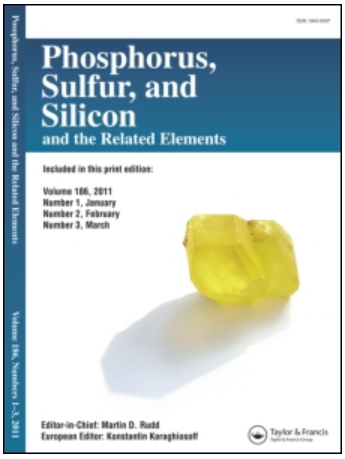

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Pentagon Stability in Cycloarsanes

Jing Ma[a]; Atsushi Hozaki[b]; Satoshi Inagaki[b]
[a] Department of Chemistry, Nanjing University, Nanjing, P. R. China [b] Department of Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan

Online publication date: 27 October 2010

To cite this Article Ma, Jing , Hozaki, Atsushi and Inagaki, Satoshi(2002) 'Pentagon Stability in Cycloarsanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1705 — 1708
To link to this Article: DOI: 10.1080/10426500212314
URL: http://dx.doi.org/10.1080/10426500212314

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1705–1708

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290093388

PENTAGON STABILITY IN CYCLOARSANES

Jing Ma,[a] *Atsushi Hozaki,*[b] *and Satoshi Inagaki*[b]
Department of Chemistry, Nanjing University, Nanjing, P. R. China[a] *and Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu, Japan*[b]

(Received August 7, 2001; accepted December 25, 2001)

The orbital phase theory leads to the prediction that the saturated arsenic cyclic molecules prefer pentagons, which is substantiated by the negative strain energy of cyclic As_5H_5. The puckered five-membered arsenic ring is an important structural unit for the pentagon stability. Possible structures and conformers of polycycloarsanes As_8H_4, $As_{11}H_3$, "roof-like" and "cage-like" $As_{12}H_4$, $As_{13}H_3$, $As_{14}H_2$, and $As_{15}H_3$ with relatively low strain energies were predicted due to many puckered pentagon units in them. The low stability of the dodecahedron As_{20} with 12 planar pentagon units was suggested by the high strain energy.

Keywords: Arsenic ring compounds; orbital phase; strain energy

INTRODUCTION

The orbital phase theory[1,2] has been developed over the past 25 years into a useful tool for providing insights into various molecular properties and reaction mechanisms and for understanding the known experimental results and designing new experiments. The continuity-discontinuity of the orbital phase was shown to underlie the cyclic conjugated systems, i.e., the Hückel rule for the aromaticity and the Woodward-Hoffmann rule for the pericyclic reactions. Applications were recently made to the unusually short distance between the silicon atoms in disilaoxiranes and 1,3-cyclodisiloxanes[3] and to the geminal bond participation in organic reactions.[4] The orbital phase theory was also applied to propose the pentagon stability in cyclophophanes.[5] Cyclic delocalization of the lone pair electrons on the five-membered ring atoms through the vicinal σ bonds was shown to be favored by the orbital phase properties. The bond model analysis and calculated strain energies substantiated the significant pentagon stability of P_5H_5.[5] Then

Acknowledgment is made to Chinese Education Ministry for the financial support.

a question arises: *does the pentagon stability still hold for arsenic rings?* Here, we will answer this question by examining the relative stability between the five- **1** and six-membered **2** arsenic rings. Finally, the concept of the pentagonal stability is employed to design some potential polycycloarsanes, As_8H_4 **3**, $As_{11}H_3$ **4**, "roof-like" **5** and "cage-like" **6** $As_{12}H_4$, $As_{13}H_3$ **7**, $As_{14}H_2$ **8**, and $As_{15}H_3$ **9**, and to discuss the possibility of the existence of the dodecahedral cluster As_{20} **10**.

ORBITAL PHASE PREDICTION

Electron delocalizations in cyclic conjugated systems involve the cyclic interaction of orbitals. The delocalization is under the control of the orbital phase property. The orbital phase continuity requirement[1] is the simultaneous satisfaction of the following conditions: (1) the electron-donating orbitals are out of phase; (2) the accepting orbitals are in phase; (3) the donating and accepting orbitals are in phase. If the conditions are satisfied or the orbital phase is continuous, the delocalization takes place effectively, and consequently the system is stabilized. Recently, we have demonstrated that cyclic delocalization of lone pair electrons of phosphorus on the five-membered ring through the vicinal σ bonds, i.e., cyclic (n, σ^*, σ^*) interaction in cyclopentaphosphane, is favored by the phase continuity.[5] The similar cyclic (n, σ^*, σ^*) interaction is also expected to exist in pentagonal arsane as displayed in Figure 1. The electron-donating orbital n, can be in phase with the both of the accepting orbitals σ^*, and the accepting orbitals σ^* can be in phase with each other at the same time, as is required. Thus it can be anticipated that saturated cyclic arsenic molecules prefer pentagons.

PENTAGON STABILITY: EVIDENCE FROM STRAIN ENERGY

The orbital phase continuity suggests low strain energies of arsenic pentagon. Homodesmotic reactions[6] are employed to evaluate the strain energies of mono- and polycyclic arsanes. The optimized most

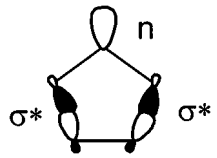

FIGURE 1 The cyclic orbital interaction in the saturated pentagon ring.

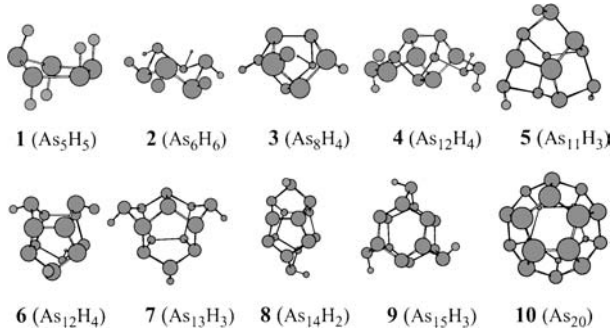

FIGURE 2 The most stable conformations of arsenic ring compounds.

stable structures of all the studied cycloarsanes **1–10** are depicted in Figure 2. The strain energy of As_5H_5 **1** is surprisingly found to be *negative* (−2.01 kcal/mol at HF/LanL2DZ + p, −2.80 kcal/mol at B3LYP/6-311G**, −2.56 kcal/mol at MP2/6-311G**). The hexagonal As_6H_6 **2** has larger strain energy (3.76 kcal/mol at HF/LanL2DZ + p, 1.12 kcal/mol at B3LYP/6-311G**, 0.55 kcal/mol at MP2/6-311G**) than the pentagon, which substantiates the orbital phase prediction of pentagon stability. In Figure 2, the most favorable structure of As_5H_5 **1** is puckered, in which the cyclic (n, σ^*, σ^*) interaction is most effective, as was previously demonstrated for cyclopentaphosphane.[5] The puckered structure should be important for the pentagonal stability.

In contrast to the rich family of polycyclophosphanes,[7] polycyclic arsanes are still hardly known.[8] Here, we design some novel polycyclic molecules **3–9** composed of puckered arsenic pentagons as shown in Figure 2. We calculate the strain energies of those polycycloarsanes at HF/LanL2DZ + p level and list the results in Table I, since the HF/LanL2DZ + p calculations produce strain energies close to those from B3LYP and MP2 with 6-311G** basis but with less computational cost. As_8H_4 **3** and "roof-like" $As_{12}H_4$ **5**, arsenic analogous to the structural units of Hittorf's phosphorus, as well as "ufosan" $As_{11}H_3$ **4** are predicted to have very low strain energies of 0.99, −3.15, and −2.32 kcal/mol, respectively. A little higher strain energies of

TABLE I Strain Energies (SE, in Units of kcal/mol) of Polycycloarsanes Calculated at the RHF/LanL2DZ + p

Molecules	SE	Molecules	SE	Molecules	SE
As_8H_4 **3**	0.99	$As_{12}H_4$ **6**	7.03	$As_{15}H_3$ **9**	20.54
$As_{11}H_3$ **4**	−2.32	$As_{13}H_3$ **7**	4.64	As_{20} **10**	81.46
$As_{12}H_4$ **5**	−3.15	$As_{14}H_2$ **8**	4.96		

"cage-like" $As_{12}H_4$ **6**, $As_{13}H_3$ **7**, $As_{14}H_2$ **8**, and $As_{15}H_3$ **9** are obtained, which increases in the order of $As_{13}H_3$ **7** < $As_{14}H_2$ **8** < $As_{12}H_4$ **6** < $As_{15}H_3$ **9** in strain energies. There was a similar relative order in the corresponding polycyclophosphanes. Hence, the same reason based on the concept of pentagon stability as that addressed for phosphanes[5] can be applied to rationalize the strain energies of polycyclic arsanes. Analogous to the dodecahedron P_{20}, the low stability of As_{20} **10** was suggested by the high strain energy of 81.46 kcal/mol due to its planar pentagon units.

REFERENCES

[1] K. Fukui and S. Inagaki, *J. Am. Chem. Soc*., **97,** 4445 (1975).
[2] S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc*., **98,** 4693 (1976).
[3] J. Ma and S. Inagaki, *J. Phys. Chem. A*, **104,** 8989 (2000).
[4] H. Ikeda, T. Kato, and S. Inagaki, *Chem. Lett*., 270 (2001).
[5] J. Ma, A. Hozaki, and S. Inagaki, *Inorg. Chem.*, **41,** 1876 (2002).
[6] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron*, **32,** 317 (1976).
[7] M. Baudler and K. Glinka, *Chem. Rev*., **93,** 1623 (1993).
[8] M. Baudler and S. Wietfeldt-Haltenhoff, *Angew. Chem. Int. Ed. Engl*., **24,** 991 (1985).