

Ring Strain Energy of Tetrphosphacubane. An Ab Initio Study.

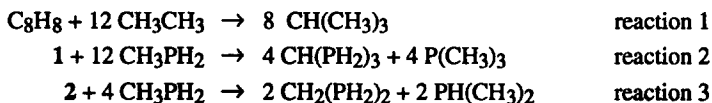
Steven M. Bachrach* and Laureta M. Perriott

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115

Abstract: The structure of tetrphosphacubane was optimized at the HF/6-31G* level. The small ring strain energy of tetrphosphacubane (62.84 kcal mol⁻¹) is understood in terms of geometric parameters and charge distribution.

Tetra-*tert*-butyltetrphosphacubane was first prepared in 1989 by the tetramerization of *tert*-butylphosphaethyne.¹ The crystal structure of this novel compound was reported and confirmed to be a distorted cube structure. Continuing our theoretical study of organophosphorus compounds, particularly the ring strain energy (RSE) of phosphorus-substituted small rings,² we report here an ab initio calculation of the RSE of the parent compound, tetrphosphacubane **1**, which is compared to the RSE of cubane and 1,2,3,4-tetrahydro-1,3-diphosphate **2**.

Ring strain cannot be uniquely defined, but can generally be related to the energy difference between the ring and unstrained analogues. In this work, we use the group equivalent reaction to evaluate the RSE.³ The RSE of cubane, using reaction 1 and experimental heats of formation, is 165.1 kcal mol⁻¹.⁴ The group equivalent reactions needed to evaluate the RSE of tetrphosphacubane and 1,3-diphosphacyclobutane are reactions 2 and 3, respectively.



The structures of all of the compounds in reactions 2 and 3 were completely optimized at the HF/6-31G* level using GAUSSIAN-90.⁵ Our previous studies of organophosphorus compounds indicate that this computational level is sufficient for obtaining geometries in excellent agreement with experiment.⁶ Further, RSE is little affected by inclusion of electron correlation through MP2.² Although the optimization of **1** was restricted to C_{2v} symmetry, it optimized to the T_d structure. We optimized two isomers of **2** – the *trans* form **2t** which has C_s symmetry and a *cis* form **2c** which has C_{2v} symmetry. A variety of conformations of all the other compounds were explored; we have selected only the lowest energy conformation. Zero-point energies were obtained by calculating the analytical frequencies and scaling them by 0.89.

The optimized geometry of **1** is drawn in Figure 1. The C-P distance is 1.8854 Å, which compares quite favorably with the C-P distance of 1.881 Å found in the x-ray crystal structure of tetra-*tert*-butyltetrphosphacubane.¹ The structure of **1** has been optimized at HF/4-31G* and its C-P distance is longer than our structure by 0.058 Å.⁷ Unlike cubane, which has C-C-C angles of about 90°, the interior angles of **1** distort to accommodate the ability of phosphorus to form small bond angles. Our HF/6-31G* structure agrees

with the x-ray structure in that the angles about P are small (84.8° calculated, 85.6° exp.) and the angles about C expand relative to cubane to 95.0° (94.4° exp.).

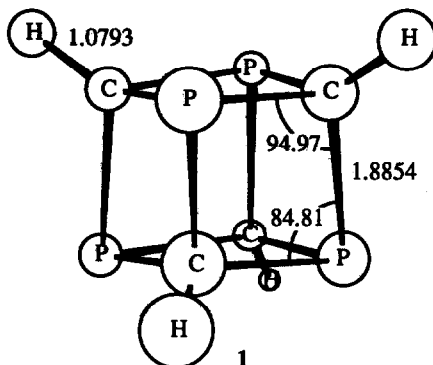


Fig. 1 Optimized geometry of **1** at HF/6-31G*. All distances in Å and all angles in deg.

The two isomers of **2** are drawn in figure 2. The *trans* isomer is $0.11 \text{ kcal mol}^{-1}$ lower in energy than the *cis* isomer, due to the decreased repulsion between the phosphorus lone pair electrons in the former. Outside of the orientation of the lone pairs, the geometries of **2c** and **2t** are very similar. The P-C distance is about 1.875 Å and the angles about P and C are 84.3 and 93.6° , respectively. Crystal structures have been obtained for substituted analogues of both **2c**⁸ and **2t**⁹. As before, the calculated structures are in excellent agreement with the experimental structures, with the C-P distances differing by less than 0.01 Å .

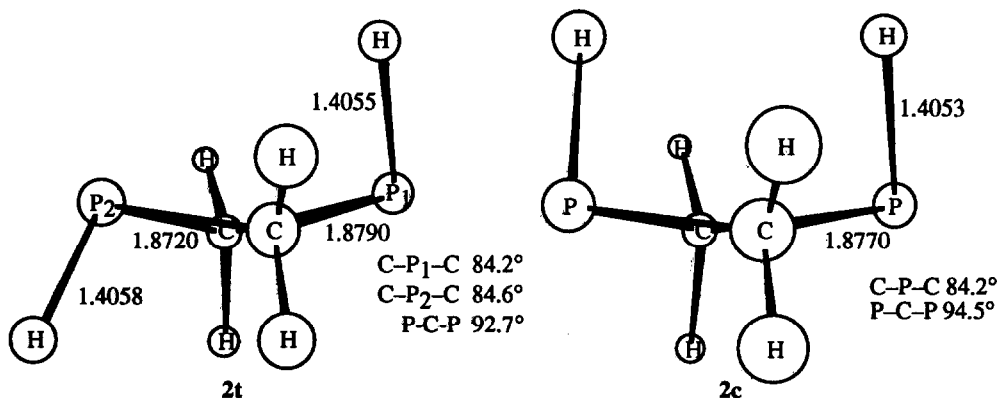


Fig. 2. Optimized geometries of **2t** and **2c** at HF/6-31G*. All distances in Å and all angles in deg.

The calculated RSEs of **1**, **2t**, and **2c** are listed in Table 1, along with some other reference compounds. We have previously noted that replacement of a carbon by a phosphorus atom in a strained ring greatly reduces the strain energy (compare cyclobutane with RSE of $26.6 \text{ kcal mol}^{-1}$ to phosphetane² having RSE of $17.9 \text{ kcal mol}^{-1}$). Not unexpectedly, we find the RSE of **2** to be smaller than either phosphetane or

cyclobutane. The slightly greater RSE of **2c** versus **2t** is due to the larger repulsive interaction of the lone pairs in the former.

Table 1. Ring Strain Energy Using Reactions 1-3.

| compound | RSE (kcal mol ⁻¹) |
|-------------|-------------------------------|
| cubane | 165.1 ^a |
| cyclobutane | 26.6 ^a |
| 1 | 62.84 ^b |
| phosphetane | 17.9 ^c |
| 2t | 12.63 ^b |
| 2c | 12.74 ^b |

^aCalculated using experimental data from Ref. 4.

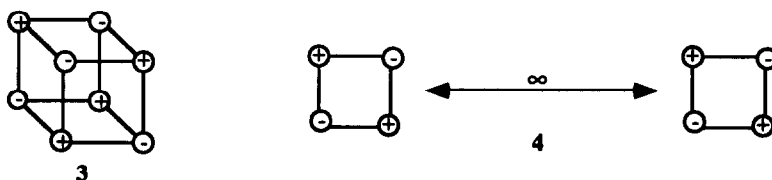
^bThis work.

^cRef. 2.

The RSE of **1** is only 62.84 kcal mol⁻¹, more than 100 kcal mol⁻¹ below that of cubane. This amazing reduction in strain energy is attributable to the ability of phosphorus to accommodate small bond angles, particularly angles near 90°, due to the high p character in its bonds. With the angles about phosphorus less than 90°, the angles about carbon expand to about 94°, thereby relieving some of the cage strain. Nagase¹⁰ has examined group IV cubane analogues, which are also less strained than cubane. Interestingly, the lead analogue Pb₃H₈ is calculated to be only 3 kcal mol⁻¹ less strained than **1**, while the other analogues are more strained than **1**.

Can the small RSE of **1** be attributed solely to the hybridization of P and larger angles about C? We examined the electron density distribution of **1** using the topological method of Bader.¹¹ The value of the electron density at the C–P bond critical point ($\rho(r_c)$) is 0.1490 e au⁻³, which corresponds to a bond order of 0.92 using the exponential relationship previously reported.^{2c} The value of $\rho(r_c)$ for the C–P bond in **2c** and **2t** is 0.1505 and 0.1514 e au⁻³, respectively. The value of $\rho(r_c)$ at any of the ring critical points of **1** is 0.0519 e au⁻³, indicating little surface electron delocalization, just as for phosphetane. The bond paths in **1** are only 0.28% longer than the internuclear distances. Therefore, the electron density distribution in **1** is very similar to the density in unstrained phosphoalkanes.

On the other hand, we can compare **1** with **2c**, in that there are six four-membered rings comprising **1**. Using this comparison, **1** is *less* strained than six molecules of **2c**. In contrast, cubane is more strained than six molecules of cyclobutane, reflecting the very narrow angles about carbon in cubane. The unusual stability of **1** may be due to charge distribution about the molecule. Based on the integrated charges of phosphoalkanes,⁶ the C–P bond is strongly polarized, with carbon bearing a negative charge and phosphorus a positive charge. The alternating charges about the cube structure of **1** is quite electrostatically favorable (see 3). This arrangement is lower in energy than two isolated structures having alternating charges in a rectangle (see 4), a model of two isolated four-membered rings. Therefore, the angle strain relief due to phosphorus does not solely contribute to the stability of **1**; the charge alternation contributes to its lack of RSE.



In conclusion, we find that tetraphosphacubane has the remarkably small ring strain energy of approximately 63 kcal mol^{-1} . The relatively small RSE of 1 can be attributed to two factors: (1) the ability of phosphorus to accommodate small angles allowing the angles about carbon to exceed 90° and (2) the high ionic character of the C-P bonds which leads to a stable electrostatic environment.

Acknowledgment is made to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(Received in USA 14 June 1993; accepted 30 July 1993)