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Remarkable Deprotonation Energies of Tetraphosphacubanes

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Among all of the chemical properties of cubane, perhaps the most interesting is its enhanced acidity.[1] Strain has long been known to increase carbon acidity, and has been rationalized in terms of increased s-character of the hybrid orbital used by carbon to form the bond to hydrogen.[2] Recently, Kass and Eaton were successful in experimentally determining the gas-phase deprotonation energy (DPE) of cubane.[3] The DPE of cubane is 404 ± 3 kcal mol^{-1}, which is in perfect agreement with the computational estimates. Given that phosphorus is known to stabilize adjacent carbanions,[4] and that tetraphosphacubane is a strained molecule (though substantially less strained[5] than cubane itself), we thought that it too should possess enhanced acidity. The tetraoxide and tetrasulfide tetraphosphacubanes should be even more acidic, due to the ability of the oxygen and sulfur to accept charge. We report here computational evaluations of the deprotonation energies of these compounds.

The first tetraphosphacubane was prepared by thermal tetramerization of *tert*-butylphosphaethyne.[6] An improved synthetic method involves catalytic cyclooligomerization of the phosphaethyne in the presence of bis(cyclopentadienyl)zirconium chloride.[7] The tetraoxide is prepared by oxidation of the tetraphosphacubane with bis(trimethylsilyl)peroxide and the tetrasulfide is synthesized by reaction with sulfur and triethylamine.[8] The basicity of these compounds have been explored.[9,10]

Computational estimates of carbon acidity can be very accurate as long as the following procedures are followed: polarization and diffuse functions are included in the basis set, energies are obtained at least at the MP2 level (and, preferably, geometries are optimized at this level as well), and zero-point energies are added to the electronic energies. Calculated DPEs are then usually within a couple of kcal mol^{-1} of experimental values.[11−14] Consequently, we have determined the DPE for the parent molecules tetraphosphacubane (**1**), tetraoxotetraphosphacubane (**2**), and tetrathiotetraphosphacubane (**3**) at MP2/6-31+G*//MP2/6-31+G*

with ZPE evaluated at HF/6-31+G* and scaled by 0.9646. All calculations were performed with use of GAUSSIAN-94.[15]

Optimization of the structures of **1**−**3** was carried out in C_{2v} symmetry, but each converged to T_d symmetry. Some important geometrical parameters for these compounds are listed in Table 1. The C−P distance is shorter in the oxide and sulfide than in the parent. Also, bond angles around C and P are closer to 90° in **2** and **3** than in **1**. We have previously reported that the ring strain energy of **1** is about 100 kcal mol^{-1} less than that of cubane, and argued that this reduction is primarily attributable to the larger angle about C in **1** compared to cubane.[5] The geometries of **2** and **3** suggest that they are more strained than **1**, which generally indicates enhanced acidity.

The structures of the conjugated bases of **1**−**3** (designated with a trailing **A**) were optimized by invoking C_{3v} symmetry. Analysis of the Hessian matrix confirmed that these structures are at local minima. Selected distances and angles for these three anions are listed in Table 2. The changes in the angles upon deprotonation suggest increased strain in the molecules. Even more intriguing are the changes in bond distances. The distance between the carbon formally carrying the negative charge (C_1) and the neighboring P atom shortens dramatically upon deprotonation: −0.063 Å for **1** → **1A**, −0.083 Å for **2** → **2A**, and −0.066 Å for **3** → **3A**. In addition, the P−O and P−S distances are longer in the anions than in the neutrals, including the ones across the body diagonal from the anionic carbon. These changes are suggestive of delocalization of the negative charge from C to P in **1**, and onto O and S in **2** and **3**. This delocalization should stabilize the anion and therefore lead to low DPE.

The calculated DPE of **1**−**3** are listed in Table 3. These DPEs are remarkably small (particularly the DPE of **2**) and need to be placed within a proper context.[16] Toward that end, we have calculated the DPE of four model compounds (2-methylpropane, trimethylphosphine, trimethylphosphine oxide, and trimethylphosphine sulfide) at the same level as was done for the phosphacubanes. These are also listed in Table 3. The recently measured value of the DPE of cubane in the gas phase is 404 kcal mol^{-1}.[3] The calculated DPE of **1** is 382.8 kcal mol^{-1}, similar to the DPE of methanol (381.2 kcal mol^{-1}),[17] and 21 kcal mol^{-1} less than for cubane. This reduction is comparable to the difference in the DPEs of Me$_3$CH and Me$_3$P, reflecting the ability of P to stabilize adjacent anionic charge. The calculated DPE of **3** is 328.9 kcal mol^{-1}, which is close to the DPE of *p*-nitrobenzoic acid[18] and dibromoacetic acid.[19] The difference in the DPE of **3** and **1** is slightly smaller than four times the difference in the DPEs of their unstrained models, Me$_3$P=S and Me$_3$P. Even smaller is the DPE of **2**, calculated to be 320.2 kcal mol^{-1}, which is 62 kcal mol^{-1} *lower* than for **1** and more than 80 kcal mol^{-1} lower than the DPE of cubane. Moreover, the difference in DPE between **1** and **2** is more than four times the difference between trimethylphosphine and its oxide. In fact, these calculations indicate that **2** is about as acidic as HBr[18] and nitric acid![20]

What gives rise to the remarkable acidity of the phosphacubanes? The answer resides in a number of factors. First, the

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Table 1. Selected Geometrical Parameters of **1**−**3** at MP2/6-31+G* [a]

geometrical parameters	**1**	**2**	**3**
$r(P-C)$	1.897	1.872	1.876
$r(P\cdots C)$[b]	3.276	3.241	3.248
$r(C-H)$	1.092	1.092	1.092
$r(P-X)$		1.495	1.919
$A(P-C-P)$	95.8	91.8	92.6
$A(C-P-C)$	83.8	88.2	87.4

[a] All distances are in Å and all angles are in deg. [b] Distance between the P and C along the body diagonal.

Table 2. Selected Geometrical Parameters of **1A**−**3A** at MP2/6-31+G* [a]

1A : X = lone pair
2A : X = O
3A : X = S
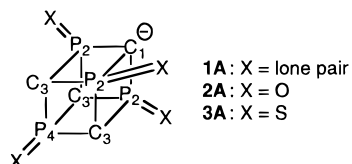
geometrical parameters	**1A**	**2A**	**3A**
$r(C_1-P_2)$	1.834	1.789	1.810
$r(C_3-P_2)$	1.912	1.884	1.885
$r(C_3-P_4)$	1.896	1.862	1.864
$r(P_2-X)$		1.506	1.939
$r(P_4-X)$		1.509	1.941
$r(C_1\cdots P_4)$	3.180	3.146	3.193
$A(P_2-C_1-P_{2'})$	96.7	93.7	92.4
$A(P_2-C_3-P_{2'})$	92.3	87.6	87.7
$A(C_3-P_2-C_3)$	89.3	89.2	88.2
$A(C_3-P_4-C_{3'})$	86.8	90.6	89.5

[a] All distances are in Å and all angles are in deg.

Table 3. DPEs (kcal mol^{-1}) of **1**−**3** and Model Compounds at MP2/6-31+G* + ZPE(HF/6-31+G*)

compd	DPE	compd	DPE
1	382.85	Me$_3$P	389.70
2	320.22	Me$_3$P=O	378.89
3	328.91	Me$_3$P=S	372.89
Me$_3$CH	412.44		

s-character leads to higher acidity, though the s-character here is not enough to produce the dramatically low DPEs.

The acidity is largely attributable to significant charge delocalization in the anion, leading to a very stable carbanion. The C−P bond is quite polar, with essentially a full negative charge on C and a full positive charge on P, as determined by either the topological method[23] or natural population analysis (NPA). According to NPA, each P atom gains 0.08 e when the proton is lost from **1** and 0.04 e when the proton is lost from **2**. In addition, **2A** is stabilized by each oxygen accepting about 0.05 e. The principal charge delocalization is to S in **3A**, where each S picks up about 0.1 e, while the charge on P remains unchanged. These delocalizations are reflected in the structure of the anions, which all have very short C_1-P_2 distances and lengthened P_2-X bonds.

We should emphasize that all four O or S atoms accept electrons in the anions, even the ones remote from the anionic center. A through-space interaction between the anionic center and the P, P=O, or P=S across the cube transfers density to this remote acceptor. The contraction of this body diagonal distance in the anions relative to the parent reflects this interaction. The interaction is strongest in the oxide, where the cross cube distance is short, and more charge is transferred to this remote O than to the adjacent O atoms. This interaction is less in the sulfide, and the remote S gains less charge than the other S atoms.

Therefore, due to the ability of P and O or S to accept charge, the resulting anions of the tetraphosphacubanes are highly delocalized and stable. The delocalization of charge is more extensive in the oxide (with all P and O atoms gaining charge in the anion) than in the sulfide (where only S gains electrons), leading to the exceptionally stable oxide conjugate base. These compounds should act as strong acids, but we are unaware of any experimental studies of this activity.

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C−H bond is composed of a hybrid on C that is largely of s-character; based on natural bond order[21,22] analysis the C hybrid of the C−H bond is sp$^{2.14}$ in **1**, sp$^{2.07}$ in **2**, and sp$^{2.18}$ in **3**. Greater