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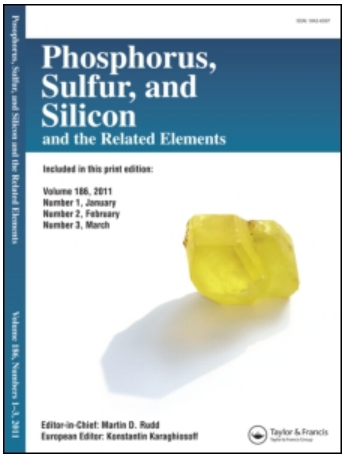

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Strain Energies of the Cyclophosphanes

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STRAIN ENERGIES OF THE CYCLOPHOSPHANES

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Abstract Strain energies of $(PH)_n$ rings, n = 3-8, are obtained from geometry optimized ab initio total energies of $(PH)_n$ rings and $H(PH)_mH$ chains. These quantities are then compared with strain energies of O_n, S_n, $(NH)_n$, $(SiH_2)_n$, and $(CH_2)_n$ rings.

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INTRODUCTION

In organic chemistry, where the concept has a long history, strain energies are known for rings of different sizes and an additivity rule allows strain energies of polycyclic systems to be estimated by summing up the strain energies of component monocycles.[1] In contrast, strain energies of inorganic rings are largely unknown. Here we report the calculation of strain energies of the cyclophosphanes, $(PH)_n$,[2,3] and compare them with values for $(NH)_n$, O_n, and S_n,[4-7] and with $(CH_2)_n$,[1] and $(SiH_2)_n$.[8]

Strain energy can be defined as the experimental energy change for a strain-releasing process compared with the energy change for the same process as obtained by a model that does not include strain. We use ab initio calculated energies to approximate experimental results and the bond additivity model as the strain-free model. Equation (1) is the s-homodesmotic reaction that converts $(PH)_n$ rings into $H(PH)_mH$ chains.

$$(PH)_n + nH(PH)_{s+1}H \rightarrow nH(PH)_{s+2}H \quad (1)$$

Energy changes can be taken as differences in ab initio calculated total energies of products and reactants. For $s \geq 0$, Equation (1) conserves numbers of P-P and P-H bonds; therefore the bond additivity model gives zero as the energy change for Equation (1). But experience leads us to expect an energy release as the ring is converted to chains, therefore the experimentally determined energy change measures the strain energy of the ring. For $s \geq 1$, Equation (1) preserves the valence environment at each atom in reactants and products, allowing some of the basis set and electron correlation errors to cancel as

differences in total energies are taken. For larger s, the PH units of the ring fit into longer chains that more adequately express the conformational preferences of an unstrained chain. Experience shows that calculated strain energies are about the same for $s \geq 1$.

CALCULATIONS

Using the GAUSSIAN 92 program package,[9] we have carried out geometry optimized ab initio calculations for reactants and products of Equation (1) at RHF and MP2 levels with the 6-31G** basis set. We chose those conformations of $(PH)_n$ rings and $H(PH)_mH$ chains that we found to have minimum energies for the comparable nitrogen systems.[7] The ring conformations are illustrated in Table I. The chains prefer to adopt helical shapes. Relative energies of the various ring and chain conformers can be rationalized

TABLE I Total energies (in hartrees) of most stable cyclophosphane conformers.

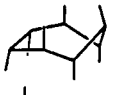
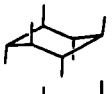
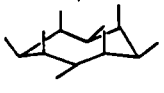
n	(PH)n	-E(RHF)	-E(MP2)
3		1023.9029129	1024.2682102
4		1365.2123275	1365.6915876
5		1706.5384639	1707.1480463
6		2047.8367958	2048.5709048
7		2389.1111983	2389.9688109
8		2730.4390919	2731.4145441

TABLE II Total energies (in hartrees) of most stable chain conformers.

m	H(PH)mH	-E(RHF)	-E(MP2)
0	H_2	1.1313335	1.1576611
1	PH_3	342.4541897	342.5901429
2	H_2PPH_2	683.7605003	684.0145790
3	$H_2P(PH)PH_2$	1025.0673833	1025.4429193
4	$H_2P(PH)_2PH_2$	1366.3737551	1366.8714071
5	$H_2P(PH)_3PH_2$	1707.6802491	1708.3003137
6	$H_2P(PH)_4PH_2$	2048.9867024	2049.7293332

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in terms of the Gauche effect.[7,10] Total energies of $(PH)_n$ rings appear in Table I; those for $H(PH)_mH$ chains are in Table II. Using these quantities to calculate energy changes for Equation (1) gives strain energies directly. Table III contains strain energies for s=0-3 for RHF and MP2 results. MP2 results are usually more reliable since they include some of the effects of electron correlation which is neglected at the RHF level. Larger values of s denote longer reference chains.

DISCUSSION

Strain energies for the cycloalkanes, $(CH_2)_n$, and for S_n rings $n \geq 5$, have been estimated using experimental thermochemical data.[1,5] Allen and coworkers have calculated the strain energies of $(SiH_2)_3$ and $(SiH_2)_4$ at the s = 1 level based on RHF/6-31G* calculated total energies for rings and chains.[8] Figure 1 shows strain energies of (a) $(CH_2)_n$ and

TABLE III Calculated strain energies of the cyclophosphanes, $(PH)_n$.

Ring Size n	Strain Energies (kcal/mol) RHF s = 0	1	2	3	MP2 s=0	1	2	3
3	10.1	11.1	10.2	10.4	3.2	10.6	10.8	11.6
4	8.1	9.5	8.3	8.6	3.9	13.7	14.0	15.1
5	-4.3	-2.5	-4.1	-3.8	-16.2	-4.0	-3.5	-2.2
6	0.7	2.8	0.9	1.4	-15.2	-0.5	0.0	1.6
7	20.7	23.2	21.0	21.5	1.4	18.6	19.2	21.0
8	7.2	10.2	7.5	8.1	-12.0	7.7	8.4	10.5

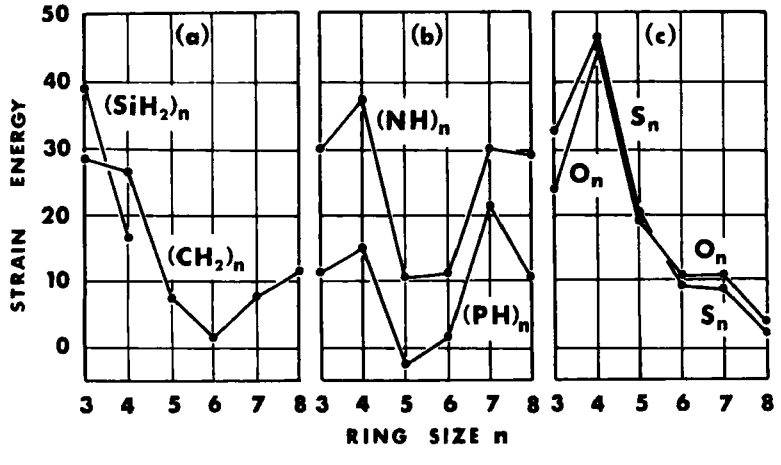

FIGURE 1 Strain energies (kcal/mol) of monocyclic structures.

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$(SiH_2)_n$, (b) $(NH)_n$ and $(PH)_n$, and (c) O_n and S_n. Compared to other monocyclic systems that have been studied, $(PH)_n$ rings have low strain energies. At n=3 compare 10 kcal/mol for $(PH)_3$ with 25 to 35 kcal/mol for $(NH)_3$, S_3, O_3, and $(CH_2)_3$. The minimum strain energy for $(PH)_n$ occurs at n=5 compared to n=5 or 6 for $(NH)_n$, n=6 for $(CH_2)_n$, and n=8 for O_n and S_n. For O_n, S_n, and $(NH)_n$, rings with n=4 are more strained than those with n=3, while for $(CH_2)_n$, the n=4 ring is slightly less strained than that with n=3. $(SiH_2)_4$ is much less strained than $(SiH_2)_3$. The $(PH)_n$ comparisons are equivocal: the n=4 ring is more strained at the MP2 level while the order is reversed for RHF results.

Although the $(PH)_n$ ring strain energies are much smaller than those of the other monocycles discussed here, they are still larger than strain energies of P_n rings deduced from the strain energy additivity rule and based on calculated strain energies of various isomeric forms of polycyclic P_4, P_6, and P_8 clusters.[11,12] Two effects might explain why the additivity rule strain energies from polycyclic clusters are smaller than those calculated directly for $(PH)_n$ rings. First, the polycyclic clusters are compared to branched reference structures which are probably slightly strained relative to the helical $H(PH)_mH$ chains that serve as reference structures for $(PH)_n$ rings. Second, the deconstruction of cluster strain energies using the ring strain additivity rule allows the effects of lone pair-lone pair interactions to be divided and apportioned among several contiguous rings.

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