Computational Study on the Characteristics of the Interaction in Naphthalene···$(H_2X)_{n=1,2}$ (X = O, S) Clusters

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The characteristics of the interaction between the π cloud of naphthalene and up to two H_2O or H_2S molecules were studied. Calculations show that clusters formed by naphthalene and one H_2O or H_2S molecule have similar geometric features, and also present similar interaction energies. Our best estimates for the interaction energy amount to −2.95 and −2.92 kcal/mol for H_2O and H_2S, respectively, as obtained with the CCSD(T) method. Calculations at the MP2 level employing large basis sets should be avoided because they produce highly overestimated interaction energies, especially for hydrogen sulfide complexes. The MPWB1K functional, however, provides values pretty similar to those obtained with the CCSD(T) method. Although the magnitude of the interaction is similar with both H_2X molecules, its nature is somewhat different: the H_2O complex presents electrostatic and dispersion contributions of similar magnitude, whereas for H_2S the interaction is dominated by dispersion. In clusters containing two H_2X molecules several minima were characterized. In water clusters, the total interaction energy is dominated by the presence of a O−H···O hydrogen bond and, as a consequence, structures where this contact is present are the most stable. However, clusters containing H_2S show structures with no interaction between H_2S moieties which are as stable as the hydrogen bonded ones, because they allow an optimal H_2S···naphthalene interaction, which is stronger than the S−H···S contact. Therefore it is possible that in larger polycycles hydrogen sulfide molecules will be spread onto the surface maximizing S−H···π interactions rather than aggregated, forming H_2S clusters.

1. Introduction

Intermolecular interactions involving aromatic rings are crucial in a variety of chemical and biological processes. Their understanding is essential for the rational design of drugs and other functional materials. On the basis of these intermolecular interactions not only theoretical design but also experimental realization of novel functional receptors has become possible. Therefore, the study of the fundamental intermolecular interactions and new types of interaction is important for aiding the design of new materials as well as for understanding cluster formation.[1–6] In particular, novel types of interaction involving aromatic rings have been an important subject in the past decade.[7–9] In this regard, if the interaction involves the aromatic system it is usually one of the following three types: cation···π, π···π or X−H···π.[2,3]

The properties of aromatic polycyclic compounds have attracted much interest from a fundamental point of view but also regarding the many expected applications in the field of electronics and optoelectronics. Also, the intermolecular interaction between polycyclic aromatic compounds is also important for the structures of biological systems.[2,3,10] Therefore, a complete understanding of the characteristics and magnitude of these interactions is essential in these fields, as also is for developing appropriate force fields for these molecules. The experimental and computational aspects of π−π, cation−π, alkyl−π, and amino−π interactions have been a subject of much recent interest.[2–5]

Most studies of this kind have been carried out by employing benzene as a model for aromatic systems,[11–16] but there exists a lack of studies employing larger aromatic systems, though works in larger polycycles have been carried out as a way to interpret graphite interactions.[17–24] In the case of X−H···π interactions, benzene has also been employed as the main model for aromatic systems. Most studies are devoted to the interaction between benzene and water clusters of different size.[11,25] Indole has also been frequently considered as a possible candidate for these studies because it forms part of tryptophan.[26–30] However, interactions with other polycycles can be of interest in different areas, ranging from molecular recognition, because naphthalene and other units are employed as a constituent part of molecular tweezers,[31–33] to chromatography, because this kind of interactions can be employed for separating polycyclic aromatic hydrocarbons.[34]

Naphthalene is one of the simplest polycyclic aromatic hydrocarbons, so it is one of the first choices to extend the studies of interaction with aromatic rings to polycycles. However, the studies devoted to the interaction with naphthalene molecules are relatively scarce.[17,19–24] Very recently, Tsuzuki et al. studied naphthalene dimers employing high level ab initio calculations and found significant differences with respect to benzene dimer interaction.[17] Mainly, naphthalene dimer exhibits a larger dispersion component for the interaction, and a more acute orientation dependence of the interaction energy than benzene.

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One type of interaction that has not received as much attention from a computational point of view is the sulfur$-\pi$ interaction,[12–16] partly because it is not as common as others in natural systems but also because the presence of the sulfur atom increases the computational expense.[2] Besides, for sulfur containing systems, it has been shown that basis set effects are especially important, so large basis sets and high level calculation methods must be employed.[15]

Therefore, in the present work the interaction in systems containing a naphthalene molecule and one or two water or hydrogen sulfide molecules was computationally studied. This kind of study allows determining the following aspects: (1) The geometries of clusters formed between naphthalene and water or hydrogen sulfide have not been determined to date. (2) The size of the interaction energy of these clusters is also unknown. (3) In larger clusters the balance between $C_{10}H_8\cdots H_2X$ and $H_2X\cdots H_2X$ interactions could play a relevant role. The systems studied allow estimating the relative importance of these contributions. (4) A comparison between water and hydrogen sulfide clusters allows revealing the main differences of the interaction with hydroxyl and thiol containing molecules.

2. Computational Details and Procedure

Starting structures were constructed by attending to chemical intuition, trying to represent the possible $X-H\cdots\pi$ favorable contacts. To our knowledge, no experimental determination of the structures of the clusters studied has been carried out. Only the structures of complexes formed by water and the naphthalene radical anion have been reported; however, taking into account the large differences in electronic structure between neutral naphthalene and its radical anion, these results do not constitute a good guidance for the complexes studied in this work.[35,36] Several initial structures were therefore fully optimized by using the MP2 method together with the 6-31+G* basis set. For systems of the size of those studied in this work, and having in mind possible extension to even larger polycycles, it is interesting to test the performance of density functional theory (DFT) methods for this kind of interaction. After preliminary tests, a widely used functional as B3LYP reveals significant differences in structures when compared to MP2. This is not surprising because it is a well-known fact that B3LYP usually fails in the description of this kind of complexes.[11,27,37] In fact, the main problem comes from the large dispersive contribution to interaction energy, which has been a goal for functional developers. Recently, several functionals have been proposed for studying this kind of interaction. Among them, we opted to employ the MPWB1K functional proposed by Thrular's group. as it is recommended as a well-balanced functional with a good average performance in different kinds of systems, including dispersion bound ones.[38] Also, previous calculations in indole−water complexes have shown that a similar functional gives good results.[29] Therefore, the geometries of the complexes were also optimized with the MPWB1K functional together with the 6-31+G* basis set. All points were characterized as minima by calculating the harmonic vibrational frequencies.

After locating the stationary points of the potential energy surface of each cluster and having characterized them as minima by performing a vibrational analysis, the interaction energies were calculated by means of the counterpoise method to avoid basis set superposition error.[39,40] Thus, the interaction energy is obtained by subtracting from the energy of the whole system the energies of the fragments that constitute the clusters, employing the geometry and the whole basis set of the cluster

$$\Delta E_{\text{int}} = E_{ij}(ij...) - \sum_i E_i^{\text{clus}}(ij...) \qquad (1)$$

As the geometry of the molecules changes when the cluster is formed, an additional contribution describing this effect must be included, obtained as the energy difference between the molecules in the cluster geometry and in isolation.[40]

$$E_{\text{def}} = \sum_i (E_i^{\text{clus}}(i) - E_i^{\text{isol}}(i)) \qquad (2)$$

The total complexation energy results from adding these two contributions, but deformation effects are usually small and negligible,[41,42] so in the discussion we will not consider them. In any case, the results are available as Supporting Information.

Though the 6-31+G* basis set has been chosen as a compromise between accuracy and computational effort, it cannot be expected to give good values for interaction energies.[11] Therefore, to estimate basis set effects, interaction energies were also computed by employing a larger basis set: aug-cc-pVDZ in heavy atoms and cc-pVDZ in hydrogen atoms (henceforth AVDZ). Finally, selected high level computations were performed; that is, interaction energies of complexes with one H_2X molecule were obtained with the MP4(SDTQ) and CCSD(T) methods. A deeper analysis of the interaction has also been carried out in the case of complexes with two H_2X molecules by calculating interaction energies for each pair of molecules that constitute the cluster. This analysis allows estimating three-body effects by subtracting the interaction energies for each pair of molecules from the interaction energy of the whole cluster.

The supermolecule method gives a plain number as result, so a perturbational analysis was carried out to have more insight into the nature of the interaction.[43] A Symmetry Adapted Perturbation Theory (SAPT) analysis was performed to compute the different contributions to the interaction energy. To reduce the cost of SAPT calculations, density functional theory has been employed to describe the intramonomer correlation correction, in the so-called SAPT(DFT) approach.[43–45] These calculations were performed by using the SAPT2006 code of Szalewicz and coworkers,[45] using Dalton[46] to perform the DFT calculations. CCSD(T) calculations were performed with Orca[47] and Gaussian03[48] was employed for all other calculations.

3. Results

3.1. Naphthalene$\cdots H_2X$ Clusters. Figure 1 shows the minimum energy structures found after optimization, which correspond to minima of the potential energy surface. Other possibilities where H_2X molecules interact as acceptors of in-plane $C-H\cdots X$ hydrogen bonds have not been considered because our aim is to focus on the $X-H\cdots\pi$ interaction. In any case, previous work in indole−water clusters showed this kind of structures to be secondary minima.[30]

It can be observed from Figure 1 that the minima correspond to structures where the H_2X molecule is located over naphthalene in a roughly perpendicular position with respect to the central C−C axis. Therefore, the minimum energy structure for the cluster with one H_2O molecule corresponds to the structure shown in Figure 1, where the hydrogen atoms of water point down toward the aromatic ring. However, because the structure is not symmetric, the distances between hydrogen and the center of the rings differ by 0.1−0.2 Å. In the case of the MPWB1K minimum, the position of the water molecule is more displaced over one ring, so distances to ring centers differ more markedly.

In the naphthalene$\cdots H_2S$ dimer, the situation is similar. In this case both MP2 and MPWB1K methods produce structures

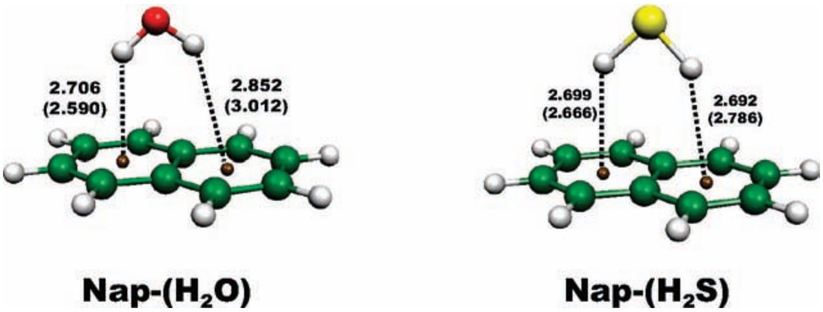

Figure 1. Geometries of the minima found for naphthalene$\cdots H_2X$ clusters with X$-$H$\cdots\pi$ contact. Distances to ring centers in Å from MP2/6-31+G* optimizations. Numbers in parentheses correspond to MPWB1K/6-31+G* level.

TABLE 1: Interaction Energy (kcal/mol) Obtained for the Clusters with One H_2X Unit with Different Levels of Calculation

	Nap$-$(H_2O)	Nap$-$(H_2S)
MPWB1K/6-31+G*	-3.01	-2.77
MP2/6-31+G*	-2.63	-2.49
MPWB1K/AVDZ//MPWB1K/6-31+G*	-2.99	-2.71
MP2/AVDZ// MP2/6-31+G*	-3.37	-4.32
MP4/AVDZ// MP2/6-31+G*	-3.25	-3.42
CCSD/AVDZ// MP2/6-31+G*	-2.56	-2.24
CCSD(T)/AVDZ// MP2/6-31+G*	-2.95	-2.92

where the H_2S molecule is located over the molecule roughly above the central C$-$C bond. However, slight differences are observed as the MP2 structure presents a bit tilted H_2S molecule in the direction of the C$-$C bond. In any case, these differences are not especially significant and they are not strange, taking into account the flatness of the potential energy surface over the ring. In previous work, Sherrill et al. studied the interaction of H_2S with benzene and found that the energy is almost constant upon rotations of H_2S, with energy differences smaller than 0.06 kcal/mol.[15] Also, tests were carried out for estimating the effect of basis set in optimized geometries. Optimizations were also performed with the AVDZ basis set. The results indicate that geometries are similar to those found with the 6-31+G* basis set, though slight changes in distances occur. In any case, the interaction energies computed in both geometries show values which differ by less than 0.1 kcal/mol, so we decided to employ 6-31+G* basis for geometry optimization in clusters with two H_2X molecules.

Table 1 lists the results obtained for the interaction energy of the clusters containing one H_2X molecule. Deformation effects are not included, but they are marginal and amount to at most 0.1 kcal/mol. It can be observed that the interaction energy amounts to -2.6 kcal/mol at the MP2/6-31+G* for the water complex. The MPWB1K gives similar results, though interaction energies are a bit larger. Interaction energies are pretty similar for H_2O and H_2S complexes, though interaction with H_2S seems to be a bit weaker at these levels of calculation.

Increasing the size of the basis set to aug-cc-pVDZ, including only diffuse functions on heavy atoms (AVDZ), dramatically changes the results obtained for interaction energies, which become more negative, indicating a more intense interaction. However, this increase of intensity is moderate for a H_2O complex, reaching an interaction energy of -3.4 kcal/mol, whereas in the case of H_2S complex the interaction energy decreases -1.8 kcal/mol, reaching -4.3 kcal/mol. This effect could be related to the more dispersive character of H_2S interaction, which is more difficult to recover and needs much larger basis sets. However, it has been noted that the MP2 method tends to overestimate interaction energies, especially when dispersion bound complexes are studied.[3,15,49] Therefore, calculations were performed by using more advanced correlation treatments. The results are also shown in Table 1. Employing the MP4(SDTQ) method interaction energies present values of -3.2 and -3.4 kcal/mol for H_2O and H_2S, respectively. Therefore, it seems that MP2 results fail to describe H_2S interaction. The coupled cluster results allow concluding similarly. CCSD results are similar to MP2 ones, though the interaction is less intense; however, the inclusion of triple excitations produces an increase of intensity leading to interaction energies which amount to -2.95 and -2.92 kcal/mol for H_2O and H_2S, respectively. Thus, our best estimation indicates that both complexes show similar interaction energies reaching almost -3 kcal/mol. Of course, increasing the basis set would lead to changes in these values due to basis set incompleteness. In conclusion, we can state that the MP2 method overestimates interaction energy, especially in H_2S complexes, in accordance with other authors.[3,15,49] Thus, more elaborated methods are necessary for describing this interaction. However, it is worth noting that the MPWB1K functional gives a quite acceptable estimation of the interaction energies at a much lower cost when compared to CCSD(T) results, and could be an interesting alternative when studying larger polycyclic systems.

Though it is difficult to compare results, because different authors employ different levels of calculation, the obtained values indicate that H_2X molecule interacts more strongly with naphthalene than with benzene, though differences are not large.[15,49] This could be expected taking into account the probable larger contribution of dispersion interaction in naphthalene, as noted by Tsuzuki et al.[17]

Supermolecule calculations produce values for interaction energy as a whole. Though the total interaction energy for both H_2O and H_2S complexes is similar, its source is somewhat different. First, whereas at the HF level the complex with water is stable by -0.8 kcal/mol at the MP2/6-31+G* minimum, the complex with hydrogen sulfide is clearly repulsive by 1.3 kcal/mol. Therefore, the attractive interaction in H_2S complexes has its origins mainly in correlation effects, to a larger extent than H_2O complexes.

A deeper physical interpretation can be obtained by partitioning the interaction energy on different components by means of perturbational calculations. Among the different methods, SAPT gives the most robust approach by performing a double perturbation series on inter and intra correlation effects.[43] Figure 2 shows the results obtained by means of SAPT(DFT) calculations performed with the 6-31+G* and AVDZ basis sets at the MP2/6-31+G* optimized geometry.

All contributions are larger in H_2S complexes, especially exchange, but this should be related to the larger size of the sulfur atom. Regarding attractive interactions, it can be observed

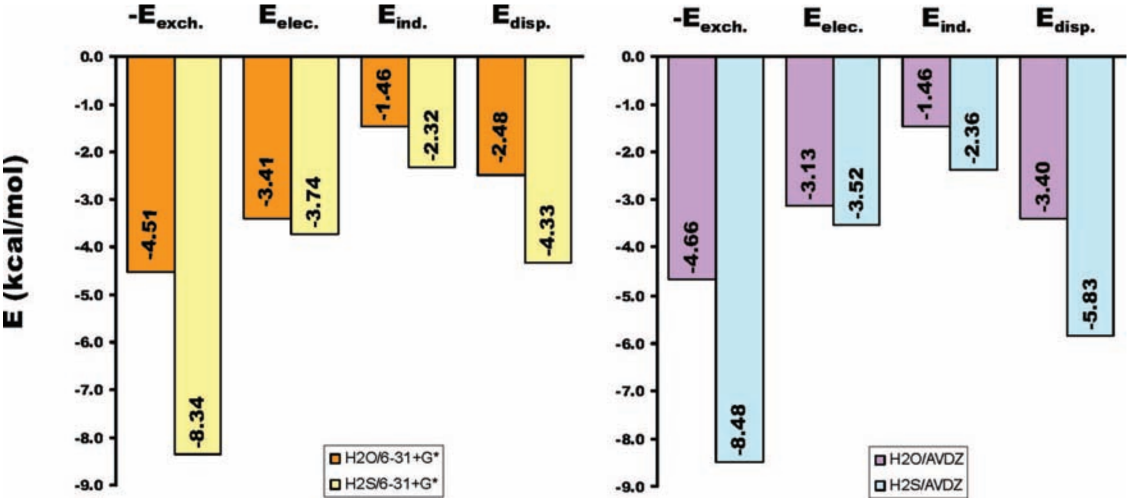

Figure 2. SAPT(DFT) decomposition of the interaction energy for the clusters formed by naphthalene and one H_2X molecule. Values obtained with 6-31+G* and AVDZ basis sets at the MP2/6-31+G* optimized geometry.

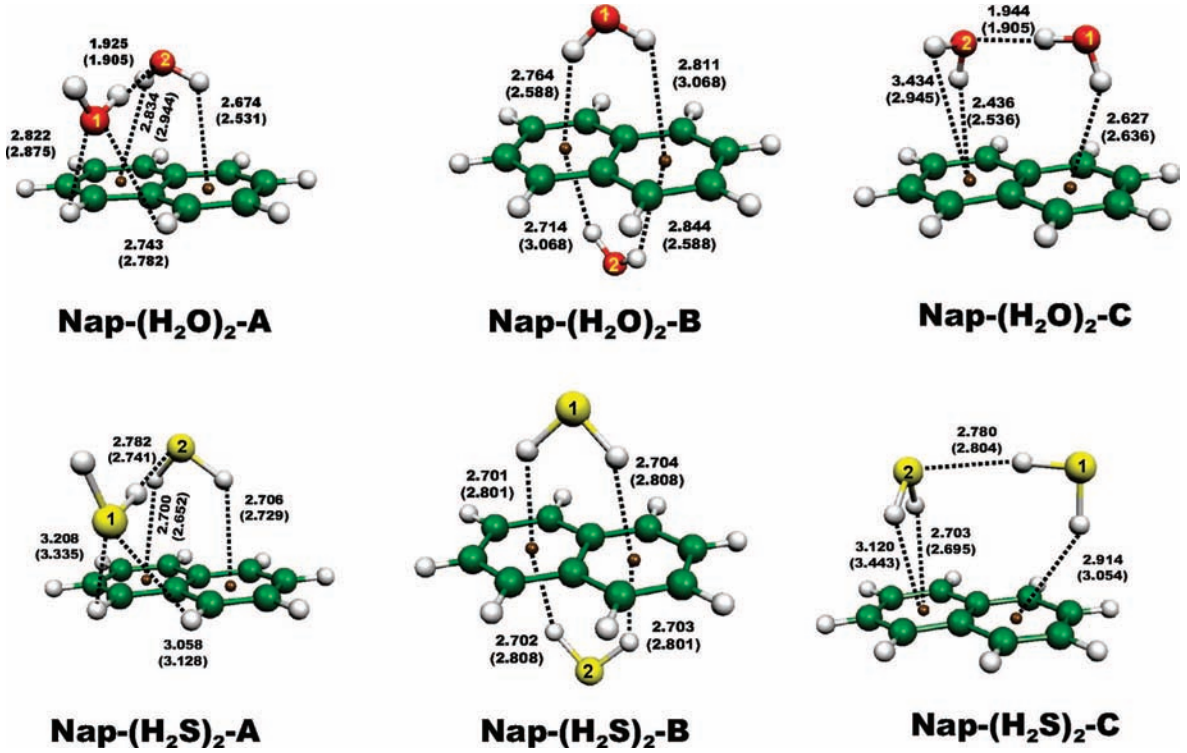

Figure 3. Geometries of the minima found for naphthalene$\cdots$$(H_2X)_2$ clusters. Distances to ring centers in Å from MP2/6-31+G* optimizations. Numbers in parentheses correspond to MPWB1K/6-31+G* level.

that for the H_2O cluster the leading term is the electrostatic contribution, though the dispersion contribution is almost as large. Therefore, the water complex is dominated by the electrostatic contribution but also by dispersion effects as was also observed in other X−H$\cdots$aromatic interactions.[50] On the other hand, the interaction in the H_2S cluster is dominated by a larger dispersion interaction which contributes about −2.4 kcal/mol more than in the H_2O complex, though electrostatic contribution is still important. When the basis set is enlarged, it can be observed from the data in Figure 2 that all contributions remain almost unchanged, and only dispersion energy exhibits a significant variation. That is, all contributions are saturated with respect to the basis set, but the dispersion term still increases. Therefore, it can be expected that for even larger basis sets, the dispersion contribution will be even more significant. The total SAPT interaction energies amount to −3.33 and −3.24 kcal/mol for H_2O and H_2S.

3.2. Naphthalene$\cdots$$(H_2X)_2$ Clusters. Figure 3 shows the minimum energy structures located for the clusters containing two H_2X molecules. These structures appear as a compromise between two stabilizing patterns, which correspond to the $H_2X$$\cdots$$H_2X$ interactions and to the naphthalene$\cdots$$H_2X$ interaction. Therefore, several structures are found where the basic motifs are hydrogen bonds between H_2X molecules but also X−H$\cdots$$\pi$ contacts. Structures A correspond to the interaction of a H_2X dimer with naphthalene; the hydrogen bond between H_2X molecules is favored in these structures, though contacts with the π cloud of naphthalene are also possible. Structures C are similar, but in this case the H_2X dimer has all free hydrogen atoms pointing downward to the naphthalene molecule. Also,

TABLE 2: Interaction Energy and Pair Energy Decomposition Obtained for the Clusters with Two H_2X Units (MPWB1K/AVDZ//MPWB1K/6-31+G* Results)

	Nap−$(H_2O)_2$−A	Nap−$(H_2O)_2$−B	Nap−$(H_2O)_2$−C	Nap−$(H_2S)_2$−A	Nap−$(H_2S)_2$−B	Nap−$(H_2S)_2$−C
ΔE_{int} (kcal/mol)	−9.95	−5.46	−8.51	−5.49	−5.15	−3.91
ΔE_{zpe} (kcal/mol)	−6.16	−2.95	−5.21	−3.00	−3.03	−2.07
ΔH_{298} (kcal/mol)	−6.64	−2.69	−5.47	−2.76	−2.46	−1.41
ΔS (cal/mol)	−52.78	−46.18	−50.48	−52.49	−48.51	−45.64
$\Delta E_{12}{}^{a}$ (kcal/mol)	−4.61	0.33	−3.61	−1.10	0.00	−1.05
$\Delta E_{\text{Nap-1}}{}^{a}$ (kcal/mol)	−1.54	−2.96	−2.17	−1.11	−2.70	−1.10
$\Delta \mathrm{E}_{\text{Nap-2}}{}^{a}$	−2.50	−2.96	−2.56	−2.62	−2.70	−1.73
$\Delta E_{\text{3-body}}{}^{b}$	−1.30	0.13	−0.17	−0.66	0.24	−0.03
$\Delta E_{\text{Nap-(1-2)}}{}^{a}$	−5.34	−5.80	−4.90	−4.39	−5.15	−2.86

[a] Molecules 1 and 2 correspond to H_2X moieties as shown in Figure 3. [b] Obtained as $\Delta E_{\text{int}} - \Delta E_{12} - \Delta E_{\text{Nap-1}} - \Delta E_{\text{Nap-2.}}$

the orientation of H_2X dimer is roughly perpendicular to that shown in structures A. Finally, structures B correspond to a situation where no hydrogen bonding between H_2X molecules is possible and only interaction with the naphthalene aromatic cloud is allowed. It can be expected that for H_2O clusters, structures with O−H···O hydrogen bond will be favored due to the great predisposition to association of water molecules. However, H_2S has a lesser tendency to association[12] and structures as B are also plausible.

Table 2 lists the interaction energies calculated for the clusters shown in Figure 3. Only results for the MPWB1K method are shown by taking into account that, as concluded from the values commented in the preceding section, they would probably be similar to CCSD(T)/AVDZ ones. Values obtained with the MP2 method are also available as Supporting Information, though they reproduce the behavior shown for complexes with one H_2X molecule, suggesting a large overestimation of interaction energies in hydrogen sulfide complexes. First of all, it can be observed that H_2O clusters are much more stable than the corresponding structures containing H_2S. This is a consequence of the stronger O−H···O hydrogen bond when compared to the analogous S−H···S contact in hydrogen sulfide clusters. In fact, only for B structures are the interaction energies similar due to the absence of hydrogen bond between H_2X molecules. The most stable structure for water clusters is A, with an interaction energy of about −10 kcal/mol, followed by C (−8.51 kcal/mol) and the much less stable structure B (−5.5 kcal/mol). In the case of hydrogen sulfide clusters the sequence is slightly different. Structure A is still the most stable one, but B is almost isoenergetic with it (only 0.3 kcal/mol difference); the less stable structure is C in this case.

Including zero point energy or thermal corrections introduces no differences in the stability sequences, as concluded from Table 2. However, the entropic correction favors B structures, so they will become more stable as temperature increases. It can be expected that this effect will not affect water clusters because the B structure is much less stable than A, but in the case of H_2S clusters it could be significant.

Also in Table 2 values are presented obtained by calculating the pair interaction energies of the trimers shown in Figure 3. That is, interaction between each pair of molecules is calculated and the difference with respect to the whole interaction energy gives information about three body effects. In structure A the main stabilizing contribution comes from the H_2O···H_2O interaction which gives −4.6 kcal/mol to the whole interaction energy of the cluster. This value is consistent with the interaction energy calculated for the water dimer, revealing that for this structure the water molecules can interact almost freely, and finally this water dimer interacts with naphthalene. One of the water molecules adopts a position similar to the minimum found in clusters containing one water molecule. However, the geometry is not optimal and the interaction amounts to −2.5 kcal/mol, instead of the −3.0 calculated for the naphthalene···H_2O cluster. The second water molecule interacts in a nonoptimal position, establishing contacts with the C−H units of naphthalene, and contributing with −1.5 kcal/mol. In structure B, water molecules do not interact directly, thus no water dimer is properly formed. Therefore, individual water molecules are able to interact with naphthalene in a similar way to that found in naphthalene···H_2O cluster. In structure C water dimer does not adopt such an optimal geometry, so the contribution to the total interaction energy is only −3.6 kcal/mol, still the most important one. However, the two water molecules can interact more favorably with naphthalene, contributing with 2−2.5 kcal/mol. That is, in this structure water−water interactions are penalized with respect to water-naphthalene interactions, resulting in a less stable cluster.

Also listed in Table 2 is the interaction energy between the naphthalene molecule and the H_2O dimer. It can be observed that the most stable interaction corresponds in this case to B, though all interaction energies are close in the three structures. Thus, the preference for structure A comes from water−water interactions, whereas in B the interaction between naphthalene and water is more favorable. It can also be observed that only in structure A are three body effects significant.

In the case of H_2S clusters, the balance between different stabilizing contributions is different. In structure A the interaction is strongest between naphthalene and hydrogen sulfide molecule 1, amounting to −2.6 kcal/mol, a value similar to that obtained in the complex with one H_2S molecule. The contribution of the interaction between naphthalene and the other molecule is similar to that given by the interaction between H_2S molecules (about −1 kcal/mol). That is, the interaction between H_2S molecules is quite weak and, in fact, is weaker than the interaction between H_2S and naphthalene molecule. Therefore, the most favorable structures will be those that optimize naphthalene···H_2S interactions. In structure B no interaction between H_2S molecules is observed because they are quite far apart. However, H_2S molecules can adopt the optimal geometric arrangement for interacting with naphthalene molecule almost freely, contributing to the interaction energy with −2.7 kcal/mol each. Finally in structure C none H_2S molecule is at a geometrical arrangement optimal for interaction with naphthalene and thus the contributions to interaction energy are less important. If the interaction between naphthalene and H_2S dimer is considered, the most stable situation corresponds to B, as in water clusters, but the energy difference with respect to other structures is larger. Also, if only pair energies are considered, structure B is the most stable one. However, only for structure A do three-body effects contribute significantly to the interaction energy, stabilizing the complex and making it the most stable one, as also happens in other clusters.[41] In any case, taking into account the small energy difference between A and B it is possible that H_2S molecules could be distributed over large polycycles without interacting among them rather than forming a cluster, thus favoring an optimal $H_2S\cdots\pi$ interaction. This would be the case for molecules with lesser tendency to self-association.

4. Conclusions

Intermolecular interaction for the naphthalene complexes with one and two H_2O or H_2S molecules was studied by means of ab initio and density functional theory calculations. Calculations show that the minimum energy structures are similar for both H_2O and H_2S complexes. Only one structure implying the aromatic cloud of naphthalene was found for the complex with one H_2X molecule. In this structure, the H_2X molecule is located over the ring and oriented almost perpendicularly to the central C═C bond of naphthalene.

Different computation levels were employed for obtaining the interaction energies of these structures. As a result, it is clear that MP2 overestimates the interaction energy of the complexes, in an especially dramatic way in the case of H_2S complex. For this system, the use of MP2 with large basis sets is not appropriate. Our best estimates for the interaction energy obtained at the CCSD(T)/AVDZ level amount to −2.95 and −2.92 kcal/mol for the complexes with H_2O and H_2S, respectively. It is also worth noting the excellent predictions of MPWB1K functional, which performs much better than MP2, especially in H_2S clusters, suggesting that it could represent a good choice for studying this kind of interaction in larger systems.

Both molecules bind with similar intensity to naphthalene. However, the nature of the interaction is somewhat different. SAPT calculations show that interaction with H_2O is mainly dominated by electrostatics though dispersion contribution is also important. On the other hand, interaction with H_2S is dominated by dispersion, but still with a significant electrostatic contribution. Also, the stabilization of H_2S complex totally comes from correlation effects.

The results obtained for complexes with two H_2X molecules reveal structures consequence of a balance between $H_2X\cdots H_2X$ interactions and those with naphthalene. Interaction energy in water clusters is thus dominated by hydrogen bonding and therefore the most stable clusters are those where water dimer is formed. However, in H_2S clusters the lower tendency to self-association of H_2S produces structures with no hydrogen bonding between H_2S molecules which are competitive with hydrogen bonded ones. In fact, interactions between H_2S moieties and naphthalene are stronger in Nap−$(H_2S)_2$−B, but the contribution of three body effects makes structure A the most stable. Therefore, in water−naphthalene clusters the most favorable arrangement clearly corresponds to the interaction between water dimer and naphthalene, whereas for H_2S clusters structures where H_2S molecules interact independently with naphthalene are also possible.

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Supporting Information Available: Tables containing detailed information about interaction energies as obtained with the different methods employed in this work. Listings of all optimized geometries of the clusters studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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