



Guest-host complexes of 1-iodochlordecone and β -1-iodo-pentachlorocyclohexane with cyclodextrins as radiotracers of organochlorine pesticides in polluted water

Ulises Jáuregui-Haza^{1,2} · Anthuan Ferino-Pérez² · Juan José Gamboa-Carballo² · Sarra Gaspard³

Received: 29 March 2019 / Accepted: 23 January 2020 / Published online: 13 February 2020
© Springer-Verlag GmbH Germany, part of Springer Nature 2020

Abstract

The chlordecone (CLD) and the β -hexachlorocyclohexane (β -HCH) are persistent organic pollutants with a great environmental stability that cause severe affectations to health. The concentration of these pesticides in the environment is low, which represent a problem for their determination, even for the modern analytical methods. The labeling of these compounds with an iodine radioisotope for their use as radiotracers is a potential solution to this problem. The present work studies the interaction of 1-iodochlordecone (I-CLD) and β -1-iodo-pentachlorocyclohexane (I- β -HCH) with cyclodextrins (CDs), during the formation of molecular inclusion complexes pesticide@CDs. The methodology of multiple minima hypersurfaces, quantic calculations based on density functional theory and a topologic study of electronic density were used to corroborate the stability of I-CLD@CDs and I- β -HCH@CDs complexes. Three main types of guest-host complexes in relation to the occlusion grade were observed: with total occlusion, with partial occlusion and external interaction without occlusion. The more stable complexes are obtained when the γ -CD is the host molecule. The formed complexes with radiolabelled pollutants are analogous with the ones reported in previous works. These results confirm the utility of these complexes for the removal of organochlorine pesticides from polluted water and, also, demonstrate the possibility of using the I-CLD and the I- β -HCH as possible radiotracers for these pollutants in further studies with environmental proposes.

Keywords Labelled organochlorine pesticides · Host-guest complexes · Radiotracers · Multiple minima hypersurfaces · Density functional theory · Quantum theory of atoms in molecules

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11356-020-07862-w>) contains supplementary material, which is available to authorized users.

✉ Ulises Jáuregui-Haza
ulises.jauregi@intec.edu.do

¹ Instituto Tecnológico de Santo Domingo (INTEC), Santo Domingo, Dominican Republic

² Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Universidad de La Habana, 10600 La Habana, Cuba

³ Laboratoire COVACHIM M2E, Université des Antilles, 97157 Pointe à Pitre, Guadeloupe, France

Introduction

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.

Chlordecone (CLD, $C_{10}Cl_{10}O$, CAS: 143-50-5) is a POP produced and used between 1951 and 1993 in agriculture for controlling several plagues such as *Cosmopolitus Sordidus* in banana plantations of Guadeloupe and Martinica (Vilardebo et al. 1974) and as well in domestic traps for ants and cockroaches (Newhouse et al. 2009). The CLD presents a great affinity for the soils rich in organic matter, evidenced by its high absorption coefficient on organic carbon ($\log K_{oc} \approx 4.2$)

(Phillips et al. 2005). In the meanwhile, its bioaccumulation and biomagnification respond to an elevated octanol-water partition coefficient ($\log K_{ow} \approx 4.5$) (Xiao et al. 2004). This pollutant is not volatilized in a significant manner and does not experience direct photodegradation in the atmosphere (Fernandez-Bayo et al. 2013; Sakakibara et al. 2011). The molecule is found to be distributed in the different environmental compartment of the polluted areas of Guadeloupe and Martinica (Della Rossa et al. 2017; Robert 2012), contaminating the local food chain (Clostre et al. 2015; Fournier et al. 2017). Indeed, over the period 1972–1978, 300 tons of chlordecone was spread on the soils of the two islands, 120 tons from 1972 to 1978 and 180 tons from 1981 to 1993 (Le Déaut and Procaccia 2009). A simple leaching model established that CLD pollution will last several decades to half a millennium depending on soil type (Cabidoche et al. 2009). It has been addressed as a POP by the Stockholm Convention since May 2009 (Listing of POPs in the Stockholm Convention: Annex A (Elimination) 2011).

The hexachlorocyclohexane (HCH, $C_6H_6Cl_6$) is also used as an organochlorine pesticide. It is composed of an isomers' mixture of which only the γ -HCH (lindane, CAS 58-89-9) has insecticide properties. However, the commercial mixture contains up to 87% of other isomers, mainly α -HCH, β -HCH and δ -HCH, even though all of these are toxic and carcinogenic (Onogbosele and Scrimshaw 2014). Around 600,000 tons of technical HCH were used in several countries between decades of 1940–1990 with the aim of controlling a wide range of agricultural and health plagues (Li 1999; Vijgen et al. 2006). The HCH isomers can be detected in all environmental compartments including water, soil, air and biota (Willett et al. 1998). As a result of the water cycle, the terrestrial contamination of HCH is progressively transferred to aquatic ecosystems. Its high absorption coefficient on organic carbon ($\log K_{oc} \approx 3.57$) (Phillips et al. 2005) reflects its great affinity by soils rich in organic matter. While α and γ isomers are the most disperse in the environment, the β -HCH (CAS 319-85-7) results also very important because it is the one with the greatest tendency to bioaccumulate, it could be transported by air and has the higher stability (Willett et al. 1998). Furthermore, the β -HCH's relatively high octanol/air partition coefficient ($K_{oa} = 5.1 \cdot 10^8$) (Xiao et al. 2004) promotes the accumulation from the air in environmental organic compartments. All the aspects previously discussed made that β -HCH was also included in the list of POPs by the Stockholm Convention (Listing of POPs in the Stockholm Convention: Annex A (Elimination) 2011). Figure 1 shows a graphical representation of CLD and β -HCH.

In the last years, the search for strategies for water decontamination centered on organochlorine pesticide removal was prompted (Onogbosele and Scrimshaw 2014; Vallack et al. 1998; Wycisk et al. 2013). The decontamination methods used range from advanced oxidation process (Cruz-Gonzalez et al.

2018) and biodegradation treatments (Johri et al. 2000; Johri et al. 1998; Phillips et al. 2005), to the use of activated carbon for the treatment of polluted water by adsorption (Durimel et al. 2013; Durimel et al. 2015; Enriquez-Victorero et al. 2014; Gamboa-Carballo et al. 2016a). 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 (Allabashi et al. 2007; Arkas et al. 2006; Benfeito et al. 2013; Liu et al. 2011; Rana et al. 2016; Sawicki and Mercier 2006; Schäfer et al. 2017).

Cyclodextrins (CDs) are a family of cyclic oligosaccharides consisting of a number of α -D-glucopyranose subunits linked by (1 \rightarrow 4) glycosidic bonds. The more common CDs, called α -, β - and γ -CDs, are formed, respectively, by six, seven and eight glucopyranose units (Mura 2014). The remarkable encapsulation capacity of the CDs causes a type of host-guest interaction (Sifaoui et al. 2016; Steed and Atwood 2009; Szejtli 1998) that has allowed their use in applications for many sectors of society, like agriculture and environment (Bilensoy 2011; Duca and Boldescu 2008). Particularly interesting for purposes of this work, their use in innovative alternatives to remove pollutants from waters and soils should be highlighted, based on the formation of non-soluble inclusion complexes in water and in most of the organic solvents (Cruickshank et al. 2013; Duca and Boldescu 2008; Garrido et al. 2012; Xiaoguang Zhang et al. 2016). Recently, Rana et al. (2016) demonstrated that cyclodextrin is a good complexation agent for the removal of chlordecone from water, forming 1:1 guest-host complex with β - and γ -CDs.

The determination of CLD and HCH in water represents a challenge for the analytical chemistry due to pesticide low concentrations in nature that in occasions are found below the quantification limit of many modern analytical methods. The labelling 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.

The labelling of compounds with radioactive isotopes is a quite employed technique in cases where conventional procedures for analysis are not suitable. In the case of studied pesticides, the labelling with radioactive isotopes presents several alternatives. The first one is the labelling with isotopes of the same element C and Cl that are common for both pesticides; O and H present only in CLD and β -HCH, respectively (Fig. 1). In the cases of positronic isotopes, their short half-life time is a limitation for this kind of study as well as for labelling the molecules, which discard very popular isotopes as ^{11}C , ^{15}O or other less known, like ^{34m}Cl . Other options are ^{14}C and 3H , but due to their relatively long half-life time (5730 years and 12.32 years, respectively), problems of radiologic protection appear. The second option is the use of radioisotopes of

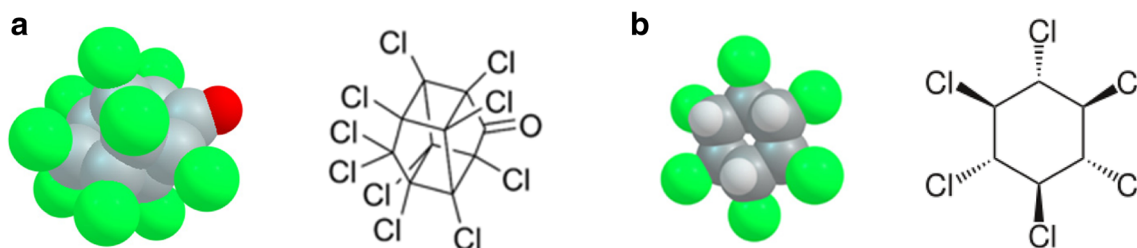


Fig. 1 Chlordecone (**a**, CLD) and β -hexachlorocyclohexane (**b**, β -HCH)

different elements mainly halogen for the interest of this work. ^{18}F , another very popular positronic radionuclide, also decays very fast and Br radioisotopes are not generally commercially available (Browne et al. 1986).

In the case of studied pesticides, the labelling with iodine radioisotopes looks like a viable alternative. Isotopes ^{131}I , ^{123}I and ^{125}I stand out due to their commercial availability and their nuclear characteristics. The employment of ^{125}I has several advantages. The first one, tracers with high specific activities, could be obtained. It presents gamma emission, which allows using simple and relatively cheap measurement equipment. In addition, its half-life time of 60 days makes it very convenient for environmental studies (Baldwin 1986). Also, ^{123}I and ^{131}I could be used for the evaluation of technological applications at a laboratory scale for its minor half-life time.

The mathematical modelling is a useful tool for predicting if the labelled compound modifies or not its interactions with the matrix compared with the non-labelled molecule of interest. Previous studies of Gamboa-Carballo et al. (2016b) with 1-iodo-CLD has demonstrated the viability of *in silico* studies for the proposal of a new radiotracer and its interactions with surface groups of activated carbon. The aim of this investigation is to study the interactions of iodine analogous of CLD and β -HCH (e.g. 1-iodochlordecone (I-CLD) and β -1-iodopentachlorocyclohexane (I- β -HCH), respectively) with cyclodextrins aiming of evaluating their usefulness as possible radiotracers of the molecular inclusion complexes formed with CDs.

Materials and methods

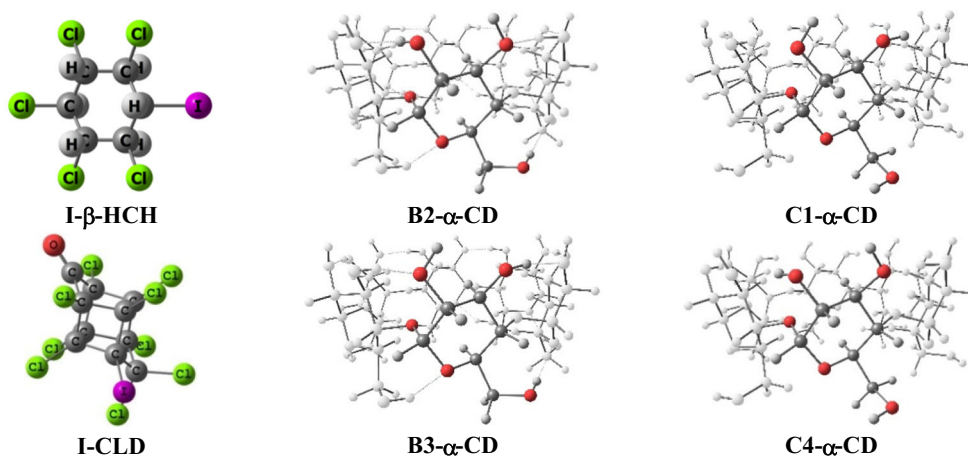
System under study

Practical (Rana et al. 2016) and theoretical (Ferino-Pérez et al. 2019; Gamboa-Carballo 2018) studies done in the last years demonstrated the capacities of CDs for the removal of CLD and β -HCH from polluted water through the formation of stable and non-soluble molecular inclusion complexes. It must be pointed out that due to the size of labelled pollutants, only complexes of stoichiometry 1:1 were considered, taking into account the previous finding (Rana et al. 2016).

According to the results of previous theoretical works (Ferino-Pérez et al. 2019; Gamboa-Carballo 2018), for this study, only the four CD conformers that form the more stable complexes with CLD and β -HCH (conformers type B and C) were selected (Fig. 2). These conformers, recently characterized by Gamboa-Carballo et al. (2017), differ in the orientation patterns of intramolecular hydrogen bonds.

In the case of labelled pollutants, the iodine atom will substitute one of the chlorine atoms of the studied molecules. In the case of β -HCH, all chlorine atoms are equivalent, being all in an equatorial position. For the CLD molecule, the iodine position was selected taking into account the diminution of electronic repulsion, as well as its distance to the carbonyl functional group. In all cases, iodine atomic mass was assumed as iodine natural mass. Figure 2 shows the molecules under study.

Fig. 2 Representation of molecules under study. In the case of CDs, only conformers for α -CD are shown. A glucopyranose unit is highlighted in all CD structures



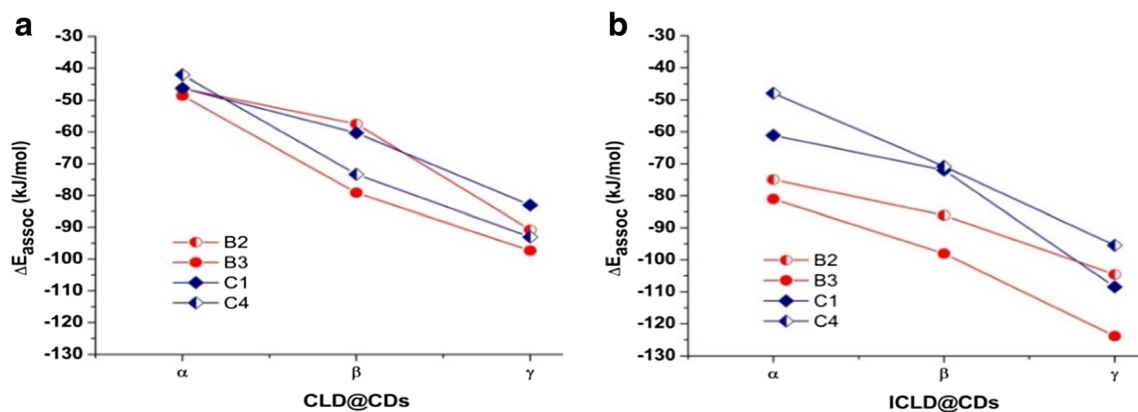


Fig. 3 Mean association energies for molecular inclusion complexes **a** CLD@CDs (Gamboa-Carballo 2018) and **b** I-CLD@CDs

Multiple minima hypersurface calculations

In the energetic spectrum of a system, different conformations and configurations with similar energies could be found. In consequence, in a canonic ensemble, these will contribute in a similar manner to the system macroscopic properties. The use of multiple minima hypersurface (MMH) methodology allows, by one side, exploring the possible sites of interactions of CD conformers with I-CLD and I- β -HCH, and by the other, calculating thermodynamic properties of the interacting system. In this work, 200 non-redundant configurations were randomly generated for each one of the conformers of the systems I-CLD@CDs and I- β -HCH@CDs, from the structures of the separated molecular models.

For generating the 200 configurations per system, the GRANADA software (Montero-Cabrera 2000) was used. The supermolecules generated were taken as input files for the semi-empirical software package MOPAC2016 (Stewart 2016), from which the structures of minimum energy were obtained. For the optimization of these structures, the semiempirical Hamiltonian PM6-D3H4X (Brahmkshatriya et al. 2013; Řezáč and Hobza 2011a, 2011b; Stewart 2007) was used.

The structures of minimal energy obtained were processed employing the program Q3 (Montero-Cabrera et al. 2000b) with the aim to obtain the system thermodynamic magnitudes of association and to select the most important non-redundant structures for the description of the system. Q3 calculates the system partition function and its thermodynamic properties such as the energy of association, entropy of association and Helmholtz's free energy of association. The standard procedure of this methodology has been previously described in other works (Codorniu-Hernández et al. 2005; Montero et al. 1998). After mathematical treatment, according to the statistical thermodynamic equations, configurations with the higher populations according to a Boltzmann distribution were selected for its refinement (Montero-Cabrera et al. 2000a; Montero et al. 1998).

Re-optimization of distinctive structures

The representative structures (e.g. the most stable global minima of complexes between CDs and iodine substituted pollutant) were re-optimized using calculations based on density functional theory (DFT) (Hohenberg and Kohn 1964; Kohn

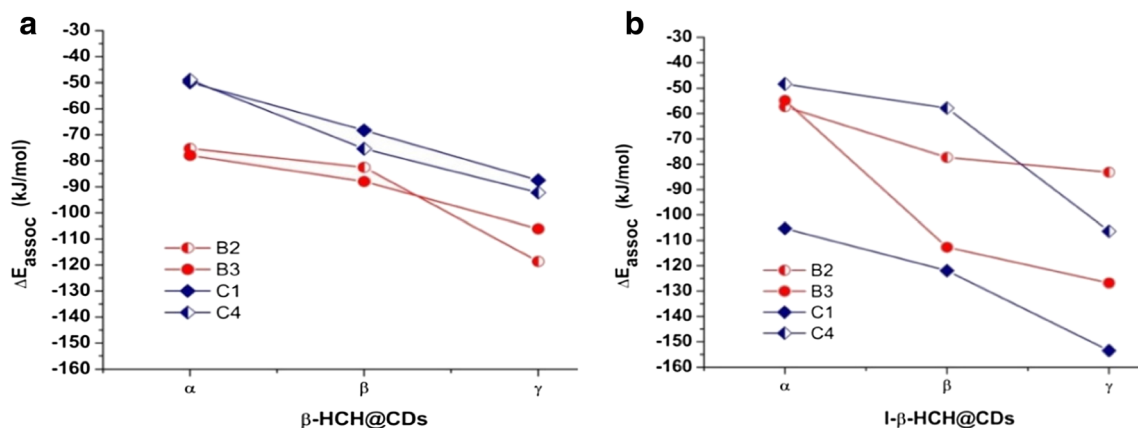


Fig. 4 Mean association energies for molecular inclusion complexes **a** β -HCH@CDs (Ferino-Pérez et al. 2019) and **b** I- β -HCH@CDs

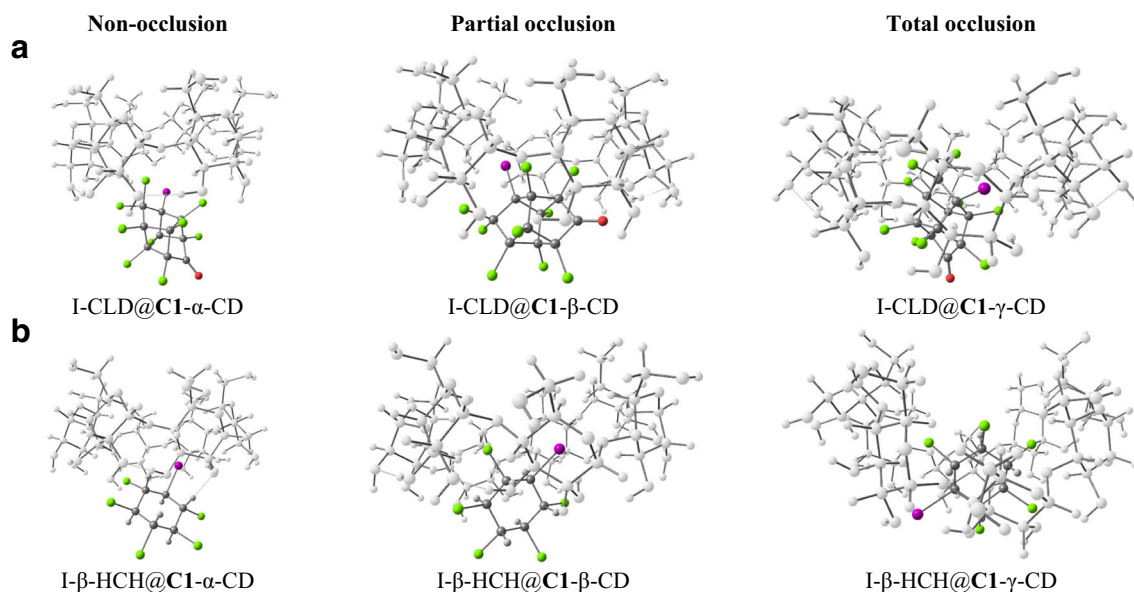


Fig. 5 Progressive increment of occlusion grade of labelled pesticide, **a** I-CLD and **b** I-β-HCH, as increase the size of CDs internal cavity for conformer C1

and Sham 1965). For refining previously optimized structures, a hybrid functional that employs the metageneralized gradient approximation, M06-2X (Johnson et al. 2009; Zhao and Truhlar 2008), along with the Pople basis 6-31G for all the light atoms, was used. It is known that this combination correctly describes the interactions found in non-covalent bond dimers (Johnson et al. 2009) as in the case of van der Waals interactions that should be present in the system under study. The solvent effects were taken into account using SMD (Marenich et al. 2009) as an implicit solvent model and DFT-D3 dispersive corrections (Grimme et al. 2011) were applied to all DFT calculations. In the case of iodine, the effective core potential or pseudopotential LANL2DZ (Check et al. 2001; Roy et al. 2008) were used with the

objective of considering the core electrons without the great computational effort. In this way, the effects of core electrons are taken into account, avoiding their explicit consideration in the optimization of system wavefunction. All calculations were performed employing the Gaussian09 software package (Frisch et al. 2009).

Topologic analysis of electronic density

In order to make a rigorous characterization of all existing interactions between CDs and iodine substituted pesticides, the electronic density of complexes was recalculated with 6-31G(d,p) basis. The distinctive structures of I-CLD@γ-CD and I-β-HCH@γ-CD complexes were studied using the

Table 1 Distribution of occlusion grade for each conformer of α-, β- and γ-CD obtained through MMH methodology for CLD (Gamboa-Carballo 2018) and I-CLD. The percentages are based in the minima summing over 99% of the total population based in a Boltzmann energy distribution

| Host CD conformers | % Total occlusion | | % Partial occlusion | | % Non-occlusion | |
|--------------------|-------------------|-------|---------------------|-------|-----------------|-------|
| | CLD | I-CLD | CLD | I-CLD | CLD | I-CLD |
| B2-α-CD | 0.00 | 0.00 | 1.56 | 0.00 | 97.54 | 99.96 |
| B3-α-CD | 0.00 | 0.00 | 0.00 | 16.00 | 99.09 | 83.92 |
| C1-α-CD | 0.00 | 0.00 | 54.29 | 17.44 | 44.74 | 82.47 |
| C4-α-CD | 0.00 | 0.00 | 9.76 | 82.39 | 89.45 | 17.52 |
| B2-β-CD | 0.00 | 0.00 | 99.07 | 97.97 | 0.00 | 1.93 |
| B3-β-CD | 0.00 | 0.00 | 95.92 | 99.90 | 3.52 | 0.00 |
| C1-β-CD | 0.00 | 0.00 | 99.72 | 96.55 | 0.00 | 3.37 |
| C4-β-CD | 0.00 | 0.00 | 99.46 | 99.92 | 0.00 | 0.00 |
| B2-γ-CD | 99.37 | 99.84 | 0.00 | 0.10 | 0.00 | 0.00 |
| B3-γ-CD | 86.05 | 99.95 | 6.48 | 0.00 | 6.55 | 0.00 |
| C1-γ-CD | 92.86 | 99.47 | 5.74 | 0.45 | 0.63 | 0.00 |
| C4-γ-CD | 97.98 | 69.78 | 1.14 | 30.13 | 0.00 | 0.00 |

quantum theory of atoms in molecules (QTAIM) (Bader 1991, 2010). This permits the analysis of interactions nature based on Nakanishi criteria (Nakanishi et al. 2008, 2009) and to compare them with the existing in the non-labelled complexes (Ferino-Pérez et al. 2019; Gamboa-Carballo 2018), which is one of the main goals of this investigation. QTAIM allows describing the topology of electronic density (ρ) and its Laplacian ($\nabla^2\rho$) in the bond critical points (BCPs). In addition, other ρ -dependent functions such as total energy density (H_{BCP}), the rate of potential and kinetic energy density (V_{BCP}/G_{BCP}) and the ellipticity of electronic density (ϵ) were analyzed. This study was made using the Multiwfn 3.3.6 (Lu and Chen 2012) software package.

Results and discussion

MMH calculations

The exploration of the configuration space corresponding to interactions between labelled pesticides (I-CLD and I- β -HCH) with the four different conformers of the three natural CDs (α -, β -, and γ -CD) was performed for a total of 24 studied systems. Figures 3 and 4 show the behavior of mean association energies obtained for the non-labelled pesticides (CLD and β -HCH) (Ferino-Pérez et al. 2019; Gamboa-Carballo 2018) and the iodine substituted ones at 298.15 K.

As it becomes clear when Figs. 3 a and b are compared, the tendency of association is similar for B and C type conformers in their interactions with CLD and I-CLD. In both graphs, the decrease of ΔE_{assoc} is monotonous for the four compared conformers. Figures 4 a and b show that the behavior in the

case of β -HCH and I- β -HCH is very similar, presenting, in the same way, a monotonous descent of ΔE_{assoc} .

Figure 5 illustrates, according to the classification established in the previous works (Ferino-Pérez et al. 2019; Gamboa-Carballo 2018), the different occlusion grades that exist in complexes formed between labelled pollutants and the different studied CDs. As it could be seen, when the size of the CD internal cavity increases from α to γ CDs, a greater occlusion grade is favored.

Tables 1 and 2 show the distribution of occlusion grades obtained through MMH methodology for complexes formed between each one of conformers of α , β and γ -CD and the pesticides (Ferino-Pérez et al. 2019; Gamboa-Carballo 2018) and their iodine substituted analogous. The selection of representative configurations was made based on 99% of the sum of populations. It is possible to appreciate that occlusion grades (%) of complexes formed between β -CD and γ -CD with I-CLD are very similar to the ones obtained for CLD (Gamboa-Carballo 2018) (Table 1). In the case of this pollutant, the main variations are observed when α -CD is the host molecule. The α -CD having the smaller cavity is more susceptible to the changes in the size of the guest molecule, a size that in the studied cases was increased changing a chlorine atom with a bigger iodine atom.

Data reported in Table 2 reflects that I- β -HCH complexes exhibit structures with occlusion grades very similar to the ones obtained for non-labelled complexes in the case of conformers type B (B2 and B3). In the other hand, complexes with type C conformers (C1 and C4) display a greater variability of their occlusion grades overall in cases of the smaller CDs (α -CD and β -CD) which is an indicator that the formation of inclusion complexes with these conformers is more prone to variations when the size of the occluded molecule changes.

Table 2 Distribution of occlusion grade for each conformer of α -, β - and γ -CD obtained through MMH methodology for β -HCH (Ferino-Pérez 2019) and I- β -HCH. The percentages are based in the minima summing over 99% of the total population based in a Boltzmann energy distribution

| Host CD conformers | % Total occlusion | | % Partial occlusion | | % Non-occlusion | |
|--------------------------|-------------------|-----------------|---------------------|-----------------|-----------------|-----------------|
| | β -HCH | I- β -HCH | β -HCH | I- β -HCH | β -HCH | I- β -HCH |
| B2 - α -CD | 0.00 | 0.00 | 99.67 | 86.85 | 0.22 | 13.07 |
| B3 - α -CD | 0.00 | 0.00 | 99.59 | 85.18 | 0.33 | 14.50 |
| C1 - α -CD | 0.00 | 0.00 | 94.25 | 42.26 | 5.65 | 57.65 |
| C4 - α -CD | 0.00 | 0.00 | 96.69 | 36.57 | 3.22 | 63.34 |
| B2 - β -CD | 0.26 | 0.22 | 99.67 | 99.76 | 0.00 | 0.00 |
| B3 - β -CD | 0.00 | 0.00 | 99.72 | 99.92 | 0.19 | 0.00 |
| C1 - β -CD | 46.67 | 37.00 | 50.67 | 10.83 | 2.57 | 52.07 |
| C4 - β -CD | 0.00 | 94.36 | 46.80 | 5.01 | 53.18 | 0.53 |
| B2 - γ -CD | 99.97 | 99.97 | 0.00 | 0.00 | 0.00 | 0.00 |
| B3 - γ -CD | 28.70 | 0.74 | 70.19 | 99.15 | 0.56 | 0.03 |
| C1 - γ -CD | 94.55 | 90.38 | 0.85 | 9.54 | 4.53 | 0.00 |
| C4 - γ -CD | 92.44 | 99.98 | 0.00 | 0.00 | 7.53 | 0.00 |

Additionally, Figs. 3 and 4 show that, in all studied cases, the more stable complexes with iodine substituted pesticides are formed when γ -CD is the host molecule. The greater association energies are obtained for the formation of complexes with I- β -HCH. For both pesticides, the more thermodynamic favorable interactions occur with conformers B3 and C1. In consequence, for the re-optimization of the geometries of formed complexes, the global minima according to MMH methodology for these two conformers were selected for each guest molecule.

Refining of representative structures

In order to achieve a better description of geometries and electronic densities, the four structures corresponding to

inclusion complexes formed with studied pesticides and conformers B3 and C1 of γ -CD were re-optimized. Figure 6 allows making a comparison between structures obtained by the two methods previously mentioned.

In our knowledge, until now, there is not any study that describes the formation of these complexes with iodine substituted pesticides by DFT calculations. Comparing the results of both methods (semiempirical and DFT), presented in Fig. 6, it is possible to conclude that the geometric differences between the results of both methods are minor for the case of I-CLD. In the case of complexes formed with I- β -HCH, only small differences exist between structures obtained by PM6-D3H4X and M06-2X increasing this last method the occlusion grade of the pollutant (Fig. 6c) similar to the study of Ferino-Pérez et al. (2019). Spite of the considerable differences

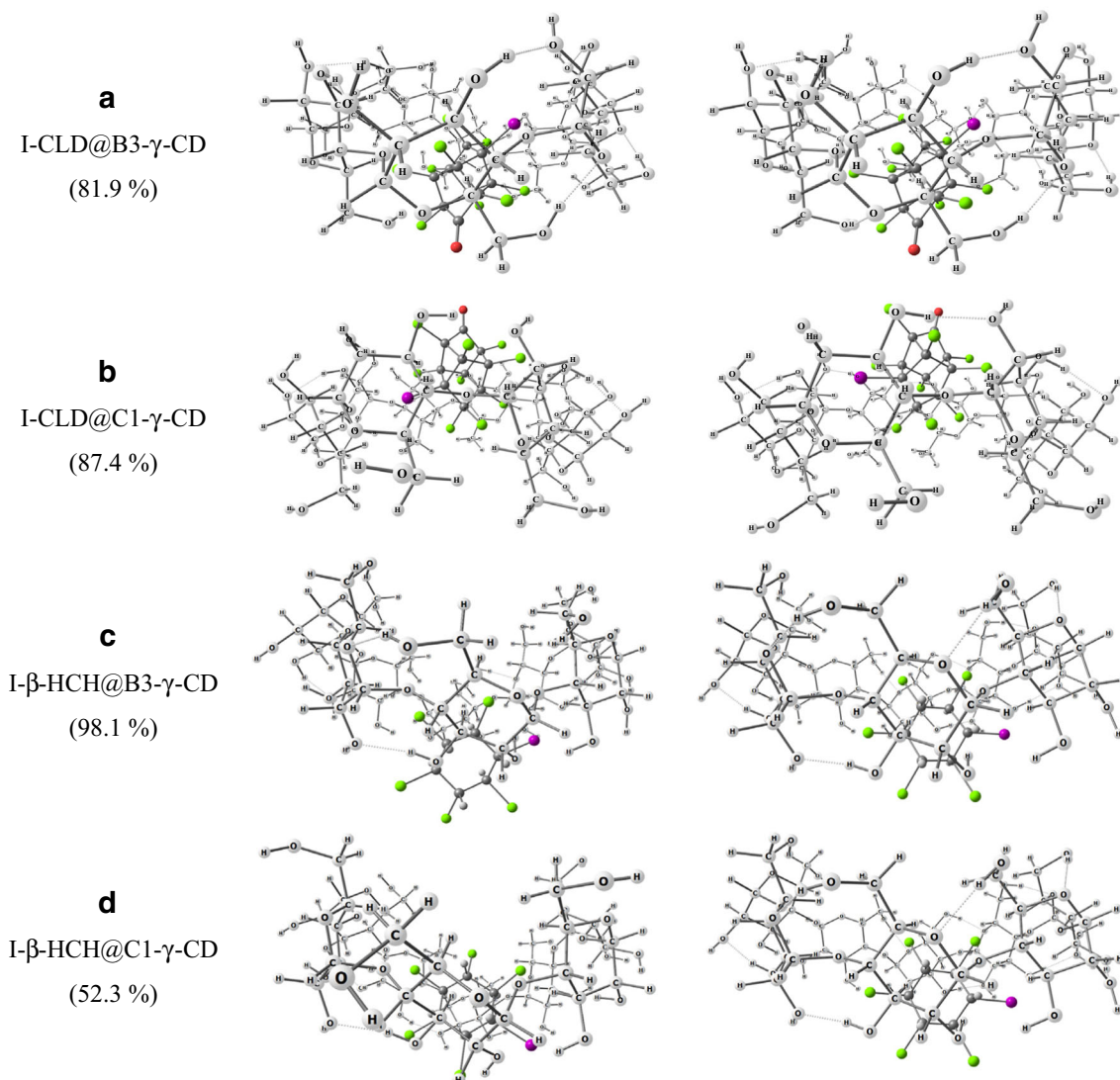


Fig. 6 Distinctive structures of complexes I-CLD@ γ -CD (**a**, **b**) and I- β -HCH@ γ -CD (**c**, **d**). I-CLD and I- β -HCH are shown in colors while γ -CD is in gray. In each couple displayed, the global minimum obtained

through MMH/PM6-D3H4X (left) and the one obtained through M06-2X/6-31G (right). In parentheses, the population according to Boltzmann distribution for MMH structure

between the initial structures of I- β -HCH@CD γ -CDs complexes before the DFT re-optimizations, the obtained structures present a great similarity for both conformers of the host molecule (Fig. 6).

Quantitative description of interactions. QTAIM analysis

Figure 7 shows the representations of BCPs for four molecular inclusion systems: CLD@C1- γ -CD and I-CLD@C1- γ -CD (Fig. 7a), and β -HCH@C1- γ -CD and I- β -HCH@C1- γ -CD (Fig. 7b). Tables 3 and 4 show the QTAIM analysis for I-CLD@C1- γ -CD and I- β -HCH@C1- γ -CD, respectively. Tables S3 and S4 of Supporting Information show the results of this analysis for the systems I-pesticide@B3- γ -CD. If the existing interactions in molecular inclusion complexes pesticide@ γ -CD are compared with their respective iodine substituted analogous, it is possible to appreciate that, in both cases, a great number of interactions are established between the pollutant and the interior cavity of γ -CD. It is valid to assume that this great amount of interactions favors the formation of stable complexes in spite of the fact that all

have a non-covalent nature. It could also be observed that interactions established in complexes are mainly of dispersive nature (vdW), although there are present several interactions classifiable as halogen bonds (XB), a product of electron density anisotropy around halogen atoms, or also hydrogen bonds (HB).

In the case of I-CLD@C1- γ -CD complex, HB appears as weak hydrogen bonds and several new XB are established. This is a direct consequence of a diminishing in interactions distances produced by the greater size of I-CLD with respect to CLD. In contrast, in I- β -HCH@C1- γ -CD complex, in spite of the resemblance between the “interaction patterns”, the absence of HB is remarkable, which are present in the β -HCH@C1- γ -CD complex. That occurs because the iodine atom introduced push away, through steric hindrance, the atoms that form the CD interior cavity. This steric hindrance causes a different effect from the observed for I-CLD where, as discussed above, iodine atom inclusion increases the number of HB and XB established with the CD cavity. In the complex I- β -HCH@C1- γ -CD, a widening of this cavity is also observed, while it adopts an ovoid shape (Fig. 7b). In spite of the differences previously described, it is possible to

Fig. 7 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 from the wavefunction values obtained by M06-2X/6-31G(d,p). The different types of interactions are identified as dispersive (vdW, in yellow), hydrogen bond (HB, in red) and halogen bond (XB, in purple)

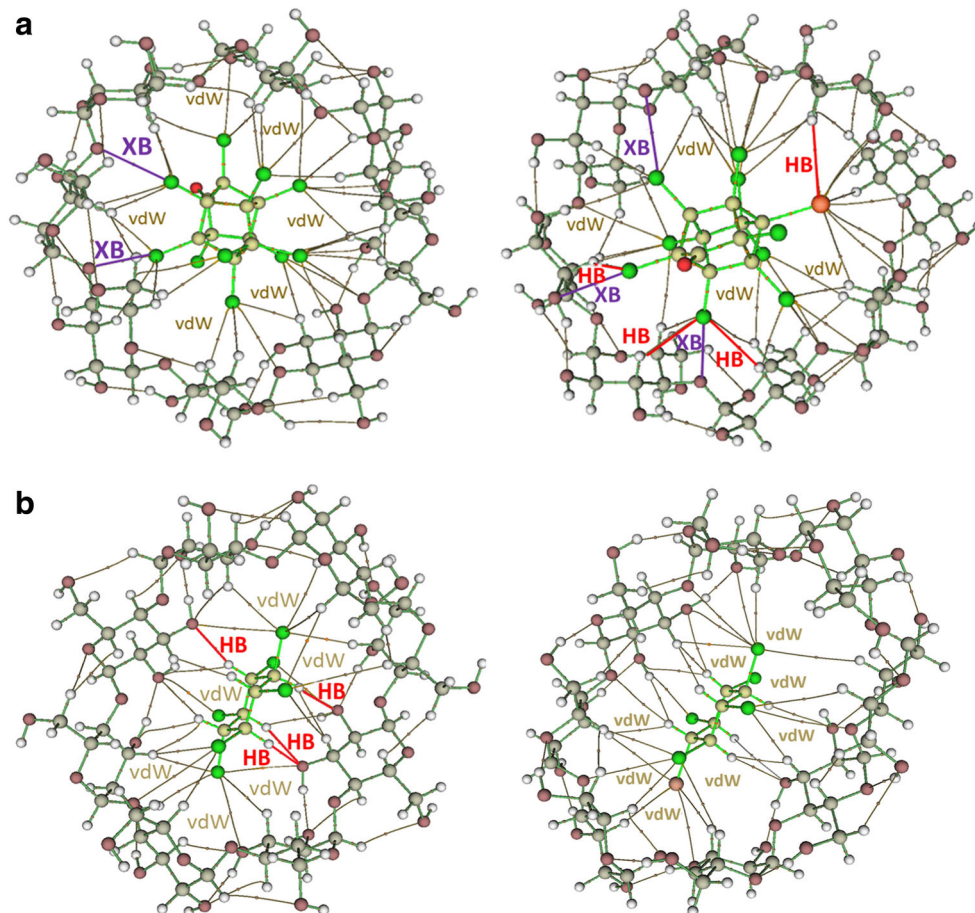


Table 3 Interatomic distances (d), electronic density (ρ), electronic density Laplacian ($\nabla^2\rho$), total energy density (H) and electron density ellipticity (ϵ) in BCPs for I-CLD@C1- γ -CD complex. Interaction distance is expressed in Å and the rest of values in atomic units

| Interactions | Atoms ^a | $d(\text{Å})$ | ρ | $\nabla^2\rho$ | H | ϵ | Type ^b |
|--------------|--------------------|---------------|--------|----------------|--------|------------|-------------------|
| 1 | I...H | 2.95 | 0.010 | 0.028 | 0.0009 | 0.06 | HB |
| 2 | I...H | 3.11 | 0.005 | 0.017 | 0.0010 | 0.21 | vdW |
| 3 | I...O | 3.33 | 0.009 | 0.032 | 0.0008 | 0.09 | vdW |
| 4 | I...H | 2.84 | 0.009 | 0.031 | 0.0013 | 0.06 | vdW |
| 5 | I...H | 3.20 | 0.006 | 0.018 | 0.0009 | 0.04 | vdW |
| 6 | I...O | 3.78 | 0.005 | 0.017 | 0.0007 | 0.12 | vdW |
| 7 | I...O | 3.65 | 0.006 | 0.021 | 0.0007 | 0.35 | vdW |
| 8 | I...H | 3.14 | 0.008 | 0.022 | 0.0010 | 0.05 | vdW |
| 9 | Cl...H | 3.45 | 0.002 | 0.006 | 0.0004 | 0.12 | vdW |
| 10 | Cl...O | 4.10 | 0.001 | 0.006 | 0.0004 | 0.64 | vdW |
| 11 | Cl...H | 3.39 | 0.002 | 0.008 | 0.0005 | 0.12 | vdW |
| 12 | Cl...H | 2.76 | 0.009 | 0.031 | 0.0014 | 0.01 | vdW |
| 13 | Cl...O | 3.11 | 0.009 | 0.035 | 0.0011 | 0.06 | vdW |
| 14 | Cl...O | 3.41 | 0.005 | 0.022 | 0.0010 | 0.19 | vdW |
| 15 | Cl...H | 2.93 | 0.007 | 0.023 | 0.0012 | 0.26 | vdW |
| 16 | Cl...H | 2.63 | 0.011 | 0.037 | 0.0014 | 0.03 | HB |
| 17 | Cl...H | 3.20 | 0.004 | 0.013 | 0.0008 | 1.95 | vdW |
| 18 | Cl...O | 2.91 | 0.013 | 0.050 | 0.0012 | 0.07 | XB |
| 19 | Cl...H | 3.18 | 0.004 | 0.014 | 0.0009 | 0.36 | vdW |
| 20 | Cl...H | 2.67 | 0.010 | 0.037 | 0.0017 | 0.02 | HB |
| 21 | Cl...H | 3.38 | 0.003 | 0.008 | 0.0005 | 0.38 | vdW |
| 22 | Cl...H | 3.16 | 0.003 | 0.011 | 0.0008 | 0.32 | vdW |
| 23 | Cl...H | 2.87 | 0.007 | 0.023 | 0.0011 | 0.03 | vdW |
| 24 | Cl...H | 3.18 | 0.004 | 0.012 | 0.0008 | 0.00 | vdW |
| 25 | Cl...O | 3.00 | 0.012 | 0.044 | 0.0010 | 0.06 | XB |
| 26 | Cl...H | 2.66 | 0.011 | 0.042 | 0.0019 | 0.11 | HB |
| 27 | Cl...H | 3.34 | 0.002 | 0.007 | 0.0005 | 0.41 | vdW |
| 28 | Cl...H | 2.85 | 0.006 | 0.022 | 0.0012 | 0.06 | vdW |
| 29 | Cl...O | 3.06 | 0.011 | 0.040 | 0.0011 | 0.11 | XB |
| 30 | Cl...H | 2.87 | 0.008 | 0.029 | 0.0015 | 0.37 | vdW |
| 31 | Cl...H | 3.17 | 0.004 | 0.013 | 0.0007 | 0.06 | vdW |
| 32 | Cl...H | 3.25 | 0.002 | 0.009 | 0.0006 | 0.20 | vdW |
| 33 | Cl...O | 3.91 | 0.002 | 0.008 | 0.0006 | 0.98 | vdW |
| 34 | Cl...H | 3.57 | 0.002 | 0.005 | 0.0003 | 0.08 | vdW |
| 35 | Cl...H | 3.01 | 0.006 | 0.019 | 0.0010 | 0.10 | vdW |
| 36 | Cl...O | 3.35 | 0.006 | 0.023 | 0.0011 | 0.10 | vdW |
| 37 | Cl...O | 3.83 | 0.002 | 0.011 | 0.0007 | 1.57 | vdW |
| 38 | Cl...O | 3.54 | 0.004 | 0.017 | 0.0010 | 0.59 | vdW |
| 39 | Cl...H | 3.10 | 0.005 | 0.017 | 0.0009 | 0.44 | vdW |

^a Atoms between which the interaction is established. At left, I-CLD atom, at right, the corresponding to CD

^b Interaction types characterized were dispersive (vdW), hydrogen bonds (HB) and halogen bonds (XB)

appreciate the existence of a great number of interactions that should stabilize the labelled compound.

The results of this work show that, like in CLD and HCH, their iodine analogs form inclusion complexes with cyclodextrins. Therefore, the formation of these

complexes can be a way for the separation of I-CLD and I-HCH from water. Thus, the CLD and HCH labelled with an iodine radioisotope could be added to polluted waters as a way to track cyclodextrin-mediated removal of these pesticides. This will allow to study the efficiency

Table 4 Interatomic distances (d), electronic density (ρ), electronic density Laplacian ($\nabla^2\rho$), total energy density (H) and electron density ellipticity (ε) in BCPs for I- β -HCH@Cl- γ -CD. Interaction distance is expressed in Å and the rest of values in atomic units

| Interactions | Atoms ^a | $d(\text{Å})$ | ρ | $\nabla^2\rho$ | H | ε | Type ^b |
|--------------|--------------------|---------------|--------|----------------|--------|---------------|-------------------|
| 1 | Cl...H | 3.16 | 0.005 | 0.015 | 0.0008 | 0.22 | vdW |
| 2 | Cl...O | 3.62 | 0.004 | 0.017 | 0.0009 | 0.55 | vdW |
| 3 | Cl...O | 3.83 | 0.002 | 0.011 | 0.0007 | 0.84 | vdW |
| 4 | Cl...O | 3.52 | 0.004 | 0.017 | 0.0009 | 0.17 | vdW |
| 5 | Cl...H | 2.97 | 0.005 | 0.018 | 0.0011 | 0.06 | vdW |
| 6 | Cl...H | 4.31 | 0.001 | 0.001 | 0.0001 | 0.09 | vdW |
| 7 | H...O | 2.68 | 0.006 | 0.023 | 0.0010 | 0.41 | vdW |
| 8 | Cl...H | 3.92 | 0.001 | 0.007 | 0.0002 | 1.78 | vdW |
| 9 | Cl...O | 3.85 | 0.002 | 0.010 | 0.0006 | 0.86 | vdW |
| 10 | Cl...H | 2.80 | 0.008 | 0.027 | 0.0011 | 0.04 | vdW |
| 11 | H...O | 3.21 | 0.002 | 0.009 | 0.0006 | 16.77 | vdW |
| 12 | H...H | 2.29 | 0.006 | 0.026 | 0.0014 | 7.00 | vdW |
| 13 | H...O | 2.57 | 0.008 | 0.027 | 0.0005 | 0.10 | vdW |
| 14 | Cl...H | 3.47 | 0.002 | 0.007 | 0.0004 | 0.17 | vdW |
| 15 | Cl...H | 2.67 | 0.009 | 0.032 | 0.0014 | 0.06 | vdW |
| 16 | Cl...O | 3.77 | 0.003 | 0.012 | 0.0007 | 2.28 | vdW |
| 17 | Cl...H | 3.00 | 0.005 | 0.017 | 0.0010 | 0.06 | vdW |
| 18 | I...H | 3.05 | 0.009 | 0.025 | 0.0010 | 0.02 | vdW |
| 19 | I...O | 3.59 | 0.006 | 0.023 | 0.0007 | 0.38 | vdW |
| 20 | I...H | 3.01 | 0.009 | 0.024 | 0.0009 | 0.08 | vdW |
| 21 | I...H | 3.53 | 0.003 | 0.010 | 0.0005 | 0.62 | vdW |
| 22 | H...H | 2.40 | 0.004 | 0.016 | 0.0010 | 0.28 | vdW |
| 23 | H...O | 3.20 | 0.002 | 0.009 | 0.0007 | 4.09 | vdW |
| 24 | H...H | 2.29 | 0.004 | 0.015 | 0.0010 | 0.13 | vdW |
| 25 | Cl...H | 3.25 | 0.003 | 0.012 | 0.0008 | 0.42 | vdW |
| 26 | H...O | 2.88 | 0.005 | 0.019 | 0.0012 | 0.34 | vdW |
| 27 | H...H | 2.38 | 0.005 | 0.019 | 0.0011 | 0.25 | vdW |
| 28 | H...O | 2.88 | 0.004 | 0.017 | 0.0009 | 2.42 | vdW |
| 29 | H...H | 2.25 | 0.006 | 0.020 | 0.0011 | 0.07 | vdW |

^a Atoms between which the interaction is established. At left, I-CLD atom, at right, the one corresponding to CD

^b Interaction types characterized were dispersive (vdW), hydrogen bonds (HB) and halogen bonds (XB)

of this process on a greater scale than the laboratory, easing the detection and following these compounds in treatment plants or environmental compartments.

Conclusions

MMH methodology coupled with PM6-D3H4x semiempirical Hamiltonian allows computationally to verify the formation of molecular inclusion complexes I-CLD@CDs and I- β -HCH@CDs. As in the complexes formed with CLD and β -HCH, more stable complexes with iodine substituted pesticides are formed when γ -CD is the host molecule. SMD/M06-2X/6-31G scheme was employed for the refinement of geometries of studied systems. QTAIM analysis demonstrated

that predominant interactions in complexes formed, as for non-labelled pesticides, have a dispersive nature. The comparison between CLD@CDs and β -HCH@CDs with their labelled analogous taking into account the geometries obtained by DFT and interactions detected in QTAIM analysis, proved the great similarity of CLD and β -HCH with I-CLD and I- β -HCH, respectively, in the formation process of molecular inclusion complexes. The possibility of using I-CLD and I- β -HCH as a way to track cyclodextrin-mediated removal of CLD and β -HCH was theoretically proved.

Acknowledgements Computational calculations were performed using *Wahoo*, the cluster of the *Centre Commun de Calcul Intensif* of the *Université des Antilles*, Guadeloupe, France. The authors wish to thank Raphael Pasquier, Jacques Laminie and Pascal Poulet for their support with the calculation facilities. The Informatics service of InSTEC at

Havana, Cuba, is also gratefully acknowledged. AFP thanks the Cooperation Service of the French Embassy in Cuba for supporting his stay in Guadeloupe.

Funding information The financial support was from the project CIMPest (CBA-330810-2018-P-1, INTEC, Dominican Republic) and project TATARCOP (InSTEC, Cuba).

References

- Allabashi R, Arkas M, Hörmann G, Tsiourvas D (2007) Removal of some organic pollutants in water employing ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers. *Water Res* 41:476–486
- Arkas M, Allabashi R, Tsiourvas D, Mattausch EM, Perfler R (2006) Organic/inorganic hybrid filters based on dendritic and cyclodextrin “nanosponges” for the removal of organic pollutants from water. *Environ. Sci. Technol.* 40:2771–2777
- Bader RFW (1991) A quantum theory of molecular structure and its applications. *Chem Rev* 91:893–928
- Bader RFW (2010) The density in density functional theory. *J Mol Struct* 943:2–18
- Baldwin RM (1986) Chemistry of radioiodine. *Int J Rad Appl Instr A* 37: 817–821
- Benfeito S, Rodrigues T, Garrido J, Borges F, Garrido EM (2013) Host-guest interaction between herbicide oxadiargyl and hydroxypropyl- β -cyclodextrin. *Scientific World J* 2013. <https://doi.org/10.1155/2013/825206>
- Bilensoy E (ed) (2011) Cyclodextrins in pharmaceuticals, cosmetics, and biomedicine: current and future industrial applications. John Wiley & Sons, Inc., Hoboken, pp 440
- Brahmkshatriya PS, Dobeš P, Fanfrlík J, Paruch K, Bronowska A, Lepšík M, Hobza P (2013) Quantum mechanical scoring: structural and energetic insights into cyclin-dependent kinase 2 inhibition by pyrazolo [1, 5-a] pyrimidines. *Curr Comput-Aided Drug Des* 9(1): 118–129
- Browne E, Firestone RB, Shirley VS (1986) Table of radioactive isotopes. John Wiley & Sons, Inc., Hoboken, pp 1050
- Cabidoche YM, Achard R, Cattani P, Clermont-Dauphin C, Massat F, Sansoulet J (2009) Long-term pollution by chlordecone of tropical volcanic soils in the French West Indies: a simple leaching model accounts for current residue. *Environ Pollut* 157:1697–1705
- Check CE, Faust TO, Bailey JM, Wright BJ, Gilbert TM, Sunderlin LS (2001) Addition of polarization and diffuse functions to the LANL2DZ basis set for p-block elements. *J Phys Chem A* 105: 8111–8116
- Clostre F, Cattani P, Gaude JM, Carles C, Letourmy P, Lesueur-Jannoyer M (2015) Comparative fate of an organochlorine, chlordecone, and a related compound, chlordecone-5b-hydro, in soils and plants. *Sci Total Environ* 532:292–300
- Codorniu-Hernández E, Mesa-Ibérico A, Hernández-Santiesteban R, Montero-Cabrera LA, Martínez-Luzardo F, Santana-Romero JL, Borrmann T, Stohner W-D (2005) Essential amino acids interacting with flavonoids: a theoretical approach. *Int J Quantum Chem* 103: 82–104
- Cruickshank DL, Rougier NM, Maurel VJ, Rossi RH, Buján EI, Bourne SA, Caira MR (2013) Permethylated β -cyclodextrin/pesticide complexes: X-ray structures and thermogravimetric assessment of kinetic parameters for complex dissociation. *J Incl Phenom Macrocycl Chem* 75:47–56
- Cruz-Gonzalez G, Julcour C, Chaumat H, Bourdon V, Ramon-Portugal F, Gaspard S, Jauregui-Haza UJ, Delmas H (2018) Degradation of chlordecone and beta-hexachlorocyclohexane by photolysis, (photo-)Fenton oxidation and ozonation. *J. Environ. Sci. Health. Part B* 53:121–125
- Della Rossa P, Jannoyer M, Mottes C, Plet J, Bazizi A, Arnaud L, Jestin A, Woignier T, Gaude JM, Cattani P (2017) Linking current river pollution to historical pesticide use: insights for territorial management? *Sci Total Environ* 574
- Duca G, Boldescu V (2008) Cyclodextrins – fields of application. Part I *Chem J Mold Gen Ind Eco Chem* 3:30–37
- Durimel A, Altenor S, Miranda-Quintana R, Couespel Du Mesnil P, Jauregui-Haza U, Gadiou R, Gaspard S (2013) pH dependence of chlordecone adsorption on activated carbons and role of adsorbent physico-chemical properties. *Chem Eng J* 229:239–249
- Durimel A, Passé-Coutrin N, Jean-Marius C, Gadiou R, Enriquez-Victorero C, Hernández-Valdés D, Jauregui-Haza U, Gaspard S (2015) Role of acidic sites in beta-hexachlorocyclohexane (β -HCH) adsorption by activated carbons: molecular modelling and adsorption-desorption studies. *RSC Adv* 5:85153–85164
- Enriquez-Victorero C, Hernández-Valdés D, Montero-Alejo AL, Durimel A, Gaspard S, Jáuregui-Haza U (2014) Theoretical study of γ -hexachlorocyclohexane and β -hexachlorocyclohexane isomers interaction with surface groups of activated carbon model. *J. Mol. Graphics Modell.* 51:137–148
- Ferino-Pérez A, Gamboa-Carballo JJ, Ranguin R, Levalois-Grützmacher J, Bercion Y, Gaspard S, Miranda-Quintana RA, Arias M, Jáuregui-Haza UJJR (2019) Evaluation of the molecular inclusion process of β -hexachlorocyclohexane in cyclodextrins. *RSC Adv* 9:27484–27499
- Fernandez-Bayo JD, Saison C, Voltz M, Disko U, Hofmann D, Berns AE (2013) Chlordecone fate and mineralisation in a tropical soil (andosol) microcosm under aerobic conditions. *Sci Total Environ* 463-464:395–403
- Fournier A, Feidt C, Lastel ML, Archimede H, Thome JP, Mahieu M, Rychen G (2017) Toxicokinetics of chlordecone in goats: implications for risk management in French West Indies. *Chemosphere* 171: 564–570
- Frisch MJ et al (2009) Gaussian 09, revision a. 01. Gaussian, Inc., Wallingford
- Gamboa-Carballo JJ (2018) Molecular inclusion complexes of chlordecone and 1-iodinechlordecone with natural cyclodextrins. Quantum description of association process. Master thesis, Instituto superior de Teconologías y Ciencias Aplicadas, Universidad de La Habana, 124 pp
- Gamboa-Carballo JJ, Melchor-Rodríguez K, Hernandez-Valdes D, Enriquez-Victorero C, Montero-Alejo AL, Gaspard S, Jauregui-Haza UJ (2016a) Theoretical study of chlordecone and surface groups interaction in an activated carbon model under acidic and neutral conditions. *J Mol Graphics Modell* 65:83–93
- Gamboa-Carballo JJ, Melchor-Rodríguez K, Hernández-Valdés D, Jáuregui-Haza UJ (2016b) Interaction of 1-iodochlordecone, as radioactive tracer, with carboxylate group on activated carbon. *Nucleus* 59:14–18
- Gamboa-Carballo JJ, Rana VK, Levalois-Grützmacher J, Gaspard S, Jauregui-Haza U (2017) Structures and stabilities of naturally occurring cyclodextrins: a theoretical study of symmetrical conformers. *J Mol Model* 23:318
- Garrido EM, Santos M, Silva P, Cagide F, Garrido J, Borges F (2012) Host-guest complexes of phenoxy alkyl acid herbicides and cyclodextrins. MCPA and β -cyclodextrin. *J Environ Sci Health Part B* 47: 869–875
- Grimme S, Ehrlich S, Goerigk L (2011) Effect of the damping function in dispersion corrected density functional theory. *J Comput Chem* 32: 1456–1465
- Hohenberg P, Kohn W (1964) Inhomogeneous Electron gas. *Phys Rev* 136:B864–B871

- Johnson ER, Mackie ID, DiLabio GA (2009) Dispersion interactions in density-functional theory. *J Phys Org Chem* 22:1127–1135
- Johri AK, Dua M, Tuteja D, Saxena R, Saxena DM, Lal R (1998) Degradation of alpha, beta, gamma and delta-hexachlorocyclohexanes by *Sphingomonas paucimobilis*. *Biotechnol Lett* 20:885–887
- Johri AK, Dua M, Saxena DM, Sethunathan N (2000) Enhanced degradation of hexachlorocyclohexane isomers by *Sphingomonas paucimobilis*. *Curr Microbiol* 41:309–311
- Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. *Phys Rev* 140:A1133–A1138
- Le Déaut JY, Procaccia C (2009) In: Nationale A (ed) Les impacts de l'utilisation de la chlordécone et des pesticides aux Antilles: bilan et perspectives d'évolution. OPECST, Paris, p 487
- Li YF (1999) Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Sci Total Environ* 232:121–158
- Listing of POPs in the Stockholm Convention: Annex A (Elimination) (2011)
- Liu H, Cai X, Wang Y, Chen J (2011) Adsorption mechanism-based screening of cyclodextrin polymers for adsorption and separation of pesticides from water. *Water Res* 45:3499–3511
- Lu T, Chen F (2012) Multiwfn: a multifunctional wavefunction analyzer. *J Comput Chem* 33:580–592
- Marenich AV, Cramer CJ, Truhlar DG (2009) Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J Phys Chem B* 113:6378–6396
- Montero LA, Esteva AM, Molina J, Zapardiel A, Hernández L, Márquez H, Acosta A (1998) A theoretical approach to analytical properties of 2,4-Diamino-5-phenylthiazole in water solution. Tautomerism and Dependence on pH. *J Am Chem Soc* 120:12023–12033
- Montero-Cabrera LA (2000) GRANADA User's Manual. Available at the web site: <http://karin.fq.uh.cu/mmh.htm>
- Montero-Cabrera LA, Llano J, Molina J, Fabian J (2000a) Multiple minima hypersurfaces of water clusters for calculations of association energy. *Int J Quantum Chem* 79:8–16
- Montero-Cabrera LA, Sanchez E, Cruz R (2000b) Q3 program. Calculation of thermodynamic quantities of association in NVT ensembles. Available at the web site: <http://karin.fq.uh.cu/mmh.htm>
- Mura P (2014) Analytical techniques for characterization of cyclodextrin complexes in aqueous solution: a review. *J Pharm Biomed Anal* 101:238–250
- Nakanishi W, Hayashi S, Narahara K (2008) Atoms-in-molecules dual parameter analysis of weak to strong interactions: behaviors of electronic energy densities versus Laplacian of electron densities at bond critical points. *J Phys Chem A* 112:13593–13599
- Nakanishi W, Hayashi S, Narahara K (2009) Polar coordinate representation of $H_b(rc)$ versus $(h/2\pi m)^{1/2} \nabla^2 \rho_b(rc)$ at BCP in AIM analysis: classification and evaluation of weak to strong interactions. *J Phys Chem A* 113:10050–10057
- Newhouse K, Berner T, Mukerjee D, Rooney A (2009) Toxicological review of chlordécone (kepone). EPA/635/R-07/004F, U.S. Environmental Protection Agency, Washington, DC
- Onogbesele CO, Scrimshaw MD (2014) Hexabromocyclododecane and hexachlorocyclohexane: how lessons learnt have led to improved regulation. *Crit Rev Environ Sci Technol* 44:1423–1442
- Phillips TM, Seech AG, Lee H, Trevors JT (2005) Biodegradation of hexachlorocyclohexane (HCH) by microorganisms. *Biodegradation* 16:363–392
- Rana VK, Kissner R, Gaspard S, Levalois-Grützmacher J (2016) Cyclodextrin as a complexation agent in the removal of chlordécone from water. *Chem Eng J* 293:82–89
- Řezáč J, Hobza P (2011a) Advanced corrections of hydrogen bonding and dispersion for semiempirical quantum mechanical methods. *J Chem Theory Comput* 8:141–151
- Řezáč J, Hobza P (2011b) A halogen-bonding correction for the semiempirical PM6 method. *Chem Phys Lett* 506:286–289
- Robert S (2012) Historique de la contamination des sédiments littoraux des Antilles françaises par la chlordécone (ChloSed), Rapport final de convention MAAP-Ifremer. L'Houmeau Ifremer, pp 92
- Roy LE, Hay PJ, Martin RL (2008) Revised basis sets for the LANL effective core potentials. *J Chem Theory Comput* 4:1029–1031
- Sakakibara F, Takagi K, Kataoka R, Kiyota H, Sato Y, Okada S (2011) Isolation and identification of dieldrin-degrading *Pseudonocardia* sp. strain KSF27 using a soil-charcoal perfusion method with aldrin trans-diol as a structural analog of dieldrin. *Biochem Biophys Res Commun* 411:76–81
- Sawicki R, Mercier L (2006) Evaluation of mesoporous cyclodextrin-silica nanocomposites for the removal of pesticides from aqueous media. *Environ. Sci. Technol.* 40:1978–1983
- Schäfer AI, Stelzl K, Faghih M, Sen Gupta S, Krishnadas KR, Heißler S, Pradeep T (2017) Poly (ether sulfone) nanofibers impregnated with β -Cyclodextrin for increased micropollutant removal from water. *ACS Sustain Chem Eng* 6:2942–2953
- Sifaoui H, Modarressi A, Magri P, Stachowicz-Kusnierz A, Korchowiec J, Rogalski M (2016) Formation of beta-cyclodextrin complexes in an anhydrous environment. *J Mol Model* 22:207
- Steed J, Atwood J (2009) Supramolecular chemistry. John Wiley & Sons, Ltd, Chichester
- Stewart JJ (2007) Optimization of parameters for semiempirical methods V: modification of NDDO approximations and application to 70 elements. *J Mol Model* 13:1173–1213
- Stewart JJP (2016) MOPAC2016. Stewart Computational Chemistry, Colorado Springs
- Szejtli J (1998) Introduction and general overview of cyclodextrin chemistry. *Chem Rev* 98:1743–1754
- Vallack HW, Bakker DJ, Brandt I, Broström-Lundén E, Brouwer A, Bull KR, Gough C, Guardans R, Holoubek I, Jansson B, Koch R, Kuylentierna J, Lecloux A, Mackay D, McCutcheon P, Mocarelli P, Taalman RDF (1998) Controlling persistent organic pollutants—what next? *Environ Toxicol Pharmacol* 6:143–175
- Vijgen J, Yi LF, Forter M, Lal R, Weber R (2006) The legacy of lindane and technical HCH production. *Organohal Compd* 68:899–904
- Vilardebo A, Beugnon M, Melin P, Lecoq J, Aubert B (1974) Chlordécone et autres insecticides dans la lutte contre le charançon du bananier *Cosmopolites sordidus* GERM. *Fruits* 29:267–278
- Willett KL, Ulrich EM, Hites RA (1998) Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environ Sci Technol* 32:2197–2207
- Wycisk P, Stollberg R, Neumann C, Gossel W, Weiss H, Weber R (2013) Integrated methodology for assessing the HCH groundwater pollution at the multi-source contaminated mega-site Bitterfeld/Wolfen. *Environ Sci Pollut Res* 20:1907–1917
- Xiao H, Li N, Wania F (2004) Compilation, evaluation, and selection of physical-chemical property data for α -, β -, and γ -hexachlorocyclohexane. *J Chem Eng Data* 49:173–185
- Zhang X, Liu J, Hou W, Tong J, Ren L, Sun G, Sun Y (2016) Preparation and properties of pesticide/cyclodextrin complex intercalated into ZnAl-layered double hydroxide. *Ind Eng Chem Res* 55:1550–1558
- Zhao Y, Truhlar DG (2008) A prototype for graphene material simulation: structures and interaction potentials of coronene dimers. *J Phys Chem C* 112:4061–4067

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.