Tracing environment effects that influence the stability of anion–anion complexes: The case of phosphate–phosphate interactions

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ABSTRACT

The effect of the environment on the stability of the $(H_3PO_4)_2$, $(H_2PO_4^-)_2$ and $(HPO_4^{2-})_2$ hydrogen bonded dimers has been explored by the topological analyses of the theoretical electron density and the electrostatic potential. The environment has little effect on the hydrogen-bonding interaction, while it induces a significant one on the Coulombic component of the dimer. The interaction energy is represented in terms of hydrogen-bond and non-hydrogen-bond contributions, being only the latter affected by the charge or the environment. While the non-hydrogen bond contribution dominates the interaction energy in the gas phase, it becomes balanced in a polarizable environment.

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Hydrogen bond (HB) is one of the strongest intermolecular interactions, only surpassed by ionic forces. Theoretical calculations [1] and experimental results [2] demonstrate that anions can eventually aggregate in the gas phase, forming hydrogen bonded complexes. The potential energy surface (PES) of these complexes present local minima with positive values of the interaction energy (E_i), indicating that the equilibrium conformations are stable although energetically unfavorable. While at longer distances only repulsive ion–ion forces are significant, at shorter distances attractive HB forces prevail, being both behaviors separated by an energetic barrier that must be overcome in order to create or dissociate the complex.

Among the anions able to form these dimers, phosphate represents a relevant case because of its importance in biochemical processes and in materials science. In a recent study exploring the potential energy surface of $(H_2PO_4^-)_2$ by ab initio methods [3], seven stable dimers were found exhibiting energy barriers of formation in the range 165–180 kJ mol^{-1}. While the formation of such dimers in the gas phase should be regarded as improbable, it cannot be discarded that an adequate environment can lower or even remove the energetic barrier, allowing the anions aggregation. Indeed, phosphate aggregation in oversaturated aqueous solution has been observed by Raman spectroscopy [4], and the stability of polyphosphates in biological media is only possible with the presence of cations such as Mg^{2+}.

To explore the effect of the environment on the stability of phosphate dimers, the equilibrium geometries of several complexes containing H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} units were determined by ab initio calculations (Figure 1). The studied systems were two $(H_3PO_4)_2$ dimers, one showing four (**1**) and another two (**2**) HBs, two $(H_2PO_4^-)_2$ dimers with geometries similar to **1** (**3**) and **2** (**4**), and one $(HPO_4^{2-})_2$ dimer with geometry similar to **2** (**5**). Dimers **1**, **2** and **5** were built by adding or removing H-atoms in complexes **3** and **4**, which are stable in gas phase [3]. The effect of adjacent cations was explored by complexing **3** and **4** with two Na$^+$ (**6** and **7**), and **5** with two Mg^{2+} ions (**8**). The geometries of the complexes were optimized in gas phase and with a polarizable continuum model (PCM) representing an aqueous environment, except for complex **5**, which is not stable in gas phase.

In Table 1, the interaction energies (E_i) and the O$\cdots$H distances (d_{OH}, all the HBs in the same complex are equivalent by symmetry) of the complexes at their equilibrium configurations are presented. As expected, E_i depends strongly on the charge and the environment. Thus, E_i is positive for $(H_2PO_4^-)_2$ in gas phase, while adjacent cations make the value of E_i negative. The PCM reduce the range of E_i values, which are actually negative in all cases. Charge and/or polarizing environment do not lead to significant effects on the HB distance d_{OH}.

Within the framework of the quantum theory of atoms in molecules (QTAIMs) [6], the topological analysis of the electron distribution in the HB region exhibits a bond critical point (BCP), which is a saddle distribution of $\rho(\mathbf{r})$ at the interatomic surface between the acceptor and the hydrogen atoms. $\rho(\mathbf{r})$ at BCP is a minimum along the direction of the HB and a maximum in the perpendicular plane. The electron density properties at BCP provide information about the characteristics of the HB [5,7–10]. The QTAIM analysis of the complexes clearly demonstrates that the external influence of the charge and/or the polarizing environment has little effect

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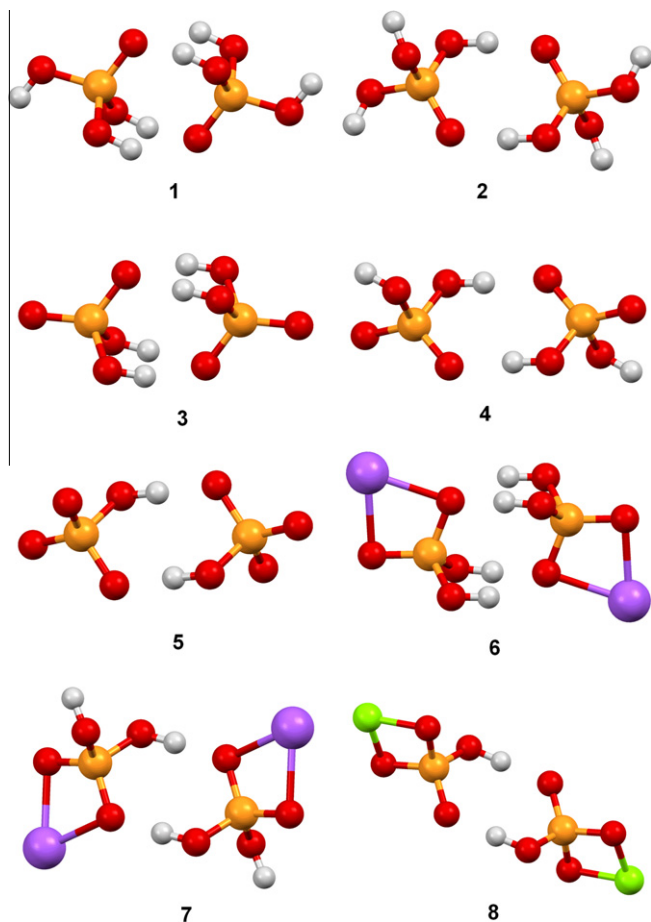   E-mail address: enrique.espinosa@crm2.uhp-nancy.fr (E. Espinosa).

Figure 1. Geometries of the complexes **1–8**. All geometries have been optimized in gas phase with the only exception of **5**, which has been optimized using an aqueous model (PCM).

Figure 2. $\rho_b, \nabla^2\rho_b$ and C_b vs d_{OH} for the hydrogen bonded complexes **1–8** in gas phase (white) and using PCM (black). Solid lines are the empirical dependencies derived from a set of neutral complexes in gas phase [5]. The dotted line in the bottom panel marks the boundary between pure closed shell (below the line) and closed shell with partial shared character (above the line) interactions. The three panels indicate that $\rho(\mathbf{r})$ is more localized in the HB than expected from the empirical dependencies, all the represented HBs therefore presenting a partial shared character.

Table 1
E_i and d_{OH} of the complexes at equilibrium geometries.

	Gas phase		PCM	
	E_i (kJ mol^{-1})	d_{OH} (Å)	E_i (kJ mol^{-1})	d_{OH} (Å)
1	−109.07	2.017	−60.89	2.053
2	−100.82	1.610	−72.97	1.592
3	105.40	1.894	−83.34	1.866
4	146.51	1.712	−75.50	1.607
5			−58.39	1.641
6	−156.46	1.899	−90.34	1.881
7	−141.21	1.609	−82.44	1.594
8	−93.61	1.581	−75.90	1.596

on the topological properties of $\rho(\mathbf{r})$ in the HB regions. Three of these properties at BCP are the electron density (ρ_b), the laplacian of the electron density ($\nabla^2\rho_b$) and $C_b = |V_b|/G_b$ [10], where V_b and G_b are, respectively, the electron potential and kinetic energy densities. The dependencies of these properties with d_{OH} for all the HBs in the complexes **1–8** are represented in Figure 2.

The ρ_b and $\nabla^2\rho_b$ values follow single exponential dependencies with d_{OH} that are similar to those derived empirically for H···O HBs from a set of neutral complexes in the gas phase [5]. In all cases, small and systematic differences from the expected values of ρ_b and $\nabla^2\rho_b$ are observed, suggesting a more concentrated character of $\rho(\mathbf{r})$ [11]. The C_b ratio indicates the pure closed shell ($C_b < 1$) or shared (covalent) ($C_b > 2$) character of the interaction, while
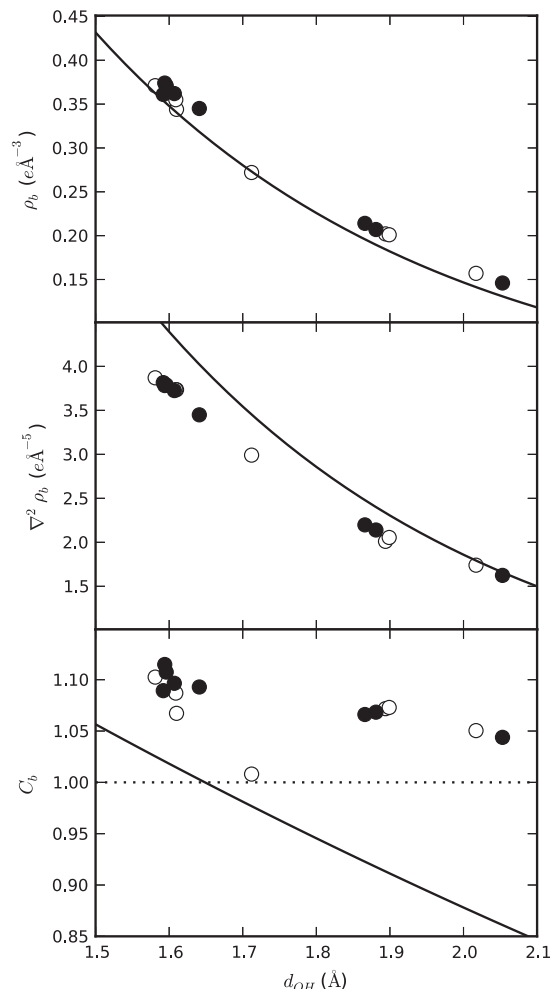
intermediate values ($1 < C_b < 2$) correspond to mixed interactions defined as closed shell with a partial covalent character [10]. In the case of complexes **1–8**, C_b is significantly larger than expected [5]. This indicates a partial shared character that extends along the observed range of d_{OH}, including long distances where a pure closed shell interaction is expected. The partial shared character of these HBs cannot be attributed to the net charge of the complexes or the polarizing environment, as it is observed even for the neutral complexes in gas phase. Consequently, it should be attributed to the tuning of the HB properties by intramolecular influence. Groups that form very polar or ionic bonds on the HB donor side, as the P–O bond [12], are at the origin of this effect, favoring the shared character of the HB [13].

The small effect of the charge and the environment on the HB properties can also be visualized by analyzing the topology of the electrostatic potential $\varphi(\mathbf{r})$ [14]. The representation of the negative gradient of $\varphi(\mathbf{r})$ (namely the electric field, $\mathbf{E}(\mathbf{r})$), indicates the direction of the Coulombic forces acting on $\rho(\mathbf{r})$ [15], which is a useful method for detecting the electrophilic and nucleophilic parts of a molecule [16] and for delimiting their influence zones [17].