

# Resonance-Assisted Intramolecular Chalcogen–Chalcogen Interactions?

Pablo Sanz, Manuel Yáñez, and Otilia Mó\*<sup>[a]</sup>

**Abstract:** High-level B3LYP/6-311+G(3df,2p) density functional calculations have been carried out for a series of saturated chalcogenoaldehydes: CH(X)-CH<sub>2</sub>-CH<sub>2</sub>YH (X, Y = O, S, Se, Te). Our results indicate that in CH(X)-CH<sub>2</sub>-CH<sub>2</sub>YH (X = Y = O, S, Se) the X–H···X intramolecular hydrogen bond (IHB) competes in strength with the X···XH chalcogen–chalcogen interaction, while the opposite is found for the corresponding tellurium-containing analogues. For those derivatives in which X ≠ Y, X being the more electronegative atom, the situation is more complicated due to the existence of two non-equivalent X–H and Y–H tautomers. The Y–H tautomer is found to be lower in energy than the X–H tautomer,

independently of the nature of X and Y. For X = O, S, Se and Y = S, Se the most stable conformer **b** is the one exhibiting a Y–H···X IHB. Conversely when Y = Te, the chelated conformer **d**, stabilized through a X···YH chalcogen–chalcogen interaction is the global minimum of the potential energy surface. Systematically the IHB and the chalcogen–chalcogen interactions observed for saturated compounds are much weaker than those found for their unsaturated analogues. This result implies that the

nonbonding interactions involving chalcogen atoms, mainly Se and Te, are not always strongly stabilizing. This conclusion is in agreement with the fact that intermolecular interactions between Se and Te containing systems with bases bearing dative groups are very weak. We have also shown that these interactions are enhanced for unsaturated compounds, through an increase of the charge delocalization within the system, in a mechanism rather similar to the so call Resonance Assisted Hydrogen Bonds (RAHB). The chalcogen–chalcogen interactions will be also large, due to the enhancement of the X→Y dative bond, if the molecular environment forces the interacting atoms X and Y to be close each other.

**Keywords:** density functional calculations • chalcogen–chalcogen interactions • hydrogen bonds • resonance assisted interactions

## Introduction

Weak interactions play a crucial role in the structural organization of chemical and biochemical systems and in molecular recognition. Many of these weak interactions are directly associated with the formation of inter- or intramolecular hydrogen bonds (IHBs),<sup>[1–3]</sup> while others are due to nonbonding interactions between heavy atoms. Among the latter chalcogen–chalcogen interactions have received a particular attention. These weak bonds are responsible for the enhanced stability of chelated structures with respect to open ones, as it is the case for instance in malonaldehyde<sup>[4–8]</sup> and in thiomalonaldehyde (TMA),<sup>[9, 10]</sup> and modulate their intrinsic reactivity. Tropolone,<sup>[11]</sup> resorcinol,<sup>[12]</sup> and acid anhydrides<sup>[13]</sup> are paradigmatic examples of systems where the existence or the formation of IHBs affects the intrinsic

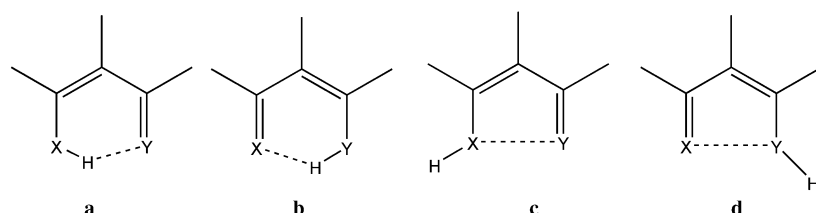
basicity and/or acidity of the system. Chalcogen–chalcogen attractive forces also play an important role as far as the preferred conformation and reactivity of some chalcogen derivatives is concerned, as it has been shown many years ago by Adcock, Angyan et al. and Bürgi and Dünitz,<sup>[14–16]</sup> and more recently by Minyaev and Minkin.<sup>[17, 18]</sup> Also recently, Komatsu et al.<sup>[19]</sup> showed that <sup>17</sup>O and <sup>77</sup>Se NMR spectroscopic data provide strong evidence for intramolecular nonbonded interaction between Se and O in hydroxy-selenenyl compounds. These interactions seem to play also an important role in some reaction mechanisms.<sup>[20]</sup>

Very recently, using β-chalcogenovinylaldehydes as suitable model compounds, we have investigated<sup>[21]</sup> the competition between X–H···Y (or X···H–Y) IHBs (structures **a** and **b** in Scheme 1) and Y→X (or X→Y) chalcogen–chalcogen nonbonded interactions (structures **c** and **d**, respectively in Scheme 1) on the stability of these systems.

A possible mixture of rapidly interconverting tautomers **a** and **b** through the IHB is another important characteristic of this kind of compounds. As a matter of fact, for thiomalonaldehyde high level ab initio calculations predict both tautomers to be very close in energy,<sup>[9]</sup> and thiomalonaldehyde and its derivatives have been successfully used as model systems to investigate ultrafast hydrogen transfer through pulsed lasers.<sup>[22–24]</sup> Also, the existence of both forms **a** and **b**

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Scheme 1. Tautomers for X = O, S and Y = Se, Te.

has been well established by means of UV,<sup>[25]</sup> UV photoelectron,<sup>[26]</sup> IR,<sup>[25]</sup> and <sup>1</sup>H NMR spectroscopy.<sup>[27, 28]</sup> However, our results indicated that, although selenovinylaldehyde and selenothiovinylaldehyde resemble closely thiomalonaldehyde, in the sense that the O-H...Se and the S-H...Se intramolecular hydrogen bonds compete in strength with the O...Se and the S...Se interactions, the opposite is found for the corresponding tellurium-containing analogues. These dissimilarities are due to dramatic differences between Se and Te as far as the X...Y (X = O, S; Y = Se, Te) interactions are concerned, which for Se derivatives are rather small, while for Te compounds are very strong. As a consequence, while for selenium containing compounds the global minima of the potential energy surface (PES) correspond to **a**-type tautomers, for Te containing systems the global minima correspond to **d**-type tautomers. In a recent paper,<sup>[29]</sup> we have also shown that these weak interactions play a crucial role in the intrinsic basicity and acidity of these systems.

The enhanced stability of the IHB in thiomalonaldehyde has been often associated with the so-called Resonance Assisted Hydrogen Bond (RAHB) phenomenon,<sup>[1, 30–32]</sup> that is, the stabilization resulting from the charge delocalization triggered by the formation of the IHB. An open question, is whether similar resonance effects may be responsible for the enhanced stability of **d**-type tautomers in the case of Se- and Te-containing compounds, that is, whether chalcogen–chalcogen interactions observed in  $\beta$ -chalcogenovinylaldehydes containing Se and Te are enhanced by a possible charge delocalization effect. In order to analyze this possibility we will compare along this paper the structure, stability and bonding characteristics previously reported in the literature<sup>[21]</sup> for  $\beta$ -chalcogenovinylaldehydes, with those of the corresponding saturated analogues, namely CH(X)-CH<sub>2</sub>-CH<sub>2</sub>YH (X, Y = O, S, Se, Te), where delocalization effects are absent.

## Computational Methods

The geometries of the different conformers of CH(X)-CH<sub>2</sub>-CH<sub>2</sub>YH (X, Y = O, S, Se, Te) species were optimized using the B3LYP density functional theory (DFT) approach, as it is implemented in the Gaussian 98 suite of programs.<sup>[33]</sup> The B3LYP method combines Becke's three-parameter nonlocal hybrid exchange potential<sup>[34]</sup> with the non-local correlation functional of Lee, Yang and Parr<sup>[35]</sup> and yields optimized geometries in fairly good agreement with experimental ones<sup>[5, 36–42]</sup> and, harmonic vibrational frequencies that are closer to experiment than those obtained by using other correlated methods such as the MP2 formalism.<sup>[43, 44]</sup> A

6-31G\* basis set expansion was used for the geometry optimization and harmonic vibrational frequency calculations for all compounds, except for those containing Te. For tellurium derivatives, we have employed a mixed base, which includes a SKBJ relativistic potential of Stevens et al.<sup>[45]</sup> for

Te, which accounts for the most important relativistic effects, together with the [4,1]+d basis described in ref. [21] and a 6-31G(d) basis set for the remaining atoms of the system. Hereafter, for the sake of simplicity this mixed basis set, will be named for extension 6-31G(d).

Final energies were obtained on single point B3LYP/6-311+G(3df,2p) calculations on the aforementioned optimized geometries. It must be indicated that for Se the 6-311+G(3df,2p) basis set corresponds to that reported by Curtiss et al.<sup>[46]</sup>

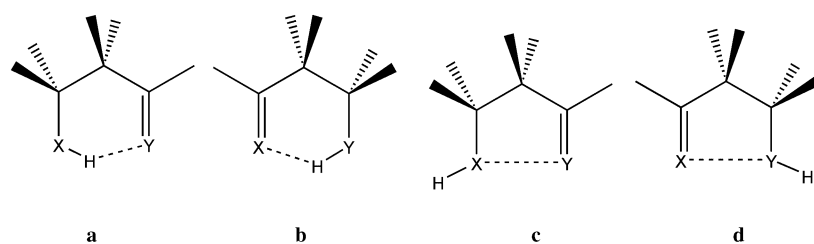
For Te-containing compounds, again a mixed basis set was used. It combines an all-electron 6-311+G(3df,2p) basis set expansion for all atoms except Te, for which the SKBJ effective core potential is combined with the (6s,6p,3d,1f) basis set developed in a previous paper.<sup>[21]</sup> Again for the sake of simplicity this mixed basis set will be named hereafter as 6-311+G(3df,2p) basis. In a previous paper<sup>[21]</sup> we have shown, for the set of  $\beta$ -chalcogenovinylaldehydes that this approach yields results in good agreement with those obtained by means of high-level G2(MP2) ab initio calculations, but at a much lower cost.

The bonding characteristics of the different tautomers were analyzed by using two alternative procedures, namely the atoms in molecules (AIM) theory of Bader<sup>[47]</sup> and the Natural Bond Order (NBO) analysis of Weinhold et al.<sup>[48]</sup> The first method is based on a topological analysis of the electron charge density and its Laplacian. Within this approach we have located for each bond the bond critical points (bcp) the charge density of which is a good indication of the strength of the linkage.

The NBO analysis will allow us to obtain reliable charge distributions, as well as to evaluate quantitatively the intramolecular attractive orbital interactions which would be responsible for the stability of **c**- and **d**-type structures (see Scheme 1). These analyses will be complemented with those carried out in terms of the lengthening or shortening of the bond lengths and in terms of the shifting of the corresponding stretching frequencies. We have carried out also a Natural Resonance Theory (NRT)<sup>[49–51]</sup> analysis to estimate the weight of the most important resonance structures that may contribute to the enhancement of the strength of the IHB or that of the chalcogen–chalcogen interaction.

## Results and Discussion

Since the main goal of our study is to analyze in detail the strength of IHBs and chalcogen–chalcogen interactions, we shall restrict our survey to tautomers **a**–**d** (see Scheme 2).



Scheme 2. Tautomers for X = O, S, Se, Te and Y = O, S, Se, Te.

Furthermore, in preliminary calculations carried out at the B3LYP/6-31G(d) level we have verified that, in the gas phase, conformers **a–d** are systematically lower in energy than other conformers in which the aliphatic chain is more extended. In order to make more systematic our discussion the following nomenclature will be adopted hereafter. The different compounds will be identified by naming the two chalcogen atoms **XY** followed by the letter which identifies each tautomer (**a–d**). In all cases **Y** designates the less electronegative of the two chalcogen atoms. It must be noted that for the particular cases in which **X = Y**, tautomer **a** is identical to tautomer **b** and tautomer **c** is identical to tautomer **d**. It is also important to realize that, although for the unsaturated compounds, tautomers **a** and **b** are directly connected through a hydrogen transfer through the IHB, that is not the case for tautomers **a** and **b** of the corresponding saturated analogues.

The optimized geometries of the different conformers of the compounds under investigation have been schematized in Figure 1. Their total energies are given as supporting information. Figure 1 includes also their relative stabilities for the sake of a better comparison.

**Relative stabilities of compounds with X = Y:** From the values in Figure 1, it can be easily observed that for O, S and Se-containing compounds the chelated structure stabilized through the X–H...X intramolecular hydrogen bond is the global minimum of the PES, although the energy gap between conformers **a** and **c** decreases steadily from O to Se. For the Te derivative the structure exhibiting a Te...Te nonbonding interaction is more stable than that with a Te–H...Te IHB. These results are consistent with the bonding characteristics obtained either through the use of the AIM or the NBO partition techniques. A topological analysis of their charge density reveals the existence of a bcp associated with the IHB in all conformers **a**. However, as shown in Table 1, the charge density decreases on going from O to Te, even though the Se derivative has a value slightly larger than that of the S containing compound. More importantly, only for Se- and Te-derivatives a bcp exists between the two chalcogen atoms in conformer **c**. As expected, the strength of the IHB depends on the donor and acceptor proton ability of the heteroatom. In the oxygen containing compound the O–H group is a good proton donor reflecting the high electronegativity of the oxygen atom, while the C=O group is a moderate proton acceptor. The C=S group is a better proton acceptor than the C=O group, but in contrast the S–H group is a much poorer proton donor than the O–H group, due to a much smaller electronegativity of the sulfur atom. This donor ability does

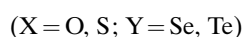
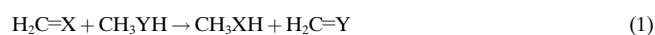
not change significantly on going from sulfur to selenium, but in general the C=Se group is slightly better proton acceptor than the C=S group. For Te-compounds, both the proton donor ability of the Te–H group and the proton acceptor ability of the C=Te group decrease and the Te-containing compound exhibits the weakest IHB. Conversely, the X–H (X = Se, Te)  $\sigma^*$  antibonding orbitals are lower in energy than the X–H (X = O, S)  $\sigma^*$  ones, favoring the formation of dative bonds. As a matter of fact, a second order perturbation NBO analysis shows that in both (**SeSe**)**c** and (**TeTe**)**c** tautomers there is a dative bond from one of the lone pairs of the chalcogen atom in the C=X group to the  $\sigma^*$  antibonding X–H (X = Se, Te) orbital, while no similar orbital interactions are detected for (**OO**)**c** and (**SS**)**c**. The energy associated with these orbital interactions is, as expected larger (10.6 kJ mol<sup>-1</sup>) for the Te derivative than for the Se-containing compound (7.0 kJ mol<sup>-1</sup>). Consistently, whereas for the Se-derivative tautomer **a** lies lower in energy than tautomer **c**, for the Te-containing compound is the other way around. This is also reflected in the Se–H and Te–H bond lengths. Although in conformer **a** the Se–H (Te–H) bond is involved in the IHB, its bond length is shorter than in tautomer **c**, reflecting the population (occupation number 0.02) of the  $\sigma^*$  antibonding X–H through the chalcogen–chalcogen interaction mentioned above, this difference being greater for the Te than for the Se-derivative. Consistently, the Se–H (Te–H) stretching frequency for tautomer **c** appears at lower values than for tautomer **a** (2387 vs 2243 cm<sup>-1</sup> for the selenium derivative and 1980 vs 2036 cm<sup>-1</sup> for the tellurium derivative).

Table 1. Charge density ( $\rho(\mathbf{r})$  in e au<sup>-3</sup>) at the bond critical points associated with the IHB and the chalcogen–chalcogen interaction in CH(X)–CH<sub>2</sub>–CH<sub>2</sub>YH (X, Y = O, S, Se, Te) compounds.

| Tautomer                 | $\rho(\mathbf{r})$ IHB <sup>[a]</sup> | Tautomer                   | $\rho(\mathbf{r})$ X...X <sup>[a]</sup> |
|--------------------------|---------------------------------------|----------------------------|---|
| X = Y                    |                                       |                            |   |
| ( <b>OO</b> ) <b>a</b>   | 1.485                                 | <b>OOc</b>                 | *                                       |
| ( <b>SS</b> ) <b>a</b>   | 0.7999                                | <b>SSc</b>                 | *                                       |
| ( <b>SeSe</b> ) <b>a</b> | 0.9457                                | <b>SeSec</b>               | 1.047                                   |
| ( <b>TeTe</b> ) <b>a</b> | 0.5364                                | <b>TeTec</b>               | 0.8472                                  |
| X ≠ Y                    |                                       |                            |   |
| ( <b>OS</b> ) <b>a</b>   | 1.329                                 | <b>OSc</b>                 | *                                       |
| ( <b>OS</b> ) <b>b</b>   | 0.8671                                | <b>OSd</b>                 | *                                       |
| ( <b>OSe</b> ) <b>a</b>  | 1.469                                 | <b>OSec</b>                | *                                       |
| ( <b>OSe</b> ) <b>b</b>  | *                                     | <b>OSe d</b>               | *                                       |
| ( <b>OTe</b> ) <b>a</b>  | 1.057                                 | <b>OTe c<sup>[b]</sup></b> | *                                       |
| ( <b>OTe</b> ) <b>b</b>  | *                                     | <b>OTe d</b>               | 1.514                                   |
| ( <b>SSe</b> ) <b>a</b>  | 1.078                                 | <b>SSec</b>                | *                                       |
| ( <b>SSe</b> ) <b>b</b>  | 0.7999                                | <b>SSe d</b>               | *                                       |
| ( <b>STe</b> ) <b>a</b>  | 0.7736                                | <b>STe c</b>               | *                                       |
| ( <b>STe</b> ) <b>b</b>  | *                                     | <b>STe d</b>               | 1.074                                   |
| ( <b>SeTe</b> ) <b>a</b> | 0.7112                                | <b>SeTe c</b>              | *                                       |
| ( <b>SeTe</b> ) <b>b</b> | 0.5545                                | <b>SeTe d</b>              | 1.099                                   |

[a] All values have been multiplied by 100. \* denotes that the corresponding bcp does not exist. [b] This tautomer is not a stationary point of the PES.

**Relative stability of compounds with  $X \neq Y$ :** The situation is obviously more complicated when both chalcogen atoms are different, because the four conformers **a–d** are different. The first conspicuous fact of Figure 1 is that the Y–H tautomers (**b**, **d**) are systematically more stable than the X–H tautomers (**a**, **c**). As illustrated in this figure, the energy gaps between these two sets of conformers depend strongly on the nature of the chalcogen atoms involved. When  $X = O$ , the gap increases from about 13 kcal mol<sup>-1</sup> if  $Y = S$ , to about 20 kcal mol<sup>-1</sup> if  $Y = Te$ . Conversely, these energy gaps decrease dramatically when  $X = S$  and  $Y = Se$ , Te or when  $X = Se$  and  $Y = Te$ . Similar stability trends were observed before for some unsaturated analogues, such as thiomalonaldehyde and some  $\beta$ -chalcogenovinylaldehydes containing sulfur, selenium and tellurium. However, for the unsaturated systems, the energy gap between Y–H type and X–H tautomers is canceled out by the existence of strong IHBs or strong chalcogen–chalcogen interactions.<sup>[29]</sup> Apparently, this is not the case when dealing with the saturated analogues, and therefore a more detailed analysis is needed. As suggested in previous papers, the relative stability of X–H versus Y–H tautomers can be analyzed through the use of the isodesmic reaction:



The results obtained (see Table 2) show that Reaction (1) is systematically endothermic reflecting the larger stability of C=O and C=S bonds as compared with C=Se and C=Te ones,

Table 2. Calculated enthalpy [kJ mol<sup>-1</sup>] for Reaction (1), showing that systematically the Y–H-type tautomers are more stable than the X–H-type ones.

| X  | Y  | $\Delta H^\circ$ |
|----|----|------------------|
| O  | S  | +54.6            |
| O  | Se | +65.5            |
| O  | Te | +81.8            |
| S  | Se | +10.8            |
| S  | Te | +27.2            |
| Se | Te | +16.4            |

which is not counterbalanced by the greater stability of O–H and S–H linkages as compared with Se–H and Te–H ones. The enthalpy values calculated when  $X = O$  are much larger than those obtained when  $C=S$ , showing the enhanced stability of a carbonyl group as compared with a thiocarbonyl group. More importantly, and in contrast with what has been found before for the unsaturated analogues,<sup>[29]</sup> these enthalpy values are rather similar to the calculated energy gaps between (**b**, **d**) and (**a**, **c**) tautomers (See Figure 1). This seems to indicate that, for saturated compounds, the relative stability trend is given primarily by the fact that the Y–H tautomers (**b**, **d**) are systematically more stable than the X–H ones (**a**, **c**), and that the possible role of IHBs or chalcogen–chalcogen interactions is very small. We shall discuss this particular point later.

Among the most stable tautomers conformer **b**, stabilized through the Y–H...X IHB (see Figure 1), is the global minimum of the PES, for compounds in which  $X = O, S, Se$  and  $Y = S, Se$ , while for all systems in which  $Y = Te$  structure **d**, stabilized through a X...Y–H chalcogen–chalcogen interaction, is the most stable conformer.

Let us analyze in more detail the bonding of these systems. As shown in Table 1, the X–H...Y IHB in tautomers **a** is systematically stronger than the Y–H...X IHB in tautomers **b**, as measured by the value of the charge density at the corresponding bcp. Actually, for some compounds, such as (**OSe**)**b**, (**OTe**)**b**, and (**STe**)**b** the interaction is so weak that no bcp is found associated with the possible IHB. This result could be qualitatively anticipated if one takes into account that, on the one hand the X–H groups should be better proton donors than the Y–H groups, because X is more electronegative than Y, and on the other hand, the C=Y groups are more polarizable than the C=X ones, because they involve bulkier atoms and therefore they behave as better proton acceptors. However, the enhanced strength of the X–H...Y IHB, is not enough to counterbalance the intrinsic greater stability of Y–H versus X–H tautomers. This is at variance with what was found for the corresponding unsaturated analogues, where for compounds in which  $X = O, S, Se$  and  $Y = S, Se$ , tautomer **a**, stabilized through a X–H...Y IHB is the most stable one, in spite of the fact that also for unsaturated compounds the Y–H tautomers are intrinsically more stable than the X–H ones. We shall come back later to this point.

A similar analysis permits to explain the stability of those species which do not present IHBs. As shown in Table 1, a bcp between the two chalcogen atoms was located only for (**OTe**)**d**, (**STe**)**d**, and (**SeTe**)**d** species. Consistently, a second order NBO perturbation analysis shows that only for these three species there is a dative bond from the lone pairs of the X (= O, S, Se) atom towards the  $\sigma^*$  Te–H antibonding orbital (see Table 3). The existence of this stabilizing chalcogen–chalcogen interaction is mirrored in shorter X...Te ( $X = O, S, Se$ ) distances (See Figure 1) than those estimated for the remaining tautomers. Also the population of the Te–H antibonding  $\sigma^*$  orbital is reflected in a clear elongation of this bond (compare structures **d** and **b** in Figure 1), and in the red-shifting (63, 59 and 71 cm<sup>-1</sup>, respectively) of the corresponding Te–H stretching frequency.

Why chalcogen–chalcogen interactions are quantitatively significant only for Te containing compounds can be understood, as explain elsewhere,<sup>[21]</sup> as the result of several factors, associated in general with the low electronegativity of Te and with its size. One of these factors is the electrostatic interaction between the negatively charged X chalcogen and the positively charged tellurium atom, which tends to bring

Table 3. Second order orbital interaction energies [kJ mol<sup>-1</sup>] obtained by means of a NBO analysis.

| System                   | $LP_X(1) \rightarrow \sigma_{Te-H}^*$ | $LP_X(2) \rightarrow \sigma_{Te-H}^*$ |
|--------------------------|---------------------------------------|---------------------------------------|
| ( <b>OTe</b> ) <b>d</b>  | 6.2                                   | 7.3                                   |
| ( <b>STe</b> ) <b>d</b>  | 2.8                                   | 9.5                                   |
| ( <b>SeTe</b> ) <b>d</b> | 3.1                                   | 12.8                                  |

both atoms closer favoring the dative bond between the occupied orbitals of X and the occupied orbitals of the YH group. On the other hand, the size of the Te orbitals also favors the overlap with the orbitals of X<sup>[48]</sup> and, finally, the  $\sigma^*$  Te–H antibonding orbital is lower in energy than  $\sigma^*$  Y–H (Y=S, Se) orbitals and behaves as a better electron acceptor. It is also worth noting that the second order interaction energies reported in Table 3 are significantly smaller than those reported in ref. [21] for the corresponding unsaturated analogues.

### Saturated versus unsaturated compounds:

The next important question to be answered is why the IHBs as well as the chalcogen–chalcogen interactions are significantly weaker for saturated compounds than for their unsaturated analogues. As far as the IHB one can invoke the so called RAHB effect. A quantitative way to measure this effect is by means of isodesmic reactions (2)–(5).

These reactions allow us to compare the strength of the IHB in unsaturated compounds [Reactions (2) and (3)] with that of the IHB in the saturated analogue [Reactions (4) and (5)]. The results obtained are summarized in Table 4. It is apparent that IHBs are extremely weak for saturated compounds. Actually, only for X=O the O–H...Y (Y=S, Se) are slightly stabilizing, while not net stabilization of the system is found when a Y–H...X IHB is formed. Most importantly, for the unsaturated compounds the relative energy associated with X–H...Y IHB is rather similar to the energy gap between X–H and Y–H-type tautomers. Accordingly, even if in general the latter are intrinsically more stable than the former, the possibility of forming a strong X–H...Y IHB tends to cancel out this difference and both, **a** and **b**

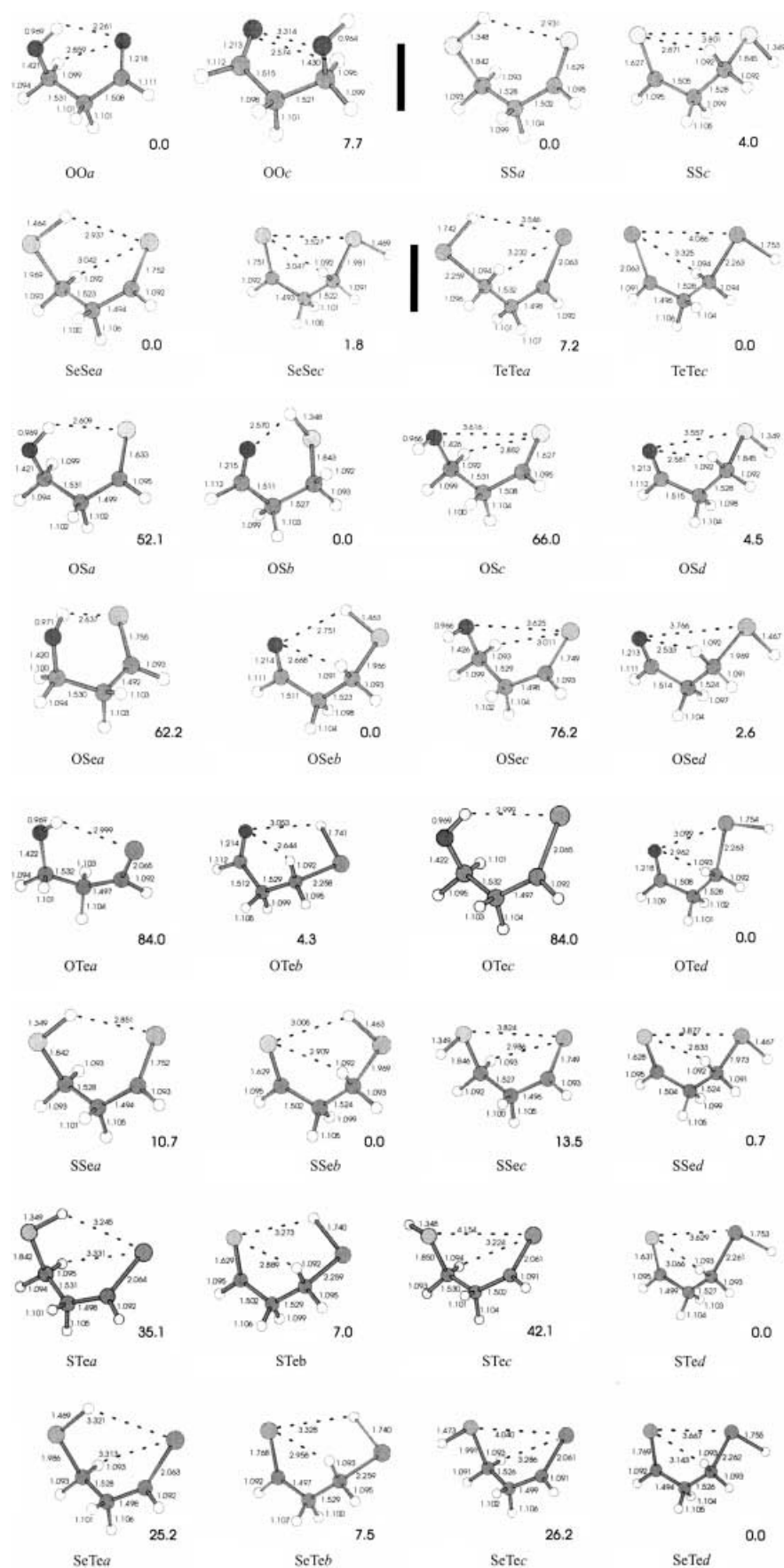


Figure 1. Optimized structures of CH(X)-CH<sub>2</sub>-CH<sub>2</sub>YH (X, Y = O, S, Se, Te) compounds (bond lengths [Å], bond angles [°]). Relative energies with respect to the most stable tautomer are in kJ mol<sup>-1</sup>. For X ≠ Y, the more electronegative chalcogen atom (X) is always the one on the left.

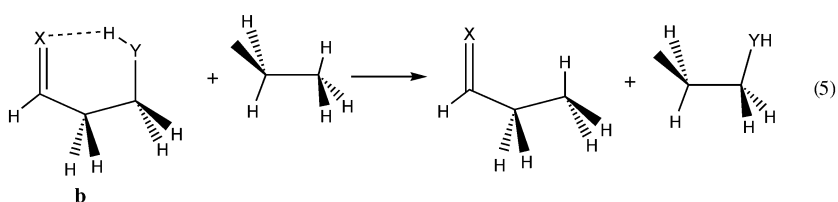
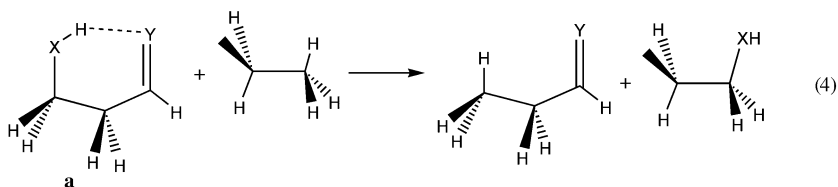
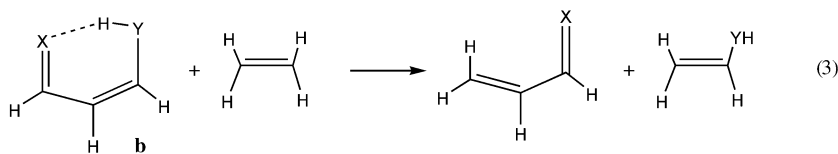
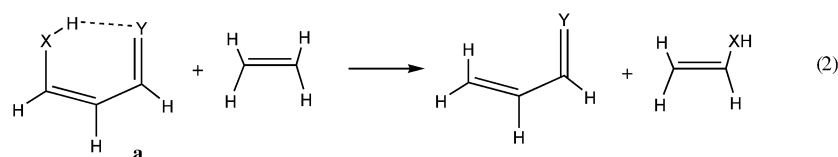


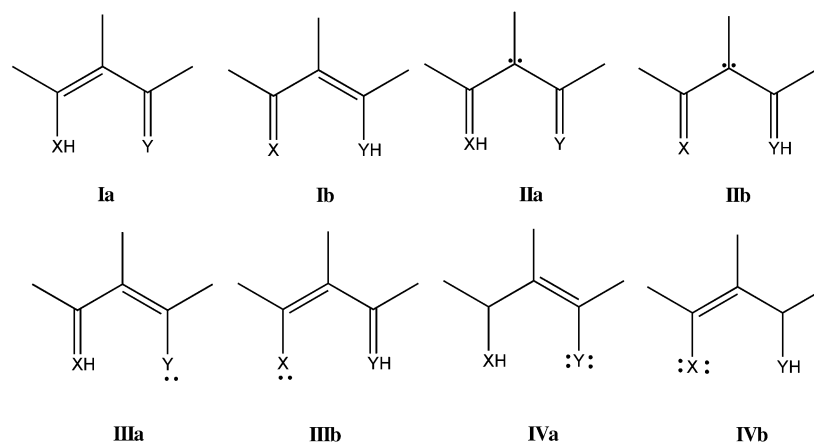
Table 4. Enthalpies of Reactions (2)–(5) [kJ mol<sup>-1</sup>] that allow to estimate the relative stability of X–H...Y and Y–H...X IHBs.

| X  | Y  | Unsaturated compounds |       | Saturated compounds |      |
|----|----|-----------------------|-------|---------------------|------|
|    |    | (2)                   | (3)   | (4)                 | (5)  |
| O  | S  | +56.6                 | +20.6 | +1.6                | -0.7 |
| O  | Se | +59.4                 | +17.6 | +1.6                | -2.5 |
| O  | Te | +53.6                 | +6.6  | -0.2                | -2.8 |
| S  | Se | +30.7                 | +19.5 | -5.0                | -6.3 |
| S  | Te | +29.7                 | +4.5  | -6.5                | -6.4 |
| Se | Te | +25.7                 | +9.0  | -7.1                | -5.5 |

tautomers, are very close in energy.<sup>[9, 21]</sup> This is not the case for saturated compounds where the extra stabilization associated with the IHB is so small that it cannot affect, in a significant way, to the relative stability of the tautomers, being the Y–H-type ones systematically lower in energy.

The question now is whether the greater strength of the IHB for unsaturated compounds is a direct consequence of charge delocalization process (RAHB effect) or it is simply a consequence of the greater rigidity of the unsaturated compound that, on the one hand forces the whole system to be planar, and on the other hand forces the X...Y distance to be smaller than in saturated compounds where the flexibility of the system does not impose any

Scheme 3.



constrain. To gain some insight into this problem we have carried out a NRT analysis of both **a**- and **b**-type unsaturated compounds. In this analysis we have considered only those resonance structures whose weight is larger than 5%. These resonance structures have been schematized in Scheme 3 and their weights in Table 5.

It can be observed that for **a**-type tautomers stabilized through a O–H...Y IHB the degree of delocalization is significantly high, the classical alternated structure **I** weighting only about 33%. Also interestingly, when the system presents a much weaker Y–H...O IHB (**b**-type conformers) the degree of delocalization significantly decreases, and the resonance structure **I** clearly dominates. These results indicate that although RAHB phenomenon is present in both O–H...Y and

Y–H...O IHBs, the delocalization is more favorable in the former than in the latter case, contributing to strengthen the O–H...Y bonds with respect to the Y–H...O ones.

A similar strategy can be carried out to analyze the strength of the chalcogen–chalcogen interactions. In this case we will limit our analysis exclusively to Te-containing compounds for which these interactions are quantitatively significant. To compare the strength of these interactions for unsaturated and saturated compounds we can use similar isodesmic reactions to those employed to analyze the relative strength of the IHBs by simply replacing tautomers **a** and **b** by tautomers **c** and **d** in Reactions (2)–(5).

The results obtained (see Table 6) show that again, the intramolecular chalcogen–chalcogen interactions are extremely weak for saturated compounds, while they are much

Table 5. Weight [%] of the most important resonance structures for  $\beta$ -chalcogenovinylaldehydes as obtained through a NRT analysis.

| Compound | I    | II   | III  | IV   |
|----------|------|------|------|------|
| (OS)a    | 34.7 | 20.3 | 12.7 | 9.2  |
| (OSe)a   | 33.0 | 20.4 | 13.3 | 9.6  |
| (OTe)a   | 32.7 | 19.3 | 14.8 | 10.3 |
| (SSe)a   | 47.8 | 20.8 | 5.6  | 9.7  |
| (STe)a   | 33.4 | 20.4 | 11.8 | 9.5  |
| (SeTe)a  | 46.6 | 18.9 | 6.1  | 10.7 |
| (OS)b    | 60.9 | 18.7 | –    | 7.1  |
| (OSe)b   | 69.5 | 11.2 | –    | 7.7  |
| (OTe)b   | 74.2 | 8.2  | –    | 6.7  |
| (OS)d    | 71.2 | 10.1 | –    | 7.2  |
| (OSe)d   | 69.8 | 10.7 | –    | 7.8  |
| (OTe)d   | 61.9 | 9.9  | –    | 8.9  |
| (SSe)d   | 56.1 | 19.1 | –    | 8.5  |
| (STe)d   | 38.8 | 14.6 | 10.7 | 7.0  |
| (SeTe)d  | 34.8 | 14.3 | 11.7 | 7.4  |

Table 6. Enthalpies of Reactions (2)–(5) [kJ mol<sup>-1</sup>] involving tautomers and **d**, that allow to estimate the relative stability of H–X...Y and X...Y–H chalcogen–chalcogen interactions for tellurium containing systems.

| X  | Y  | Unsaturated compounds |       | Saturated compounds |      |
|----|----|-----------------------|-------|---------------------|------|
|    |    | (2)                   | (3)   | (4)                 | (5)  |
| O  | Te | +8.4                  | +43.8 | –                   | +1.5 |
| S  | Te | +19.7                 | +58.4 | –13.5               | +0.6 |
| Se | Te | +27.7                 | +64.0 | –8.1                | +2.0 |

stronger for the unsaturated systems. In both cases the X...YH interactions are much stronger than the Y...XH ones. As a matter of fact, for saturated compounds, the latter do not contribute to stabilize the system.

A NRT analysis (See Table 5) indicates that for **d**-type tautomers the delocalization is also sizably large, and therefore, similarly to what has been postulated for IHBs, we can speak of resonance assisted chalcogen–chalcogen interactions. A closer analysis permits to realize that this resonance stabilization depends on the nature of the electron donor and/or on the nature of the electron acceptor. If we take for example, the **(OTe)d**, **(STe)d** and **(SeTe)d** systems, in which the acceptor group is systematically the Te–H group, it can be observed that while the oxygen derivative is not very delocalized, with a large weight of the resonance form **I**, the degree of delocalization increases significantly when O is replaced by S or Se. As a matter of fact, due to the great stability of the C=O bond, in the **(OS)d**, **(OSe)d**, and **(OTe)d** tautomers, in which the oxygen of the carbonyl group is the common electron donor, the charge distribution is quite localized through a high weight of resonance form **I**. Hence, we can conclude that although delocalization also contributes to stabilize tautomers with chalcogen–chalcogen interactions, these effects are more pronounced as the electronegativity difference between the two chalcogen atoms involved decreases.

An alternative way to assess the importance of the resonance assisted phenomenon would be to analyze what changes appear in the unsaturated system if the chalcogen–chalcogen distance is forced to be equal to that of the corresponding saturated analogue. For this purpose we have

used the **(OTe)d** unsaturated derivative. When the O–Te distance is forced to be equal to 3.1 Å, which is the distance obtained for the optimized structure of the saturated analogue, the stability of the system decreases by 10 kJ mol<sup>-1</sup>. However, the second order orbital interaction energies associated with the dative bond from the lone pairs of oxygen to the  $\sigma_{\text{TeH}^*}$  antibonding orbital decrease dramatically from 20 and 38 kJ mol<sup>-1</sup>[21] to 3.6 and 9.0 kJ mol<sup>-1</sup>, respectively. It is worth noting that these new values are similar to those reported in Table 3 for the saturated compound. This seems to indicate that this dative interaction depends strongly on the chalcogen–chalcogen distance. Conversely, changes in the delocalization are much smaller. As a matter of fact the weight of resonance structures **II** and **IV** remain almost unchanged (9.2 and 7.9%, respectively), while that of resonance structure **I** increases (70.9%). The fact that the dramatic change in the strength of the O→TeH dative interaction is not reflected in a parallel change in the stability of the system leads us to conclude that resonance is an important factor behind the strong chalcogen–chalcogen interactions observed in unsaturated compounds. This conclusion would also explain why similar intermolecular interactions, such as those calculated between H<sub>2</sub>C=O and CH<sub>3</sub>-TeH, are much weaker[21] than those observed in  $\beta$ -telluriumvinylaldehyde [**(OTe)d**]. For the intermolecular case the repulsion between the electronic distributions of both neutrals, H<sub>2</sub>C=O and CH<sub>3</sub>-TeH, prevents them to be very close each other. As a matter of fact, the O...Te distance in the corresponding complex[21] is rather similar to that calculated for the saturated **(OTe)d** compound. The consequence is that the dative O→TeH bond in the intermolecular complex is very weak (2.8 kJ mol<sup>-1</sup>), and the lack of any resonance stabilization leads to a rather weak interaction energy (5.2 kJ mol<sup>-1</sup>) between both molecules.

## Conclusion

Our results indicate that in CH(X)-CH<sub>2</sub>-CH<sub>2</sub>YH (X=Y=O, S, Se) the X–H...X IHB competes in strength with the X...XH chalcogen–chalcogen interaction, while the opposite is found for the corresponding tellurium-containing analogues.

For those derivatives in which X≠Y the situation is more complicated due to the existence of two non-equivalent X–H and Y–H tautomers. The Y–H tautomer is found to be lower in energy than the X–H tautomer, independently of the nature of X and Y. For X=O, S, Se and Y=S, Se the most stable conformer **b** is the one exhibiting a Y–H...X IHB. Conversely when Y=Te, conformer **d**, stabilized through a X...YH chalcogen–chalcogen interaction is the global minimum of the PES.

Systematically the IHB and the chalcogen–chalcogen interactions observed for saturated compounds are much weaker than those found for their unsaturated analogues. This result implies that the nonbonding interactions involving chalcogen atoms, mainly Se and Te, are not always strongly stabilizing. This conclusion is in agreement with the fact that intermolecular interactions between Se and Te containing systems with bases bearing dative groups are very weak. Our

analysis also shows that these interactions are enhanced through an increase of the charge delocalization within the system, in a mechanism rather similar to the so call RAHB. The chalcogen–chalcogen interactions will be also large, due to the enhancement of the  $X \rightarrow Y$  dative bond, if the molecular environment, for instance in a crystal, forces the interacting atoms X and Y to be close each other.

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