

Self-assembly of hydrogen-bonded cage tetramers of phosphonic acid

I.S. Giba,^{1,2} P.M. Tolstoy^{1,*}

¹ Institute of Chemistry, St. Petersburg State University, Russia

² Department of Physics, St. Petersburg State University, Russia

* – corresponding author, peter.tolstoy@spbu.ru

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Figure S1. Temperature dependencies of low-field parts of ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra (left); ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (right) of tert-butylphosphonic acid in a mixture of $\text{CDF}_3/\text{CDF}_2\text{Cl}$.

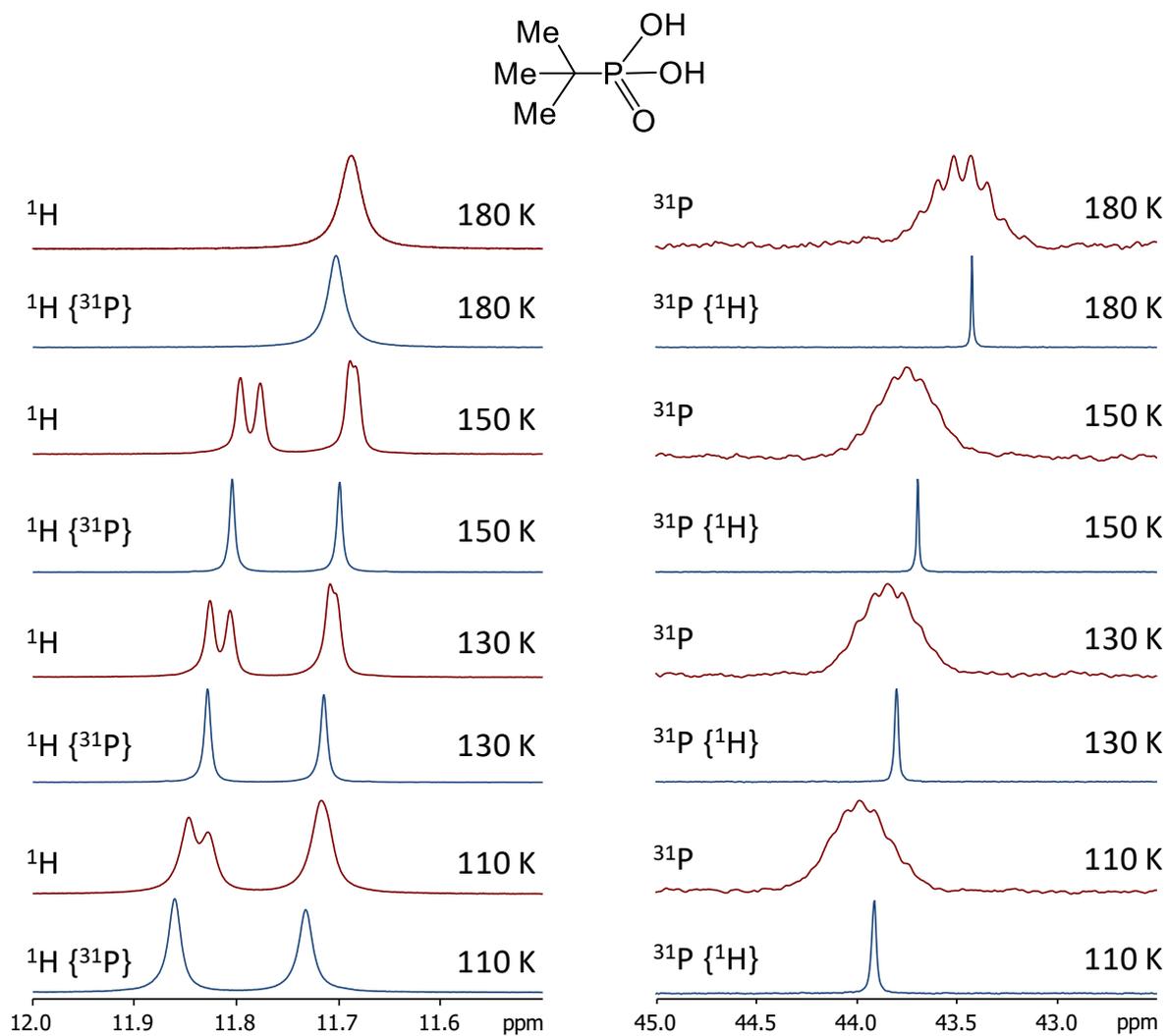


Figure S2. Unfolded papercut patterns for the assembly of the tetrahedron models showing the layout of hydrogen bonds in phosphonic acid tetramer. Orange dots at the vertices of the tetrahedra represent phosphorus atoms.

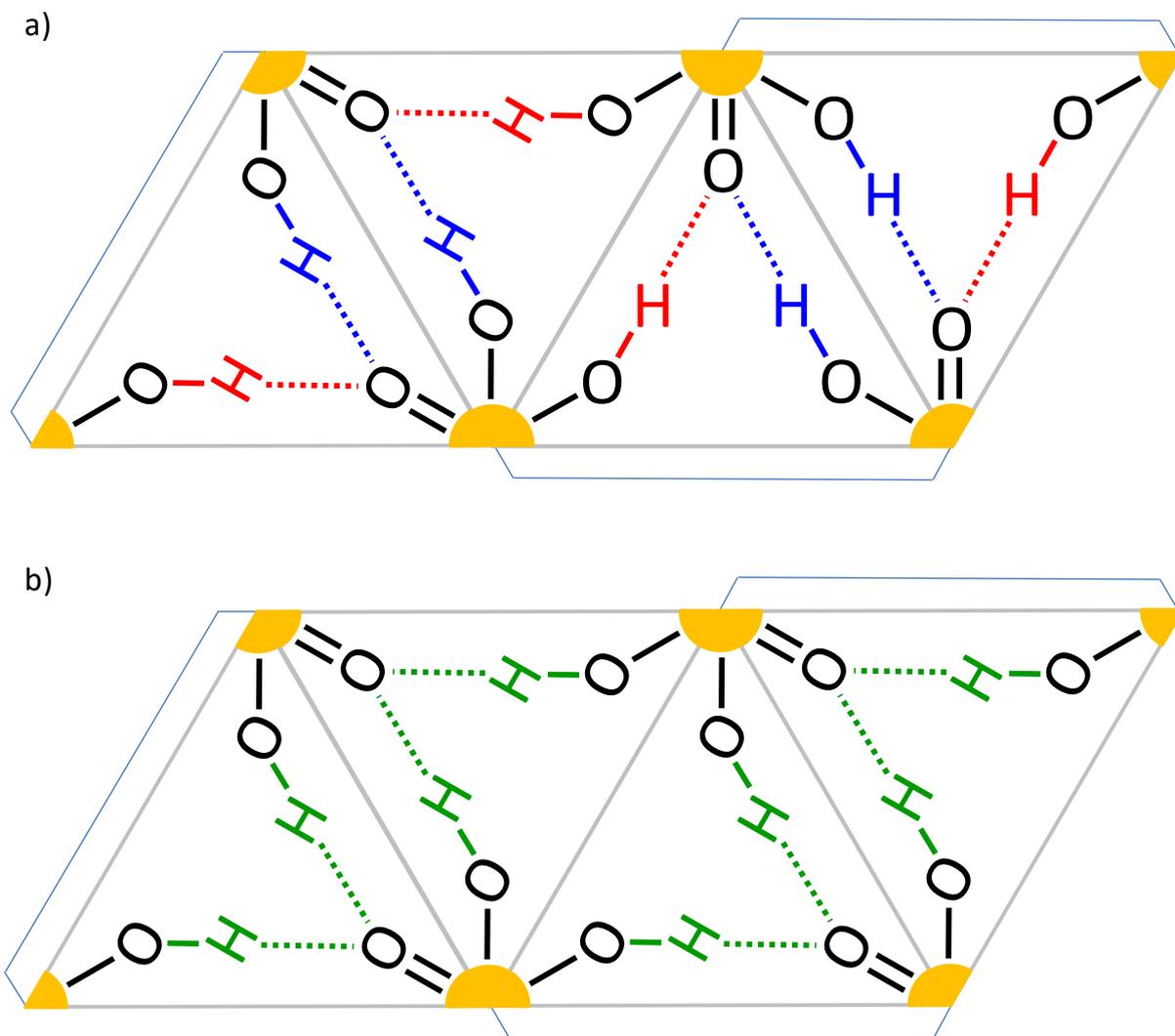
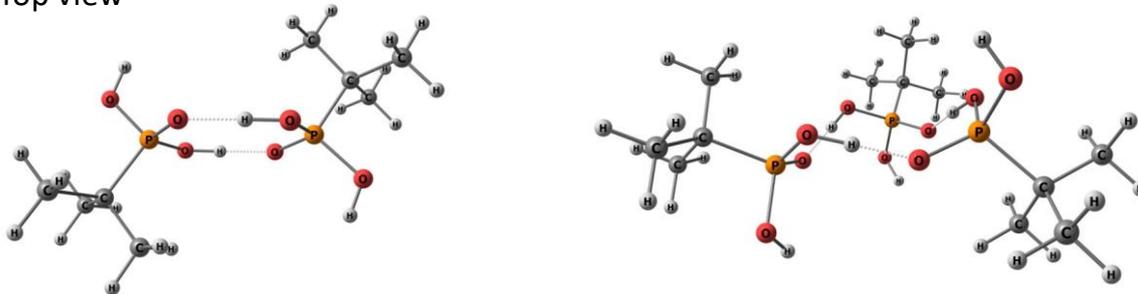
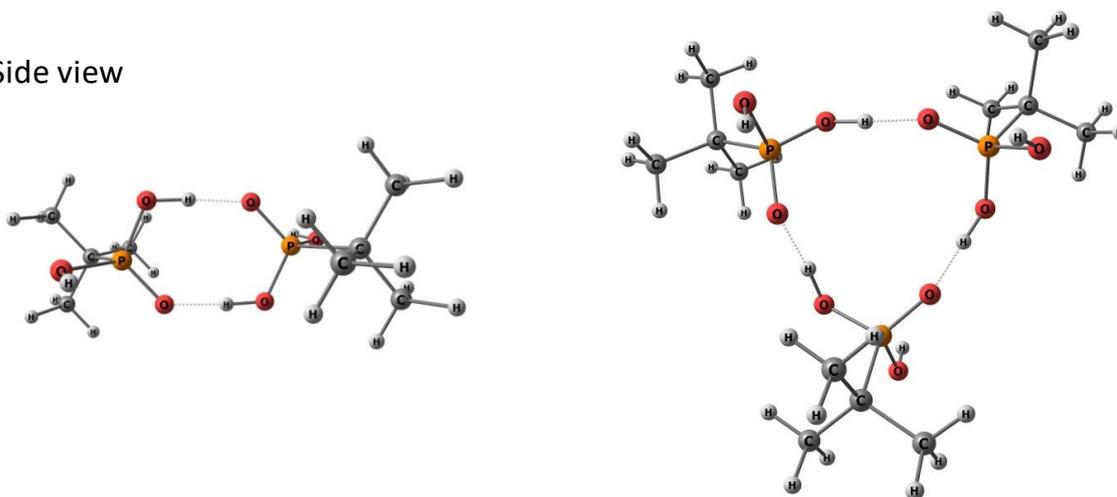


Figure S3. Two projections (a, “top view”; b “side view”) of the equilibrium structures (B3LYP/6-311++G(d,p)) of *tert*-butylphosphonic acid cyclic dimer (left) and trimer (right).

a) Top view



b) Side view



The computed structures of cyclic dimers and trimers of phosphonic, methylphosphonic and phenylphosphonic acids are similar: in each case one OH group of every acid molecule remains “free”.

The cyclic tetramer of *tert*-butylphosphonic acid is unstable in a sense that it is converted into a cage-like tetramer during the structure optimization. Similarly, the cyclic dimer of phosphonic acid with four hydrogen bonds (see the Scheme below) is converted into the cyclic dimer with two hydrogen bonds, such as shown in Figure S3a above.

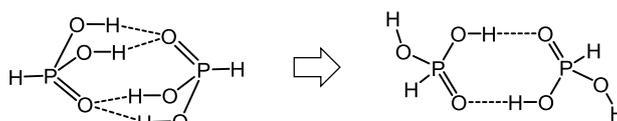


Figure S4. The visualization of calculated (B3LYP/6-311++G(d,p), vacuum) ^1H NMR chemical shifts of OH protons in cyclic dimer, cyclic trimer and cage like (“tetrahedral”) tetramer of *tert*-butylphosphonic acid. The signals are split due to $^2J(\underline{\text{P}}\text{O}\underline{\text{H}})$ and $^{2h}J(\underline{\text{P}}\text{O}\cdots\underline{\text{H}}\text{O})$ coupling constants, calculated at the same level of theory. The numerical values of calculated ^1H NMR chemical shifts are collected in Table S1 (page S7). For comparison, at the bottom of the figure the experimental low-temperature (130 K) ^1H NMR spectrum of *tert*-butylphosphonic acid is given (the same spectrum as in Figures 3 and S1).

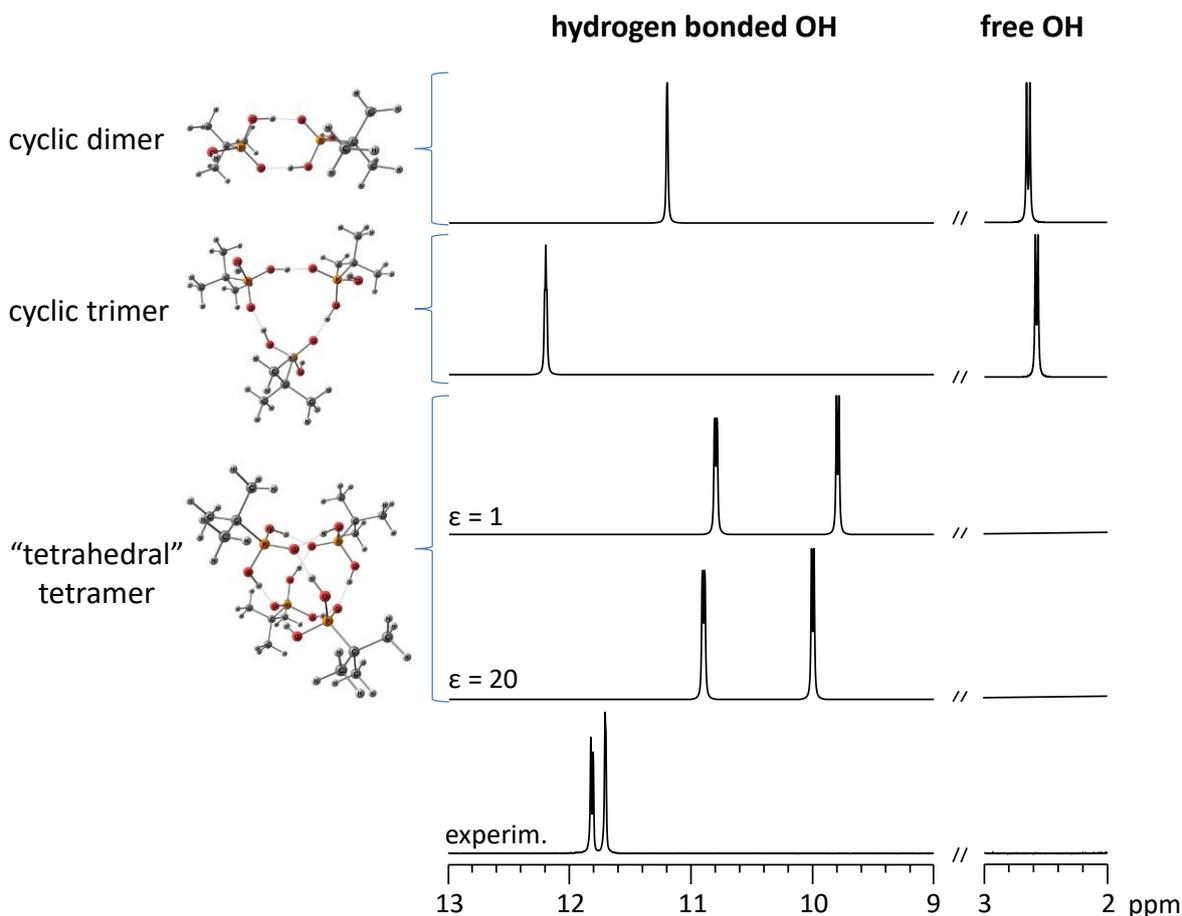
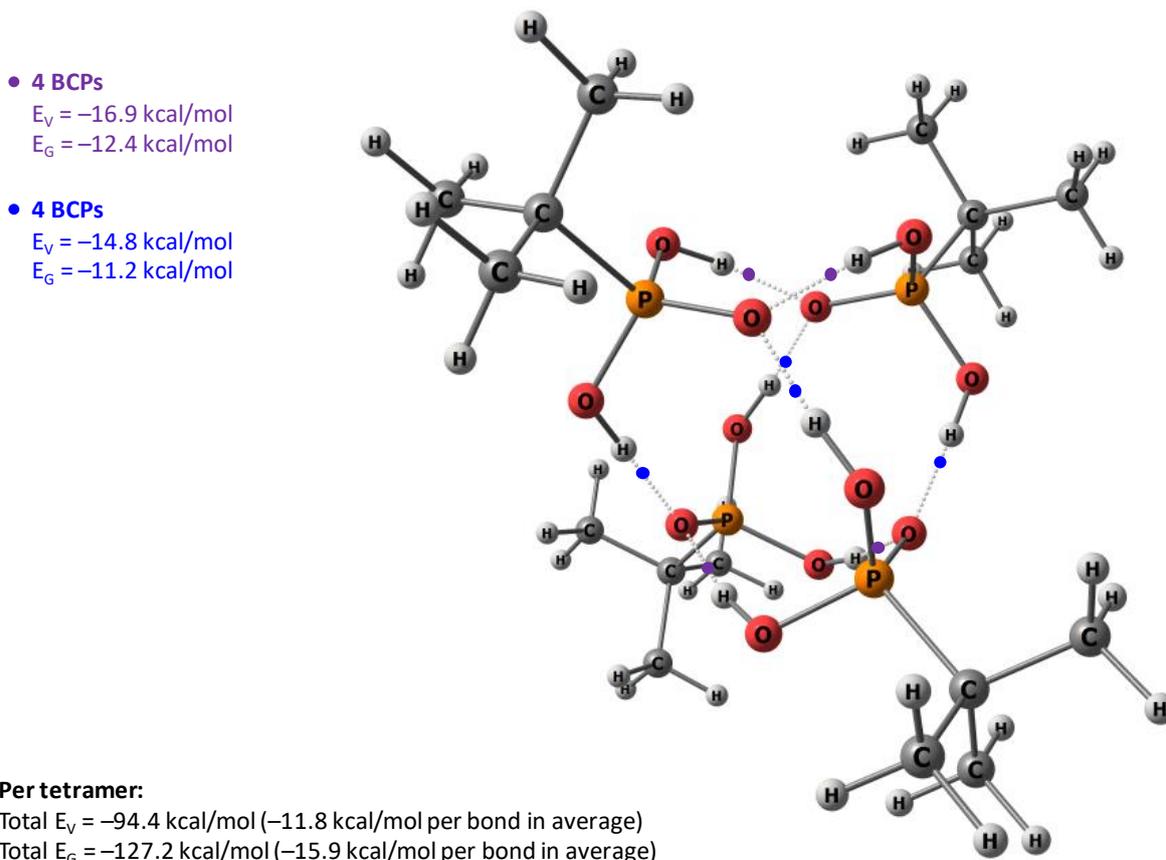


Figure S5. The QTAIM topological analysis of the electron density at the OHO hydrogen bond critical points (BCP) of *tert*-butylphosphonic acid.



Values of local potential and kinetic energies of electrons were converted into values of interaction energy according to the formulas given in [Vener et al. *J. Comput. Chem.* **2012**, 33, 2303-2309. DOI: 10.1002/jcc.23062]:

$$E_V = -0.5 V, \text{ where } V \text{ is } \text{kJ}/(\text{mol} \cdot \text{\AA}^3)$$

$$E_G = 0.429 G, \text{ where } G \text{ is } \text{kJ}/(\text{mol} \cdot \text{\AA}^3)$$

The same approach was shown in articles [Espinosa et al. *Chem. Phys. Lett.* **1998**, 285, 170–173. DOI: 10.1016/S0009-2614(98)00036-0] and [Mata et al. *Chem. Phys. Lett.* **2011**, 507, 185–189. DOI: 10.1016/j.cplett.2011.03.055].

Table S1. The thermodynamic parameters (ΔH , ΔS and ΔG at 100 K) of the dimerization, trimerization and tetramerization reaction of *tert*-butylphosphonic acid. The optimized structures of the cyclic dimer, cyclic trimer and cage-like tetramer could be found in Figure S3a, S3b and S5, respectively). In the last column the calculated numerical values of the ^1H NMR chemical shifts of OH protons are listed.

Reaction	ΔH , kcal/mol	ΔS , cal/mol/K	ΔG at 100 K, kcal/mol	δH , ppm
1) dimerization (cyclic) $\text{A} + \text{A} \rightleftharpoons \text{A}_2$	-22.7	-39.0	-18.8	11.2 (bonded) 2.64 (free)
2) trimerization (cyclic) $\text{A} + \text{A} + \text{A} \rightleftharpoons \text{A}_3$	-38.2	-76.1	-30.6	12.2 (bonded) 2.57 (free)
3) tetramerization (cage-like) $\text{A} + \text{A} + \text{A} + \text{A} \rightleftharpoons \text{A}_4$	-82.9	-146.5	-68.2	10.8 (bonded) 9.8 (bonded)

Gibbs free energy change per one acid molecule:

dimerization: -9.4 kcal/mol

trimerization: -10.2 kcal/mol

tetramerization: -17.1 kcal/mol