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# Characteristics of nonconventional hydrogen bonds and stability of dimers of chalcogenoaldehyde derivatives: a noticeable role of oxygen compared to other chalcogens†

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In this work, twenty-four stable dimers of RCHZ with R = H, F, Cl, Br, CH<sub>3</sub> or NH<sub>2</sub> and Z = O, S, Se or Te were determined. It was found that the stability of most dimers is primarily contributed by the electrostatic force, except for the dominant role of the induction term in those involving a Te atom, which has been rarely observed. Both electron-donating and -withdrawing groups in substituted formaldehyde cause an increase in the strength of nonconventional C<sub>sp<sup>2</sup></sub>-H...Z hydrogen bonds, as well as the dimers, in which the electron donating effect plays a more crucial role. The strength of nonconventional hydrogen bonds decreases in the following order: C<sub>sp<sup>2</sup></sub>-H...O ≫ C<sub>sp<sup>2</sup></sub>-H...S > C<sub>sp<sup>2</sup></sub>-H...Se > C<sub>sp<sup>2</sup></sub>-H...Te. Remarkably, a highly significant role of the O atom compared to S, Se and Te in increasing the C<sub>sp<sup>2</sup></sub>-H stretching frequency and strength of the nonconventional hydrogen bonds and dimers is found. A C<sub>sp<sup>2</sup></sub>-H stretching frequency red-shift is observed in C<sub>sp<sup>2</sup></sub>-H...S/Se/Te, while a blue-shift is obtained in C<sub>sp<sup>2</sup></sub>-H...O. When Z changes from O to S to Se and to Te, the C<sub>sp<sup>2</sup></sub>-H blue-shift tends to decrease and eventually turns to a red-shift, in agreement with the increasing order of the proton affinity at Z in the isolated monomer. The magnitude of the C<sub>sp<sup>2</sup></sub>-H stretching frequency red-shift is larger for C<sub>sp<sup>2</sup></sub>-H...Te than C<sub>sp<sup>2</sup></sub>-H...S/Se, consistent with the rising trend of proton affinity at the Z site and the polarity of the C<sub>sp<sup>2</sup></sub>-H bond in the substituted chalcogenoaldehydes. The C<sub>sp<sup>2</sup></sub>-H blue-shifting of the C<sub>sp<sup>2</sup></sub>-H...O hydrogen bonds is observed in all dimers regardless of the electron effect of the substituents. Following complexation, the electron-donating derivatives exhibit a stronger C<sub>sp<sup>2</sup></sub>-H blue-shift compared to the electron-withdrawing ones. Notably, the stronger C<sub>sp<sup>2</sup></sub>-H blue-shift turns out to involve a less polarized C<sub>sp<sup>2</sup></sub>-H bond and a decrease in the occupation at the σ\*(C<sub>sp<sup>2</sup></sub>-H) antibonding orbital in the isolated monomer.

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## 1. Introduction

The hydrogen bond is one of the most important weak interactions because of its undeniable role in various fields. The effect of hydrogen bonds is presented in stabilizing chemical structures or the crystal skeleton and participating in biochemical processes.<sup>1-4</sup> Hydrogen bonds are intimately involved in large molecules, such as proteins and nucleic acids, as well as in solvation processes and the function of enzymes.<sup>5,6</sup> The C-H...O/N, C-H...π, and C-H...Y (Y = F, Cl, Br) hydrogen bonds are detected in many clusters, enzyme mechanisms,

proteins, DNA, RNA, catalytic reactions, and material structures.<sup>7-12</sup> This indicates the essential role of hydrogen bonds in developing new drugs that serve human health. In addition, organic synthesis methods based on the activation of C-H bonds in intermediate complexes are an attractive topic today because of their importance in controlling the formation of the desired products.<sup>13,14</sup> Notably, the dominant role of hydrogen bonds in the internal cohesion of cellulose microfibrils has also been shown in recent years.<sup>15</sup> In short, the hydrogen bond plays a crucial role in our lives, and understanding the characteristics of hydrogen bonds could help scientists devise a theoretical approach to exploit the application of this weak interaction.

Up to now, hydrogen bonds in the form of X-H...Y have been classified into two types, including conventional and nonconventional hydrogen bonds.<sup>16</sup> The difference between these two types is the electronegativity of the X and Y atoms. X and Y are indeed normally large electronegative atoms, or Y can be a rich

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electron density region for conventional hydrogen bonds. Meanwhile, the X and Y atoms in nonconventional hydrogen bonds have much smaller electronegativity. Following complexation, the formation of conventional hydrogen bonds causes an elongation of the X–H bond length and a decrease in its stretching frequency to the red wavelength region, which is called a red-shifting hydrogen bond.<sup>2,17–19</sup> The red shift of the X–H stretching frequency in conventional hydrogen bonds is suggested to be due to a strong electrostatic attraction between H and Y. Remarkably, scientists have found that the stretching frequency of X–H bonds acting as a proton donor in nonconventional hydrogen bonds could shift to red or blue wavelengths upon complexation. This leads to two different properties of nonconventional hydrogen bonds, so-called red-shifting hydrogen bonds and blue-shifting hydrogen bonds. While the former is characterized by the elongation of the X–H bond and the decrease of its stretching frequency,<sup>20</sup> the latter exhibits a bond length contraction and an increase in the stretching frequency of the X–H bond.<sup>21</sup> The red-shift of nonconventional hydrogen bonds is suggested to be due to the intermolecular hyperconjugation effect from  $n(Y)$  to the  $\sigma^*(X-H)$  orbital overcoming the increase in both  $s$  character and X–H polarity.<sup>22</sup> The characteristics of the blue-shift, however, have not yet been identified. Several scientists have endeavored to further understand this novel type of hydrogen bond,<sup>23–26</sup> but some controversies regarding the origin of blue-shifting hydrogen bonds have persisted until now. Over the years, various theories and models have been proposed to explain the essence of blue-shifting hydrogen bonds.<sup>27–30</sup> Xin Chang *et al.* suggested that the blue-shift or red-shift relies on the characteristics of the X–H bond, in which the blue-shift is associated with a covalent nature of the X–H bond, while an ionic state of the X–H bond induces a red-shift.<sup>25</sup> Mao and co-workers showed that Pauli repulsion enhances the blue-shift, whereas the merging of electrostatic and dispersion effects causes the red-shift.<sup>31</sup> Another study by Mo suggested that the X–H bond contraction and its blue-shift in the stretching frequency are due to the predominance of long-range electrostatic and Pauli interactions, overcoming the electron density transfer and polarity.<sup>32</sup> In addition, Shaik *et al.* recently reported that valence bond theory could be used to give a generalized description of a hydrogen bond, including the nonconventional C–H $\cdots$ Y hydrogen bonds. Shaik pointed out that the two major interactions that makeup hydrogen bonds are polarization and charge transfer, which are significantly involved in the ionic-valence bond property.<sup>33</sup> In general, these rationalizations have both advantages and disadvantages. However, they explained the origin of nonconventional hydrogen bonds as well as their blue-shift based on complexation without considering the characteristics of the initial proton donors or acceptors and their property relationship. Therefore, studies explaining the characteristics of blue-shifting hydrogen bonds based on the intrinsic properties of the proton donors and acceptors represent potential approaches for understanding nonconventional hydrogen bonds.<sup>34–39</sup> Indeed, Alkorta *et al.*, in their latest report, evaluated the hydrogen bond dissociation energies from the properties of isolated monomers. They suggested that the more negative

minimum electrostatic region in a Lewis base (proton acceptor) and the more positive maximum electrostatic one in a Lewis acid (proton donor) cause a stronger hydrogen bond. The increase in the values of the reduced nucleophilicity of the proton acceptor and the reduced electrophilicity of the proton donor also enhance the strength of the hydrogen bond.<sup>40</sup>

Most of the research on blue-shifting hydrogen bonds has investigated the  $C_{sp^3}$ –H blue-shift, with the  $C_{sp^3}$  atom referring to the tetrahedral hybridized state. For instance, the C–H $\cdots$ Y blue-shifting hydrogen bond was found for the first time in systems between  $-CHF_2$  and some proton acceptors in 1980.<sup>21</sup> In 2001, the research group of Reimann reported the  $C_{sp^3}$ –H $\cdots\pi$  hydrogen bond in complexes containing haloforms with benzene derivatives.<sup>41,42</sup> The blue-shifting hydrogen bonds involved in  $\pi$  as a proton donor were also proposed by Oliveira *et al.* in 2009.<sup>43</sup> Besides, the C–H bond contraction during the complexation between a haloform, methane, water, and acetylene was also observed.<sup>44,45</sup> It is noteworthy that the blue-shift of large-polarized  $C_{sp^2}$ –H ( $C_{sp^2}$  stands for a triangular hybridized carbon atom) created much potential for expanding the research on  $C_{sp^2}$ –H $\cdots$ Y hydrogen bonds. The stretching frequency of the  $C_{sp^2}$ –H bond can reach  $90\text{ cm}^{-1}$  in complexes of formaldehyde and thioformaldehyde with formic acid,<sup>46</sup> which is rarely observed in previous reports. A  $C_{sp^2}$ –H blue-shift often appears in the systems of carbonyl compounds, which play an important role in organic reactions and biochemical processes thanks to hydrogen bond formation and proton transfer. Some reports have revealed individual cases of  $C_{sp^2}$ –H $\cdots$ O hydrogen bonds between carbonyl derivatives and water.<sup>47–50</sup> Chandra *et al.* explored a large blue-shift of the  $C_{sp^2}$ –H $\cdots$ O hydrogen bond with the stretching frequency values changing between 11 and  $53\text{ cm}^{-1}$  when investigating the interaction in systems of substituted formaldehyde with some  $H_2O$  molecules.<sup>47</sup> Interestingly, the complexation between RCHO and  $nH_2O/HF$  ( $R = H, F, Cl$  and  $Li$ ;  $n = 1-4$ ) in the study by Karpfen demonstrated that the  $C_{sp^2}$ –H stretching frequency could be considered for both blue-shift and red-shift.<sup>51</sup> When investigating the interactions in the RCHO dimers with  $R = H$  or  $CH_3$  at M062X/6-311++G(3df,3dp), Thakur reported complex stability and the  $C_{sp^2}$ –H blue-shift magnitude in the  $C_{sp^2}$ –H $\cdots$ O hydrogen bonded interaction is stronger for the  $CH_3CHO$  dimer than for the HCHO dimer.<sup>26</sup> This implied the important role of electron-donating substituents in complex stabilization and the  $C_{sp^2}$ –H blue-shift. A larger  $C_{sp^2}$ –H blue-shift was reported in the complex of  $HCHO\cdots HCHO$  compared to  $HCHO\cdots HCHS$  and  $HCHS\cdots HCHS$ .<sup>49</sup> This shows that the magnitude of  $C_{sp^2}$ –H blue-shift in hydrogen bonds depends strongly on the  $C_{sp^2}$ –H polarity and the gas-phase basicity of the proton acceptor.

In recent years, proton acceptors containing oxygen and sulfur have been concentrated on for a clearer understanding of the characteristics and nature of nonconventional hydrogen bonds; however, other atoms in the chalcogen series with lower electronegativity are less studied.<sup>52–54</sup> Very recently, the existence of  $C_{sp}$ –H and  $C_{sp^3}$ –H stretching frequency red-shifts of nonconventional  $C_{sp}$ –H $\cdots$ Se and  $C_{sp^3}$ –H $\cdots$ Se hydrogen bonds has been theoretically and experimentally discovered in complexes of  $C_8H_6$  and  $Se(CH_3)_2$ ,<sup>55</sup>  $Q_3CH$  and  $SeH_2$  ( $Q = Cl, H,$

and F),<sup>56</sup> and CHCl<sub>3</sub> and Se(CH<sub>3</sub>)<sub>2</sub>.<sup>57</sup> It is noteworthy that a very large C<sub>sp<sup>2</sup></sub>-H blue-shift of 104.5 cm<sup>-1</sup> was reached in the complexes between CH<sub>3</sub>CHZ and RCZOH (R = H, CH<sub>3</sub>, F; Z = O, S).<sup>54</sup> The nonconventional C<sub>sp<sup>2</sup></sub>-H...Se/Te and Z-H...Se/Te hydrogen bonds have recently been found in some systems. Indeed, O/N-H...Se/Te hydrogen bonds have been detected through experiments.<sup>58-60</sup> Cuc *et al.* also reported the existence of C<sub>sp<sup>2</sup></sub>-H...Se/Te hydrogen bonds in the complexes of chalcogenoaldehydes with water or aldehydes with hydrogen chalcogenides.<sup>61,62</sup> It is remarkable that these new hydrogen bonds can belong to either blue- or red-shifting hydrogen bonds. Therefore, the study of C<sub>sp<sup>2</sup></sub>-H...Se/Te hydrogen bonds is essential to rationalize the origin of blue-shifting hydrogen bonds. Extending the hydrogen bond study to the chalcogen-containing compounds is very consequential for clarifying the nature of hydrogen bonds and their classification.

In the present work, we investigate the interactions in dimers of RCHZ, with R = H, F, Cl, Br, CH<sub>3</sub> or NH<sub>2</sub> and Z = O, S, Se or Te, to shed light on the influence of electron-donating and electron-withdrawing substituents on the stability and characteristics of nonconventional C<sub>sp<sup>2</sup></sub>-H...Z hydrogen bonds and dimers. A notable role of O compared to other chalcogens in chalcogenoaldehydes in affecting the characteristics and strength of nonconventional hydrogen bonds is also evaluated thoroughly. Furthermore, state-of-the-art chemical quantum approaches are carried out to clarify the existence and strength of hydrogen bonds and dimers, as well as the role of various energetic components in complex stabilization.

## 2. Computational methods

The second-order perturbation theoretical method (MP2) with the aug-cc-pVTZ-PP basis set for the Te atom and 6-311++G(3df,2pd) for the remaining ones was used for geometry optimizations and harmonic vibrational frequency calculations for isolated monomers and dimers. In order to avoid vibrational coupling between the CH<sub>2</sub> stretching modes in HCHZ (Z = O, S, Se or Te), harmonic frequencies are calculated for the DCHZ isotopomers for both the monomers and complexes. All quantum chemical calculations were performed with the Gaussian 16 suite.<sup>63</sup> The interaction energy of the dimers includes the single-point energy (*E*), basis set superposition error (BSSE) correction computed at the CCSD(T) level and zero-point energy (ZPE) performed by the MP2 method in combination with the aug-cc-pVTZ-PP basis set for Te and the 6-311++G(3df,2pd) basis set for the remaining atoms. The interaction energies of the dimers ( $\Delta E^*$ ) were calculated as follows:

$$\Delta E^* = (E + ZPE)_{\text{dimer}} - \sum (E + ZPE)_{\text{monomer}} + \text{BSSE}$$

Besides, the deprotonation enthalpy (DPE) of the C<sub>sp<sup>2</sup></sub>-H bond and the proton affinity (PA) at the Z atom of the isolated monomers were also evaluated using the same level of theory.

The Quantum Theory of Atoms in Molecules (QTAIM)<sup>64,65</sup> was analysed by the AIMall program<sup>66</sup> using the wavefunctions obtained at the MP2/6-311++G(3df,2pd) level, except for the Te

atom for which the aug-cc-pVTZ-PP basis set was used, to examine the existence of bond critical points (BCPs), which indicate the presence of hydrogen bonds. Furthermore, the electron density [ $\rho(r)$ ], Laplacian electron density [ $\nabla^2(\rho)$ ], and potential energy density [ $V(r)$ ] at the BCPs were also computed. The individual hydrogen bond energy ( $E_{\text{HB}}$ ) was determined according to the formula of Espinosa-Molins-Lecomte:  $E_{\text{HB}} = 0.5V(r)$ .<sup>67</sup> In addition, Natural Bond Orbital (NBO) analysis was implemented by the NBO 7.0 program at the same level of theory used for AIM analysis to consider the electron transfer and the characteristics of nonconventional hydrogen bonds.<sup>68</sup> The ratio between the H...Z intermolecular distances and their total van der Waals radii ( $r_{\text{H...Z}}/\sum r_{\text{vdW}}$ ) was additionally calculated to clarify the relationship between intermolecular distance and the strength of nonconventional hydrogen bonds.<sup>69</sup>

Non-Covalent Interaction (NCI) plotting<sup>70</sup> and Molecular Electrostatic Potential (MEP)<sup>71</sup> analysis were also used to determine the properties of the weak interactions in the dimers. The NCI results provide a more intuitive comparison of the non-covalent properties of hydrogen bonds and their stability. MEP analysis is an appropriate approach for understanding molecular reactivity and intermolecular interactions, and recognising the active sites of the monomers. Therefore, in order to visualize the distribution of electron density on the surface of the monomers and determine the electron-rich center on them, we carried out MEP calculations at the MP2/aug-cc-pVTZ-PP level for the Te atom and MP2/6-311++G(3df,2pd) level for the remaining ones. In addition, Symmetry-Adapted Perturbation Theory (SAPT)<sup>72</sup> analysis was performed through the Psi4 program<sup>73</sup> to evaluate the contribution of energy components to the stability of the investigated dimers.

## 3. Results and discussion

### 3.1. Geometrical structure and AIM analysis

In order to evaluate the effect of different R and Z substituents on the characteristics and strength of the nonconventional C<sub>sp<sup>2</sup></sub>-H...Z hydrogen bonds and dimers formed, we first performed geometrical optimization of the HCHZ dimers with Z = O, S, Se or Te, and two stable structures were identified, including the hexagonal (I) and perpendicular (II) forms as shown in Fig. S1 of the ESI.† It is found that structures I with interaction energies in the range of -10.3 to -6.2 kJ mol<sup>-1</sup> are more stable than structures II (from -9.5 to 2.5 kJ mol<sup>-1</sup>) (*cf.* Table S1†). Notably, the perpendicular structure of the 2HCHTe dimer exhibits a positive value of the interaction energy. Consequently, only the hexagonal geometry was considered in the dimers of RCHZ, with R = H, F, Cl, Br, CH<sub>3</sub> or NH<sub>2</sub>, and Z = O, S, Se or Te. The 24 stable structures of the RCHZ dimers on the potential energy surfaces are displayed in Fig. 1. The dimers are labeled with the name in bold **2R-Z**. In general, these hexagonal ring structures are formed by two C<sub>sp<sup>2</sup></sub>-H...Z interactions, as confirmed by the ring critical points (RCPs) in the middle of the ring surface (*cf.* Fig. 2). It is noteworthy that the AIM analysis pointed out the presence of bond critical points (BCPs) between two H atoms in the interaction C<sub>sp<sup>2</sup></sub>-H...H-C<sub>sp<sup>2</sup></sub> in the **2CH<sub>3</sub>/NH<sub>2</sub>-Se/Te** dimers (*cf.* Fig. 2). Indeed, the very small electron density [ $\rho(r)$ ] values

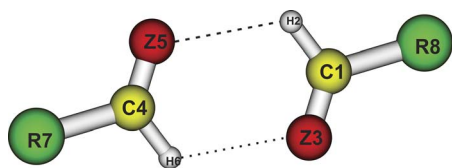


Fig. 1 Stable structures of the dimers between two RCHZ molecules, with R = H, F, Cl, Br or CH<sub>3</sub>, and Z = O, S, Se or Te.

ranging from 0.006 au to 0.009 au, along with the positive values of the Laplacian electron density [ $\nabla^2(\rho)$ ] ( $\nabla^2(\rho) = 0.02\text{--}0.04$  au) (cf. Table S2†) at these BCPs, indicate the existence of very weak C<sub>sp<sup>2</sup></sub>-H $\cdots$ H-C<sub>sp<sup>2</sup></sub> dihydrogen bonds in these dimers. This observation is also the reason for the appearance of two RCPs in the 2CH<sub>3</sub>-Se, 2CH<sub>3</sub>-Te, 2NH<sub>2</sub>-Se and 2NH<sub>2</sub>-Te dimers.

The ratio between intermolecular distance and the sum of the van der Waals radii of the two interacting atoms ( $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$ ) was calculated and gathered in Table S3.† This parameter is one of the factors that predicts the formation of hydrogen

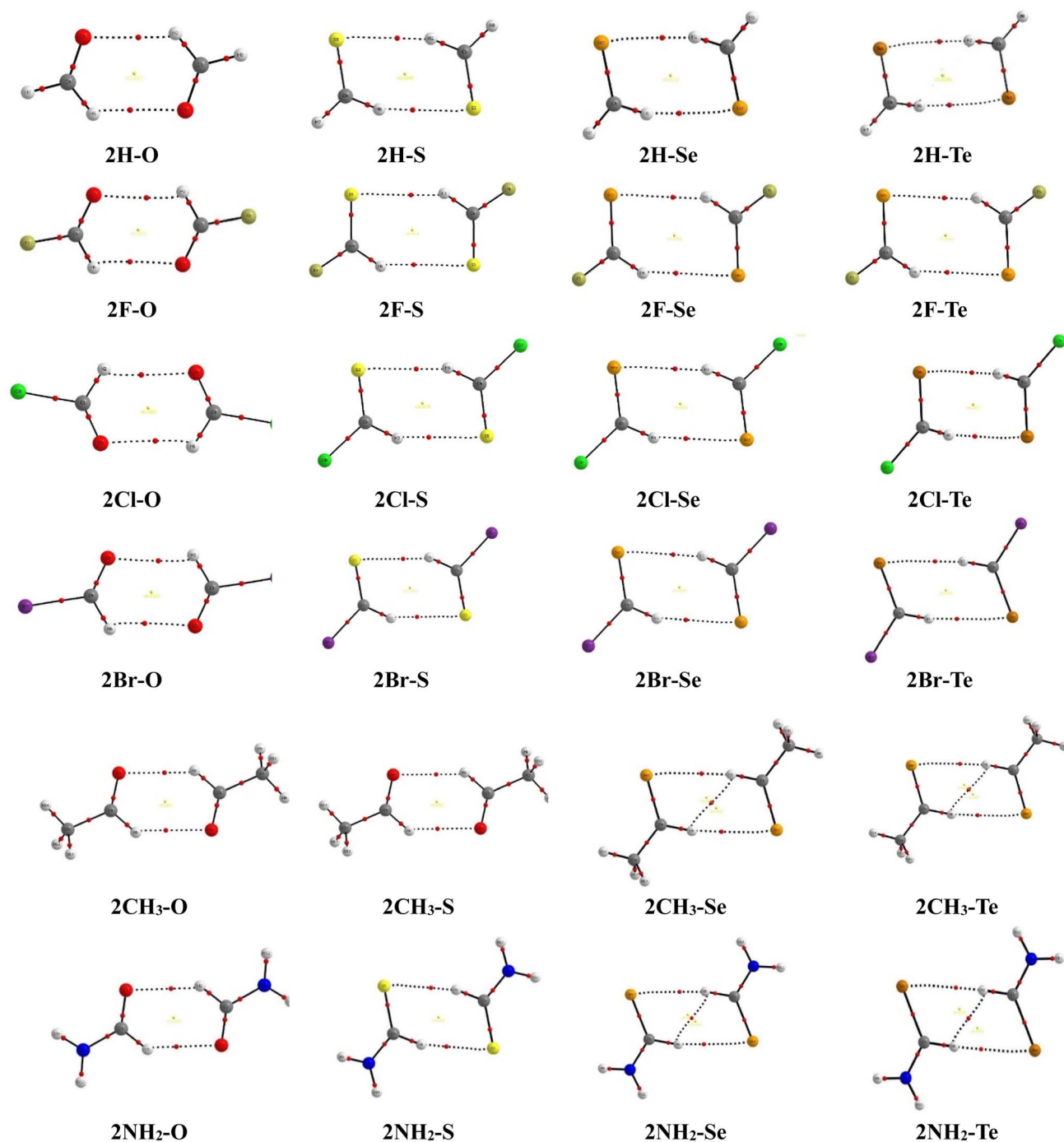


Fig. 2 The topological images of the 2R-Z dimers with R = H, F, Cl, Br, CH<sub>3</sub> or NH<sub>2</sub> and Z = O, S, Se or Te.

bonds. Thus, the smaller  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  ratio indicates the stronger H $\cdots$ Z interaction, and *vice versa*. Table S3† shows that the  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  ratios for all intermolecular interactions range from 0.87 to 0.97, indicating the smaller value of H $\cdots$ Z distance compared to the sum of the van der Waals radii. These ratios imply the existence of C<sub>sp<sup>2</sup></sub>-H $\cdots$ O/S/Se/Te nonconventional hydrogen bonds in the dimers, which is evidenced by the presence of BCPs between the interacting atoms given in Fig. 2. The  $\rho(r)$  and  $\nabla^2(\rho)$  values at the BCPs are in the ranges of 0.008–0.012 au and 0.02–0.04 au, respectively (*cf.* Table S3†). These values belong to the regions of weak non-covalent interactions.<sup>74</sup> Besides, the individual hydrogen bond energies ( $E_{\text{HB}}$ ) in the dimers have negative values, indicating the stability of all of the formed nonconventional hydrogen bonds, including C<sub>sp<sup>2</sup></sub>-H $\cdots$ O, C<sub>sp<sup>2</sup></sub>-H $\cdots$ S, C<sub>sp<sup>2</sup></sub>-H $\cdots$ Se, and C<sub>sp<sup>2</sup></sub>-H $\cdots$ Te.

There is a good agreement between the  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  ratios and the strength of the hydrogen bonds, which is presented by the relationship between the  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  ratios and  $E_{\text{HB}}$  values in Fig. 3. For the same R, the  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  ratio increases in the order of substituents O < S < Se < Te, indicating that the C<sub>sp<sup>2</sup></sub>-H $\cdots$ O hydrogen bonds are more stable than the C<sub>sp<sup>2</sup></sub>-H $\cdots$ S/Se/Te ones. The  $E_{\text{HB}}$  values of the C<sub>sp<sup>2</sup></sub>-H $\cdots$ O hydrogen bonds (from -8.1 kJ mol<sup>-1</sup> to -11.0 kJ mol<sup>-1</sup>) are indeed more negative than those of C<sub>sp<sup>2</sup></sub>-H $\cdots$ S/Se/Te (from -4.7 kJ mol<sup>-1</sup> to -9.3 kJ mol<sup>-1</sup>). This tendency was also observed in complexes of XCHO and H<sub>2</sub>Y with X = H, F, Cl, Br or CH<sub>3</sub> and Y = O, S, Se or Te, in which the  $E_{\text{HB}}$  values of the C<sub>sp<sup>2</sup></sub>-H $\cdots$ O and C<sub>sp<sup>2</sup></sub>-H $\cdots$ S/Se/Te hydrogen bonds at the MP2/aug-cc-pVDZ level are in the ranges from -10.2 to -11.2 kJ mol<sup>-1</sup> and from -3.7 to -5.5 kJ mol<sup>-1</sup>, respectively.<sup>62</sup> This is due to the larger negative value of  $V_{\text{S,min}}$  at the O atom in XCHO (-108.3 to -193.1 kJ mol<sup>-1</sup>) compared to the S, Se and Te atoms in other monomers (-70.9 to -131.0 kJ mol<sup>-1</sup>) (*cf.* Table S4, Fig. S2†), which is in line with a decrease of notable electronegativity from O (3.44) to S (2.58) *via* Se (2.55) and then to Te (2.10). Consequently, the electronegativity of chalcogen Z atoms in the monomers acts as an important factor in the stability of nonconventional C<sub>sp<sup>2</sup></sub>-H $\cdots$ Z hydrogen bonds, especially a crucial role of the O atom relative to the S, Se and Te ones. The effect of electronegativity on the strength of the hydrogen bonds was also suggested by Liu *et al.* when investigating the dimers between H<sub>2</sub>Y and HX (X = F, Cl, Br; Y = O, S, Se) at the MP2/aug-cc-pVTZ level.<sup>39</sup>

When keeping Z and changing the R substituents, the change in the strength of the nonconventional C<sub>sp<sup>2</sup></sub>-H $\cdots$ Z hydrogen bonds in the 2R-O dimers has a very distinct tendency as compared to those in the 2R-S/Se/Te ones (*cf.* Fig. 3). For Z = O, the  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  values in the dimers containing electron-donating and -withdrawing groups are smaller than those in the dimer of formaldehyde. The strength of the nonconventional C<sub>sp<sup>2</sup></sub>-H $\cdots$ O hydrogen bonds decreases in the sequence of substituents NH<sub>2</sub> > CH<sub>3</sub> > F/Cl/Br > H, in accordance with a decrease in the PA values at the O sites in the isolated monomers (*cf.* Table 1). For Z = S, Se and Te, the more stable hydrogen bonds in 2NH<sub>2</sub>/CH<sub>3</sub>-S/Se/Te and 2Cl/Br-S/Se/Te compared to 2H-S/Se/Te exhibit a smaller  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  ratio, except for 2F-S/Se/Te. Besides, larger  $r_{\text{H}\cdots\text{Z}}/\sum r_{\text{vdW}}$  values are

found for 2CH<sub>3</sub>-S/Se/Te than for the 2Cl/Br-S/Se/Te ones. This observation shows a decrease in the strength of nonconventional C<sub>sp<sup>2</sup></sub>-H $\cdots$ S/Se/Te hydrogen bonds in the order of 2NH<sub>2</sub>-Z > 2Br-Z ~ 2Cl-Z > 2CH<sub>3</sub>-Z > 2H-Z > 2F-Z, with Z = S, Se and Te.

### 3.2. Interaction energy and SAPT2+ analysis

To investigate the stability of the dimers and the factors impacting their strength, the interaction energies with both ZBE and BSSE corrections of 24 dimers are calculated and given in Table 2. The data show that the interaction energies of all dimers have negative values from -6.2 to -21.2 kJ mol<sup>-1</sup>, implying their strength on the potential energy surface. Among them, the most negative values belong to 2NH<sub>2</sub>-Z, 2–3 times as negative as those of 2H-Z. The considerable strength of complexes containing the NH<sub>2</sub> group was also obtained in the interactions of XCHY with HCOOH (X = H, F, Cl, Br, CH<sub>3</sub>, NH<sub>2</sub> and Y = O, S), with the interaction energies from -15.3 kJ mol<sup>-1</sup> to -42.2 kJ mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level.<sup>46</sup>

As seen in Table 2, for the same R = H, F, Cl, Br and CH<sub>3</sub>, the stability of the 2R-O dimers is larger than that of the 2R-S/Se/Te ones, which is due to the  $\Delta E^*$  values being from -10.3 to -13.6 kJ mol<sup>-1</sup> for 2R-O and from -6.2 to -11.5 kJ mol<sup>-1</sup> for 2R-S/Se/Te, consistent with the more negative charges at O compared to S, Se and Te (*cf.* Table S5†), affirming the greater importance of the O than S, Se and Te ones for the stabilization of the dimers. Van Dornshuld also highlighted the greater strength of (CH<sub>2</sub>O)<sub>2</sub> in comparison with (CH<sub>2</sub>S)<sub>2</sub>.<sup>49</sup> Regarding the 2NH<sub>2</sub>-Z dimers, it is noted that the interaction energies of 2NH<sub>2</sub>-S/Se/Te are more negative than those of 2NH<sub>2</sub>-O. In comparison with 2R-Z (R = H, F, Cl, Br or CH<sub>3</sub> and Z = O, S, Se or Te), the difference in negative charges at the O, S, Se and Te atoms in 2NH<sub>2</sub>-Z is negligible (*cf.* Table S5†). However, the intermolecular electron density transfer from the n(Z) to  $\sigma^*(\text{C1-H2})$  orbital in 2NH<sub>2</sub>-S/Se/Te (12.5–15.7 kJ mol<sup>-1</sup>) is much larger than that in 2NH<sub>2</sub>-O (9.6 kJ mol<sup>-1</sup>) (*cf.* Table 3). This leads to a larger strength of 2NH<sub>2</sub>-S/Se/Te compared to 2NH<sub>2</sub>-O.

For Z = O, the descending interaction energy values display an increase in the dimer stability in the order of 2H-O < 2CH<sub>3</sub>-O < 2F-O ~ 2Cl-O ~ 2Br-O < 2NH<sub>2</sub>-O. It is notable that the 2F/Cl/Br-O dimers ( $\Delta E^*$  being from -13.2 to -13.6 kJ mol<sup>-1</sup>) are more stable than 2CH<sub>3</sub>-O ( $\Delta E^*$  being -12.0 kJ mol<sup>-1</sup>), while they are less stable than 2NH<sub>2</sub>-O. The larger positive resonance effect of NH<sub>2</sub> compared to the hyperconjugation effect of CH<sub>3</sub> leads to stronger electron-donating ability of NH<sub>2</sub> relative to the CH<sub>3</sub> group. In addition, the larger proton affinity at O in NH<sub>2</sub>CHO compared to the remaining monomers (*cf.* Table 1) also contributes to the strongest stability of the 2NH<sub>2</sub>-O dimer. On the other hand, the strength tendency of the 2R-O dimers implies a large role of C<sub>sp<sup>2</sup></sub>-H polarity relative to proton affinity at the O site in substituted formaldehyde in stabilizing the dimers. The magnitude and changing tendency of PA at the O site and DPE of the C<sub>sp<sup>2</sup></sub>-H in the isolated monomers are the reason for this strength ordering (*cf.* Table 1). The stronger strength of 2F/Cl/Br-O dimers compared to the 2CH<sub>3</sub>-O one is due to the larger polarity of the C<sub>sp<sup>2</sup></sub>-H bond in F/Cl/BrCHO relative to CH<sub>3</sub>CHO, and even surpasses the proton affinity at

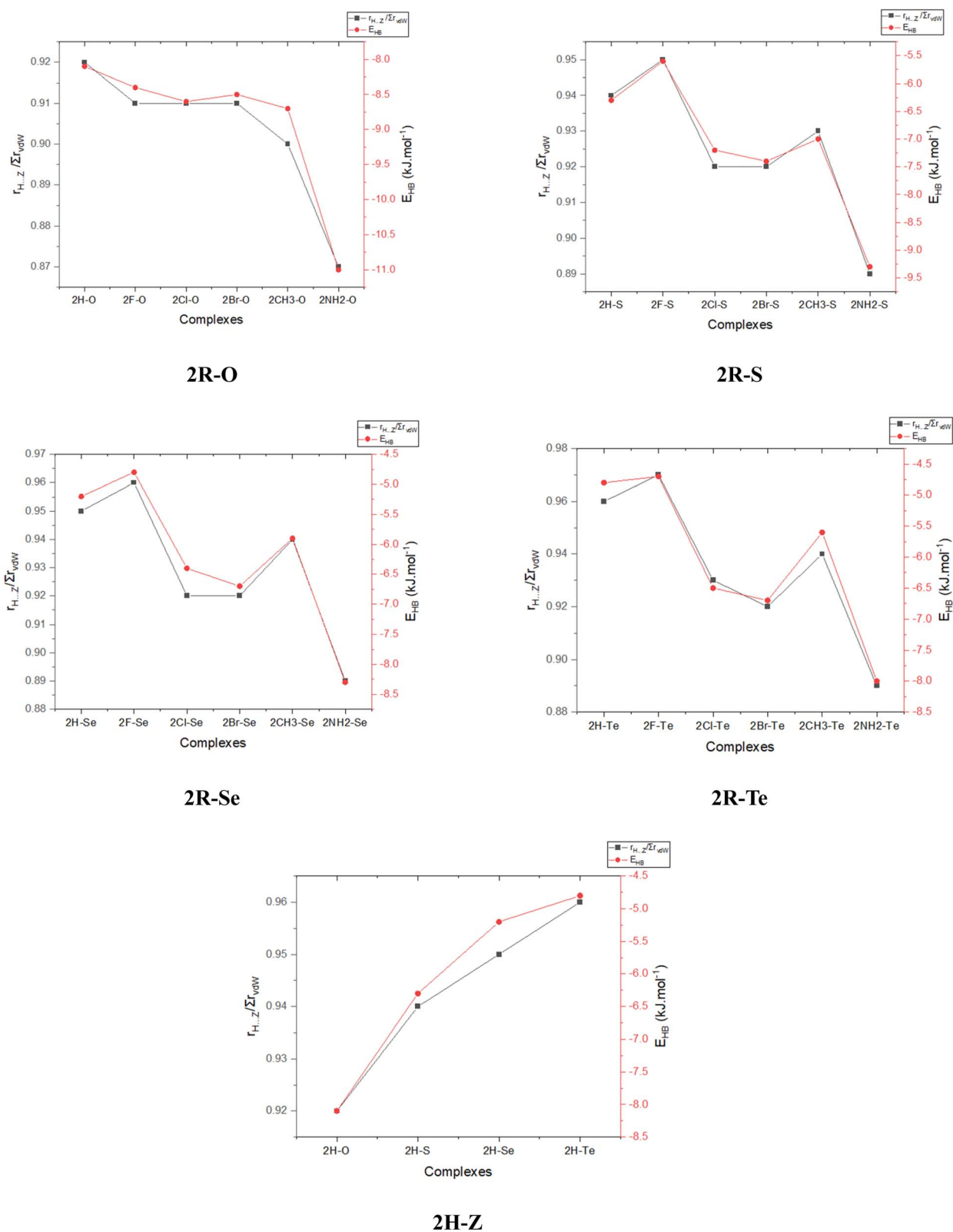


Fig. 3 The relationship between the  $r_{H...Z}/\sum r_{vdW}$  ratios and individual hydrogen bond energy ( $E_{HB}$ ) in the 2R-Z dimers (R = H, F, Cl, Br or CH<sub>3</sub>; Z = O, S, Se or Te).

**Table 1** Deprotonation enthalpies (DPEs) of the  $C_{sp^2}$ -H bond in the RCHZ monomers and the proton affinities (PA) at the Z site of RCHZ, with R = H, F, Cl, Br,  $CH_3$  or  $NH_2$ , and Z = O, S, Se or Te

	HCHO <sup>a</sup>	HCHS	HCHSe	HCHTe
DPE( $C_{sp^2}$ -H) (kJ mol <sup>-1</sup> )	1684.9	1636.5	1625.9	1611.4
PA(Z) (kJ mol <sup>-1</sup> )	696.6	753.1	754.2	770.2
	FCHO	FCHS	FCHSe	FCHTe
DPE( $C_{sp^2}$ -H) (kJ mol <sup>-1</sup> )	1583.8	1581.3	1571.2	1560.1
PA(Z) (kJ mol <sup>-1</sup> )	642.2	706.8	716.9	740.0
	ClCHO	ClCHS	ClCHSe	ClCHTe
DPE( $C_{sp^2}$ -H) (kJ mol <sup>-1</sup> )	1540.9	1557.7	1554.6	1549.7
PA(Z) (kJ mol <sup>-1</sup> )	678.2	739.3	744.8	761.7
	BrCHO	BrCHS	BrCHSe	BrCHTe
DPE( $C_{sp^2}$ -H) (kJ mol <sup>-1</sup> )	1505.0	1542.0	1542.2	1540.8
PA(Z) (kJ mol <sup>-1</sup> )	682.5	746.1	751.3	766.9
	$CH_3CHO$ <sup>b</sup>	$CH_3CHS$	$CH_3CHSe$	$CH_3CHTe$
DPE( $C_{sp^2}$ -H) (kJ mol <sup>-1</sup> )	1659.9	1629.1	1623.5	1614.4
PA(Z) (kJ mol <sup>-1</sup> )	755.6	793.4	791.4	801.2
	$NH_2CHO$	$NH_2CHS$	$NH_2CHSe$	$NH_2CHTe$
DPE( $C_{sp^2}$ -H) (kJ mol <sup>-1</sup> )	1632.8	1592.6	1575.4	1557.2
PA(Z) (kJ mol <sup>-1</sup> )	873.1	888.2	882.7	909.5

<sup>a</sup> DPE<sub>experiment</sub>( $C_{sp^2}$ -H) = 1650.7 (kJ mol<sup>-1</sup>)<sup>75</sup> and PA<sub>experiment</sub>(O) = 712.9 (kJ mol<sup>-1</sup>)<sup>76</sup> in HCHO molecule. <sup>b</sup> DPE<sub>experiment</sub>( $C_{sp^2}$ -H) = 1645.1 (kJ mol<sup>-1</sup>)<sup>77</sup> and PA<sub>experiment</sub>(O) = 768.5 (kJ mol<sup>-1</sup>)<sup>78</sup> in  $CH_3CHO$  molecule.

**Table 2** Interaction energies corrected by ZPE and BSSE ( $\Delta E^*$ , kJ mol<sup>-1</sup>) of the 2R-Z dimers (R = H, F, Cl or  $CH_3$ ; Z = O, S, Se or Te)

Complex	$\Delta E^*$	Complex	$\Delta E^*$	Complex	$\Delta E^*$	Complex	$\Delta E^*$
2H-O	-10.3	2H-S	-7.3	2H-Se	-7.9	2H-Te	-6.2
2F-O	-13.6	2F-S	-8.6	2F-Se	-9.7	2F-Te	-9.0
2Cl-O	-13.5	2Cl-S	-9.3	2Cl-Se	-10.6	2Cl-Te	-9.4
2Br-O	-13.2	2Br-S	-9.9	2Br-Se	-10.9	2Br-Te	-9.1
2 $CH_3$ -O	-12.0	2 $CH_3$ -S	-10.8	2 $CH_3$ -Se	-11.5	2 $CH_3$ -Te	-9.7
2 $NH_2$ -O	-17.7	2 $NH_2$ -S	-19.1	2 $NH_2$ -Se	-21.2	2 $NH_2$ -Te	-21.0

O in  $CH_3CHO$ . The notable importance of  $C_{sp^2}$ -H polarity in stabilizing the 2R-Z dimer is different from the dominant role of O-H polarity in both HCOOH and  $H_2O$ ,<sup>46,61</sup> overcoming the proton affinity of O in  $CH_3CHO$  and F/Cl/BrCHO in determining the strength of the complexes.

For Z = S, Se and Te, the strength of the dimers increases in the sequence of 2H-Z < 2F-Z < 2Cl-Z ~ 2Br-Z < 2 $CH_3$ -Z < 2 $NH_2$ -Z, in which a considerable stability of the dimer is found as Z =  $NH_2$  compared to the remaining substituents (*cf.* Table 2). This indicates that one H in HCHZ substituted by the electron-donating group leads to a larger increase in the strength of the 2R-Z dimers as compared to that by the electron-

**Table 3** The NBO analysis of the 2R-Z dimers, with R = H, F, Cl, Br,  $CH_3$  or  $NH_2$  and Z = O, S, Se or Te

	2H-O	2H-S	2H-Se	2H-Te
$E_{inter}[n(Z5) \rightarrow \sigma^*(C_{sp^2}-H)]^a$ (kJ mol <sup>-1</sup> )	4.1	8.6	7.5	5.9
$E_{intra}[n(Z3) \rightarrow \sigma^*(C_{sp^2}-H)]^b$ (kJ mol <sup>-1</sup> )	102.7	59.1	50.8	39.7
$\sum E_{inter}^c$ (kJ mol <sup>-1</sup> )	4.1	8.6	7.5	6.5
$\Delta E_{intra}^d$ (kJ mol <sup>-1</sup> )	-11.9	-4.7	-2.4	0.7
$\Delta\sigma^*(C_{sp^2}-H)$ ( $10^{-3}$ e)	-4.4	0.5	1.3	1.8
$\Delta\%s(C)$	0.8	0.96	0.86	0.71
	2F-O	2F-S	2F-Se	2F-Te
$E_{inter}[n(Z5) \rightarrow \sigma^*(C_{sp^2}-H)]^a$ (kJ mol <sup>-1</sup> )	4.4	10.3	9.7	9.0
$E_{intra}[n(Z3) \rightarrow \sigma^*(C_{sp^2}-H)]^b$ (kJ mol <sup>-1</sup> )	100.9	62.6	48.0	34.9
$\sum E_{inter}^c$ (kJ mol <sup>-1</sup> )	4.4	10.3	9.8	9.9
$\Delta E_{intra}^d$ (kJ mol <sup>-1</sup> )	-9.4	-6.9	-3.4	-4.4
$\Delta\sigma^*(C_{sp^2}-H)$ ( $10^{-3}$ e)	-3.0	0.5	1.3	2.0
$\Delta\%s(C)$	0.5	0.8	0.9	0.9
	2Cl-O	2Cl-S	2Cl-Se	2Cl-Te
$E_{inter}[n(Z5) \rightarrow \sigma^*(C_{sp^2}-H)]^a$ (kJ mol <sup>-1</sup> )	3.5	12.2	11.9	10.2
$E_{intra}[n(Z3) \rightarrow \sigma^*(C_{sp^2}-H)]^b$ (kJ mol <sup>-1</sup> )	114.2	70.1	54.3	40.8
$\sum E_{inter}^c$ (kJ mol <sup>-1</sup> )	3.5	12.2	11.9	11.8
$\Delta E_{intra}^d$ (kJ mol <sup>-1</sup> )	-9.8	-7.5	-6.0	-3.9
$\Delta\sigma^*(C_{sp^2}-H)$ ( $10^{-3}$ e)	-3.5	0.5	1.6	2.9
$\Delta\%s(C)$	0.5	1.0	1.1	1.0
	2Br-O	2Br-S	2Br-Se	2Br-Te
$E_{inter}[n(Z5) \rightarrow \sigma^*(C_{sp^2}-H)]^a$ (kJ mol <sup>-1</sup> )	2.7	11.7	11.3	9.5
$E_{intra}[n(Z3) \rightarrow \sigma^*(C_{sp^2}-H)]^b$ (kJ mol <sup>-1</sup> )	115.0	71.7	56.3	43.2
$\sum E_{inter}^c$ (kJ mol <sup>-1</sup> )	2.7	11.7	11.3	11.4
$\Delta E_{intra}^d$ (kJ mol <sup>-1</sup> )	-9.8	-7.5	-5.3	-2.8
$\Delta\sigma^*(C_{sp^2}-H)$ ( $10^{-3}$ e)	-3.5	0.3	1.5	3.0
$\Delta\%s(C)$	0.5	1.1	1.2	1.0
	2 $CH_3$ -O	2 $CH_3$ -S	2 $CH_3$ -Se	2 $CH_3$ -Te
$E_{inter}[n(Z5) \rightarrow \sigma^*(C_{sp^2}-H)]^a$ (kJ mol <sup>-1</sup> )	5.8	9.3	7.8	5.9
$E_{intra}[n(Z3) \rightarrow \sigma^*(C_{sp^2}-H)]^b$ (kJ mol <sup>-1</sup> )	115.6	68.9	54.8	42.7
$\sum E_{inter}^c$ (kJ mol <sup>-1</sup> )	6.1	9.3	8.0	6.8
$\Delta E_{intra}^d$ (kJ mol <sup>-1</sup> )	-15.2	-4.7	-2.2	1.5
$\Delta\sigma^*(C_{sp^2}-H)$ ( $10^{-3}$ e)	-5.3	0.4	1.3	2.2
$\Delta\%s(C)$	0.9	1.0	0.9	0.7
	2 $NH_2$ -O	2 $NH_2$ -S	2 $NH_2$ -Se	2 $NH_2$ -Te
$E_{inter}[n(Z5) \rightarrow \sigma^*(C_{sp^2}-H)]^a$ (kJ mol <sup>-1</sup> )	9.6	15.7	15.0	12.5
$E_{intra}[n(Z3) \rightarrow \sigma^*(C_{sp^2}-H)]^b$ (kJ mol <sup>-1</sup> )	113.2	66.7	51.3	38.4
$\sum E_{inter}^c$ (kJ mol <sup>-1</sup> )	9.9	15.8	15.5	15.4
$\Delta E_{intra}^d$ (kJ mol <sup>-1</sup> )	-20.0	-7.5	-5.0	-1.9
$\Delta\sigma^*(C_{sp^2}-H)$ ( $10^{-3}$ e)	-5.8	1.7	3.4	4.9
$\Delta\%s(C)$	1.0	1.3	1.2	1.1

<sup>a</sup> The hyperconjugative interaction energy of the intermolecular electron transfer from lone pair n(Z5) to the  $\sigma^*(C_{sp^2}-H)$  orbital. <sup>b</sup> The hyperconjugative interaction energy of the intramolecular electron transfer from lone pair n(Z3) to the  $\sigma^*(C_{sp^2}-H)$  orbital. <sup>c</sup> The total hyperconjugative interaction energies of the intermolecular electron transfers to the  $\sigma^*(C_{sp^2}-H)$  orbital. <sup>d</sup> The change in energy of the intramolecular electron transfers to the  $\sigma^*(C_{sp^2}-H)$  orbital.

withdrawing group. Accordingly, for  $Z = \text{S, Se and Te}$ , the strength of  $2\text{R-Z}$  is contributed by both  $\text{C}_{\text{sp}^2}\text{-H}$  polarity and proton affinity at the  $Z$  site in the monomers, in which a larger role of the latter relative to the former is proposed.

A SAPT2+ analysis was carried out using the def2-TZVPD basis set to clarify the role of the energetic components in the dimer stabilization. The obtained data are gathered in Table S6† and visualized in Fig. 4. The  $2\text{R-O/S/Se}$  dimers are stabilized by three main components: electrostatic, dispersion and induction terms. The contribution of the electrostatic component is the largest (32.0–54.5%), surpassing the two remaining terms, including the induction (16.3–54.2%) and the dispersion (0.2–32.7%). The percentage of electrostatic terms for  $2\text{R-O}$  is much higher than those for  $2\text{R-S/Se/Te}$ , indicating the significant contribution of the electrostatic component to the stability of  $2\text{R-O}$  compared to  $2\text{R-S/Se/Te}$ . The contributing percentage of the dispersion and induction terms in  $2\text{R-Z}$  is negligibly changed as  $Z$  goes from  $\text{O}$  via  $\text{S}$  to  $\text{Se}$ , while they shift quickly for  $2\text{R-Te}$ . Remarkably, the induction component is *ca.* 52% and the dispersion decreases suddenly to *ca.* 1.0% in the  $2\text{R-Te}$  dimers (*cf.* Table S6†). Therefore, the strength of  $2\text{R-Te}$  is contributed by both induction and electrostatic terms, in which a larger contribution of the former is observed. This observation is confirmed when the SAPT2+ calculations for  $2\text{R-Te}$  are recalculated using different basis sets, including def2-TZVPPD for all atoms, def2-TZVPPD for the  $\text{Te}$  atom and aug-cc-pVTZ for the remaining ones, and def2-QZVPPD for all atoms (*cf.* Table S7 and Fig. S3a and b†).

### 3.3. NBO and NCI analysis

NBO analysis was conducted to gain a clearer view of the intermolecular electron density transfer and electron distribution during the formation of dimers. The selected data are given in Table 3.

As seen in Table 3, for the same  $\text{R}$ , the intermolecular hyperconjugative interaction energies of  $n(\text{Z5}) \rightarrow \sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  increase considerably when replacing the  $\text{O}$  in  $2\text{R-O}$  by  $\text{S, Se, and Te}$ . This result is in line with the smaller value for  $E_{\text{inter}}[n(\text{O}) \rightarrow \sigma^*(\text{C}_{\text{sp}^2}\text{-H})]$  than  $E_{\text{inter}}[n(\text{S/Se/Te}) \rightarrow \sigma^*(\text{C}_{\text{sp}^2}\text{-H})]$  in the  $\text{XCHO} \cdots n\text{H}_2\text{Z}$  complexes with  $\text{X} = \text{H, F, Cl, Br or CH}_3$ ,  $\text{Z} = \text{O, S, Se or Te}$  and  $n = 1-2$ , calculated at the  $\omega\text{B97X-D/aug-cc-pVDZ}$

level.<sup>62</sup> It is noteworthy that there is a significant decrease in the total intramolecular interaction energies of electron transfers from  $n(\text{O}), \pi(\text{C}=\text{O})$  and  $\sigma(\text{C-R})$  to the  $\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  orbital (from  $-20.0 \text{ kJ mol}^{-1}$  to  $-9.4 \text{ kJ mol}^{-1}$ ) in the  $2\text{R-O}$  dimers, overcoming their total intermolecular hyperconjugative interaction energies (from  $2.7 \text{ kJ mol}^{-1}$  to  $9.9 \text{ kJ mol}^{-1}$ ). This implies a significant contribution of intramolecular electron transfer to the rearrangement of the electron density in the  $\text{RCHO}$  monomers during the complexations, leading to a decrease in occupation at the  $\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  orbital of  $2\text{R-O}$ . In contrast, positive values of  $\Delta\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  are obtained in the dimers of  $2\text{R-S/Se/Te}$  because of the dominance of the hyperconjugative interaction energies over the decrease in intramolecular interaction energy. Indeed, the  $\sum E_{\text{inter}}$  and  $\Delta E_{\text{intra}}$  values of the electron transfers in  $2\text{R-S/Se/Te}$  are in the ranges from  $6.5$  to  $15.8 \text{ kJ mol}^{-1}$  and from  $-7.5$  to  $1.5 \text{ kJ mol}^{-1}$ , respectively. These data lend support to a prediction that a strong  $\text{C}_{\text{sp}^2}\text{-H}$  blue-shift is observed for the  $\text{C}_{\text{sp}^2}\text{-H} \cdots \text{O}$ , while a  $\text{C}_{\text{sp}^2}\text{-H}$  red-shift is found for  $\text{C}_{\text{sp}^2}\text{-H} \cdots \text{S/Se/Te}$ . Despite the smaller intermolecular electron density transfer from  $n(\text{O})$  relative to that from  $n(\text{S/Se/Te})$  to the  $\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  orbital, the  $\text{C}_{\text{sp}^2}\text{-H} \cdots \text{O}$  is more stable than the  $\text{C}_{\text{sp}^2}\text{-H} \cdots \text{S/Se/Te}$  due to the highly negative charge density on the  $\text{O}$  site (*cf.* Table S5†). Therefore, the strength of nonconventional  $\text{C}_{\text{sp}^2}\text{-H} \cdots \text{Z}$  hydrogen bonds is contributed by both intermolecular electron density transfer and electrostatic attraction, in which a more dominant role of the latter is presented.

For  $\text{Z} = \text{O}$ , the intermolecular electron density transfer from  $n(\text{O})$  to the  $\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  orbital in the dimers containing electron-donating substituents is stronger than in those with electron-withdrawing ones. Furthermore, the  $\Delta\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  values become less negative in the order of  $2\text{NH}_2\text{-O} \sim 2\text{CH}_3\text{-O} > 2\text{H-O} > 2\text{Cl/Br/F-O}$ , corresponding to the more significantly negative  $\Delta E_{\text{intra}}$  of the  $2\text{NH}_2/\text{CH}_3\text{-O}$  dimers than the  $2\text{H-O}$  and  $2\text{Cl/Br/F-O}$  ones (*cf.* Table 3). This indicates that the greater contribution of electron-donating groups relative to electron-withdrawing ones exhibits an enhancement of the  $\text{C}_{\text{sp}^2}\text{-H}$  blue-shift. Regarding  $\text{Z} = \text{S, Se and Te}$ , the  $E_{\text{inter}}$  values of  $n(\text{Z5}) \rightarrow \sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  descend in the order of the substituents  $\text{NH}_2 > \text{Cl} \sim \text{Br} > \text{F} > \text{CH}_3 > \text{H}$ , implying that the electron density transfer from  $n(\text{Z5})$  to the  $\sigma^*(\text{C}_{\text{sp}^2}\text{-H})$  orbital in the  $2\text{R-S/Se/Te}$  dimers lessens along that order.

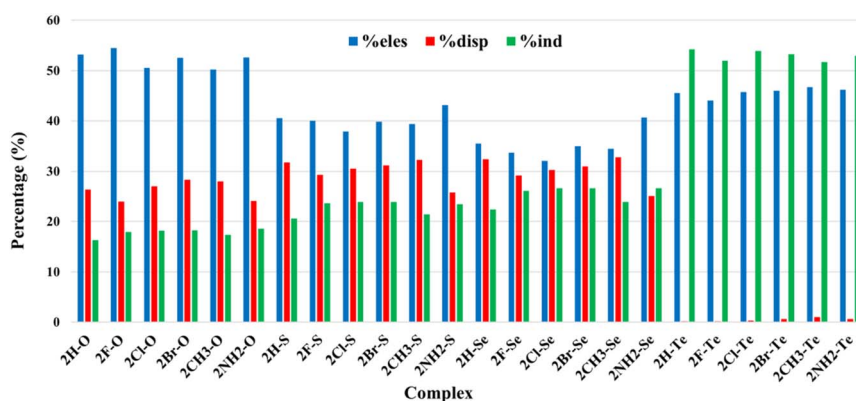


Fig. 4 The percentage contribution (%) of the energy components to the stability of the  $2\text{R-Z}$  dimers at the def2-TZVPD level, with  $\text{R} = \text{H, F, Cl, Br, CH}_3$  or  $\text{NH}_2$  and  $\text{Z} = \text{O, S, Se or Te}$ .



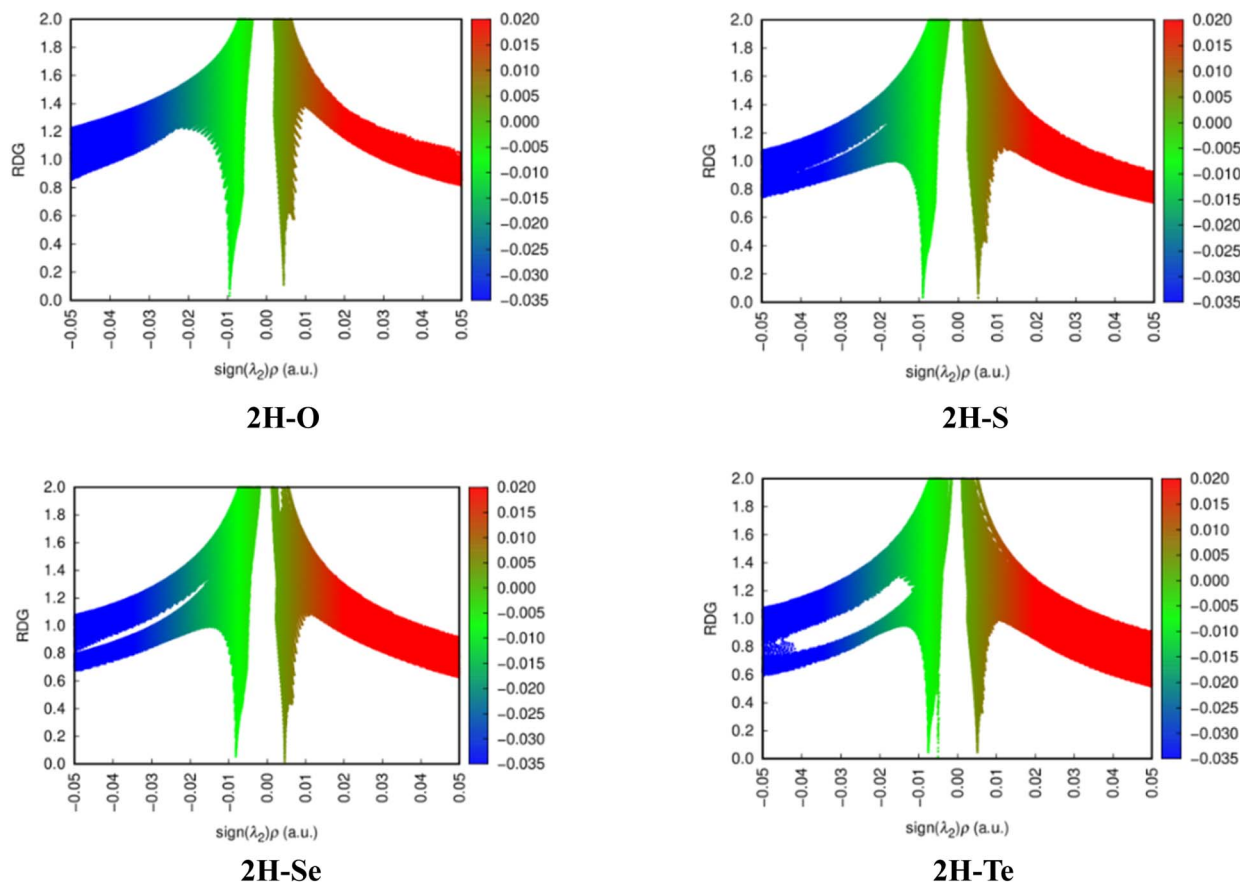


Fig. 5 Plots of the reduced density gradient (s, au) versus the electron density multiplied by the sign of the second Hessian eigenvalue ( $\text{sign}(\lambda_2)\rho$ , au) for the 2H-Z dimers (Z = O, S, Se or Te).

In addition, the results from the NCI plot (*cf.* Fig. 5 and S4a, b, and Table S8<sup>†</sup>) show that the reduced density gradient (RDG) of  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{Z}$  interaction spikes ranges from 0.086 to 0.179 au (RDG  $\approx 0$ ), confirming that the nonconventional  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{Z}$  hydrogen bonds in the dimers belong to weak non-covalent interactions (*cf.* Table S8<sup>†</sup>). For the same R, the spikes of the  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{O}$  hydrogen bonds are located in a more negative region of  $\text{sign}(\lambda_2)\rho(r)$  as compared to those of the  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{S/Se/Te}$  ones, validating the more attractive interaction of the  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{O}$  hydrogen bonds. For Z = O, the most negative  $\text{sign}(\lambda_2)\rho(r)$  regions of  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{O}$  are observed for the spikes of **2NH<sub>2</sub>-O** ( $\text{sign}(\lambda_2)\rho(r) = -0.0119$  au), and the least negative ones belong to the spikes of **2H-O** ( $\text{sign}(\lambda_2)\rho(r) = -0.0095$  au). In the case of Z = S, Se and Te, the spikes of  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{S/Se/Te}$  tend to the left as R goes from F/H to CH<sub>3</sub> to Cl/Br and then to NH<sub>2</sub>, confirming the increase in the strength of the hydrogen bonds in the order of substituents  $\text{F} \sim \text{H} < \text{CH}_3 < \text{Cl} \sim \text{Br} < \text{NH}_2$ , as found from the AIM analysis.

### 3.4. Changes in the $\text{C}_{\text{sp}^2}\text{-H}$ bond lengths and their stretching frequencies

The changes in the  $\text{C}_{\text{sp}^2}\text{-H}$  bond lengths and their stretching frequencies in the **2R-Z** dimers compared to the relevant RCHZ monomers are calculated to evaluate the characteristics of the nonconventional  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{Z}$  hydrogen bonds. The obtained results are gathered in Fig. 6 and Table S9.<sup>†</sup> The results show that

the changes in the stretching frequencies of the  $\text{C}_{\text{sp}^2}\text{-H}$  bonds are negative with the values from  $-0.3$  to  $-38.6$   $\text{cm}^{-1}$ , along with the  $\text{C}_{\text{sp}^2}\text{-H}$  elongation of 0.3–2.4 mÅ for the **2R-S**, **2R-Se** and **2R-Te** dimers (*cf.* Table S9<sup>†</sup>), demonstrating the  $\text{C}_{\text{sp}^2}\text{-H}$  stretching frequency red-shift of the nonconventional  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{S/Se/Te}$  hydrogen bonds. The  $\text{C}_{\text{sp}^2}\text{-H}$  red-shift of the nonconventional

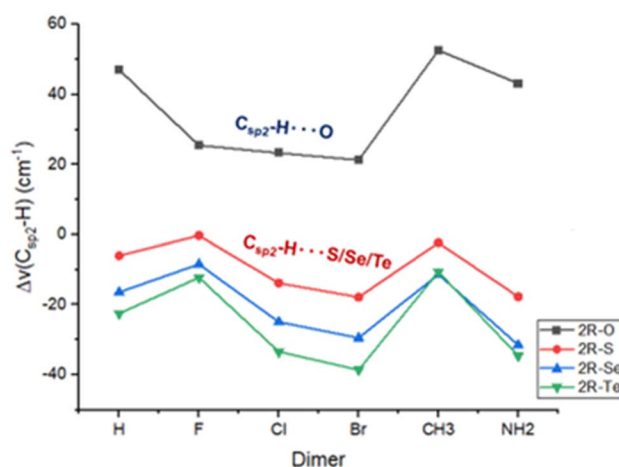


Fig. 6 The tendency of red-shifting and blue-shifting of the nonconventional  $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{Z}$  hydrogen bonds in the **2R-Z** dimers with R = H, F, Cl, Br, CH<sub>3</sub> or NH<sub>2</sub> and Z = O, S, Se or Te.

$C_{sp^2}\text{-H}\cdots\text{Se}$  hydrogen bonds in the  $[\text{C}_8\text{H}_8\cdots\text{Se}(\text{CH}_3)_2]$  complex has been recently determined by the experimental and theoretical results of  $101\text{ cm}^{-1}$  and  $89\text{ cm}^{-1}$ , respectively.<sup>55</sup> It was reported that the  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$  hydrogen bonds were red-shifted up to  $36.1\text{ cm}^{-1}$  in the complexes of aldehydes and hydrogen chalcogenides, in which the blue-shift of  $C_{sp^2}\text{-H}\cdots\text{Te}$  is stronger than that of  $C_{sp^2}\text{-H}\cdots\text{S/Se}$ .<sup>62</sup> Conversely, the  $C_{sp^2}\text{-H}$  blue-shift is observed in the nonconventional  $C_{sp^2}\text{-H}\cdots\text{O}$  hydrogen bonds with the values of  $\Delta\nu(C_{sp^2}\text{-H})$  and  $\Delta r(C_{sp^2}\text{-H})$  from  $21.3$  to  $52.6\text{ cm}^{-1}$  and from  $-3.5$  to  $-0.9\text{ mÅ}$ , respectively (cf. Table S9†). The difference in the characteristics between  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$  and  $C_{sp^2}\text{-H}\cdots\text{O}$  hydrogen bonds results from the greater role of the noticeable intermolecular transfer of electron density from  $n(\text{S/Se/Te})$  to the  $\sigma^*(C_{sp^2}\text{-H})$  orbital compared to that from  $n(\text{O})$  to the  $\sigma^*(C_{sp^2}\text{-H})$  one. This highlights a noticeably different role of O compared to S, Se, and Te in changing the  $C_{sp^2}\text{-H}$  bond length and its stretching frequency upon complexation.

The enhancement of the electron density occupation at the  $\sigma^*(C_{sp^2}\text{-H})$  orbital (cf. Table 3) leads to an increase in  $C_{sp^2}\text{-H}$  bond length and a decrease in its stretching frequency in the  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$  hydrogen bonds. For the same R, the  $C_{sp^2}\text{-H}$  red-shift of the stretching frequency decreases in the sequence of  $C_{sp^2}\text{-H}\cdots\text{Te} > C_{sp^2}\text{-H}\cdots\text{Se} > C_{sp^2}\text{-H}\cdots\text{S}$  following complexation (cf. Fig. 6). The larger  $\Delta\sigma^*(C_{sp^2}\text{-H})$  values (cf. Table 3) indeed lead to an increase in the  $\Delta r(C_{sp^2}\text{-H})$  values as Z changes from S to Te, which is accompanied by the more negative  $\Delta\nu(C_{sp^2}\text{-H})$  values in this order. This tendency of  $C_{sp^2}\text{-H}$  red-shift is in good agreement with the increase in the proton affinity at the S/Se/Te site and the more polarization of the  $C_{sp^2}\text{-H}$  bonds in the sequence of isolated monomers  $\text{RCHS} < \text{RCHSe} < \text{RCHTe}$ . For the same Z being S, Se and Te, the  $\Delta\nu(C_{sp^2}\text{-H})$  values of the  $C_{sp^2}\text{-H}$  bond become more negative in the order of substituents  $\text{F} < \text{CH}_3 < \text{H} < \text{Cl} < \text{Br} \sim \text{NH}_2$  (cf. Fig. 6), indicating the enhancement of the  $C_{sp^2}\text{-H}$  red-shift in the nonconventional  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$  hydrogen bonds according to this trend. Therefore, the rule of the effect of electron-donating and withdrawing groups on the characteristics of  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$  should not be presented in the **2R-S/Se/Te** dimers. The reason for its characteristics could be suggested by the rearrangement of the electron density during the formation of the dimers.

For  $Z = \text{O}$ , the blue-shift of the nonconventional  $C_{sp^2}\text{-H}\cdots\text{O}$  hydrogen bonds is proposed by the considerable decrease in the occupation of the  $\sigma^*(C_{sp^2}\text{-H})$  orbital upon complexation, leading to the contraction of the  $C_{sp^2}\text{-H}$  bond and an increase in its stretching frequencies. Indeed, the stretching frequency blue-shifts of the  $C_{sp^2}\text{-H}$  bond in the **2R-O** dimers are found to lie between  $21\text{ cm}^{-1}$  and  $53\text{ cm}^{-1}$  (cf. Table S9†). The approximate  $C_{sp^2}\text{-H}$  blue-shifts of the  $C_{sp^2}\text{-H}\cdots\text{O}$  hydrogen bonds were reported in the  $\text{YCHO}\cdots\text{H}_2\text{O}$  complexes ( $\text{Y} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{or } \text{CH}_3$ ) with the values of  $\Delta\nu(C_{sp^2}\text{-H})$  being  $21\text{--}52\text{ cm}^{-1}$ .<sup>61</sup> For the complexes of  $\text{XCHO}$  ( $\text{X} = \text{H}, \text{F}$  and  $\text{Cl}$ ) with  $\text{H}_2\text{O}$ , the blue-shifts of the  $C_{sp^2}\text{-H}$  stretching frequencies were in the range of  $20\text{--}45\text{ cm}^{-1}$  calculated at the MP2/aug-cc-pVTZ level.<sup>51</sup> Fig. 6 shows that the  $C_{sp^2}\text{-H}$  blue-shifting of the  $C_{sp^2}\text{-H}\cdots\text{O}$  hydrogen bonds is observed in all dimers, regardless of the electron effect of the substituents, in which the electron-donating derivatives exhibit a stronger  $C_{sp^2}\text{-H}$  blue-shift compared to electron-withdrawing

ones. The smaller magnitude of the  $C_{sp^2}\text{-H}$  blue-shift in the nonconventional hydrogen bonds was also found in the complexes of  $\text{XCHO}$  with  $\text{HF}$ ,  $\text{H}_2\text{Z}$  and  $\text{H}_2\text{O}$  (with  $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$  or  $\text{CH}_3$ , and  $\text{Z} = \text{O}, \text{S}, \text{Se}$  or  $\text{Te}$ ). The **2CH<sub>3</sub>-O** dimer in this work shows the strongest blue-shift with a  $\Delta\nu(C_{sp^2}\text{-H})$  value of *ca.*  $53\text{ cm}^{-1}$  (cf. Table S9†). Large  $C_{sp^2}\text{-H}$  blue-shifts of  $\text{CH}_3\text{CHO}\cdots\text{H}_2\text{O}$  ( $52\text{ cm}^{-1}$ ) and  $\text{CH}_3\text{CHO}\cdots\text{HCOOH}$  ( $96\text{ cm}^{-1}$ ) have been reported.<sup>46,62</sup> A very large  $C_{sp^2}\text{-H}$  blue-shift of the stretching frequency up to  $104.5\text{ cm}^{-1}$  was also found in  $\text{CH}_3\text{CHO}\cdots\text{FCOOH}$  calculated at the MP2/6-311++G(3df,2pd) level.<sup>54</sup> Consequently, the substitution of one  $\text{CH}_3\text{CHO}$  molecule in the dimer of  $\text{CH}_3\text{CHO}$  by one carboxylic acid, like  $\text{HCOOH}$  or  $\text{FCOOH}$ , induces a significant increase in the magnitude of the  $C_{sp^2}\text{-H}$  stretching frequency blue-shift upon complexation. As seen in Table 1, the polarity of  $C_{sp^2}\text{-H}$  in the  $\text{F/Cl/BrCHO}$  monomers is greater than that in the  $\text{H/CH}_3/\text{NH}_2\text{CHO}$  ones. This suggests that following complexation, the less polar  $C_{sp^2}\text{-H}$  bond in the isolated monomer causes a larger magnitude of the  $C_{sp^2}\text{-H}$  blue-shift and *vice versa*.

## 4. Concluding remarks

The stable structures of **2R-Z** dimers ( $\text{R} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$  or  $\text{NH}_2$  and  $\text{Z} = \text{O}, \text{S}, \text{Se}$  or  $\text{Te}$ ) were found on the potential energy surface. It is notable that the stability of the dimers increases when replacing H in **2H-Z** with both electron-withdrawing and electron-donating groups, and decreases upon changing Z from O to S, Se and Te. This implies an important role of the O atom compared to the S, Se and Te ones in the strength of the nonconventional  $C_{sp^2}\text{-H}\cdots\text{Z}$  hydrogen bonds and dimers. The greater electrostatic attraction of  $\text{O}\cdots\text{H}$  than  $\text{S/Se/Te}\cdots\text{H}$  leads to the stronger strength of **2R-O** compared to **2R-S/Se/Te** in most cases. In contrast, a dominant role of intermolecular electron transfer is the reason for the stronger stability of **2NH<sub>2</sub>-S/Se/Te** relative to **2NH<sub>2</sub>-O**. Remarkably, while the electrostatic component contributes significantly to the strength of **2R-O/S/Se**, a dominant role of the induction term is observed in **2R-Te**, which has been rarely observed.

The strength of the nonconventional hydrogen bonds lessens in the order of  $C_{sp^2}\text{-H}\cdots\text{O} > C_{sp^2}\text{-H}\cdots\text{S} > C_{sp^2}\text{-H}\cdots\text{Se} > C_{sp^2}\text{-H}\cdots\text{Te}$ , which indeed ranges from  $-8.1$  to  $-11.0\text{ kJ mol}^{-1}$  for  $C_{sp^2}\text{-H}\cdots\text{O}$  and from  $-4.7$  to  $-9.3\text{ kJ mol}^{-1}$  for  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$ . Hydrogen bonds are mainly stabilized by both the electrostatic interaction between the H and Z atoms and the intermolecular electron density transfer from  $n(\text{Z})$  to the  $\sigma^*(\text{C1-H2})$  orbital. Besides, replacing H in **2H-S/Se/Te** by electron-donating and -withdrawing groups results in an improvement in the nonconventional hydrogen bond strength, except for the F substituent, which causes an opposite effect.

It is found that a  $C_{sp^2}\text{-H}$  stretching frequency red-shift is observed in nonconventional  $C_{sp^2}\text{-H}\cdots\text{S/Se/Te}$  hydrogen bonds, while the  $C_{sp^2}\text{-H}\cdots\text{O}$  ones display a blue-shifting of their stretching frequency following complexation. When Z changes from O *via* S to Se and then to Te, the  $C_{sp^2}\text{-H}$  blue-shift in the nonconventional  $C_{sp^2}\text{-H}\cdots\text{Z}$  hydrogen bonds tends to decrease gradually and eventually turn to a red-shift, in agreement with the enhancement of the proton affinity at the Z site in the order

of  $O < S < Se < Te$ . In addition, a rearrangement of electron density in the dimers induces an enhancement of the  $C_{sp^2}$ -H red-shift in the sequence of substituents  $F < CH_3 < H < Cl < Br < NH_2$ . The magnitude of  $C_{sp^2}$ -H stretching frequency red-shift in  $C_{sp^2}$ -H $\cdots$ S/Se/Te increases in line with the enhancement of the proton affinity at the Z site and the polarity of the  $C_{sp^2}$ -H covalent bond in the isolated monomer. Noticeably, the  $C_{sp^2}$ -H blue-shifting of nonconventional  $C_{sp^2}$ -H $\cdots$ O hydrogen bonds is weaker for electron-withdrawing substituents than electron-donating ones.

## Conflicts of interest

There are no conflicts to declare.

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