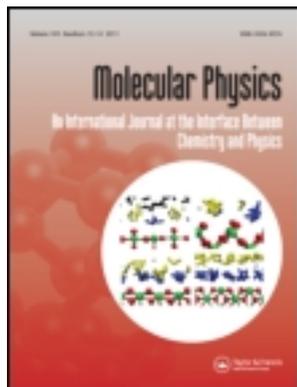


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RESEARCH ARTICLE

Theoretical study of the HXYH dimers (X, Y = O, S, Se). Hydrogen bonding and chalcogen–chalcogen interactions

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A theoretical study of the HXYH (X, Y = O, S and Se) monomers and dimers has been carried out by means of MP2 computational methods. For the monomers, isomerization ($H_2X=Y//HXYH$) and rotational transition state barriers have been calculated. Additionally, the molecular electrostatic potential of the isolated monomers has also been analysed. Due to the chiral nature of these compounds, homo and heterochiral dimers have been explored. The number of minima found for the dimers range between 13 and 22. The electron density of the complexes has been characterized with the Atoms in Molecules (AIM) methodology finding a large variety of interactions. The DFT-SAPT method has been used to analyse the components of the interaction energies. Concerning chalcogen–chalcogen interactions, although the most stable minima are formed through hydrogen bonds (especially if OH groups are present in the molecules) as the size of the atoms involved in the interaction increase, the chalcogen–chalcogen contacts become more important.

Keywords: hydrogen peroxide; hydrogen bond; Chalcogen interaction; MP2; DFT-SAPT

1. Introduction

Among the weak interactions, hydrogen bond (HB) is without any doubt the most important one. In recent years, a variety of new groups that can be involved in this interaction have been described. In fact, IUPAC has issued a new definition of HB in order to cope with all the new information [1]. In parallel with these advances, new kind of interactions have been described such as halogen bonds [2], hydride bonds [3,4] or chalcogen–chalcogen interactions [5–14].

Chalcogen–chalcogen interactions are probably the weak interaction that is less known although several theoretical papers have been published on this topic [5–14]. Several of the systems there studied deal with the intramolecular competition of chalcogen–chalcogen interactions with other stabilization forces as HBs [5–8] while, in other cases these chalcogen–chalcogen interactions were considered in intermolecular complexes [9–14].

HXYH molecules, where X and Y are atoms of the group VIA of the periodic table, are simple models of systems with axial chirality [15]. The smallest of these molecules, HOOH, has been widely studied theoretically, specially regarding chiral related properties [16–19] in complex formation via hydrogen bonding [20–28] or in metallic clusters [29]. The rest of the molecules of this family (X, Y = O, S, Se, Te)

can present chalcogen–chalcogen contacts in addition to HB interactions. The rotational barriers of these H-X-Y-H monomers have been studied theoretically [30–32], as well as the nature and bond strength [33] and its Vibrational Circular Dichroism (VCD) spectra [34]. The monomers, dimers and trimers of sulfoxides (X-S-O-H) have been explored in relation with their chiral discrimination [35]. Finally, the HSSH molecule has been extensively studied both experimentally and computationally [30,31,36–38].

In the present article, the electronic properties of the HXYH monomers, where X, Y = O, S, Se except X=Y=O, have been characterized and the homo-dimers minima have been evaluated at the MP2 computational level. Special attention has been paid to the different interactions present in the complexes (hydrogen bonds vs. chalcogen–chalcogen interactions) and the chiral discrimination between the homo and heterochiral dimers.

2. Computational details

The geometries of the monomers and complexes were fully optimized at MP2 computational level [39] with the 6-311++G** basis set [40]. Frequency calculations were carried out at the same level in order to verify that the structures obtained were energetic minima.

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The interaction energies have been calculated as the difference of the total energy of the complex and the sum of the isolated monomers. They have been corrected for the inherent basis set superposition error (BSSE) using the Boys–Bernardi counterpoise technique [41]. All the calculations have been carried out with Gaussian09 program [42].

The bonding characteristics were analysed by means of the atoms in molecules (AIM) theory [43]. For this purpose we have located the most relevant bond critical points (BCP), and evaluated the electron density at each of them, by means of the AIMPAC and MORPHY programs [44,45]. The chalcogen–chalcogen and HB interaction were characterized by the formation of a BCP between the X–Y chalcogen atoms or the hydrogen atom and the HB acceptor atom which are connected by the corresponding bond path.

The molecular electrostatic potential (MEP) of the isolated monomers have been calculated with the facilities of the Gaussian-09 program. Regions with negative MEP values are susceptible to interact with electron deficient moieties, such as HB donors, while positive regions can interact with electron rich areas.

Density Functional Theory-Symmetry Adapted Perturbation Theory (DFT-SAPT) calculations [46] have been carried out in order to obtain detailed information of the different contributions to the total interaction energy. The SAPT methodology separates the interaction energy into several components, related to physical variables such as dispersion, electrostatic, induction, and exchange. The SAPT interaction energy can be written as the sum of the truncated expansion terms as in the Equation (1):

$$E_{\text{int}} = E_{\text{pol}}^{(1)} + E_{\text{ex}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{ex-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{ex-disp}}^{(2)} + d(\text{HF}) \quad (1)$$

Those terms can be associated to some physical quantities using the following relationships:

$$E_{\text{elec}} = E_{\text{pol}}$$

$$E_{\text{ind}} = E_{\text{ind}}^{(2)} + E_{\text{ex-ind}}^{(2)}$$

$$E_{\text{disp}} = E_{\text{disp}}^{(2)} + E_{\text{ex-disp}}^{(2)}$$

$$E_{\text{ex}} = E_{\text{ex}}$$

where $E_{\text{pol}}^{(1)}$ is the electrostatic energy of monomers with the unperturbed electron distribution, $E_{\text{ex}}^{(1)}$ is the first-order valence repulsion energy of the monomers

Table 1. Relative energy (kJ mol^{-1}) of the $\text{H}_2\text{X}=\text{Y}$ and $\text{X}=\text{YH}_2$ isomers with respect to the HXYH ones calculated at the MP2/6-311++G(d,p) computational level and those previously reported in the literature.

	E_{rel}	Literature results
H_2SS	140.12	143 [MP4/6-311G(d,p)//MP2/6-311G(d,p)] [48] 131.67 (MP2/MIDI-4*) [49]
H_2SeSe	121.36	125.64 (MP2/MIDI-4*) [49]
H_2SO	112.85	106.2 [(MP4SDTQ(FC)/6-311++G(d,p)//MP2(Full)/6-311++G(d,p)] [50] 133.8 (HF/6-31G(d,p) [51], 66 (CCSD(T)/CBS) [52], 73.9 (B3LYP/aug-cc-pVQZ) [53]
H_2SeO	157.25	158.39 [QCISD/LANLSDZ(d)] [54]
H_2SeS	146.06	137.68 (MP2/MIDI-4*) [49]
H_2SSe	114.48	119.30 (MP2/MIDI-4*) [49]

due to the Pauli exclusion principle, $E_{\text{ind}}^{(2)}$ denotes the second-order energy resulting from the induction interaction, and, $E_{\text{ex-ind}}^{(2)}$ accounts for the repulsion change caused by the electronic cloud deformation, $E_{\text{disp}}^{(2)}$ stands for the second-order dispersion energy, and finally, $E_{\text{ex-ind}}^{(2)}$ represents the second-order correction for a coupling between the exchange repulsion and the dispersion interactions. The $d(\text{HF})$ term is a Hartree–Fock correction, which includes higher order induction and exchange corrections. These computations have been carried out using PBE0/aug-cc-pVTZ computational level within the MOLPRO program [47].

3. Results and discussion

3.1. Monomers

The case of the HOOH dimers will not be considered in the present work since it has been extensively studied previously by us and by other authors [20–27].

Initially, the energy of the HXYH molecules has been compared with those of the $\text{H}_2\text{X}=\text{Y}$ and $\text{X}=\text{YH}_2$ isomer (Table 1). Obviously, the $\text{H}_2\text{O}=\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$) tautomers have not been considered because the oxygen does not have the ability to form more than two bonds, while the opposite is true for S and Se. In all cases, the HXYH configuration is the most stable by more than 100 kJ mol^{-1} . All the theoretical data obtained from the literature are in agreement with this fact, with less than 8% of difference between the resulting energy barriers, with the exception of the HSOH case. Therefore, the structures with a double bond will not be considered in the present article for the formation of the dimers.

Table 2. Bond distance (Å), dihedral angle (°) of the minima obtained (experimental data in parenthesis) and Transition State barriers (kJ mol⁻¹) of the isomers with respect to the minimum for all the monomers calculated at MP2/6-311++G(d,p) level.

	XY bond distance	HXYH dihedral angle	TS _{cis} (kJ mol ⁻¹)	TS _{trans} (kJ mol ⁻¹)
HOOH	1.451 (1.475) [55]	121.5 (119.8)	37.5	4.1
HOSH	1.691 (1.6616) [56]	93.9 (90.41)	28.6	16.4
HSSH	2.084 (2.055) [57]	91.0 (90.36)	32.9	22.1
HOSeH	1.844	91.6	23.0	15.8
HSSeH	2.223	90.8	29.8	21.3
HSeSeH	2.356	90.8	28.5	21.1

Some of the geometrical parameters of the isolated HXYH molecules and their isomerization barrier have been gathered in Table 2. In addition to the monomers considered in the present article, and for comparative purposes, the characteristics of hydrogen peroxide have been included at the same computational level in Table 2. The optimized structures of the systems considered present non-planar configurations with dihedral angles close to 90° except for the HOOH with a dihedral angle of 121°. Experimental geometries are only available for three of the systems considered, HOOH, HSOH, HSSH, and our computational results are able to reproduce the experimental data.

All the TS structures present the four atoms in the same plane and for all the compounds two different TS are obtained, that towards the *cis* isomer and that towards the *trans* one. In all cases, the TS_{trans} barrier is smaller than the corresponding TS_{cis}. However, while in HOOH, the TS_{trans} is very small (4 kJ mol⁻¹), in the rest of the compounds it ranges from 16 to 22 kJ mol⁻¹. In the same way, the largest TS_{cis} barrier corresponds to the hydrogen peroxide with a value of 38 kJ mol⁻¹ and in the rest of the systems it varies between 23 and 33 kJ mol⁻¹. These results are in agreement with the experimental barrier observed for the HSSH (*cis* barrier 33.49 kJ mol⁻¹; *trans* barrier 23.80 kJ mol⁻¹) [48] and previous computational studies [49,50].

Among the different electronic properties of these molecules, the MEP has been chosen since it provides information for those regions where the molecule could interact with electron deficient systems and the relative strength of this interaction [51]. In Figure 1, the MEPs of the HXXH molecules are presented. In all HXYH monomers, for each heavy atom, two negative regions

are found that can be associated with the atomic lone pairs (Table 3), except in the HSOH system where only one MEP minima is located around the oxygen atom. The disposition of the MEP minima around the oxygen atom is very different to those found for the sulfur and selenium. Thus, in the case of the oxygen the two MEP minima are very close to each other with an angle MEPmin-O-MEPmin of about 90°, while for sulfur and selenium the analogous angle is 133° and 152°, respectively. In general, one of the MEP minima of X (or Y) is eclipsed by the hydrogen atom bonded to Y (or X). This MEP minimum has been denoted with the superscript 'a' in Table 3. In all the cases, this MEP shows less negative values than the other MEP minimum which is alternated to the hydrogen atom (denoted by 'b' in Table 3).

Another interesting difference between the MEP minima in oxygen, in sulfur and in selenium is the fact that in the former they are located much closer to the atom than in other ones. Similarly, the values obtained for the oxygen MEP minima are more negative than those of the larger atoms. Thus, the region between MEP minima in the oxygen atom is always negative while in the sulfur and selenium positive regions can be found.

The features of the MEP will determine the orientation of the molecules when the dimers are formed. Hence, an atom like S or Se will present two different zones; one opposite to the H bound which will be a region with positive values of the MEP and another perpendicular to the molecular bond axis with negative MEP values indicating that these atoms can act as dual donor-acceptor systems.

3.2. Dimers

The dimers (HXYH)₂ of all the combinations of X, Y = O, S and Se (except those where X=Y=O) have been studied.

The number of minima found for each of these five systems ranges from 13 to 22. To simplify the analysis of the minima, they have been divided into homochiral and heterochiral systems based on the HXYH dihedral angle. When the dihedral angle of the two molecules within the dimer shows the same sign, the dimers are designated as homochiral and they are heterochiral when the two constituent monomers show dihedral angles with opposite sign. In addition, the same numbering has been assigned for the homo- and heterochiral dimers that present similar interactions. For example, Min-1 in HSOH system presents one OH...O and one SH...S interactions, in both homo- and heterochiral dimers. The ordering of the minima

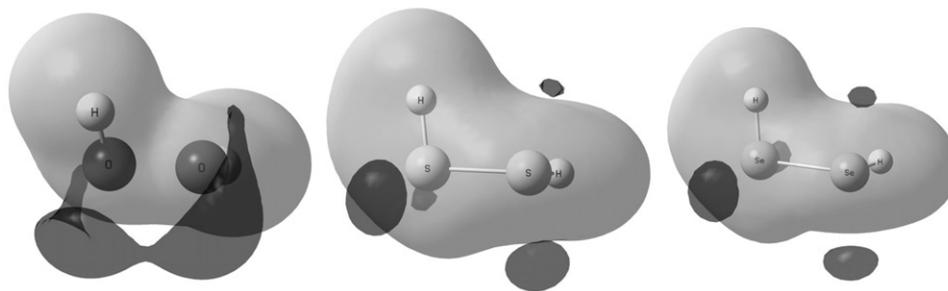


Figure 1. MEP for HXXH (X = O, S, Se). Dark and light regions indicate negative and positive values of the MEP, respectively. The values of the isosurfaces are 0.045, for HOOH, and 0.020 for HSSH and HSeSeH.

Table 3. Molecular electrostatic potential minima values (au) calculated at MP2/6-311++G(d,p) level.

HXYH	HOOH	HOSH	HOSeH	HSSH	HSSeH	HSeSeH
X ^a	-0.048	-	-0.068	-0.025	-0.025	-0.022
X ^b	-0.067	-0.072	-0.070	-0.031	-0.029	-0.027
Y ^a	-0.048	-0.022	-0.020	-0.025	-0.022	-0.022
Y ^b	-0.067	-0.035	-0.030	-0.031	-0.028	-0.027

Table 4. Contacts observed within the AIM methodology, Interaction and chiral discrimination energies (kJ mol⁻¹) for HSOH dimers optimized at MP2/6-311++G(d,p) level.

Interactions	Homochiral Heterochiral		ΔE_{chiral}
	ΔE_{I}	ΔE_{I}	
Min-1 OH...O, SH...S	-20.52	-21.23	-0.71
Min-2 OH...O	-19.84	-18.78	1.06
Min-3 (S...HO) × 2	-16.38	-17.25	-0.87
Min-4 (SH...O) × 2	-14.79	-13.84	0.95
Min-5 S...HO, O...SH	-10.55	-10.11	0.44
Min-6 OH...S, S...S	-9.99	-11.72	-1.73
Min-7 OH...S, S...O	-8.19	-7.95	0.24
Min-8 SH...O, S...O	-	-6.93	-
Min-9 (S...O) × 2, O...O	0.39	-4.00	-4.39

has been based on their stability, thus, the most stable homochiral dimer has been named Min-1.

3.2.1. HSOH dimer

Eight homochiral and nine heterochiral minima have been characterized for the dimers of this compound (Table 4). The BSSE corrected interaction energies found ranges from -21 to 0.4 kJ mol⁻¹. A variety of interactions are found in the AIM analysis of the electron density of the dimers. Four different types of hydrogen bond (OH...O, OH...S, SH...O

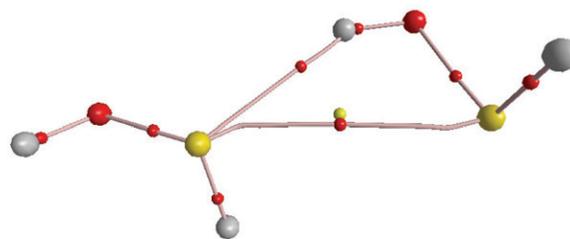


Figure 2. AIM molecular graph of the Min-6 of (HSOH)₂ (Heterochiral). The red and yellow dots indicate the position of the bond and ring critical points respectively. The bond paths are shown.

and SH...S) as well as three different chalcogen-chalcogen contacts (O...O, O...S and S...S) are observed.

The most stable minima, Min-1, presents one OH...O and one SH...S bond critical points (BCPs) in the AIM analysis. The heterochiral configuration of this minimum is 0.71 kJ mol⁻¹ more stable than the corresponding homochiral one.

Min-2, which is 2.77–1.41 kJ mol⁻¹ less stable than the minimum, presents only one O...H–O interaction. Thus, the difference between Min-1 and Min-2 can be used to estimate the stabilization energy of an S...H–S bond.

The HBs in Min-5 are similar to those found in Min-3 and Min-4. However, the stabilization energy of Min-5 is not approximately half of those of Min-3 and Min-4. The reason being that the disposition of the OH...S interaction with an angle of 108°, which is quite unfavourable, makes this interaction weaker and the dimer more unstable.

Min-6 presents a curious structure (Figure 2) in which the S performs a dual interaction, one S...S interaction at 3.482 Å, and another S...H–O at 2.466 Å, both characterized by the existence of a BCP between the corresponding atoms. This interaction is possible for the S, and Se, because, as mentioned, there

Table 5. Intermolecular contacts observed within the AIM methodology, interaction and chiral discrimination energies (kJ mol^{-1}) for the HSSH dimers optimized at MP2/6-311++G(d,p) level.

Interactions		Homochiral ΔE_1	Heterochiral ΔE_1	ΔE_{chiral}
Min-1	(SH...S) \times 2	-7.10	-7.22	-0.12
Min-2	(SH...S) \times 3	-6.21		
Min-3	(SH...S) \times 4		-6.19	
Min-4	S...S, SH...S	-5.56	-6.24	-0.68
Min-5	(SH...S) \times 2		-5.07	
Min-6	(S...S) \times 2, (SH...S) \times 2		-4.56	
Min-7	(S...S) \times 2, SH...S/S...S, SH...S ^a	-4.18	-3.78	0.4
Min-8	(S...S) \times 2, SH...S	-3.32		
Min-9	(S...S) \times 2/(S...S) \times 4 ^a	-0.12	-0.48	-0.36

^aThe first set of interactions corresponds to the homochiral dimer while the second to the heterochiral one.

are two zones in the atoms, one with positive values of electron density (acceptor zone) and another with negatives values (donor zone) due to the electron lone pairs. A similar case has been described for some halogen atoms that can act as electron donor and acceptors simultaneously [62].

Finally, Min-9 is the only minimum which presents exclusively chalcogen–chalcogen. The positive value of the interaction energy indicates that this isomer is not stable and therefore the chalcogen interaction is not strong enough to bind the two monomers.

Overall, the minima found show different types of interactions, and based on the energetic results, these contacts can be ordered in terms of strength as OH...O > OH...S > SH...O > S...S > S...O > O...O.

3.2.2. HSSH dimer

The characteristics of the 13 minima found for the HSSH dimers (6 homochiral and 7 heterochiral) have been gathered in Table 5. The interaction energies found for these dimers varies between -7.2 and -0.1 kJ mol^{-1} . The most stable dimer, Min-1, shows the presence of two symmetrical SH...S interactions. Each of the molecules in these configurations act as HB donor with one SH while the other sulfur atom acts as HB acceptor. The homochiral complex shows C_2 symmetry and the heterochiral one C_i . The small stability of these minima when compared with the analogous of HSOH are due to the poor ability of the SH and S moieties as HB donor and HB acceptor, respectively [63].

Other minima show more HBs but the disposition of the moieties involved in them is not optimal for the interaction. For instance, the heterochiral dimer Min-3 shows S_4 symmetry with the four SH moieties acting as

Table 6. Intermolecular contacts observed within the AIM methodology, interaction and chiral discrimination energies (kJ mol^{-1}) for the HSeOH dimers calculated at MP2/6-311++G(d,p) level.

Interactions		Homochiral ΔE_1	Heterochiral ΔE_1	ΔE_{chiral}
Min-1	OH...O, SeH...Se	-21.82	-22.01	-0.19
Min-2	OH...O	-21.20	-20.75	0.45
Min-3	(O-H...Se) \times 2	-19.81	-20.04	-0.23
Min-4	(SeH...O) \times 2	-15.29	-14.23	1.06
Min-5	Se...Se, OH...Se	-14.85	-15.88	-1.03
Min-6	Se...O, SeH...O	-11.74	-10.86	0.88
Min-7	SeH...O, OH...Se	-11.47	-11.22	0.25
Min-8	Se...O, OH...Se	-10.00	-9.55	0.45
Min-9	(O...Se) \times 2, O...O	-7.16	-9.60	-2.44

HB donor and acceptor being the SH...S angle 127° in all the contacts. Min-2 resembles to Min-3 but with only three SH...S contacts. Similarly, Min-5 shows one of the molecules acting as double HB donor while the other is double HB acceptor. Finally, in the case of Min-4 and Min-6, in addition to chalcogen–chalcogen interactions, one of the SH moieties acts as HB acceptor and donor simultaneously.

In general, the S...S chalcogen–chalcogen interactions does not seem to be very stabilizing, and for instance Min-9, the weaker complex found in this set, shows exclusively chalcogen–chalcogen interactions.

3.2.3. HSeOH dimer

The energetic values of the 18 minima found for the HSeOH dimers, 9 homochiral and 9 heterochiral, are gathered in Table 6. As in the case of the HSOH, the most stable minimum, Min-1, shows two HB

Table 7. Intermolecular contacts observed within the AIM methodology, interaction and chiral discrimination energies (kJ mol^{-1}) for the HSeSH dimers calculated at MP2/6-311++G(d,p) level.

Interactions		Homochiral ΔE_1	Heterochiral ΔE_1	ΔE_{chiral}
Min-1	(SH...Se) $\times 2$	-10.14	-10.00	0.14
Min-2	Se...Se, SH...Se	-9.59	-10.23	-0.64
Min-3	SeH...S, SH...Se, SeH...Se, SH...S		-9.30	
Min-4	SeH...S, SH...Se, SeH...Se	-8.64		
Min-5	SeH...Se, SH...S	-8.45	-8.34	0.11
Min-6	SeH...Se, SH...Se, Se...S		-7.73	
Min-7	Se...Se, SH...S	-7.43	-7.41	0.02
Min-8	Se...Se, S...S, SeH...S, SH...Se		-7.35	
Min-9	Se...Se, Se...S, SH...S, SH...Se		-7.17	
Min-10	Se...Se, S...S, Se...S, SH...Se	-7.04		
Min-11	(SeH...S) $\times 2$	-6.93	-7.08	-0.15
Min-12	S...S, SeH...S	-6.34	-6.12	0.22
Min-13	SeH...S, Se...S	-5.80	-5.66	0.14
Min-14	(Se...S) $\times 2$	-4.06	-4.44	-0.38

interaction, a OH...O plus a SeH...Se one. The values of the interaction energies of these complexes are slightly larger than those of the most stable configuration of HOSH indicating that, in both cases, the dominant interaction is the OH...O one. In agreement with this, Min-2, which contains only an O...HO intermolecular interaction shows similar stabilization energies to that of Min-1. Based on the energies of these two minima, it can be concluded that the SeH...Se is a very weak HB ($\approx 1 \text{ kJ mol}^{-1}$) and in fact, it is not observed in any other of the minima found for this set.

It is interesting to notice that Min-3, which presents two OH...Se interactions, shows a stabilization energy similar to the two most stable minima with an OH...O interaction, even though the Se atom is a poor HB acceptor.

As previously, the dimer with only chalcogen-chalcogen interactions, Min-9, is the least stable one. However, in this case the interaction energies obtained are much larger than those found for the HSOH or HSSH dimers. Another interesting point of the interaction energies of the Min-9 complex is that they present the largest chiral discrimination of all the complexes of HSeOH.

3.2.4. HSeSH dimer

A total of 22 minima, 10 homochiral and 12 heterochiral, have been found for the (HSeSH) $_2$. This is the dimer with the largest number of minima of those studied in the present article. The increment in the size and polarizability of the heavy atoms within the monomers allows the possibility of a larger number

of interactions. Among the interactions observed, the chalcogen-chalcogen one is present in half of the minima found including the most stable minimum, Min-2 (heterochiral) (Table 7).

The range of interaction energies obtained for the dimers was from -10.2 to -4.4 kJ mol^{-1} . The most stable homochiral dimer, Min-1, shows two SH...Se HB interactions. The second most stable minimum shows SeH...S HB and Se...Se chalcogen-chalcogen interactions, the heterochiral configuration being slightly more stable than the homochiral Min-1.

Regarding the nature of the interaction established, two sets of the dimers calculated should be highlighted: (i) Min-4 which shows the four possible types of XH...Y HBs (SeH...S, SH...Se, SeH...Se, and SH...S) and (ii) Min-9, Min-10 and Min-11, which combine two different chalcogen-chalcogen interactions and two HBs as evaluated within the AIM methodology.

3.2.5. HSeSeH dimer

In this case 14 minima have been found, 7 homochiral and 7 heterochiral ones (Table 8). The interaction energies for all of them range from -11.8 to -6.9 kJ mol^{-1} . The narrow interval of interaction energies is due to the weak HB formed within the dimers and the stronger chalcogen-chalcogen interactions previously discussed.

The most stable configuration, Min-1, corresponds to a heterochiral dimer with four simultaneous SeH...Se interactions which shows S_4 symmetry. The homochiral Min-2 is only 0.8 kJ mol^{-1} less stable showing a similar disposition of the two molecules but

Table 8. Intermolecular contacts observed within the AIM methodology, interaction and chiral discrimination energies (kJ mol^{-1}) for the HSeSeH dimers optimized at MP2/6-311++G(d,p) level.

	Interactions	Homochiral ΔE_I	Heterochiral ΔE_I	ΔE_{chiral}
Min-1	(SeH...Se) \times 4		-11.84	
Min-2	(SeH...Se) \times 3, Se...Se	-11.04		
Min-3	(SeH...Se) \times 2, (Se...Se) \times 2		-10.07	
Min-4	(SeH...Se) \times 2	-9.76	-9.26	0.50
Min-5	Se...Se, she...Se	-9.60	-13.74	-4.14
Min-6	(SeH...Se) \times 2, (Se...Se) \times 2		-9.55	
Min-7	(Se...Se) \times 2, SeH...Se	-8.89		
Min-8	Se...Se, SeH...Se	-8.32	-10.99	-2.67
Min-9	(Se...Se) \times 4		-7.91	
Min-10	(Se...Se) \times 2	-7.01	-6.95	0.06

in this case with three HB and one chalcogen–chalcogen interaction.

The two less stable minima, Min-9 and Min-10, show exclusively Se...Se interactions. Their interaction energies (between -7.0 and -7.9 kJ mol^{-1}) are larger than those found for the rest of the dimers described in the present article bound only with chalcogen–chalcogen interactions.

3.3. General discussion

A total of 84 minima have been characterized for the dimers of the five molecules considered in the present article [(HXYH)₂ with X, Y = O, S, Se except X=Y=O]. In all cases considered here, the most stable minima are formed by HB interactions. However, as the size of the heavy atoms in the HXYH molecules increases, the chalcogen–chalcogen interactions become more important. The chiral discrimination between the homo and heterochiral pairs obtained is, in general, small.

A rich variety of interactions are observed in these minima. All the possible XH...Y HBs and X...Y chalcogen–chalcogen interactions (9 and 6 respectively) have been observed. The total number of interactions studied was 163, 99 HBs and 64 chalcogen–chalcogen interactions. In the case of the HBs they can be grouped based on the atom that acts as HB acceptor (O, S or Se) and the interatomic distances of the atoms involved in the HBs range from 1.83 to 3.32 Å. All the interactions are within the closed shell regimen with positive values of the Laplacian and values of the electron density around 10^{-3} units.

Exponential relationships have been obtained between the electron density at the BCP and the interatomic distance for each of these groups as shown

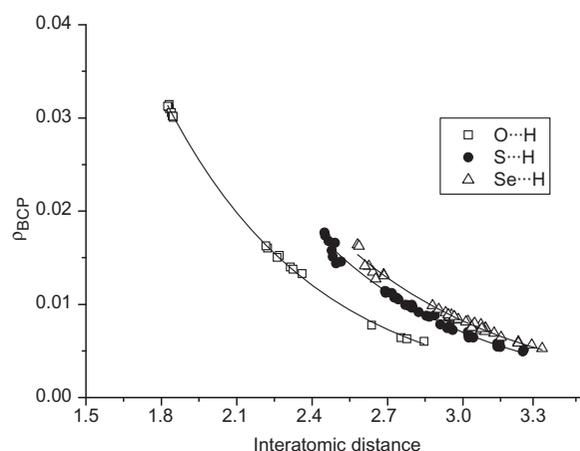


Figure 3. Relationships found between the interatomic distances (Å) and the value of the electron density at the BCP (a.u.) for the HB interactions. The fitted exponential relationships present $R^2=0.999$, 0.988 and 0.984 for the O...H, S...H and Se...H data, respectively.

in Figure 3. Similar relationships have been described for other HBs [64,65].

In the case of the chalcogen–chalcogen interactions only in two of the cases are more than 10 interactions (S...S and Se...Se with 16 and 24 interactions, respectively) observed. For these two cases, the range of interatomic distances found was from 3.32 to 4.18 Å. In addition, similar exponential relationships to those found for the HBs are calculated (Figure 4).

The NBO analysis carried out for all the minima reveals that there is a small charge transfer, being 0.05 the highest value, which corresponds to an OH...O interaction. These values are similar to what is found in other hydrogen bonded systems [66]. All the NBO data have been gathered in the supplementary material.

A DFT-SAPT study of the most stable configurations of each dimer and those that show only chalcogen–chalcogen interactions have been carried out (Table 9). In the cases where OH...O interactions are present, the dominant attractive term is the electrostatic one, $E_{\text{el}}^{(1)}$, representing about 52% of the attractive terms. In those complexes the $E_D^{(2)}$ contribution is 27% and that of the $E_i^{(2)}$ term about 11%. As the size of the heavy atoms involved in the HB interactions increases, the $E_D^{(2)}$ term is more important and the $E_{\text{el}}^{(1)}$ one became smaller. Thus, in those complexes with SH...S interactions, the $E_{\text{el}}^{(1)}$

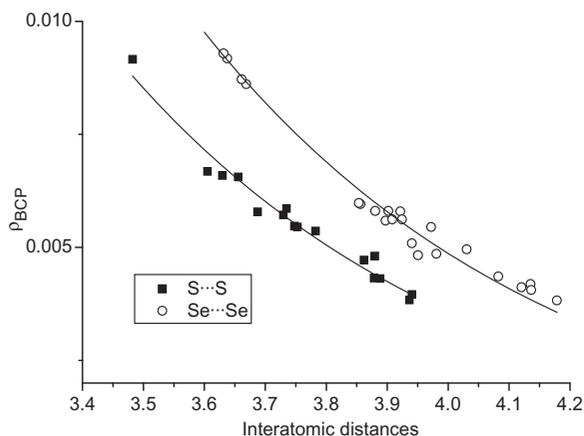


Figure 4. Relationship between the interatomic distances (Å) and the value of the electron density at the BCP (a.u.) for chalcogen–chalcogen interactions. The fitted exponential relationships present $R^2=0.96$ and 0.99 the S...S and Se...Se data, respectively.

represents between 38 and 40% of the total attractive terms and $E_D^{(2)}$ about a 44%. In the complexes with SH...Se and SeH...Se, the $E_D^{(2)}$ increases even more, up to 57%, while the $E_{\text{el}}^{(1)}$ is only 37%.

The attractive terms of the complexes that show only chalcogen–chalcogen interactions are dominated by the $E_D^{(2)}$ followed by the $E_{\text{el}}^{(1)}$, being the contribution of the $E_i^{(2)}$ very small.

4. Conclusions

A theoretical study of the monomers and dimers formed by the chiral HXYH molecules, where X, Y = O, S and Se (except X=Y=O), have been carried out using MP2/6-311++G(d,p) level computational level. A large number of minima are found for each case (between 13 and 22). Both homochiral and heterochiral complexes are characterized. In general, small chiral discrimination was found for pairs of complexes with the same interaction type.

The most stable minima are those formed through HB interactions, especially if OH groups are involved. However, as the size of the atoms interacting increases, the chalcogen–chalcogen forces become more important.

The analysis of the electron density with the AIM methodology shows the presence, both HB and chalcogen–chalcogen contacts. Exponential relationships have been found between the electron density at the BCP and the interatomic distance in both HB and chalcogen–chalcogen interactions when a sufficient number of cases was available.

Table 9. Energy components of the interaction energy (kJ mol^{-1}) evaluated with the DFT-SAPT method.

X-Y	Min	Conf	$E_{\text{el}}^{(1)}$	$E_{\text{ex}}^{(1)}$	$E_i^{(2)}$	$E_D^{(2)}$	$\delta(\text{HF})$	Interactions
(HSOH) ₂	1	Homochiral	-41.75	54.45	-9.59	-21.44	-7.40	OH...O, SH...S
	1	Heterochiral	-40.78	51.42	-9.06	-19.87	-6.80	OH...O, SH...S
	9	Homochiral	-8.57	23.64	-1.38	-15.42	-1.45	(S...O)×2, O...O
	9	Heterochiral	-15.69	26.67	-1.41	-15.16	-1.43	(S...O)×2, O...O
(HSSH) ₂	1	Homochiral	-16.97	28.86	-3.06	-19.69	-4.79	(SH...S)×2
	1	Heterochiral	-16.56	26.73	-2.58	-18.04	-4.00	(SH...S)×2
	9	Homochiral	-8.38	21.22	-0.75	-17.46	-1.85	(S...S)×2
	9	Heterochiral	-9.50	22.13	-0.79	-17.96	-1.87	(S...S)×4
(HSeOH) ₂	1	Homochiral	-41.09	53.19	-9.25	-21.69	-7.57	OH...O, SeH...Se
	1	Heterochiral	-40.75	51.68	-8.93	-20.93	-7.22	OH...O, SeH...Se
	9	Homochiral	-18.02	31.90	-2.68	-18.78	-2.13	(O...Se)×2, O...O
	9	Heterochiral	-20.17	29.51	-2.22	-16.84	-1.76	(O...Se)×2, O...O
(HSeSH) ₂	1	Homochiral	-16.41	26.61	10.20	-2.72	-18.24	(SH...Se)×2
	1	Heterochiral	-16.73	27.49	10.75	-2.91	-18.90	(SH...Se)×2
	14	Homochiral	-11.78	24.04	-1.29	-18.95	-2.05	(Se...S)×2
	14	Heterochiral	-10.98	22.02	-1.08	-18.28	-1.89	(Se...S)×2
(HSeSeH) ₂	1	Heterochiral	-19.50	32.95	-2.12	-27.00	-4.62	(SeH...Se)×4
	10	Homochiral	-12.22	23.15	-1.27	-18.58	-1.95	(Se...Se)×2
	10	Heterochiral	-11.28	21.73	-1.10	-18.54	-1.84	(Se...Se)×2

The DFT-SAPT energy analysis shows the influence of the atoms involved in the interaction in the different terms of the partition. In the case of HBs, the contribution of the dispersion energy increases with the size of heavy atoms involved and the electrostatic term decreases. In the chalcogen–chalcogen interactions the dominant term is always the dispersion one.

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