

Evaluation of the Molecular Inclusion Process of Organochlorine Pesticides at Cyclodextrins

Anthuan Ferino-Pérez^{a1}, Juan José Gamboa-Carballo^{1,2}, and Ulises Jáuregui Haza³

¹Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Universidad de La Habana, Cuba

²Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland

³Instituto Tecnológico de Santo Domingo (INTEC), República Dominicana

The molecular inclusion process of two organochlorine pesticides and its radiolabeled analogous with cyclodextrins is a perspective technology for the removal of these pollutants from water.^b

Persistent organic pollutants (POPs) are those substances that, in addition to their toxicity, present an elevated residence time in the environment due, principally, to a high chemical or biological resistance to degradation and to the fact that they were poured to nature in quantities that overcome the capacity of the natural media to degrade them. Specifically organochlorine pesticides such as chlordecone (CLD, C₁₀Cl₁₀O, CAS: 143-50-5) and β -hexachlorocyclohexane (β -HCH, C₆H₆Cl₆, CAS: 319-85-7) are of great concern because they were profusely used around the world, they have an extremely high environmental stability and cause severe affectations to human, animals, and environmental health. Due to these facts, they were included since 2009 in the list of POPs by Stockholm's Convention.

In the last years, the search for strategies for water decontamination centered on organochlorine pesticides removal was prompted. The decontamination methods used range from advanced oxidation process and biodegradation treatments, to the use of activated carbon for the treatment of polluted water by adsorption. In spite of these efforts, it is still necessary to increase the efficiency of the separation methods used, which has promoted the search for new alternatives, like the formation of host-guest complexes with cyclodextrins (CDs) [1].

The mathematical modeling of the interactions pollutant/decontaminant-agents through the application of computational chemistry methods allow saving material resources while optimizing the time and security of the researchers. Particularly, the molecular inclusion complexes formed between the CDs and different molecules have been studied by several computational methods. However, in previous works, the authors directly set the molecule of interest in contact with the interior of the CD cavity in certain configurations based, largely, on chemical intuition. Also, generally, only the β -CD is considered as a host molecule, ignoring the possibility of better encapsulation capacities of other CDs, especially the γ -CD. In our works, a more general approach was used, based on the random exploration of the configurational space of the host-

guest complexes of pesticides at each of the three natural occurring CDs (α -, β -, and γ -CD).

Nanoaggregates of CLD and β -HCH with CDs

In order to correctly evaluate the chemical behavior of CDs a theoretical study of their conformational equilibria was performed by Gamboa-Carballo et al [2]. Eight symmetrical conformers, which differ in their intermolecular H-bond patterns were found and characterized for each CD. The results obtained are in agreement with X-ray diffraction data helping to validate the results of this work. These calculations showed that four of the eight studied conformers for each CD are the most populated in aqueous solution. The eight conformers are showed in Figure 1.

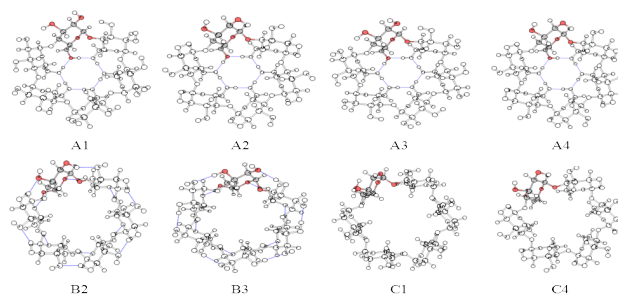


Figure 1: CDs' symmetrical conformers. Only the α -CD is presented and a glucopyranose unit is highlighted in each conformer.

Multiple Minima Hypersurface methodology, which combine a semiempirical Hamiltonian with statistical thermodynamic calculations, was employed for performing a thorough exploration of the configuration space of the nanoaggregates and evaluating the association thermodynamic properties that describe the molecular inclusion process. Figures 2a and 2b show the mean association energy for the complexes CLD@CDs [3] and β -HCH@CDs [4] respectively.

As could be seen, there is a remarkable stabilization of the systems when γ -CD is the host molecule for all evaluated conformers. In both cases, there is a progressive stabilization of nanoaggregates as the size of the CDs cavity increase for the conformers B2, B3,

C1, and C4. Of these conformers, representative structures of inclusion complexes were selected for posterior refinement. In all the cases, the global minima and additional structures of interest for the presented geometry were selected. This selection was made always taking into account that these structures had a population greater than 10% according to a Boltzmann distribution.

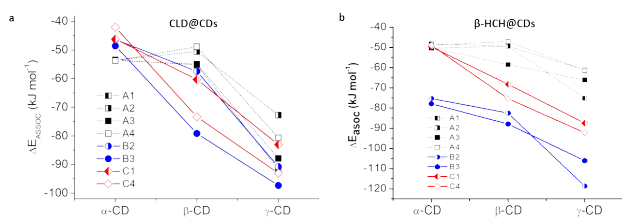


Figure 2: Mean association energies (calculated by MMH methodology) of (a) CLD and (b) β -HCH with the conformers of studied CDs.

The refinement of complexes geometries, association energies, and wavefunctions was performed through DFT calculations using the meta-GGA hybrid functional M06-2X with the Pople's basis 6-31G(d,p). SMD was employed as implicit solvent model and Grimmer dispersive corrections were applied for all calculations. The association energy here calculated was corrected for mitigating Basis Set Superposition Error (BSSE) with a method developed by the authors [3]. These calculations confirmed that the more stable complexes are formed when γ -CD is the host molecule. The conformers B3 and C1 are the more stable ones for both pesticides.

For characterizing the interactions present in these complexes Quantum Theory of Atom in Molecules was applied using the Nakanishi criteria for determinate the type of the interactions from density dependent functions. With this analysis we concluded that the great number of dispersive interactions (with a minimum of 17 interactions between the pollutant and the CD) together with the presence of other interactions of greater strength as H-bonds, dihydrogen bonds, and halogen bonds contribute to explain the stability of this complexes in spite of the absence of covalent interactions. Theoretical results for CLD@CDs system are in agreement with the experimental results obtained in 2016 by Rana et al. [1], while the ones of β -HCH@CDs complexes were confirmed through spectroscopic measurements and microscopy analysis performed by Ferino-Pérez et al. [4].

Radiolabeled analogous as radiotracers of the system

The determination of CLD and HCH in water represents a challenge for the analytical chemistry due to pesticides low concentrations in nature that in occasions are found below the quantification limit of many modern analytical methods. The labeling with a radioactive isotope might be an effective approach for

studying their distribution in nature and its biodistribution in several living organisms, as well as for evaluating several remediation technologies for the CLD and the β -HCH in their typical concentrations' conditions. However, for a compound would be a suitable radio-tracer it should resemble the behavior of its analogous inside the study system.

The work of Jáuregui-Haza et al [5] theoretically evaluated the feasibility of using radio-iodine labelled analogous of these pollutants as radiotracers of the systems under study. Results obtained in this investigation allow us to verify this hypothesis. Figure 3 shows the similarity that exists in the geometries and interactions present when compared the complexes formed with the pesticide with the ones of their iodine analogous.

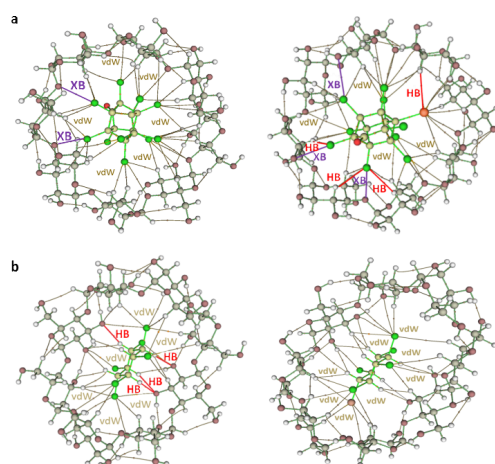


Figure 3: Intermolecular interactions of molecular inclusion complexes (a) CLD@C1- γ -CD and I-CLD@C1- γ -CD and (b) β -HCH@C1- γ -CD and I- β -HCH@C1- γ -CD determined by QTAIM analysis. The different types of interactions are identified as: dispersive (vdW, in yellow), hydrogen bond (HB, in red) and halogen bond (XB, in purple).

Notes

a. Email: anthuanferp@gmail.com

b. Original version of this article is Ref. [4]

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