

Ring strain energies of tetraphospha- and tetraarsacubanes

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Abstract

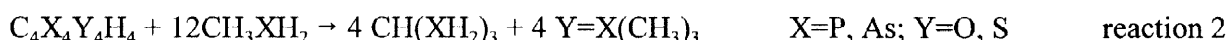
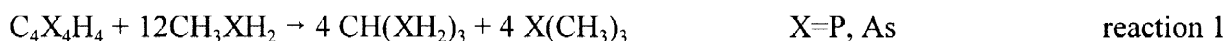
The ring strain energies of tetraphosphacubane and tetraarsacubane, along with their tetraoxide and tetrasulfide derivatives, were estimated at the MP2/6-31G* and MP2/LANL2DZ levels. The parents exhibit small strain energies, while the strain energy is quite large in the oxides and sulfides. These results are interpreted in terms of the hybridization at the heteroatom. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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The Platonic solids remain a dominant theme in synthetic chemistry, millennia after their elucidation in solid geometry. A highlight in the history of synthetic chemistry was the preparation of cubane by Eaton 1964.^{1,2} In recent years, we have seen the synthesis of heterosubstituted cubanes; of interest here will be the cubanes containing four phosphorus or arsenic atoms.^{3,4} Of the many interesting theoretical and chemical properties of cube-like structures, the ring strain energy (RSE) of these compounds has commanded central attention. The contraction of bond angles at the atoms occupying the corners in order to construct the cube demands a substantially destabilized system. In fact, the RSE of cubane is 690.8 kJ/mol, an extraordinarily high value.⁵ A few years ago we estimated that the RSE of tetraphosphacubane is only 262.9 kJ/mol, arguing that the substantial reduction in RSE relative to cubane is attributable to the ability of phosphorus to accommodate small bond angles.⁶ In this article, we extend the study of RSE to the arsenic analogue, along with their tetraoxide and tetrasulfide derivatives using *ab initio* calculations.

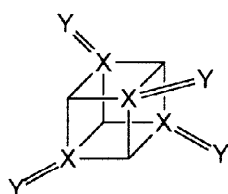
The first tetraphosphacubane was prepared by thermal tetramerization of *t*-butylphosphaethyne.³ An improved synthetic method involves catalytic cyclooligimerization of the phosphaethyne in the presence of bis(cyclopentadienyl)zirconium chloride.^{7,8} The tetraoxide is prepared by oxidation of tetraphosphacubane with bis(trimethylsilyl)peroxide and the tetrasulfide is synthesized by reaction with sulfur and triethylamine.^{9,10} Tetramerization of *t*-butylarsaethyne with a cobalt catalyst produces tetra-*t*-butyl-tetraarsacubane.⁴

Ring strain energy is obtained by comparison of the energy of the strained system with unstrained analogue(s). An effective method for this is accomplished using the group equivalent reaction.¹¹ The group equivalent reactions for evaluating the ring strain energy of tetraphosphacubane **1** and tetraarsacubane **2**, their tetraoxides (**1o** and **2o**), and their tetrasulfides (**1s** and **2s**) are given in reactions 1-2.



The structure of all phosphorus-containing compounds in reactions 1 and 2 were completely optimized at the HF/6-31G* and confirmed to be local energy minima via analytical frequency analysis. The cubanes were optimized within the C_{2v} point group, though each converged to a T_d structure. The structures were reoptimized at the MP2/6-31G* level, with only minor changes in the geometrical parameters observed. Finally, energies were obtained by adding to the MP2 results the HF zero-point vibrational energy (ZPE) scaled by 0.9646. The arsenic-containing compounds were optimized at the HF and MP2 levels using the LANL2DZ basis set, which includes an effective core for arsenic, supplemented with polarization functions on all heavy atoms. The arscubanes also optimized to T_d geometries, though only C_{2v} symmetry was enforced. Analytical frequency analysis is not available within the program employed (GAUSSIAN-94¹²) for systems where an effective core potential is utilized.

Geometric parameters of the optimized structures of the tetraphospha- and tetraarsacubanes are listed in Table 1. The calculated geometries are in good agreement with the two experimental structures, which are the crystal structures of the tetra-*t*-butyl derivatives of **1**³ and **2**.⁴ Some trends for the angles at the corner atoms are worth noting. The angle at C in cubane is 90°. Substitution of the heteroatom allows this angle to expand; all of the cubanes examined here have angles at C greater than 90°. The angle is widest in the parent, contracts in the sulfide, and is smallest in the oxide. The angles at the heteroatom are smaller than 90° and vary in a similar pattern as substitution occurs, except that the angle expands in the oxide and sulfide. In addition, the angles at C are wider in the arsenic analogues than in the phosphacubanes.



- 1**: X = P **2**: X = As
1o: X=P, Y=O **2o**: X=As, Y=O
1s: X=P, Y=S **2s**: X=As, Y=S

Table 1

Relevant distances (Å) and angles (deg) in the MP2/6-31G* Optimized Structures of 1-2.

	1		1o	1s
	calc	expt. [3] ^a		
r(C-P)	1.896	1.881	1.868	1.877
r(P-X)			1.494	1.911
a(C-P-C)	83.8	85.6	87.7	87.3
a(P-C-P)	95.9	94.4	92.3	92.6
	2		2o	2s
	calc.	expt. [4] ^a		
r(C-As)	2.027	2.012	2.007	2.009
r(As-X)			1.625	2.025
a(C-As-C)	83.2	83.9	86.9	86.0
a(As-C-As)	96.5	95.8	93.1	93.8

^aX-ray structure of the tetra-*t*-butyl derivative.

We have argued that the low RSE of **1** can be largely attributable to the ability of P to accommodate small bond angles, allowing the angles at C to expand and thereby reduce their strain.^{6,13-16} The changes in bond angles upon oxidation or sulfination, whether of **1** or **2**, suggest greater strain at C and the heteroatom. Further, the arsenic compounds should be less strained than the phosphacubanes.

Our previous estimate of the RSE of **1** was 262.9 kJ/mol, evaluated at HF/6-31G*.⁶ We list in Table 2 the RSE for **1** and **2** evaluated as described above. While only small changes in geometry were observed in reoptimization of **1** at MP2 from HF, its RSE increased by 50 kJ/mol. It should also be noted that the correction for ZPE has not been made for the arsenacubanes; this correction amounts to 30-40 kJ/mol in the phosphacubanes, so that the RSE reported in Table 2 for the arsenic compounds should be further reduced by approximately this amount. The parent tetraaracubane **2**, therefore, has a relatively small RSE of about 240 kJ/mol, approximately 450 kJ/mol less strained than cubane.

Table 2
RSE (kJ/mol) of **1-2**.

compound	RSE	compound	RSE
1	312.9	2	288.0
1o	474.9	2o	461.7
1s	438.2	2s	395.9

As predicted by the degree of bond angle deviation from 90°, the arsenacubanes are less strained than the phosphacubanes. Further, the sulfides are more strained than the parents, and the oxides further strained still. What then determines the bond angles and therefore the strain in these molecules?

Angle strain results from a distortion from the standard angle. The typical angle at an sp³ carbon is 109.5°, while trivalent P and As compounds have angles near 90°. Substitution of these heteroatoms for carbon typically reduces the RSE of a cyclic molecule for two reasons. First, the heteroatoms better accommodate the small angle than carbon. Second, the substitution usually allows the angles at any remaining carbons to widen and be less strained. This is observed in both the phosphacubanes: the angle at C is larger in **1** and **2** than in cubane, thanks to the small angle at P and As. In the oxides, the angles at P and As increase, accompanied by a contraction at C that leads to a large increase in RSE. The sulfides, slightly less strained than the oxides, have wider angles at C and smaller angles at the heteroatom than in the oxides.

The basis for this argument lies in maximizing the overlap of hybrid orbitals on adjacent atoms. The cubane bond angles are best accommodated by hybrids that are 90° apart, such as pure p orbitals. Natural bond orbital (NBO) analysis provides a direct means for obtaining the hybridization of an atom in a molecule.¹⁷⁻¹⁹ These hybrids for the C-P and C-As bonds are listed in Table 3.

Table 3
NBO Hybrids

compound	C hybrid	P hybrid	compound		
			d	C hybrid	As hybrid
1	sp ^{3.40}	sp ^{6.65}	2	sp ^{3.40}	sp ^{6.21}
1o	sp ^{3.45}	sp ^{3.33}	2o	sp ^{3.54}	sp ^{3.47}
1s	sp ^{3.38}	sp ^{2.5} d ^{1.15}	2s	sp ^{3.46}	sp ^{2.44} d ^{1.17}

The hybridization of C in all of these cubanes is nearly equivalent. The p-character is slightly larger in the oxides than in the others, suggesting perhaps less strain, but that is not what is observed in the RSE trends.

The hybridization at P and As changes dramatically with the substituent. In the parent cases, both P and As have large p-character in the bonds to C, thereby using a hybrid that is well-suited for overlapping with atoms 90° apart, leading to little strain at these atoms. Since the small angles here allow the angles at carbon to widen, thereby reducing the strain at these atoms, the overall strain for **1** and **2** is very small.

The hybridization at P and As in the two sulfides is about $sp^{2.5}d^{1.1}$. This hybridization best accommodates angles greater than 90° and thus results in an increased RSE relative to the parents. Lastly, the hybridization at P and As in the oxides is about $sp^{3.4}$, similar to the hybridization at C. These hybrids poorly accommodate the narrow angle of a cube structure, leading to wider angles at the heteroatom, smaller angles at carbon, and an overall larger RSE.

In summary, the ring strain energies of the parent tetraphosphacubane and tetraarsacubanes are unusually small. These compounds are likely to be very stable to ring rupture. On the other hand, their tetraoxide and tetrasulfide derivatives are very strained. The degree of strain can be simply understood in terms of hybridization at the heteroatom and how best these fit the small angles of a cube compound. We note that Bent's analysis of atomic hybridization qualitatively explains these results.²⁰

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