of each complex ion to one of four possible excitations, $\pi(X) \rightarrow \sim 6s$ (Hg) or $\rightarrow \sim 6p$ (Hg). The interpretation of the MCD data narrows this to either the $^1T_2{}^B[3t_2{}^5t_2{}^*]$ or $^1T_2{}^C[e^3t_2{}^*]$ excited states, or $\pi(X) \rightarrow \sim 6p(Hg)$. The higher energy intense band of $[HgI_4]^{2-}$ was also observed, and because of its positive *A* term it is assigned to $^1T_2{}^C$ or $^1T_2{}^B$.

Registry No. $[HgCl_4]^{2-}$, 14024-34-1; $[HgBr_4]^{2-}$, 15906-07-7; $[HgI_4]^{2-}$, 14876-64-3; $(NMe_4)_2[HgI_4]$, 33615-18-8.

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Contribution from the Quantum Chemistry Group, Uppsala University, 751 20 Uppsala 1, Sweden,
and from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Theoretical Study of the Chair–Boat Conformational Barrier in *cyclo*-Hexasulfur

ZELEK S. HERMAN[1a] and KARL WEISS*[1b]

Received October 2, 1974 AIC40684Y

CNDO/2 molecular orbital calculations predict that the boat form of *cyclo*-hexasulfur exists and that its potential energy is ca. 4 kcal/mol less than that of the chair form which is found in the rhombohedral crystal. The interconversion has a barrier of 23 kcal/mol and is not forbidden by symmetry rules. A Mulliken population analysis provides a picture of the bonding in *cyclo*-hexasulfur which is consistent with thermodynamic data.

Introduction

The stereochemistry of polysulfides is a topic of continuing interest.[2] In the case of elemental sulfur, the cyclic forms S_n, n = 6, 8, and 12, are well-known and have been structurally characterized by X-ray methods.[3] Since it is the most stable form both in the crystal and in the vapor below 100°, most attention has been focused on S_8 from both the experimental and the theoretical points of view.

One problem which has received only fleeting attention is that of ring inversion and structural isomerism in sulfur rings. *cyclo*-Hexasulfur is of greatest interest since, for this compound, a chair–boat interconversion can be envisioned. It has a chair conformation in the crystal. In comparing the conformational stabilities of cyclohexanes with those of polythianes it is found that the ease of ring inversion and flexibility decrease.[4] For pentathiane, a compound which resembles *cyclo*-hexasulfur, a conformational change has been observed at elevated temperature by NMR measurements.[5]

In this paper we examine the chair–boat interconversion of *cyclo*-hexasulfur by means of theoretical calculations. Previous calculations on sulfur ring compounds including *cyclo*-hexasulfur[6–8] have been primarily concerned with the participation of sulfur 3d orbitals in bonding and with spectral properties. The conformations of cyclic sulfur rings have also been studied from purely geometrical[9] and thermodynamic[10] points of view. We have chosen the all-valence electron CNDO/2 method[11] to establish the possible stability of the boat conformer of *cyclo*-hexasulfur, to estimate the inversion barrier, and to assay bonding relationships with the aid of a Mulliken overlap population analysis.[12]

Calculations

The CNDO/2 version employed is based on the parametrization of Santry[13] modified[14] to ensure invariance to molecular rotation. The basis set includes sulfur 3d orbitals. To accomplish the overlap population analysis,[12] the CNDO basis orbitals, which are orthogonal in the zero differential overlap approximation, are transformed into a nonorthogonal set.[15] This procedure provides overlap populations in test cases involving molecules of first-row atoms which are in good agreement with the results of ab initio calculations.

The bond lengths and bond angles of *cyclo*-hexasulfur used in this work are those determined experimentally[16] (sulfur–sulfur distance 2.057 Å, S–S–S bond angle 102.2°). To investigate the various conformations encountered in the chair–boat interconversion, only the angle ϕ (cf. Figure 1) was varied. The bond lengths were kept constant since the CNDO/2 method appears to be most successful when experimental geometries are utilized.[17]

Results

(a) Energy Surface and Inversion Barrier. In Figure 2 the nuclear energy and electronic energy are plotted as a function of the bending angle ϕ. The curves were, in each case, obtained from the 13 calculated points using a standard interpolation procedure.[18] Nuclear energy refers to the nuclear–nuclear repulsion energy of all the sulfur nuclei within the Born–Oppenheimer approximation, while electronic energy refers to the sum of the electronic kinetic energy, the electronic–electronic repulsion energy, and the electronic–nuclear attraction energy. The total energy is the sum of the nuclear and electronic energies since relativistic effects are neglected in the CNDO/2 approximation.

While the nuclear energy and electronic energy vary considerably as a function of the angle ϕ, their sum is very nearly constant (Figure 2). The strong angular dependence of these energy components can be understood in terms of the variation of the internuclear distances and overlaps for the

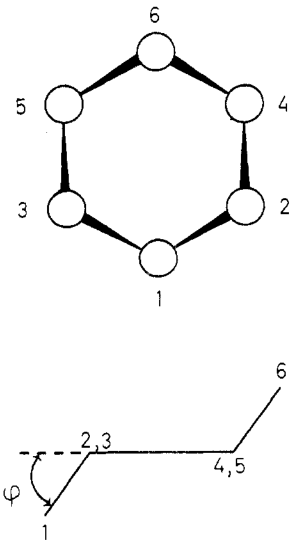

Figure 1. Top and side views of *cyclo*-hexasulfur in the D_{3d} conformation. The bending angle ϕ is determined by planes defined by nuclei 123 and 2345, with negative values signifying counterclockwise rotation. For the chair form ($\phi > 0°$, C_{2v} symmetry), the independent bond angles are angles 123, 465 (α_1) and 124, 246, 356, 135 (α_2).

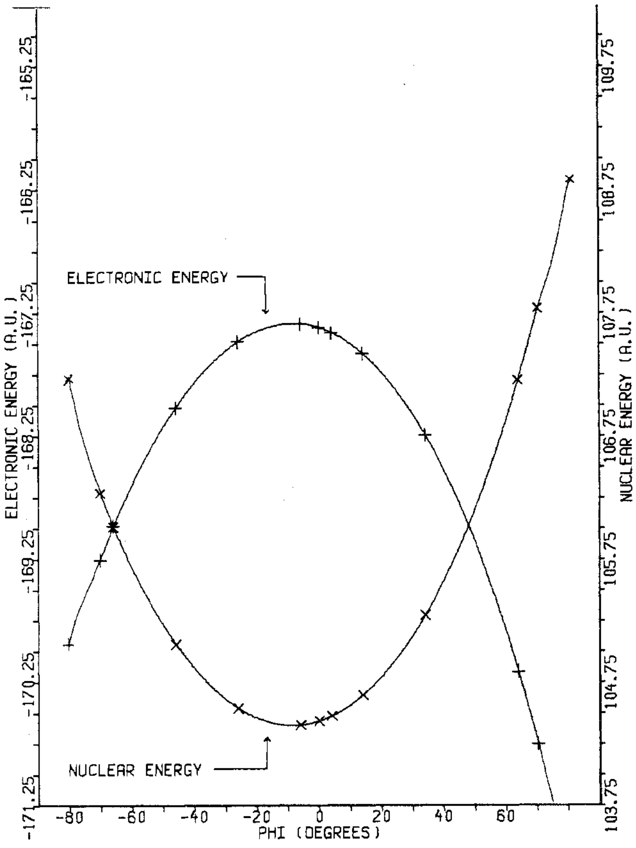

Figure 2. Electronic energy and nuclear energy of *cyclo*-hexasulfur as a function of the bending angle ϕ.

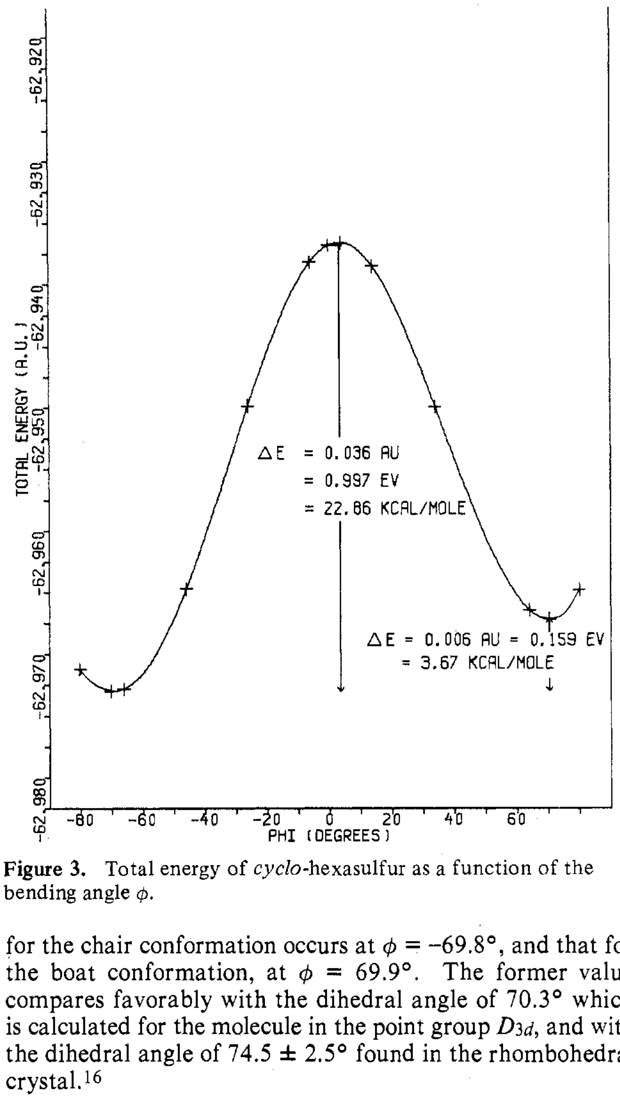

Figure 3. Total energy of *cyclo*-hexasulfur as a function of the bending angle ϕ.

different conformations. The electronic energy has a maximum value at $\phi = -8.4°$, while the nuclear energy has a minimum value for $\phi = -8.9°$.

The total energy as a function of the bending angle ϕ is shown in Figure 3. The chair and boat conformations are calculated to have nearly the same energy, the chair conformer being only 3.67 kcal/mol more stable than the boat conformer. The potential barrier for the chair–boat transformation, which corresponds to $\phi = 3.4°$, is 22.86 kcal/mol. The minimum for the chair conformation occurs at $\phi = -69.8°$, and that for the boat conformation, at $\phi = 69.9°$. The former value compares favorably with the dihedral angle of 70.3° which is calculated for the molecule in the point group D_{3d}, and with the dihedral angle of 74.5 ± 2.5° found in the rhombohedral crystal.[16]

Additional calculations for the chair (D_{3d}) and boat (C_{2v}) forms in which the S–S–S bond angles α (Figure 1) were varied show that the energies obtained with the constant experimental angle $\alpha = 102.2°$ are within less than 0.11 kcal/mol of those for optimized α values.[19] For the chair form, the energy minimum (−62.970539 au) occurs at $\alpha = 102.5°$ which, compared with −62.970526 au for $\alpha = 102.2°$, corresponds to an energy difference of 0.008 kcal/mol. For the boat form, the energies are −62.964849 au (minimum) with $\alpha_1 = 103.3°$ and $\alpha_2 = 103.0°$ and −62.964673 au with $\alpha_1 = \alpha_2 = 102.2°$, which differ by 0.11 kcal/mol. Distorted chair-like and boat-like conformations of C_s symmetry invariably have higher energies than the corresponding symmetrical forms. These results give an energy difference of 3.57 kcal/mol for the boat and chair forms with optimized bond angles. Since, with constant $\alpha = 102.2°$, this energy difference is 3.67 kcal/mol, they indicate that variation of only one angle (ϕ) provides a valid description of the interconversion process.

(b) Bonding. The results of overlap population calculations for *cyclo*-hexasulfur and H_2S_2 are presented in Table I. The latter compound is included for comparison since ab initio results are available for it. For H_2S_2 we see that the S–S bond overlap population obtained by the deorthogonalized CNDO/2 method is in good agreement with the results of an ab initio calculation in which sulfur 3d orbitals are included in the basis set.[20] Compared with an ab initio calculation in which these orbitals are excluded,[21] the CNDO/2 method provides populations which are 25–35% smaller. The trends in the various bond populations are, however, reproduced by the

Table I. Overlap Populations for *cyclo*-Hexasulfur and H_2S_2

		Overlap population		
			Ab initio	
Compd	Bond	Present work	Ref 20^b	Ref 21^c
H_2S_2^{a}	H–S	0.516		0.658
	S–S	0.291	0.304	0.449
	H–S′	−0.044		−0.057
	H–H′	0.000		0.000
cyclo-S_6 (chair)	S(1)–S(2)	0.222		
	S(1)–S(4)	−0.052		
	S(1)–S(6)	−0.003		
cyclo-S_6 (boat)	S(1)–S(2)	0.228		
	S(1)–S(4)	−0.032		
	S(1)–S(6)	−0.146		
	S(2)–S(4)	0.192		
	S(2)–S(3)	−0.055		
	S(2)–S(5)	−0.003		

^{a} R_{SS} = 2.055 Å, R_{SH} = 1.327 Å, ∠H–S–S = 91.32°, dihedral angle = 90.0°. The primes distinguish equivalent atoms. ^{b} Dihedral angle = 90.75°. The basis set includes sulfur 3d orbitals. ^{c} The basis set does not include sulfur 3d orbitals.

CNDO/2 calculation. On the basis of these findings, the results for the two *cyclo*-hexasulfur conformations are considered to provide meaningful information about the bonding in this compound.

Discussion

The calculations predict a stable boat conformation of *cyclo*-hexasulfur and, as expected, that the chair conformation has a lower energy. The barrier to interconversion is computed to be 22.9 kcal/mol. The energy difference of 3.7 kcal/mol for the two forms corresponds to a Boltzmann factor of only 1.013 at 150°.

Unfortunately, no experimental findings for *cyclo*-hexasulfur exist with which the results of the calculations can be compared. It can be noted that the chair-to-boat form barrier is substantially larger than the torsional barrier for sulfur–sulfur bonds in disulfides, which is in the range 3–15 kcal/mol.[10] For the chair-to-boat interconversion of cyclohexane, an energy difference of ca. 6 kcal/mol for the two conformers and a potential barrier of 11 kcal/mol have been reported.[22-24] While these values are similar in magnitude to those calculated for *cyclo*-hexasulfur, the two cases are not strictly comparable owing to the nonbonded interactions which are operative in the eclipsing of the hydrogen atoms during the cyclohexane transformation.

A detailed analysis of a Walsh-type[25] diagram for the molecular orbital energies as a function of the dihedral angle ϕ shows that the transformation of the chair form of D_{3d} symmetry to the boat form of C_{2v} symmetry is not accompanied by attempted crossings between occupied and unoccupied molecular orbitals of correlated symmetry. Consequently, the interconversion may be considered as symmetry allowed from the point of view of the Woodward–Hoffmann rules,[26] and the barrier is not symmetry imposed. The magnitude of the barrier is certainly consistent with this conclusion.

Figure 2 reveals that the nuclear energy and electronic energy vary substantially more (ca. 3 au (1800 kcal/mol)) with angle ϕ than does the total energy. As shown, the nuclear energy decreases as the angle ϕ approaches 0°, while the electronic energy increases, and the near cancelation of these components then produces the relatively small (23 kcal/mol) barrier for interconversion. The decrease in nuclear energy is readily understood in terms of the changing interatomic distances, as is the concomitant increase in electronic energy, which is largely due to enhanced electron–electron repulsion. Since symmetry factors are not operative (vide supra), the barrier can be viewed as arising from these repulsive interactions.

The population analysis provides further insight into the bonding relationships in the two conformers. In the case of the chair form, the internuclear separation between the second nearest neighbors (3.20 Å) is considerably less than the sum of the van der Waals radii of two sulfur atoms (3.70 Å[27]), so appreciable repulsive contact can be expected. Indeed, the overlap population for these atoms is negative (Table I) and indicative of an antibonding interaction. The overlap population for atoms 1 and 6 (Figure 1) is very small and negative, so that the interaction is clearly nonbonding. In the boat form, where all the sulfur–sulfur bonds are no longer equivalent, we find the second nearest neighbor overlap populations to be different for the 1–4 and 2–3 interactions. The former is slightly less antibonding than it is for the chair form, while the latter is essentially unchanged. The largest difference in overlap populations appears between atoms 1 and 6, for which the interaction is now strongly antibonding (−0.146 vs. −0.003 in the chair form). The interaction between atoms 2 and 5 in the boat form is the same as that between the most remote atom pairs in the chair form.

With respect to adjacent atoms, one interaction in the boat form is distinctly less bonding than it is in the chair form (overlap population 0.192 vs. 0.222). This difference is likely to be even larger if a slight change in the bond distances is taken into account. It has been noted that the molecular total overlap population, which is the sum of all atom-pair overlap populations in a molecule, is a maximum where the total calculated energy is a minimum.[28,29] In the case of *cyclo*-hexasulfur we indeed find that the molecular total overlap population is smaller for the less stable boat conformer (0.905) than it is for the chair conformer (1.015). This decreased total molecular bonding index, taken in conjunction with a smaller bond overlap population for some S–S bonds, may mean that the boat form is more prone to bond scission than the chair form. Moreover, the greater reactivity of *cyclo*-S_6 than that of *cyclo*-S_8 in certain reactions[30] may be partly due to the transformation of the former into its more labile boat conformation.

We have also calculated the sulfur–sulfur overlap population for nearest neighbors to be 0.207 for *cyclo*-octasulfur. Thus, the order of bond populations is H_2S_2 > *cyclo*-hexasulfur (chair) > *cyclo*-octasulfur. In essential agreement with this order we find the estimated sulfur–sulfur bond energies for these compounds to be close (within less than 2 kcal/mol of each other), with the bond energy for H_2S_2 (63.2 kcal/mol) larger than that for *cyclo*-hexasulfur (61.5 kcal/mol).[31]

In summary, our calculations predict that *cyclo*-hexasulfur (boat) can exist and that, as expected, it is less stable than the chair conformer. The interconversion between the conformers, which is not symmetry forbidden in the Woodward–Hoffmann sense, is apparently not associated with an excessively large barrier.

Acknowledgment. We wish to thank the members, past and present, of the Quantum Chemistry Group at Uppsala University for stimulating discussions pertaining to this work. We also thank one of the referees for suggestions regarding the effect of bond angle variations on the energy of the conformers. Financial support by a John G. Bergquist Grant of the American-Scandinavian Foundation (Z.S.H.) and a grant from the Gulf Oil Corp. (K.W.) is gratefully acknowledged.

Registry No. *cyclo*-Hexasulfur, 13798-23-7.

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Contribution from the Department of Chemistry, University of California,
and the Inorganic Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Evidence for Hyperconjugation from an X-Ray Photoelectron Spectroscopic Study of Isoelectronic Compounds

STEVEN C. AVANZINO, WILLIAM L. JOLLY,* MARC S. LAZARUS, WINFIELD B. PERRY,
RICHARD R. RIETZ, and THEODORE F. SCHAAF

Received October 23, 1974 AIC40735R

The shifts in core electron binding energies of oxygen, chlorine, and carbon atoms in some gaseous isoelectronic isostructural compounds can be readily explained in terms of simple trends in atomic charges. However the fluorine 1s binding energies for some fluoro compounds of silicon, phosphorus, sulfur, and chlorine show unusual shifts which suggest that hyperconjugation is important in the bonding of these compounds.

We have measured atomic core electron binding energies for several series of isoelectronic, isostructural compounds in the gas phase. Isoelectronic compounds were chosen for study because of the probability that the nature of the bonding in such compounds changes in a fairly systematic way with changes in the atomic numbers of the atoms in a given series of compounds. A core binding energy can be accurately represented as a linear function of three quantities: the atomic charge, the electrostatic potential due to the other atoms of the molecule, and the electronic relaxation energy.[1] To a good approximation, the electronic relaxation energy for an atom of a particular element in a series of isoelectronic, isostructural compounds can be assumed to be constant.[2] Therefore chemical shifts in binding energy can be ascribed to changes in atomic charge and changes in potential. We shall make minimal use of estimated atomic charges in our interpretations; hence our conclusions should be relatively free of the weaknesses and assumptions of theoretical methods for estimating atomic charges.

Consider the tetracovalent phosphorus compounds listed in Table I. We may imagine this series of compounds to be generated by the stepwise transfer of the three protons in the BH_3 group of $P(CH_3)_3{\cdot}BH_3$ to the boron nucleus of that molecule. Each step increases the electronegativity of the group attached to the $P(CH_3)_3$ group and causes the atomic charge of the phosphorus atom to increase. The effect of this trend in atomic charges can be seen in the phosphorus $2p_{3/2}$ binding energies, which increase on going from $P(CH_3)_3{\cdot}BH_3$ to $P(CH_3)_3O$. The methyl groups are relatively remote from the changing atoms; hence the corresponding carbon 1s binding energies are less affected, and no significant trend in their values can be seen.

Table I. Phosphorus $2p_{3/2}$ and Carbon 1s Binding Energies

	E_B, eV	
Compd	P $2p_{3/2}$	C 1s
$P(CH_3)_3{\cdot}BH_3$	137.00	290.79
$P(CH_3)_3CH_2$	137.03	290.40
$P(CH_3)_3NH$	137.39	290.63
$P(CH_3)_3O$	137.63	290.57

Next consider the five series of isoelectronic compounds listed in Table II. In the first four series, halogen atoms or methyl groups are replaced stepwise with oxygen atoms as the atomic number of the central atom is increased stepwise. The last series of compounds may be looked upon as the compounds generated by the stepwise transfer of protons from one of the fluorine nuclei of SiF_4 to the silicon nucleus of that molecule. We believe it is reasonable to assume that, on progressing down through any one of the five series, the charge of the central atom increases.[3] This increase in charge, coupled with the decrease in size, of the central atom would be expected to cause increased electron withdrawal from a given type of ligand atom. Hence the increase in the charge of the central atom is probably responsible for the observed corresponding increase in the oxygen, chlorine, and carbon binding energies within each series.

Notice, however, that the fluorine 1s binding energies do not follow the simple predicted trend. In both the fourth and fifth series, the fluorine 1s binding energies increase to a maximum value and then decrease. We believe that the increase between SiF_4 and POF_3 is caused by the dominating effect of the increased positive charge and electronegativity of the central atom. The decrease in fluorine binding energy between SO_2F_2 and ClO_3F and between POF_3 and SNF_3 is