



Theoretical study of γ -hexachlorocyclohexane and β -hexachlorocyclohexane isomers interaction with surface groups of activated carbon model

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ABSTRACT

Activated carbon (AC) is employed in drinking water purification without almost any knowledge about the adsorption mechanism of persistent organic pollutants (POPs) onto it. Hexachlorocyclohexane (HCH) is an organochlorinated contaminant present in water and soils of banana crops production zones of the Caribbean. The most relevant isomers of HCH are γ -HCH and β -HCH, both with great environmental persistence. A theoretical study of the influence of AC surface groups (SGs) on HCH adsorption is done in order to help to understand the process and may lead to improve the AC selection process. A simplified AC model consisting of naphthalene with a functional group was used to assess the influence of SGs over the adsorption process. The Multiple Minima Hypersurface (MMH) methodology was employed to study γ -HCH and β -HCH interactions with different AC SGs (hydroxyl and carboxyl) under different hydration and pH conditions. The results obtained showed that association of HCH with SGs preferentially occurs between the axial protons of HCH and SG's oxygen atom, and the most favorable interactions occurring with charged SGs. An increase in carboxylic SGs content is proposed to enhance HCH adsorption onto AC under neutral pH conditions. Finally, this work presents an inexpensive computer aided methodology for preselecting activated carbon SGs content for the removal of a given compound.

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1. Introduction

Hexachlorocyclohexane (HCH) is a monocyclic saturated chlorinated hydrocarbon of chemical formula $C_6H_6Cl_6$. HCH is synthesized, by photochemical chlorination of benzene. The synthesis product, a mixture of HCH isomers (67–70% of α -HCH (alpha-HCH), 10–12% of γ -HCH or lindane, 5–6% of β -HCH (beta-HCH), 6% of δ -HCH, traces of ϵ -, λ - and ν -HCH) is called “technical” HCH. Nearly 600,000 tons of HCH isomers were used in many countries of the world between the 1940s and the 1990s to control a wide range of agricultural, horticultural, and public health pests [1–6]. Indeed, heavily HCH contaminated sites have been

reported in several countries such as The Netherlands [7], Brazil [8], Germany [9,10], Spain [11,12], China [13], Greece [14], Canada [15], the United States [15], and India [1,16]. HCH isomers can be detected in all environmental compartments, including water, sediments, air and biota [17], where they accumulate and then enter surface water as a result of runoff from agricultural land. Because of their suspected carcinogenic, persistent, bioaccumulative and endocrine disrupting properties [18,19], the use of Lindane has been banned in at least 52 countries and HCH isomers were then included to the POP Stockholm convention [20]. Lindane is the sole isomer having insecticide properties, nearly 90% of the HCH mixture are inactive isomers [21]. Because of their low vapour pressure (4.69×10^{-3} to 1.25×10^{-3} Pa), hexachlorocyclohexane isomers evaporate slowly from soil and surface waters. Their high sorption coefficient to organic carbon ($K_{oc} \approx 3.57$) shows its excellent affinity for organic matter rich soils. The β -HCH is the isomer with the higher mobility and the α -HCH isomer is persistent in soils. The α -HCH and the γ -HCH isomer are the most dispersed in all media (air, soils, water), α -HCH and β -HCH isomers can be

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transported by air [22–25]. Technical HCH was used in banana plantation of the French West Indies Islands, Guadeloupe and Martinica, since 1951 to prevent the development of parasite such as banana weevil (*Cosmopolite sordidus*) which attacks the roots of this plant. Its use was then banned in 1972. Therefore, more than forty years after HCH has been banned the molecule can be found in soils, water and the food chain in Guadeloupe and Martinica [26]. To limit impregnation to pesticides, in the polluted areas of Guadeloupe and Martinica, drinking water production plants were equipped with activated carbon filters.

The adsorption process onto activated carbon (AC) is a very complex phenomenon driven by multiple factors that range from chemical composition to textural properties of the AC. The influence of surface group content over adsorption properties has been reported and studied to some extent both theoretically and experimentally for porous carbons, mainly AC and soot particles [27–32]. In the experimental works, either commercial AC with different SG content have been used in order to correlate this content with the adsorption capacities, or designed and tested AC with different SG contents. Even though, modifying the SGs content can lead to changes in the hydrophilic/lipophilic balance, the modifications should guarantee the specific design purpose. In this regard the computational chemistry can play a major role in designing specific modifications to obtain more efficient and specific adsorbents [31,33].

In order to get information on structural and textural properties favoring HCH adsorption on AC, Durimel et al. attempted to correlate adsorption studies data to some activated carbons surface functional groups composition. This study demonstrated that β -HCH adsorption was favored by the presence of high amounts of acidic groups at the AC surface, suggesting that hydrogen bonds were involved in adsorption mechanism [34]. To get more insight on the adsorption mechanism of HCH onto AC this work will focus on the most elementary factor i.e. the influence of some different SG over the adsorption energy. In this work, the interactions of both isomers of HCH (γ and β) with two SGs of AC are studied using multiple minima hypersurface (MMH) methodology [35–38]. MMH is a non-dynamical stochastic approach that allows estimating the thermodynamic association functions by means of the internal energy calculations with semiempirical Hamiltonians. In a previous work, exploring the interactions space through MMH methodology has helped to identify the main interactions responsible for chlordecone adsorption in a similar system [39].

This research will permit to design a methodology to evaluate the influence of SGs over the adsorption of small molecules onto AC allowing to help designing the best AC for the removal of a particular compound. It is important to note that focus is on finding the SGs improving the adsorption process.

2. System under study

Computational methods have been used widely to investigate the adsorption energies of guest molecules to idealized models of carbon-based materials. However, it is important to bear in mind that the description of the interactions between guest molecules and carbon surfaces is still challenging with current theoretical techniques. For these idealized models of carbon based materials, small polycycles and their oxidized derivatives are a common choice [27,40–50]. In fact, naphthalene [40,42] and coronene [41,45–47] have repeatedly been employed as such idealized models. The use of such small models has both advantages and disadvantages, being the most obvious of the advantages the savings in computational resources allowing either the application of relatively high level calculations or a throughout exploration of the interactions space. Small carbon models such as the naphthalene

allows the use of most quantum chemical methods and the correct description of non-local correlations as well as the evaluation of zero point and thermal contributions to the enthalpy [45] or the application of energy partition schemes to analyze binding characteristics.

Obviously, the use of these idealized models brings alone negative size effects and, in some cases, the oversimplification of the structure. The dramatic reduction in size of these models with respect to the real structures can reduce the non-local contributions to the dispersion energies. In the specific case of AC, the use of oxidized forms of polycycles completely neglects the influence of pore shape, defects, pore size and pore connectivity but in return allows a quantum chemical description of the interactions with the adsorbed molecules.

In a previous work, Durimel et al. showed that lindane adsorption onto the studied ACs is not diffusion controlled [34]. In order to center our attention in the SGs influence over the adsorption process, the selected AC model for the simulations consists of naphthalene with a functional group attached, as shown in Fig. 1 together with γ - and β -HCH structures. As surface groups, carboxylic acid (COOH) and hydroxyl (OH) both directly attached to sp² carbons were selected since these are the most commonly encountered and abundant oxygenated SGs found on AC surface [34,51,52]. To account for different pH conditions, chemical modifications to the SGs i.e. COO[−] and O[−] respectively were included. This model for AC does not take into account morphological or topological characteristics of the AC, but focuses on SG interaction with adsorbate, which is the main goal of this work.

The main advantage of this simple model is that it allows a big number of calculations while retaining the main feature of AC we are interested in (i.e. edge surface groups influence over adsorption processes).

3. Methods and procedures

In order to explore the conformational space corresponding to the interaction of each SG with water and both HCH isomers, multiple minima hypersurface procedures were applied (MMH) [35–38]. MMH is a very useful and reliable approach for localizing the minima of weakly interacting systems and, therefore, it has been successfully employed in several studies [53–60]. This procedure combines quantum mechanical methods for the calculations of energy with statistical mechanics to obtain thermodynamic quantities related to the molecular association process. The main procedure of this approach will be outlined briefly.

An appropriate construction of several random molecular geometries initially generates a set of n non-redundant cluster configurations, starting from the independently optimized structures of AC, γ -HCH, β -HCH and water. The random structures are optimized, normally following an energy gradient pathway, and a set of clusters of local minima in the configuration space is obtained. The energy, ε_i , of every i th cluster of the ensemble is thus obtained.

The partition function of molecular association is calculated by choosing the same set of non-interacting molecules as reference value for the energy scale, which means that the association process is taken as isothermal.

Thermodynamic properties such as association energy (ΔE_{assoc}), entropy (S_{assoc}), and Helmholtz free energy (A_{assoc}) are then calculated by this procedure [36,37].

The standard MMH procedure [36] put the solute in the center of a cubic box and then generates the solvent molecules in random configurations. By this procedure, the space region for generated solvent molecules cannot be restricted [38]. The above mentioned procedure combined with the model used here, would lead to an inefficient exploration of the interesting interaction

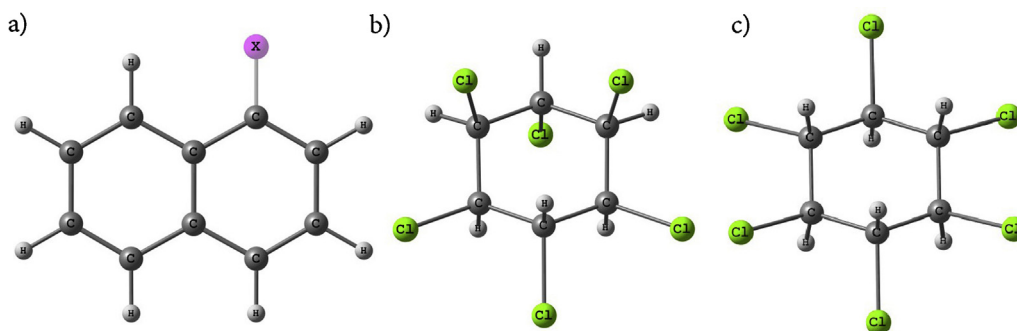


Fig. 1. (a) AC model consisting on oxidized naphthalene. The position corresponding to the SG is marked as $X = \text{COOH}, \text{COO}^-, \text{OH}, \text{O}^-$. (b) γ -HCH and (c) β -HCH.

region. In order to make a correct exploration of the interactions space corresponding to the used model, two modifications to standard MMH procedure were done. First, a modification of the program that generates the random configurations to allow specification of the region, orientation and dimensions of the solvent box [38]. This functionality can be used to make a more rational use of computational resources and improved analysis when exploring the configurational space involving an elongated shape solute molecule.

The second modification consists of an additional step to select the minimum number of random configurations needed to ensure a correct exploration of the configurational space. Convergence of thermodynamic association energy was selected as a criterion of correct hypersurface exploration. For this study the system $\text{COOH}/\beta\text{-HCH}/2$ water molecules was selected. This system was a priori selected because neutral systems have flatter potential energy surface (PES) and thus exploration becomes more complex.

Once the system is selected a sufficiently large number of random configurations are generated (i.e. 1600 configurations) and the rest of MMH procedures are applied. Then, a Fisher's test for a 95% of confidence is applied for the E_{assoc} vs. number of initial configurations considered in E_{assoc} calculation. E_{assoc} considering the full set of 1600 initial configurations was used as reference value. The E_{assoc} is assumed to be converged when at least 1000 initial configurations are considered. The variance beyond 1000 configurations is used to compare populations and identify the minimal number of initial configurations to achieve convergence.

With this procedure the minimum number of initial configurations needed to achieve convergence of ΔE_{assoc} is obtained together with the variation coefficient for the obtained ΔE_{assoc} . This procedure is repeated three times, taking the higher number of initial configurations needed and adding another 100 configurations as a security measure. This number of initial configurations is then used to explore the configurational space of all systems. By introducing this procedure the convergence of thermodynamic association energy is assessed statistically rather than by visual observation as it has been the practice until now, keeping computational cost as low as possible. Additionally, uncertainties associated with potential energy surface (PES) exploration can be statistically evaluated.

It must be noticed that the above outlined approach can provide, at the same time, important model structures with true statistical significance of the SG–HCH interaction and the role of water molecules in different hydration conditions together with the thermodynamic variables.

A plausible alternative for the calculation of supermolecules in the manner of serial procedures is the use of a semiempirical Hamiltonian. PM6 semiempirical Hamiltonian [61] with the recently introduced DH2X correction [62,63] was chosen because it has been shown that PM6-DH2 represents one of the most robust semiempirical method for describing non covalent interactions [63,64]. The

X correction implemented on top of DH2 correctly describes halogen bonding interactions [63,65], which are most likely important in our systems. To obtain energy minima structures of isolated molecules and clusters, PM6-DH2X Hamiltonian was used as implemented in MOPAC 2009 [66].

Since adsorption of HCH occurs from aqueous solution, the association energies for $\text{SG}/(\text{H}_2\text{O})_{n=0-3}$ were calculated to be used as a reference. The maximum number of water molecules was set to 3 because it has been previously reported that for similar carbonaceous clusters three water molecules are enough to saturate OH and COOH as surface groups [50]. To study the adsorption of HCH onto AC and the influence of hydration conditions, the association energies for β - and γ -HCH/SG/ $(\text{H}_2\text{O})_{n=0-3}$ systems were calculated. The procedure explained in detail and all programs for processing are available on a web site [35].

4. Results and discussion

4.1. PES exploration

As described above, the MMH procedures were applied to three sets of 1600 random independent configurations of the system $\beta\text{-HCH}/\text{naphthalene-1-carboxylic acid}/(\text{H}_2\text{O})_2$. This system was selected because it represents a hard case for convergence of association energy since it is neutral and one of the largest to be investigated in the present work. The value of the root mean square deviation (RMSD) for the three sets in the assumed converged interval (i.e. 1000–1600 starting configurations) was 0.11, 0.07 and 0.09 kJ/mol respectively. This RMSD are much lower than the accuracy of any semiempirical Hamiltonian [64,65] indicating that the assumption was right. The Fisher's test reveals that the minimum number of starting configurations needed to achieve convergence of molar association energy with a 95% of confidence for the three sets are 200, 600 and 250 respectively. Thus, in order to set the number of random configurations to be generated for each system the highest value i.e. 600 was selected and another 100 were added as a security margin, giving a total of 700 starting configurations.

To evaluate the dispersion of ΔE_{assoc} , the three values considering 700 starting configurations were chosen and, then the RMSD was calculated. The RMSD was 0.09 kJ/mol, a value lower than the RMSE of 3.3 and 3.1 kJ/mol reported for the PM6-DH2 semiempirical Hamiltonian over $\text{S66} \times 8$ and S66a8 data sets respectively [67].

4.2. Water clustering

In order to understand the role of water as solvent in the interactions of HCH with OH and COOH SGs, it is important to know how many water molecules are needed to saturate the SG (how many molecules compose the first solvation sphere). In an ab initio study of water molecules clustering on partially

Table 1
Mean adsorption energy per water molecule (ΔE_{assoc}) for small water aggregates containing n molecules of H_2O . Energies are given in kJ/mol.

SG	n	ΔE_{assoc}	$\Delta E_{\text{assoc}}^a$	$\Delta E_{\text{assoc}}^a - \Delta E_{\text{assoc}}$	SG	n	ΔE_{assoc}
COOH	1	−36.4	−38.1	−0.8	COO^-	1	−64.0
	2	−33.8	−40.3	−6.7		2	−56.8
	3	−31.1	−37.6	−6.5		3	−53.5
OH	1	−17.7	−19.3	−0.7	O^-	1	−52.1
	2	−26.8	−26.9	0.6		2	−49.7
	3	−28.3	−34.2	−5.2		3	−50.1

^a Values from Collignon et al. [50].

oxidized carbonaceous clusters, Collignon et al. showed that three and two water molecules are enough to saturate OH and COOH groups anchored on the edge of $\text{C}_{80}\text{H}_{22}$ graphite crystallites respectively [50]. For that reason, the maximum number of water molecules added was limited to three. In that work only the energies of each single configuration were considered while in the present work all local minima of each interacting hypersurfaces are explored.

In order to compare the results from both methodologies, Table 1 includes the adsorption energy per water molecule obtained in Collignon et al. study ($\Delta E_{\text{assoc}}^a$), together with the mean adsorption (association) energies (ΔE_{assoc}) for water

molecules adsorbed on the surface group for naphthalen-10l (OH) and naphthalen-1-carboxylic acid (COOH). The same information is presented for the corresponding charged forms of the SGs (O^- and COO^-) to take into account different pH conditions.

As it can be seen from Table 1, the ΔE_{assoc} is lower for COOH group than for OH group. This may be due to higher number of hydrogen bonding interactions between water molecules and SG for COOH relative to OH group. The lowest ΔE_{assoc} for COOH group is achieved with a single water molecule adsorbed, and no big differences in ΔE_{assoc} are observed after increasing the number of water molecules. This result indicates that the first water molecule saturates the COOH group and is determinant for the solvation process. For OH group the saturation corresponds to an aggregate containing two or three water molecules. This result is qualitatively different from that obtained by Collignon et al. [50], since they found saturation of SG after adding two water molecules for COOH and three for OH.

The ΔE_{assoc} given in Table 1 for charged SGs showed that affinity of water molecules increases from O^- to COO^- . Besides, as expected, ΔE_{assoc} is lower for charged SGs than for neutral SGs showing stronger coulomb-dominated interactions leading to higher affinity between water and charged SGs. For both charged SGs a single water molecule is enough to reach saturation.

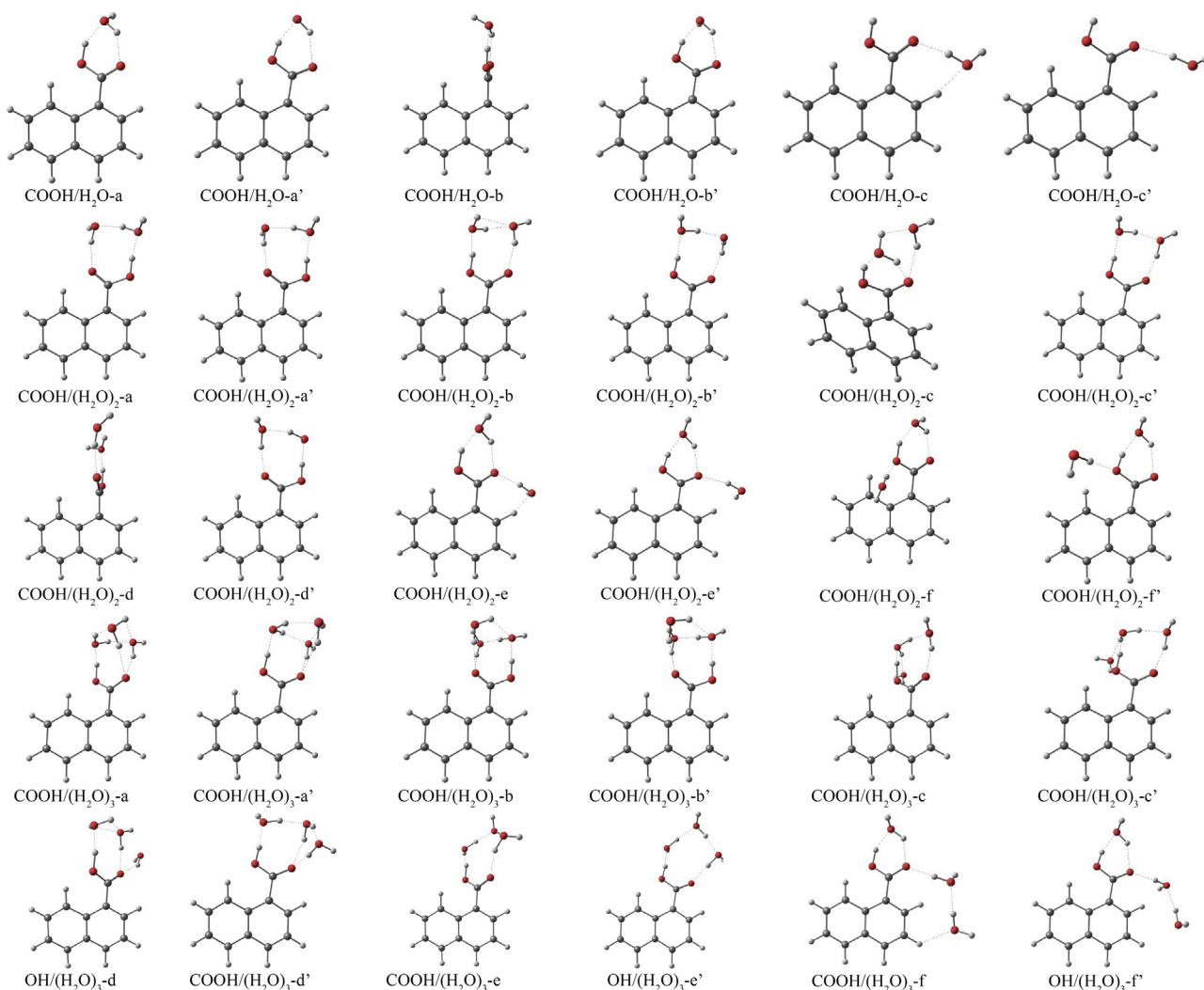


Fig. 2. Distinctive minima structures found for the systems $\text{COOH}/(\text{H}_2\text{O})_{n=1-3}$. Letters denote different structures found at PM6-DH2X and quoted letters account for the corresponding reoptimized structures at B3LYP/6311++G(2d,2p)//B3LYP/cc-PVDZ.

Note that for adsorption of a single water molecule onto neutral SG, the results obtained in this work are very close to those obtained for Collignon et al. [50], while bigger differences arisen when the number of water molecules increased. This could be related with the differences between the configurational space explorations. It is important to study the hydration of SGs and HCH interactions with SGs in a consistent fashion by using the same methodology to explore the interactions space. This is done in order to have a coherent point of comparison between the affinities of SGs for HCH or water molecules.

From the full set of minima structures, groups of distinctive minima were selected and each PM6-DH2X geometry was first re-optimized using B3LYP functional with cc-PVDZ basis set, and then, a single-point calculation with the 6-311++G(2d,2p) basis was performed to improve the electronic energies. This is the same methodology used for the inner part of the ONIOM scheme employed by Collignon et al. [50]. The goal here was to use the same scheme as the previous authors to be able to compare and demonstrate the importance of the interactions space exploration, showing that even at that level of theory, several structures must be taken into account for a correct description of the system. Table 2 summarizes association energies for the set of distinctive minima obtained using PM6-DH2X (ΔE_{assoc}), and the results from re-optimizing those

complexes using the same DFT methodology as Collignon et al. (B3LYP/6311++G(2d,2p)//B3LYP/cc-PVDZ) [50].

From Table 2 it can be seen that different minima are obtained even using Collignon's procedure, and some of those minima will have an important contribution to the partition's function. Thus, the importance of PES exploration is confirmed. Besides, it can be noticed that for some structures, the energy change is rather small when it is re-optimized. This situation has been mainly found for the COOH/(H₂O)_n systems and, as expected, corresponds with the structures suffering less changes after re-optimization (Fig. 2). On the other hand, some minima show a dramatic difference between the PM6-DH2X and the B3LYP energy. This corresponds with the structures having major changes of geometry due to the re-optimization; this change is associated with a change in the "type" of interactions. For example, in OH/H₂O-f and OH/H₂O-f' (Fig. 3) the type of interaction changes from an H- π -cloud interaction involving the H of water H (the PM6-DH2X structure) to a linear H-bond between the H of the OH SG and the O of water (B3LYP structure).

The Figs. 2 and 3 show the representative minima structures selected for COOH/(H₂O)_n and OH/(H₂O)_n systems, together with the corresponding re-optimized structures.

From Figs. 2 and 3, it can be seen that the structure of the non-covalent complexes is mainly dominated by the formation of hydrogen bonds, and the most stable structures are those with the

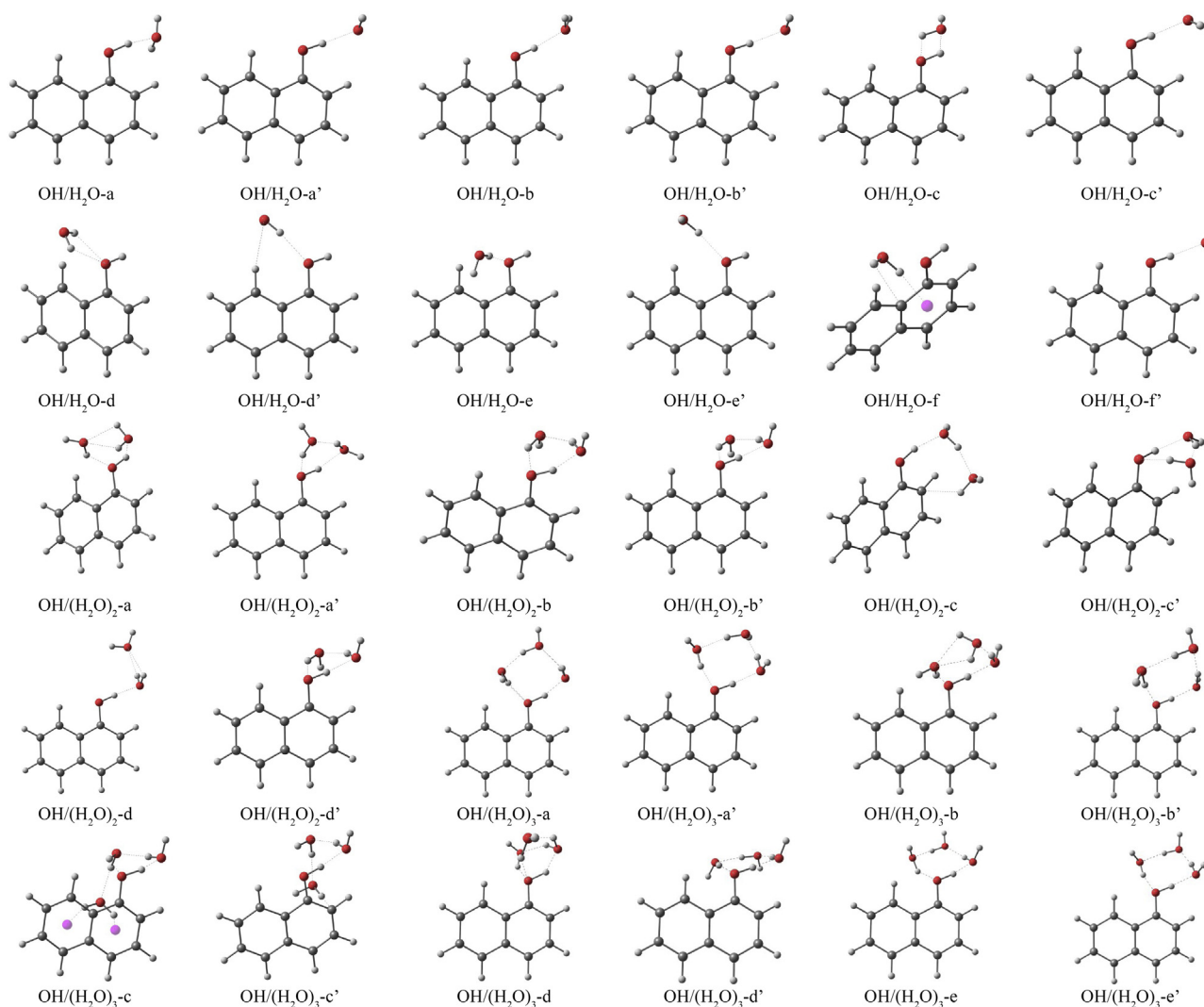


Fig. 3. Distinctive minima structures found for the systems OH/(H₂O)_{n-1-3}. Letters denote different structures found at PM6-DH2X and coated letters account for the corresponding reoptimized structures at B3LYP/6311++G(2d,2p)//B3LYP/cc-PVDZ.

Table 2

Association energy per water molecule for each selected minima, with PM6-DH2X (ΔE_{assoc}), and reoptimized using Collignon's procedure (ΔE_{assoc} (DFT)). Letters denote different minima for each system represented in Figs. 2 and 3. Energies are given in kJ/mol.

System OH/H ₂ O	ΔE_{assoc}	ΔE_{assoc} (DFT)	System COOH/H ₂ O	ΔE_{assoc}	ΔE_{assoc} (DFT)
a	-21.7	-25.7	a	-39.2	-39.1
b	-20.1	-25.7	b	-33.3	-39.0
c	-16.5	-22.2	c	-22.9	-17.3
d	-14.5	-9.6			
e	-13.0	-9.6			
f	-11.7	-25.6			

System OH/(H ₂ O) ₂	ΔE_{assoc}	ΔE_{assoc} (DFT)	System COOH/(H ₂ O) ₂	ΔE_{assoc}	ΔE_{assoc} (DFT)
a	-29.9	-28.9	a	-37.2	-43.8
b	-29.1	-30.1	b	-37.0	-41.9
c	-24.6	-26.2	c	-35.1	-40.5
d	-24.3	-30.0	d	-32.9	-43.7
			e	-29.8	-28.0
			f	-27.2	-23.3

System OH/(H ₂ O) ₃	ΔE_{assoc}	ΔE_{assoc} (DFT)	System COOH/(H ₂ O) ₃	ΔE_{assoc}	ΔE_{assoc} (DFT)
a	-32.5	-35.8	a	-36.2	-36.0
b	-30.8	-35.5	b	-35.4	-35.8
c	-29.9	-30.2	c	-33.6	-34.1
d	-29.0	-35.6	d	-33.3	-35.7
e	-27.9	-33.7	e	-32.3	-39.7
			f	-28.2	-27.4

highest number of H-bonds. That lead to the formation of H-bond networks like those observed in OH/(H₂O)₂-b and COOH/(H₂O)₃-a. Even for structures having certain degree of reorganization after re-optimization, for most complexes the nature of main interactions remains (i.e. in complex OH/H₂O-e the water molecule is moved but the hydrogen of water forming an H-bond with the oxygen of OH group is still the main interaction).

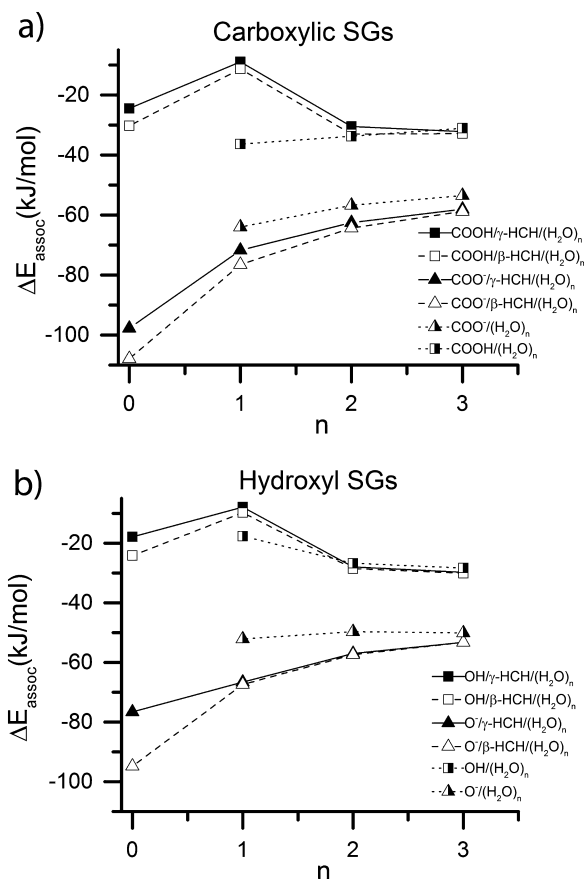
However, complexes with water molecules on top of the naphthalenic ring with the hydrogens pointing to the π cloud are eliminated in most cases. This kind of interactions has been previously reported at higher levels of theory [40,68], and thus, this change may arise from the known deficiencies of B3LYP for describing dispersive interactions rather than a failure of PM6-DH2X.

Bifurcated H-bonds between water molecules, and between water molecules and SG O, are systematically wiped and converted to linear H-bonds by re-optimization as it can be appreciated for complexes showing this feature i.e. COOH/(H₂O)₂-b, COOH/(H₂O)₃-d, OH/(H₂O)₂-a, OH/(H₂O)₂-d and OH/(H₂O)₃-b (Figs. 2 and 3). This is due to a known problem of all semiempirical methods that tend to identify the bifurcated H-bond in water dimer (actually a saddle point [69]) as minima in water clusters PES.

Additionally, after re-optimization all structures had the COOH group lying in the same plane as the naphthalenic rings. That was true even for structures like COOH/(H₂O)₂-d, where the starting geometry had the COOH group almost orthogonal to the plane of the rings.

4.3. γ -HCH and β -HCH adsorption

Graphic 1 summarizes the energy results obtained for γ and β -HCH adsorption onto AC without water and with up to three water molecules. The results for both isomers are very close; however, energy values are slightly lower for β -HCH, thus indicating a slightly more favorable association of this isomer with the SG. This is in accordance with the fact that β -HCH is less bioavailable for degradation from soils than other isomers [21]. For neutral SGs



Graphic 1. Mean adsorption energy per water + HCH molecule (ΔE_{assoc}). "n" is the number of water molecules added.

the ΔE_{assoc} obtained in the presence of the contaminant is always higher or in the same order to that obtained for water molecules alone. Besides, for both neutral SGs the system has similar stability with the HCH molecule alone or HCH plus up to three water molecules. This fact could be indicating a competition between water molecules and HCH molecules for the neutral SGs. According to this, presumably a very small fraction of the contaminant will adsorb on a surface containing mainly OH and COOH SGs under real (very diluted) conditions, as long as the pH conditions ensure neutrality of both SGs.

For both charged SGs ΔE_{assoc} values are considerably lower in the presence of the contaminant compared to the association of the AC model with water molecules alone. Moreover, the stability of the systems SG/HCH is considerably higher than SG/HCH/(H₂O)_{n=1-3} systems (although these are still energetically favored). This behavior suggests that if the HCH molecule is associated with the SG, the water molecules would not be able to compete for the adsorption sites. The behavior is similar for both SGs but the COO⁻ affinity for the contaminant seems stronger. Again, β -HCH isomer forms slightly more stable association complexes than γ -HCH. From this analysis it can be suggested that presence of charged SGs will enhance adsorption of HCH, being the adsorption of β -HCH slightly better.

The differences in association energy between both HCH isomers are higher when no water molecule is present in the system, which is when structural differences between isomers have the biggest impact. The association energy difference between both isomers is more extreme for the interaction with charged SGs (18.2 kJ/mol for O⁻/HCH and 10.2 kJ/mol for COO⁻/HCH), and particularly with O⁻ group, probably due to the role of electrostatic interactions. However, when the number of water molecules is

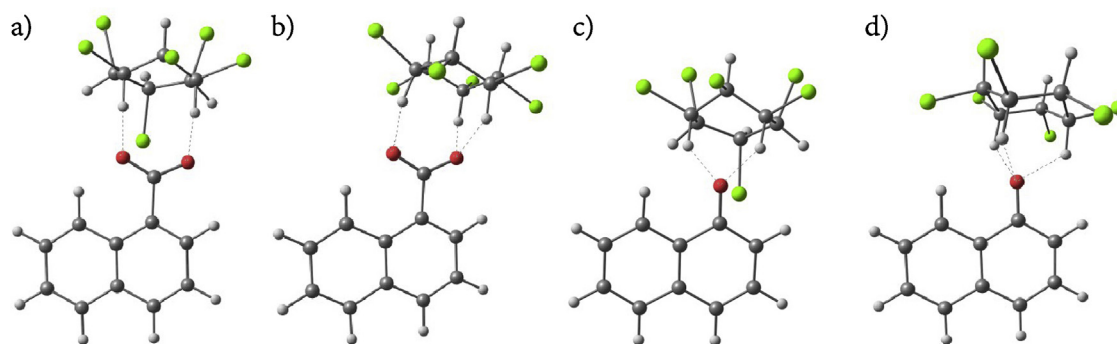


Fig. 4. Global energy minima structures for: (a) $\text{COO}^-/\gamma\text{-HCH}$, (b) $\text{COO}^-/\beta\text{-HCH}$, (c) $\text{O}^-/\gamma\text{-HCH}$ and (d) $\text{O}^-/\beta\text{-HCH}$ systems. It can be seen how $\beta\text{-HCH}$ have three H atoms in favorable position to form H-bonds with the SG while $\gamma\text{-HCH}$ have only two.

increased, the energy of the complexes for both isomers seems to merge into similar values as water interactions dominate the energy of the system and structural differences between isomers have a minor contribution.

The lower association energies for $\beta\text{-HCH}$ compared to $\gamma\text{-HCH}$ can be explained from the fact that $\beta\text{-HCH}$ has all hydrogen atoms in axial position while $\gamma\text{-HCH}$ has only two hydrogen atoms in axial position, leading to formation of three and two favorable H-bond interactions with the SG respectively (Fig. 4). The electrostatic

interactions between the negatively charged SG and HCH could be more favored for the $\beta\text{-HCH}$ isomer since this presents an area of positive electrostatic potential covering the three axial hydrogen [70].

The energy partition scheme implemented in the semiempirical method is used to get insights about the nature of the interactions that stabilize the complexes. In order to explain the different association energies between HCH isomers we analyzed those complexes with SGs of the AC models without water molecules

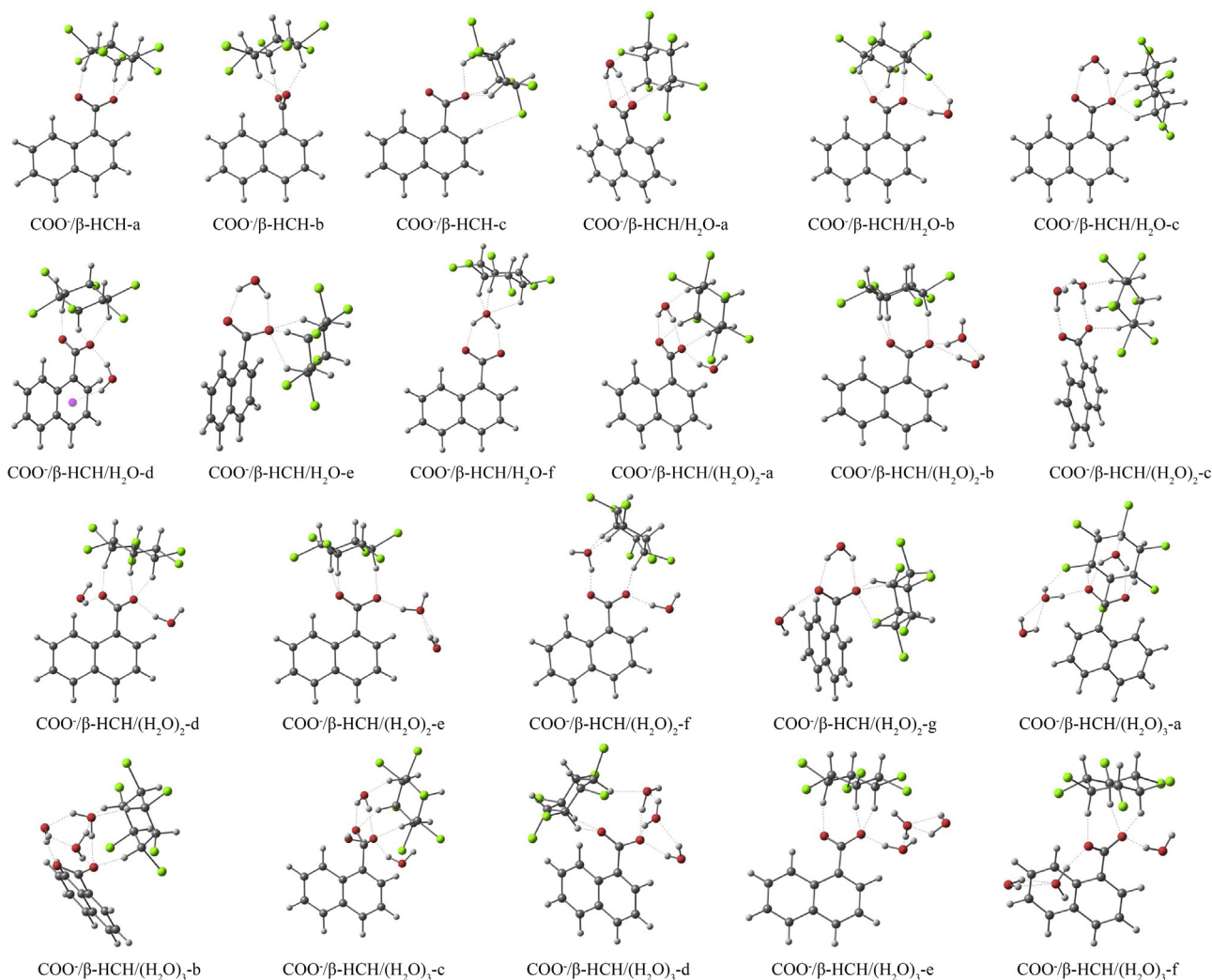


Fig. 5. Distinctive minima structures found for the systems $\text{COO}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_{n=0-3}$. Letters denote different structures found at PM6-DH2X level.

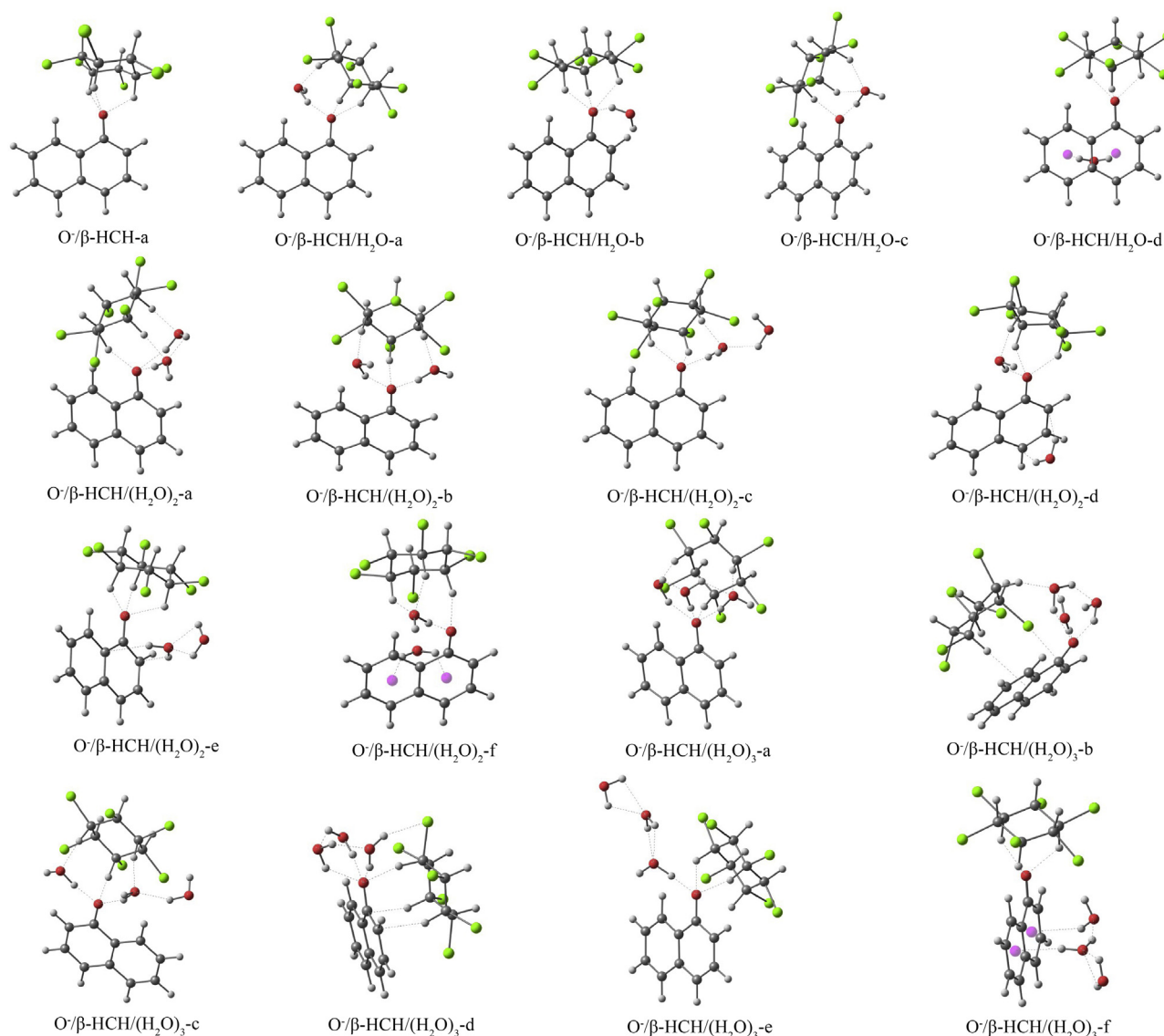


Fig. 6. Distinctive minima structures found for the systems $\text{O}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_{n=0-3}$. Letters denote different structures found at PM6-DH2X level.

that correspond to the minima of the interacting potential energy surface (see the first structural models in Figs. 5–8 and 1S–4S of the supporting information). For the PM6-DH2X semiempirical Hamiltonian, the dispersion (disp.) and Hydrogen bond (H-bond) contribution to the interaction energy is calculated and these are shown in Table 1S (supplementary information).

It is important to notice that this interaction energy does not include the molecular deformation energy required to form the complex, in contrast to the previous calculations of association energy (ΔE_{assoc}). Even though, the negative energy value of interactions in all cases refers to bound non-covalent complexes, as expected.

The dispersion terms (i.e. London forces) favorably contributed to the interaction energy of all analyzed complexes. An inspection to the percent of these contributions show that the effects are greater for the interaction of both HCH isomers with neutral SGs and within these, those complexes with the β -HCH isomer present the largest contributions. This result shows that, among other types of interactions presented, the London forces provide that β -HCH can form interaction complexes with AC models with neutral SGs more stable than the γ -HCH isomer. On the other hand, the interacting complexes of both HCH isomers with the charged SGs (where

the differences are the biggest) show similar contributions of the dispersion terms. Presumably, dispersion forces do not determine the stability of these kinds of complexes where the electrostatic factors could be playing the largest role.

The Hydrogen-bond (H-Bond) interaction terms appear unfavorable for all of SGs/HCH complexes, but these contributions can be considered negligible due to the fact that the values are in the same order of magnitude of the average error for interaction energy (for PM6-DH2 is 0.37 Kcal/mol, where $E(\text{PM6-DH2X}) = E(\text{PM6-DH2}) + E(\text{X})$) [71]. Besides the complex nature of this kind of interaction, the H-Bonds corrections in this method are limited to a parameterized scheme that fits typical H-bonds (for oxygen are $\text{O} \cdots \text{HO}$ of water, carboxyl and other HO- groups), but does not include all of the interactions observed in SGs/HCH complexes. Thus, this prediction fails for these complexes where non-conventional H-bonds (i.e. $\text{C-H} \cdots \text{O}$), as well as other electrostatic and dispersion interactions are expected. The same method achieves a large contribution of the H-bond terms that explain the stabilization of the complex $\text{COOH}/\text{H}_2\text{O}$ (see the last row in Table 1S).

An analysis of the distinctive minima structures obtained for the systems $\text{COO}^-/\gamma\text{-HCH}/(\text{H}_2\text{O})_n$, $\text{O}^-/\gamma\text{-HCH}/(\text{H}_2\text{O})_n$, $\text{COO}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_n$ and $\text{O}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_n$ (Figs. 1S, 2S, 5 and 6

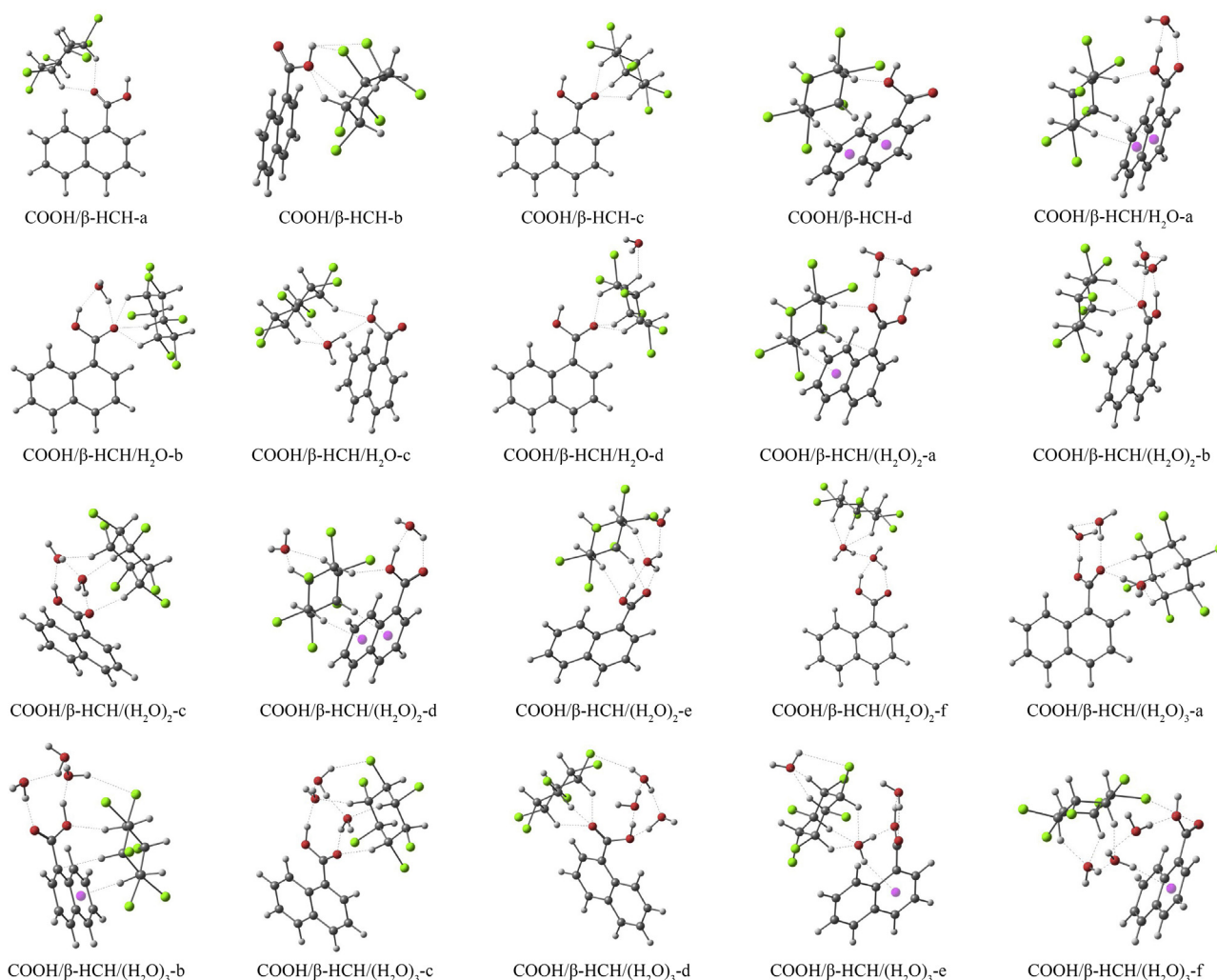


Fig. 7. Distinctive minima structures found for the systems $\text{COOH}/\beta\text{-HCH}/(\text{H}_2\text{O})_{n=0-3}$. Letters denote different structures found at PM6-DH2X level.

respectively), allows to conclude that almost all complexes show contacts between axial protons of HCH with negatively charged oxygen atoms. In addition to $\text{C-H}\cdots\text{O}^-$ interactions (Fig. 4), these complexes have water molecules interacting at the same time with negatively charged oxygen of SGs and axial protons of HCH molecules. The water molecules interact with HCH through $\text{C-H}\cdots\text{OH}_2$ hydrogen bonds (Fig. 5 $\text{COO}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_2\text{-a}$) or $\text{OH}\cdots\text{Cl}$ bifurcated H-bonds (Fig. 5 $\text{COO}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_2\text{-a}$), with the proton of water pointing to the region of negative electrostatic potential situated between chlorine atoms. A similar bifurcated H-bond has been previously reported for the HF/HCH system [70]. Also, formation of H-bond networks takes place when more than one water molecule is present. Less commonly encountered structures involve $\text{X-H}\cdots\pi$ -cloud interactions with hydrogen atoms of either water (Fig. 2S $\text{O}^-/\gamma\text{-HCH}/(\text{H}_2\text{O})_2\text{-b}$) or HCH (Fig. 6 $\text{O}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_3\text{-d}$), while chlorine atoms are involved in some $\text{C-Cl}\cdots\pi$ -cloud interactions (Fig. 6 $\text{O}^-/\beta\text{-HCH}/(\text{H}_2\text{O})_3\text{-b}$).

In general, the interactions in the non-covalent complexes formed for both HCH isomers with neutral SGs appear to be weakly favored (lowest ΔE_{assoc} values for the series: neutral $\text{SG}/\text{HCH}/(\text{H}_2\text{O})_n$) by the presence of at least two water molecules close to the interaction site (Graphic 1). This could be related to the formation of H-bond networks involving water molecules, SGs and HCH molecules, as shown in Figs. 7 and 8, 3S and 4S. For neutral complexes all interactions described above for charged ones are also present, but structures with the HCH molecules

directly situated above the SG are much less common, and that is especially true for $\gamma\text{-HCH}$. Besides, interactions involving the π -cloud of the naphthalene derivative, such as $\text{C-H}\cdots\pi$ mainly with axial protons (Fig. 8 $\text{OH}/\beta\text{-HCH-a}$) and $\text{O-H}\cdots\pi$ (Fig. 3S $\text{COOH}/\gamma\text{-HCH}/(\text{H}_2\text{O})_2\text{-c}$) are more commonly encountered compared with charged complexes. For COOH SG there are also halogen bond type interactions present (Fig. 3S $\text{COOH}/\gamma\text{-HCH}/(\text{H}_2\text{O})_2\text{-g}$), nevertheless, these interactions have a very little contribution to the overall population of the system because are very far from the corresponding global minima. For $\gamma\text{-HCH}$ complexes, the presence of axial chlorine atoms favored $\text{C-Cl}\cdots\pi$ interactions (Fig. 3S $\text{COOH}/\gamma\text{-HCH-c}$).

According to association energies, the affinity order between HCH isomers and SG is as follows: $\beta\text{-HCH} > \gamma\text{-HCH}$ and for both HCH isomers $\text{COO}^- > \text{O}^- > \text{COOH} \approx \text{OH}$.

Summing up, if the pH is acidic, then carboxylic and hydroxyl SGs will be in neutral form thus not contributing significantly to HCH adsorption. On the other hand, when pH conditions are basic both hydroxyl and carboxyl SG will contribute significantly to increase adsorption capacity of AC. If $\text{pH} \approx 7$, which is most likely the case for drinking water, a rough estimation gives a deprotonation of OH SG lower than 3% and can be neglected, while only COOH groups are deprotonated to a considerable extent ($\sim 90\%$) [72]. Taking into account that COO^- is the only charged SGs, we can state that carboxylic SGs will preferentially contribute to HCH adsorption onto AC at neutral pH conditions.

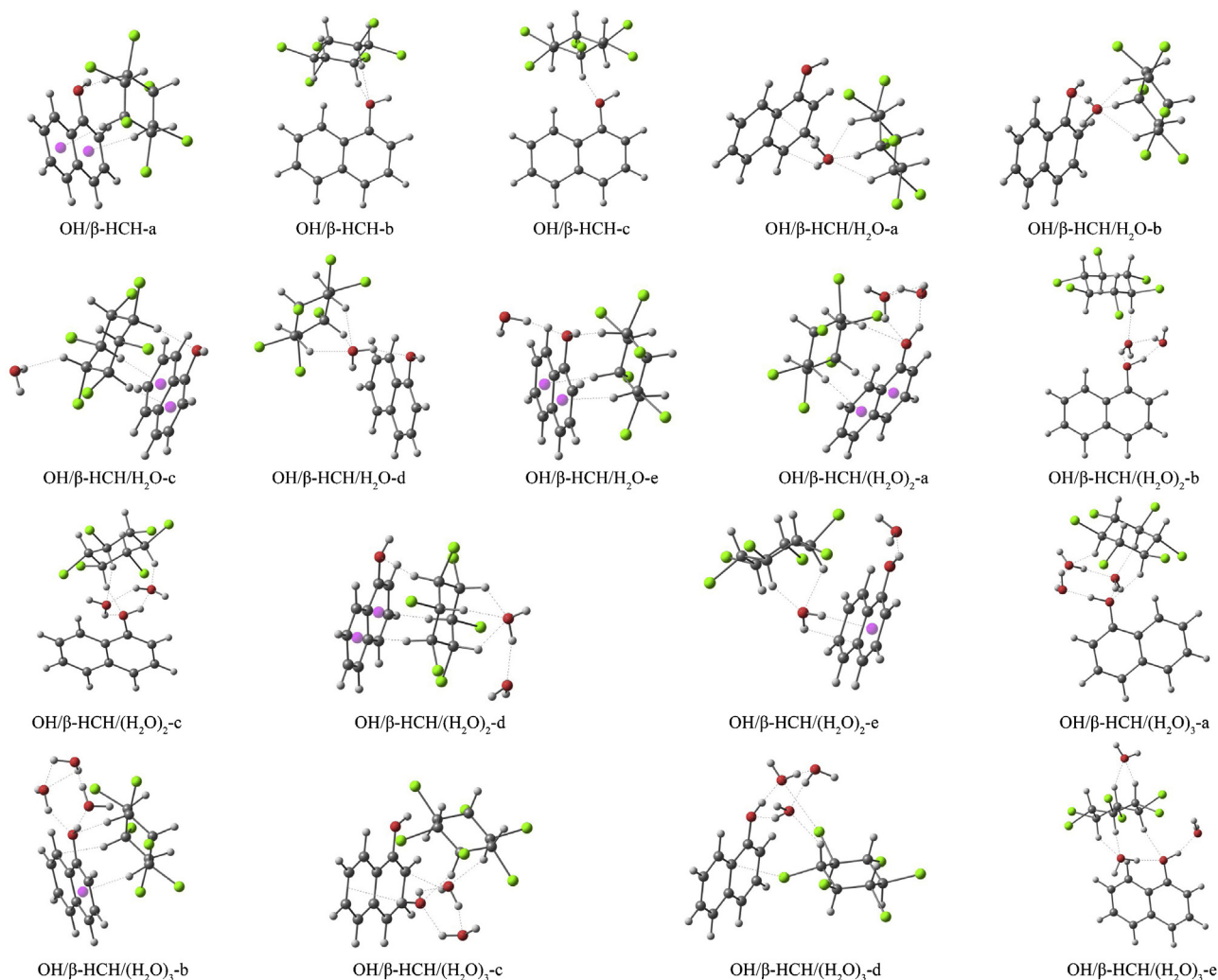


Fig. 8. Distinctive minima structures found for the systems $\text{OH}/\beta\text{-HCH}/(\text{H}_2\text{O})_{n=0-3}$. Letters denote different structures found at PM6-DH2X level.

The above result is consistent with recent experimental findings by Durimel et al. [50]. In that work, the adsorption of β -HCH onto ACs of different SGs content was tested, and the AC with the highest content of COOH SGs showed the strongest β -HCH/SG interaction.

5. Conclusions

A theoretical model for understanding the role of activated carbon SGs on the adsorption of γ - and β -HCH has been built, and this model accounts for different pH and solvation conditions. The main conclusions of this study are:

- The MMH method allows to explore the interactions space of $\text{SG}/\text{HCH}/(\text{H}_2\text{O})_n$ complexes using PM6-DH2X semiempirical Hamiltonian.
- Re-optimization of $\text{COOH}/(\text{H}_2\text{O})_n$ and $\text{OH}/(\text{H}_2\text{O})_n$ complexes demonstrated the importance of PES exploration in such weakly interacting systems.
- All analyzed association complexes are thermodynamically stable, and showed similar behavior for γ - and β -HCH.
- The performed calculations show that the association of HCH with SGs preferentially occurs between the axial protons of HCH and SG's oxygen, and the most favorable interactions occur with charged SGs.
- Only charged SGs should contribute to enhance adsorption of HCH onto AC, and under neutral pH conditions, only COOH groups

have a positive influence over the contaminant's adsorption. As a consequence, an increase in carboxylic SGs content is expected to enhance HCH adsorption onto AC.

- This work presents an inexpensive computer aided methodology for preselecting activated carbon SGs content for the removal of a given compound.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmngm.2014.05.004>.

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