO calculations for neutral As_6 in the forms of the valence isomers of benzene show that the benzvalene and prismane structures are the lowest in overall energy. The planar hexagon is the highest energy isomer. The energies of the As_6 clusters span a range of 45 kcal/mol, compared to 30–45 kcal/mol for P_6 and 120–130 kcal/mol for $(CH)_6$. Optimized bond distances for the valence isomers generally compare favorably with experimental bond distances.

For the lowest energy As_6 structure, $2As_6$ is only 28 kcal/mol higher in energy than $3As_4$ and 115 kcal/mol lower in energy than $6As_2$. HOMO–LUMO gaps are uniformly less than their P_6 counterparts by about 1/2 eV. Charge distributions for the less symmetric structures, as determined by Mulliken net atom populations, are more nearly uniform than their P_6 analogs and are qualitatively different in the case of benzvalene.

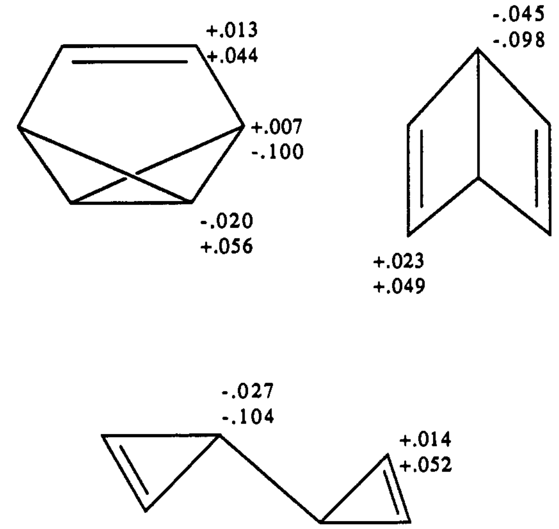


Figure 5. Mulliken net atom populations as calculated for As_6 in benzvalene, Dewar benzene, and bicyclopropenyl structures using the 752+P basis set. In each stack, the top number is the result for As_6 and the bottom number for each site is for P_6. Symmetry requires zero charges at all sites in the planar hexagon and triangular prism structures.

Table 9. Hardness of the P_6 and As_6 Valence Isomers of Benzene (hartrees)

structure	hardness, η	
	P_6	As_6
trigonal prism	0.169 56	0.155 32
benzvalene	0.147 72	0.136 57
Dewar benzene	0.155 05	0.143 48
bicyclopropenyl	0.147 33	0.137 44
planar hexagon	0.149 66	0.134 83

Homodesmotic reactions were used to estimate strain energies for As_4 and for the nonhexagonal As_6 valence isomers of benzene. The resonance stabilization energy of the planar hexagon was determined using a homodesmotic reaction similar to the P_6 reaction used by Nagase and Ito. The strain energy of tetrahedral As_4 was calculated to be 12.6 kcal/mol, slightly less than the tetrahedral P_4 strain energy of 20 kcal/mol. The strain energies of the As_6 structures range from a high of 33 kcal/mol for prismane to a low of only 2 kcal/mol for Dewar benzene. These strain energies are nearly half of their corresponding P_6 strain energies, which in turn are far lower than strain energies of the C_6H_6 analogs. The resonance stabilization energy of the As_6 planar hexagon (17.4 kcal/mol) is found to be slightly greater than the P_6 stabilization energy (14.9 kcal/mol). Subtracting out strain energies and adding in stabilization energies adjust the relative energies of the isomers to be ordered by the number of double bonds in the structure. The average As═As double bond is less than twice as strong as the average As—As single bond. An estimate of 60 kcal/mol for the energy of the As═As double bond is obtained by our results. The relative energies of the As_6 valence isomers of benzene are only slightly altered by strain energies and resonance stabilization. The finding is comparable to our result for P_6 but is in contrast to that for the $(CH)_6$ isomers. Weaker bonds, smaller strain energies, and lower charge densities are properties that are consistent with the fact that valence AO's of larger principal quantum number are more diffuse.

Acknowledgment. We thank Dr. Gustavo E. Scuseria for providing the 752+P basis set for arsenic. 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.