The Role of Chalcogen–Chalcogen Interactions in the Intrinsic Basicity and Acidity of *β*-Chalcogenovinyl(thio)aldehydes HC(=X)−CH=CH−CYH (X = O, S; Y = Se, Te)

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Abstract: The intrinsic acidity and basicity of a series of *β*-chalcogenovinyl(thio)aldehydes HC(=X)−CH=CH−CYH (X = O, S; Y = Se, Te) were investigated by B3LYP/6-311 + G(3df,2p) density functional and G2(MP2) calculations on geometries optimized at the B3LYP/6-31G(d) level for neutral molecules and at the B3LYP/6-31 + G(d) level for anions. The results showed that selenovinylaldehyde and selenovinylthioaldehyde should behave as Se bases in the gas phase, because the most stable neutral conformer is stabilized by an X−H ··· Se (X = O, S) intramolecular hydrogen bond (IHB). In contrast the Te-containing analogues behave as oxygen or sulfur bases, because the most stable conformer is stabilized by typical X ··· Y−H chalcogen–chalcogen interactions. These compounds have a lower basicity than expected because either chalcogen–chalcogen interactions or IHBs become weaker upon protonation. Similarly, they are also weaker acids than expected because deprotonation results in a significantly destabilized anion. Loss of the proton from the X−H or Y−H groups is a much more favorable than from the C−H groups. Therefore, for Se compounds the deprotonation process results in loss of the X−H ··· Se (X = O, S) IHBs present in the most stable neutral conformer, while for Te-containing compounds the stabilizing X ··· Y−H chalcogen–chalcogen interaction present in the most stable neutral conformer becomes repulsive in the corresponding anion.

Keywords: acidity · basicity · chalcogens · density functional calculations · hydrogen bonds

Introduction

The existence of intramolecular hydrogen bonds (IHBs) may significantly affect the intrinsic basicity or acidity of a given compound, as was shown for tropolone,[1], resorcinol,[2] and thiomalonaldehyde.[3] In other cases, the formation of an IHB on protonation significantly enhances the intrinsic basicity of the system.[4] Among compounds that can form IHBs, the *β*-chalcogenovinyl(thio)aldehydes HC(=X)−CH=CH−CYH (X = O, S; Y = Se, Te) are of special interest, because they can exhibit specific attractive forces between the two chalcogen atoms. These stabilizing chalcogen–chalcogen interactions have long been known[5–7] and have received particular attention in recent years, in an effort to rationalize the structural and spectroscopic peculiarities of Se- and Te-containing compounds in which these interactions are possible due to the presence of C=O or C=S donor groups. Pioneering work was performed by Minyaev and Minkin,[8] and recent experimental studies by Komatsu et al.[9] showed that ^{17}O and ^{77}Se NMR spectroscopic data provide strong evidence for intramolecular nonbonding interaction between Se and O in hydroxyselenenyl compounds. We recently investigated[10] the role of competition between X−H ··· Y (or X ··· H−Y) IHBs (***a*** and ***b***) and Y → X or X → Y chalcogen–chalcogen nonbonding interactions (***c*** and ***d***) in the stability of *β*-chalcogenovinyl(thio)aldehydes. Our results indicated that in selenovinylaldehyde and selenovinylthioaldehyde the O−H ··· Se and S−H ··· Se IHBs compete in strength with the O ··· Se and the S ··· Se interactions, while the opposite is found for the corresponding tellurium-containing analogues. These dissimilarities are due to dramatic differences between Se and Te in terms of X ··· Y (X = O, S; Y = Se, Te) interactions, which are rather weak for Se compounds, but very strong for Te compounds. Consequently, for Se-containing compounds the global minimum of the potential-energy surface (PES) corresponds to tautomers of type ***a***, and for Te-containing compounds to tautomers of type ***d***.

Our aim here is to investigate, by density functional theory (DFT) and high-level ab initio methods, the effect of protonation and deprotonation on the strength of IHBs and chalcogen–chalcogen interactions, and hence on the intrinsic basicity and acidity of these compounds.

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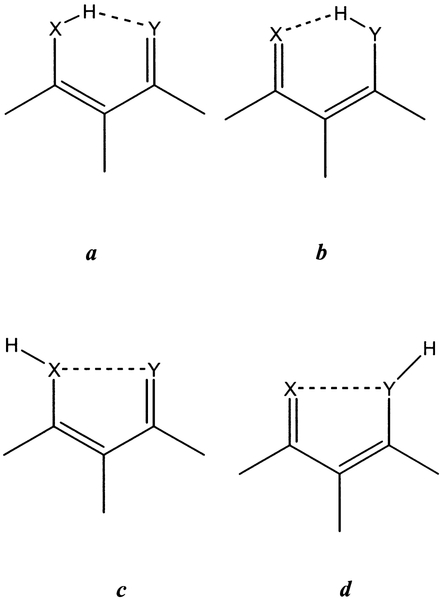

X = O, S
Y = Se, Te

Protonation and deprotonation are particularly direct methods for modulating donor or acceptor strength at each chalcogen center. Therefore, the study of these processes for the set of compounds investigated here can provide a further probe of these chalcogen–chalcogen interactions in a manner that can be experimentally tested.

Methods of Calculation

The relative stability of the different protonated and deprotonated species of the compounds under investigation was evaluated by using the B3LYP approach. This method combines Becke's three-parameter nonlocal hybrid exchange potential[11] with the nonlocal correlation functional of Lee, Yang, and Parr.[12]. In general, geometries obtained with this DFT method are in fairly good agreement with experimental values,[13–20] and the harmonic vibrational frequencies are closer to experiment than those obtained by using other correlated methods such as the MP2 formalism.[21, 22] Furthermore, we previously showed[10] that, for the neutral compounds, this approach yields results in good agreement with those obtained by means of G2(MP2) ab initio calculations, but at a much lower cost. Nevertheless, to assess the reliability of the DFT calculations, the energies of the protonated species were also evaluated at the G2(MP2) level.

The geometries of the different protonated species of Se-containing compounds were optimized at the B3LYP/6-31G(d) level, while for the deprotonated species a 6-31+G(d) expansion was used, to assure an appropriate description of the corresponding anion. The harmonic vibrational frequencies were evaluated at the same level of theory used in the geometry optimization to verify that the optimized structures corresponded to local minima of the PES and to estimate the zero-point energy (ZPE), which was scaled by the empirical factor of 0.98, proposed by Scott and Radom.[23] The final energies were obtained in single-point calculations at the B3LYP/6-311+G(3df,2p) level. The corresponding basis sets for Se were those developed by Curtiss et al.[24]

For Te-containing compounds, we used the SKBJ relativistic potential of Stevens et al.,[25] which accounts for the most important relativistic effects. For geometry optimizations and harmonic-frequency calculations, this effective core potential was used together with the [4,1]+d basis described in reference [10]. Hereafter, for the sake of simplicity this [4,1]+d basis for Te, used in conjunction with a 6-31G(d) basis set for first and second row atoms, is denoted 6-31G(d). For the particular case of anions the set of diffuse functions reported earlier[10] was added to the [4,1]+d basis. To calculate the final energies the (6s,6p,3d,1f) basis set developed in a previous paper[10] was used together with a 6-311+G(3df,2p) basis set expansion for the remaining atoms. Again for the sake of simplicity the (6s,6p,3d,1f) basis for Te is referred to hereafter as a 6-311+G(3df,2p) basis.

The bonding characteristics of the different tautomers were analyzed by using the atoms in molecules (AIM) theory of Bader,[26] which is based on a topological analysis of the electron charge density and its Laplacian. Hence, we located the various bond critical points (bcp), because the charge density at these points is a good indication of the strength of the linkage. This information was complemented with that obtained by means of the natural bond order (NBO) analysis of Weihnhold et al.[27] The NBO

Table 1. Total energies *E* [hartree], zero-point energies ZPE [hartree], and relative energies Δ*E* [kJ mol^{-1}].

Species	B3LYP			G2MP2	
	E	ZPE	Δ*E*	*E*	Δ*E*
Selenium compounds					
OSe*a*	–2593.54853	0.06479	0	–2592.01744	0.0
OSe*b*	–2593.54071	0.06076	10	–2592.01486	7
OSe*d*	–2593.54255	0.06085	5	–2592.01602	4
OSe*aH*$^{+}$	–2593.86870	0.07379	29	–2592.32461	31
OSe*bH*$^{+}$	–2593.87716	0.07445	9	–2592.33255	10
OSe*cdH*$^{+}$	–2593.88067	0.07457	0	–2592.33640	0.0
OSe*CH*$^{+}$(**1**)	–2593.82844	0.07348	134	–	–
OSe*H*$^{+}$(**2**)	–2593.85015	0.07154	72	–	–
OSe*H*$^{+}$(**3**)	–2593.79733	0.06846	203	–	–
OSe^{-}(**1**)	–2593.00739	0.05118	34	–	–
OSe^{-}(**2**)	–2593.01935	0.05166	4	–	–
OSe^{-}(**3**)	–2593.02056	0.05149	0	–	–
TS12	–2592.99099	0.04980	73	–	–
TS13	–2592.95819	0.04584	149	–	–
OSe*C*$^{-}$(**1**)	–2592.91148	0.04600	272	–	–
OSe*C*$^{-}$(**2**)	–2592.94712	0.04520	176	–	–
OSe*C*$^{-}$(**3**)	–2592.93877	0.04671	202	–	–
SSe*a*	–2916.50792	0.05927	0	–2914.75377	0
SSe*b*	–2916.50320	0.05830	10	–2914.75079	8
SSe*d*	–2916.50546	0.05896	5	–2914.75161	5
SSe*aH*$^{+}$	–2916.84050	0.06877	14	–2915.07303	16
SSe*bH*$^{+}$	–2916.84168	0.06883	11	–2915.07384	14
SSe*cdH*$^{+}$	–2916.84603	0.06885	0	–2915.07928	0
SSe^{-}(**1**)	–2915.97696	0.04968	40	–	–
SSe^{-}(**2**)	–2915.99229	0.04986	0	–	–
SSe^{-}(**3**)	–2915.99189	0.04982	1	–	–
TS12	–2915.95028	0.04741	104	–	–
TS13	–2915.94184	0.04682	123	–	–
Tellurium compounds					
OTe*a*	–199.44997	0.06369	36	–199.03393	37
OTe*b*	–199.44388	0.05792	37	–199.03372	37
OTe*d*	–199.45918	0.05911	0	–199.04788	0
OTe*aH*$^{+}$	–199.77805	0.07109	40	–199.35055	46
OTe*bH*$^{+}$	–199.78865	0.07175	14	–199.36057	19
OTe*cdH*$^{+}$	–199.79415	0.07193	0	–199.36791	0
OTe^{-}(**1**)	–198.91989	0.05045	32	–	–
OTe^{-}(**2**)	–198.93150	0.05085	2	–	–
OTe^{-}(**3**)	–198.93216	0.05065	0	–	–
TS12	–198.90620	0.04928	65	–	–
TS13	–198.86105	0.04707	177	–	–
STe*a*	–522.41120	0.05820	39	–521.77287	42
STe*b*	–522.40333	0.05599	54	–521.76743	56
STe*d*	–522.42485	0.05691	0	–521.78882	0
STe*aH*$^{+}$	–522.75027	0.06575	19	–522.10072	20
STe*bH*$^{+}$	–522.75381	0.06636	11	–522.10265	15
STe*cdH*$^{+}$	–522.75790	0.06619	0	–522.10858	0
STe^{-}(**1**)	–521.88815	0.04884	36	–	–
STe^{-}(**2**)	–521.90236	0.04899	0	–	–
STe^{-}(**3**)	–521.90177	0.04891	1	–	–
TS12	–521.86578	0.04689	91	–	–
TS13	–521.84511	0.04584	140	–	–

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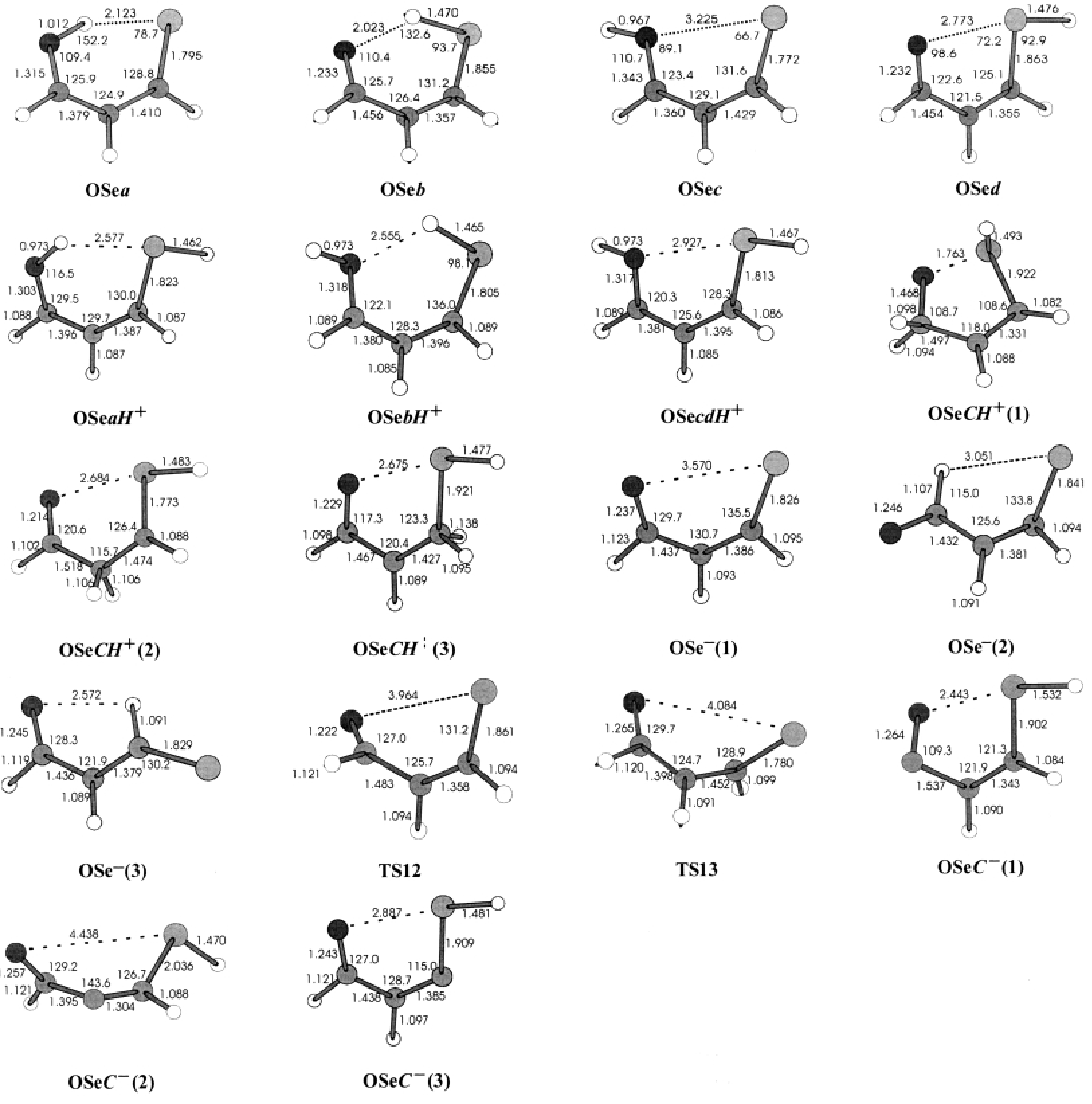
analysis will allow us to obtain reliable charge distributions, as well as quantitatively evaluating the intramolecular attractive orbital interactions which would be responsible for the stability of ***c***- and ***d***-type structures.

Results and Discussion

Preferred protonation and deprotonation sites: The compounds under scrutiny can undergo protonation at the two heteroatoms and at the carbon atoms of the unsaturated skeleton. Similarly, deprotonation can occur from a C–H, X–H, or Y–H bond. To estimate whether protonation and deprotonation processes involving the carbon atoms can compete with those involving the heteroatoms, we systematically investigated the relative stability of all possible protonated and deprotonated structures for β-selenovinylaldehyde HC(=O)–CH=CH–CSeH (**OSe**) as model compound. The structures of the species investigated are shown in Figure 1, and the corresponding total energies and relative stabilities are summarized in Table 1. Both protonation and deprotonation take place preferentially on the heteroatoms O or Se. The C-protonated species **OSe*CH***$^+$(**1**)–(**3**) lie 71–201 kJ mol^{-1} higher in energy than the O- and Se-protonated species. Similarly, the anions obtained by deprotonation of C–H bonds **OSe*C***$^-$(**1**)–(**3**) lie 176–272 kJ mol^{-1} above those produced by deprotonation of the OH or SeH group. Hence, for the remaining compounds of the set under investigation


OSe*a* **OSe*b*** **OSe*c*** **OSe*d***

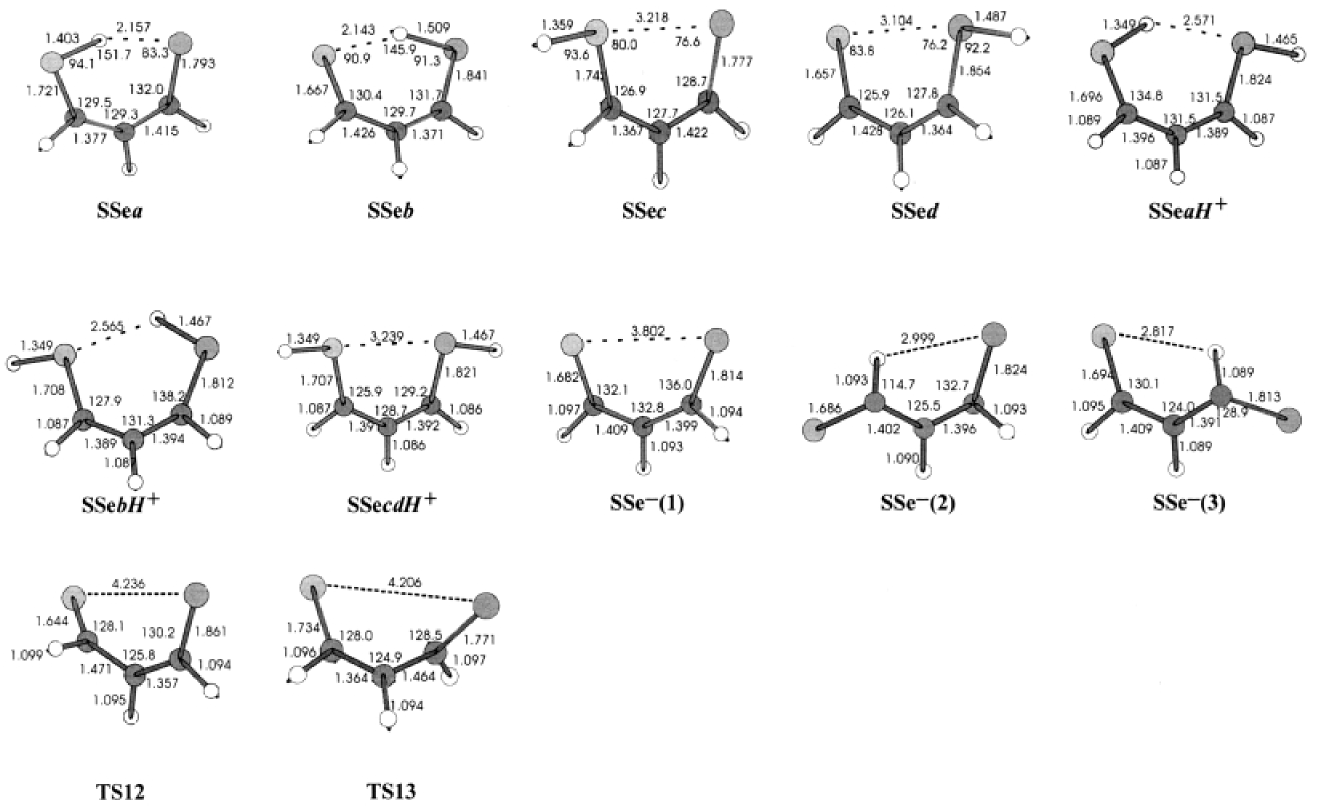
OSe*aH*$^+$ **OSe*bH***$^+$ **OSe*cdH***$^+$ **OSe*CH***$^+$**(1)**

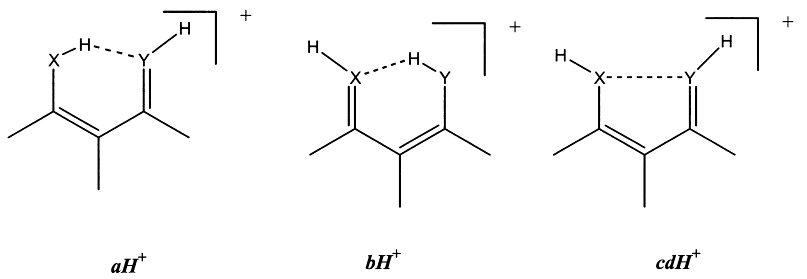
OSe*CH*$^+$**(2)** **OSe*CH***$^+$**(3)** **OSe**$^-$**(1)** **OSe**$^-$**(2)**

OSe$^-$**(3)** **TS12** **TS13** **OSe*C***$^-$**(1)**

OSe*C*$^-$**(2)** **OSe*C***$^-$**(3)**

Figure 1. Optimized geometries of β-selenovinylaldehyde and its protonated and deprotonated forms with bond lengths [Å] and angles [°]. The geometries of the neutral compounds were taken from reference [10].





X = O, S
Y = Se, Te

we concentrate exclusively on the species for which protonation and deprotonation involve the heteroatoms. For these protonated species, only conformers ***aH***$^+$, ***bH***$^+$, and ***cdH***$^+$ are possible.

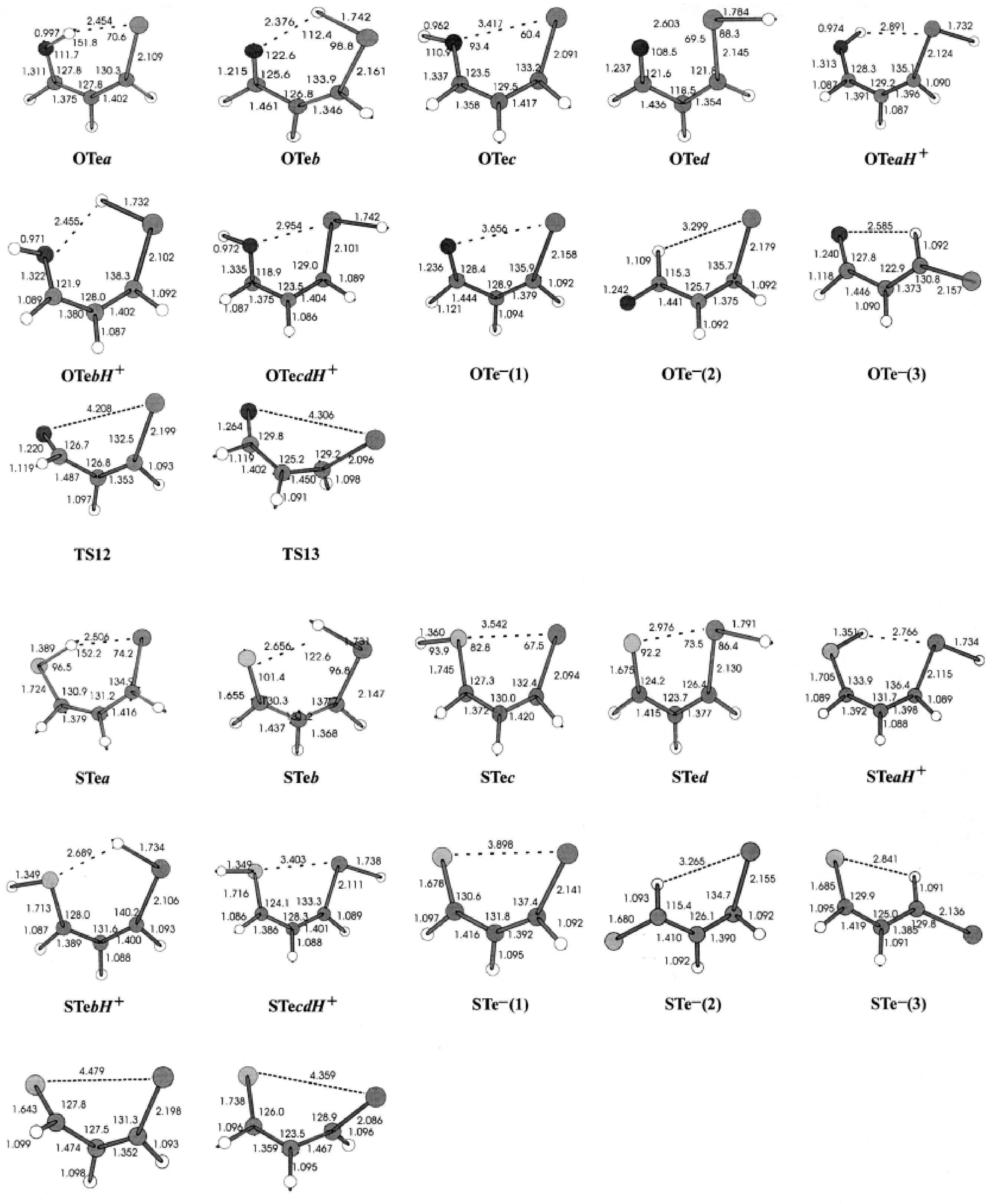
For ease of discussion the neutral molecules are identified by specifying the two chalcogen atoms **XY** followed by a letter in italics that identifies the conformer. A similar procedure is adopted for the protonated species, so that they can be easily related to the neutral structure from which they are derived. Note that protonation on X of structure ***c*** and protonation on Y of structure ***d*** yield a common cation ***cdH***$^+$.

The optimized geometries of the different protonated structures are shown in Figure 1 and Figure 2, and their total energies and relative stabilities are summarized in Table 1. The structures of the neutral compounds were taken from ref. [10] and are also included in Figure 1 and Figure 2 to facilitate the discussion.

For Se-containing compounds structure ***a*** is the most stable conformer, so gas-phase protonation of β-selenovinyl(seleno)aldehydes HC(=X)−CH=CH−CSeH (X = O, S) should yield ***aH***$^+$-type cations. Conversely, for Te compounds the most stable neutral conformer is of type ***d***, so its direct protonation should yield ***cdH***$^+$-type species. However, our results (Table 1) indicate that ***cdH***$^+$ is systematically the most stable protonated species regardless of the nature of the chalcogen atom Y, while the ***aH***$^+$-type structures are systematically less stable. Furthermore, the B3LYP/6-311+G(3df,2p) and G2(MP2) approaches both yield similar estimates for these relative stabilities.

We now analyze in more detail the origin of the relative stability changes of these compounds on protonation.

Effect of protonation on the strength of the chalcogen–chalcogen interactions: Comparing the structures of the protonated forms with those of the corresponding neutral species reveals that protonation significantly affect the strength of the chalcogen–chalcogen interactions. In fact, on going from ***d*** to the corresponding protonated form ***cdH***$^+$, the significant increase in the X$\cdots$Y distance indicates a weaker chalcogen–chalcogen interaction. This is indeed confirmed by the charge density at the corresponding bcp, which is considerably lower for the protonated than for the



OTe*a* **OTe*b*** **OTe*c*** **OTe*d*** **OTe*aH***$^+$

OTe*bH*$^+$ **OTe*cdH***$^+$ **OTe$^-$(1)** **OTe$^-$(2)** **OTe$^-$(3)**

TS12 **TS13**

STe*a* **STe*b*** **STe*c*** **STe*d*** **STe*aH***$^+$

STe*bH*$^+$ **STe*cdH***$^+$ **STe$^-$(1)** **STe$^-$(2)** **STe$^-$(3)**

TS12 **TS13**

Figure 2. Optimized geometries of β-chalcogeno(thio)vinylaldehydes HC(=X)−CH=CH−CYH (X = O, Y = Te. X = S; Y = Se, Te) and their protonated and deprotonated species with bond lengths [Å] and angles [°]. The geometries of the neutral compounds were taken from reference [10].

Table 2. Charge densities (e au^{-3}) at some relevant bcp (X = O, S; Y = Se, Te) of the neutral and protonated forms of *β*-chalcogenovinyl(thio)aldehydes

Bond	**OSe*a***	**OSe*aH*$^+$**	**OSe*b***	**OSe*bH*$^+$**	**OSe*d***	**OSe*cdH*$^+$**	**SSe*a***	**SSe*aH*$^+$**	**SSe*d***	**SSe*cdH*$^+$**
X–H	0.312	0.338	–	0.335	–	0.335	0.197	0.208	–	0.209
Y–H	–	0.171	0.177	0.172	0.171	0.172	–	0.171	0.168	0.171
XH···Y	0.048	0.010	–	–	–	–	0.042	0.013	–	–
X···HY	–	–	0.026	0.015	–	–	–	–	–	–
X···Y	–	–	–		0.021	0.014	–	–	0.020	0.011
	OTe*a*	**OTe*aH*$^+$**	**OTe*b***	**OTe*bH*$^+$**	**OTe*d***	**OTe*cdH*$^+$**	**STe*a***	**STe*a*H$^+$**	**STe*d***	**STe*cdH*$^+$**
X–H	0.293	0.338	–	0.338	–	0.336	0.191	0.207	–	0.208
Y–H	–	0.057	0.115	0.050	0.045	0.056	–	0.057	0.044	0.050
XH···Y	0.027	0.009	–	–	–	–	0.027	0.012	–	–
X···HY	–	–	0.013	0.011	–	–	–	–	–	–
X···Y	–	–	–	–	0.042	0.017	–	–	0.032	0.012

neutral species (Table 2). As we have shown[10] for the neutral compounds, two contributions are responsible for these stabilizing interactions, one associated with a $n_O-\sigma^*_{YH}$ or $n_S-\sigma^*_{YH}$ dative bond involving the lone pairs of the chalcogen atom X and the antibonding σ^*_{YH} molecular orbital, and another associated with the electrostatic interactions between the two chalcogen charge distributions. To estimate the magnitude of the electrostatic interaction, we evaluated the net atomic charges on both chalcogen atoms by NBO analysis[27]. Assuming a point-charge model in which the charges are located at the corresponding nuclei, we used these values to estimate the interaction energy between them. To estimate the strength of the $n_O-\sigma^*_{YH}$ or $n_S-\sigma^*_{YH}$ dative bond, we evaluated the corresponding orbital interaction by second-order NBO analysis.[27] Although the interaction energies thus obtained cannot be taken as an absolute measure of the electrostatic or covalent interactions, they allow us to estimate their relative importance in stabilizing the system (Table 3).

The first obvious consequence of protonation on X to yield the ***cdH***$^+$ species is a decrease in the donor ability of X. Consequently, there is a systematic decrease in the dative contribution to the chalcogen–chalcogen interaction, which is more pronounced for Te-containing species (Table 3). This is reflected, as mentioned above, in an increase in the X···Y distance and a shortening of the Y–H (Y = Se, Te) bond on going from the neutral to the protonated form (see Figure 1 and Figure 2). Hence, the Y–H stretch is blue-shifted (Table 4), and the charge density at the Y–H bcp increases (see Table 2). As expected the C–X stretching frequency is red-shifted on protonation.

Species ***cdH***$^+$ can be also viewed as the protonated form of ***c***-type neutral structures, in which the chalcogen–chalcogen interaction is repulsive.[10] In this case protonation renders this interaction attractive, because the formation of a Y–H bond makes possible the existence of a $n_X-\sigma^*_{YH}$ dative bond that cannot exist in the neutral form. In agreement with this, on

Table 3. Changes[a] in the electrostatic and covalent contributions [kJ mol^{-1}] to the chalcogen–chalcogen interaction on going from ***d***-type neutral species to ***cdH***$^+$-type protonated forms.

X = O, Y = Se		X = S, Y = Se		X = O, Y = Te		X = S, Y = Te	
Electrostatic	Dative	Electrostatic	Dative	Electrostatic	Dative	Electrostatic	Dative
−8	+10	+7	+2	−6	+38	+7	+62

[a] These changes were evaluated by subtracting from the value obtained for the protonated species the value obtained for the corresponding neutral compound. Since the interactions are attractive (negative) a positive sign indicates that the stabilizing effect decreases on protonation.

Table 4. Harmonic vibrational frequencies [cm^{-1}] of relevant vibrational modes of *β*-chalcogenovinyl(thio)aldehydes (X = O, S; Y = Se, Te) and their protonated forms.

Tautomer	X–H stretch	Y–H stretch	C–X stretch	C–Y stretch	X···Y stretch
OSe*a*	2889	–	1375	718	213
OSe*aH*$^+$	3732	2424	1398	661	134
OSe*b*	–	2326	1718	602	168
OSe*bH*$^+$	3757	2420	1542	637	168
OSe*d*	–	2304	1721	640	134
OSe*cdH*$^+$	3757	2386	1540	684	144
SSe*a*	1991	–	784	649	148
SSe*aH*$^+$	2690	2382	770	614	126
SSe*b*	–	1909	1151	615	129
SSe*bH*$^+$	2684	2387	800	606	125
SSe*d*	–	2237	1137	614	131
SSe*cdH*$^+$	2689	2373	801	618	118
OTe*a*	3077	–	1401	585	180
OTe*aH*$^+$	3691	2094	1520	536	90
OTe*b*	–	2078	1741	464	140
OTe*bH*$^+$	3776	2106	1516	513	141
OTe*d*	–	1876	1630	588	171
OTe*cdH*$^+$	3775	2060	1495	584	132
STe*a*	2128	–	762	549	139
STe*aH*$^+$	2667	2084	1147	523	100
STe*b*	–	2084	1141	439	124
STe*bH*$^+$	2691	2102	1017	496	119
STe*d*	–	1820	886	550	149
STe*cdH*$^+$	2696	2071	997	538	100

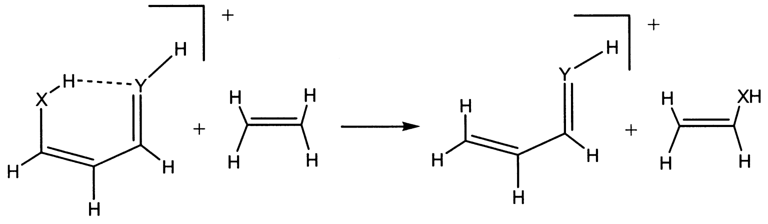
going from structures ***c*** to ***cdH***$^+$, the X$\cdots$Y distance decreases significantly, with the sole exception of the **SSe**, for which it increases very slightly (Figure 2), and the Y–H bond is slightly shorter than in the corresponding neutral form ***d***, because the $n_X-\sigma^*_{YH}$ donor interaction is weaker in the *X*-protonated species. These results seem to confirm that the stabilizing $n_X-\sigma^*_{YH}$ dative bonding only takes place from the lone pairs of the most electronegative chalcogen atom X to the σ^*_{YH} antibonding molecular orbital involving the less electronegative chalcogen atom Y.

In the S-containing compounds, the electrostatic term becomes repulsive rather than attractive due to the significant charge redistribution caused by protonation (Table 3), which also contributes to weakening of the chalcogen–chalcogen interaction.

The first conclusion of this analysis is that the existence of the chalcogen–chalcogen interaction leads to a lower intrinsic basicity than expected for these compounds in the absence of such an interaction, since its stabilizing effect is lower for the protonated than for the neutral species.

Effect of protonation on the strength of the IHBs: Protonation of structures ***a*** and ***b*** to yield ***aH***$^+$ and ***bH***$^+$ also involves weakening of the corresponding IHBs. This is mirrored in decreased charge density at the corresponding bcp (see Table 2) and in a blue shift of the X–H and Y–H stretching frequencies on going from the neutral to the protonated forms (see Table 4). To quantify these effects we can estimate the strength of XH$\cdots$Y relative to X$\cdots$HY IHBs by means of isodesmic reactions [Eqs. (1) and (2)]. The corresponding calculated energies, obtained at the G2(MP2) level, are summarized in Table 5.

The systematic endothermicity of both reactions reflects the stabilizing effect of the X–H$\cdots$Y and the X$\cdots$H-Y IHBs, as was also found for the neutral species.[10] However, while the ***a***-type forms of the neutral compounds have a stronger IHB than the ***b*** tautomers,[10] for the corresponding protonated species the opposite holds, and ***aH***$^+$ species have a weaker IHB than ***bH***$^+$-type structures. For instance, the Se–H bond shortens by only 0.005 Å on going from **OSe*b*** to **OSe*bH***$^+$, and its stretching frequency is blue-shifted by 94 cm^{-1}, while the O–H bond length decreases by 0.039 Å and its stretching frequency increases by 843 cm^{-1} on going from **OSe*a*** to **OSe*aH***$^+$.


(1)

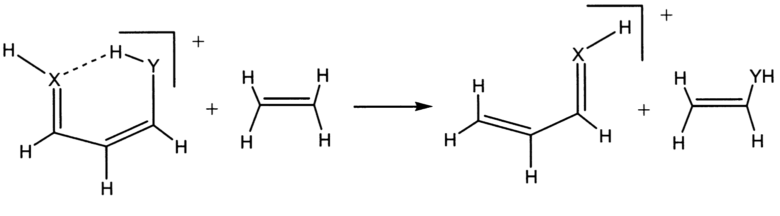

(2)

Table 5. Energies [kJ mol^{-1}] of the isodesmic reactions [Eq. (1) and (2)] evaluated at the G2(MP2) level of theory.

Y = Se				Y = Te			
X = O		X = S		X = O		X = S	
Eq. (1)	Eq. (2)	Eq. (1)	Eq. (2)	Eq. (1)	Eq. (2)	Eq. (1)	Eq. (2)
41	58	43	47	28	74	39	66

The fact that ***cdH***$^+$ is always the most stable protonated structure seems to indicate that for Se-containing compounds the destabilization of the IHBs on going from ***a*** to ***aH***$^+$ is, in relative terms, larger than the destabilization of the chalcogen–chalcogen interaction on going from ***d*** to ***cdH***$^+$. This plays an important role in the intrinsic basicities of these compounds (vide infra).

Proton affinities: In estimating the proton affinity (PA) of the Se compounds it must be taken into account that the most stable neutral form is of type ***a***, which cannot yield the most stable ***cdH***$^+$ structure by direct protonation. Hence, we estimated the activation barrier for conversion of ***aH***$^+$ and ***cdH***$^+$ structures by internal rotation about the O–H or S–H group. The values of 34 (X = O) and 60 kJ mol^{-1} (X = S) are high enough that such an isomerization should not take place under normal experimental conditions. Under these circumstances β-selenovinyl(thio)aldehydes HC(=X)–CH=CH–CSeH (X = O, S) would behave as selenium bases in the gas phase, and their proton affinities (823 and 854 kJ mol^{-1}, respectively; see Table 6) would be given by the enthalpy difference between the corresponding ***aH***$^+$ and ***a*** forms. Nevertheless, since the energy gap between the neutral forms ***a*** and ***d*** is only 5 kJ mol^{-1}, the possible presence of some ***d***-type isomers in the gas phase cannot be excluded, and therefore some ***cdH***$^+$-type protonated species could be produced on protonation. In such a case the proton affinity calculated from the enthalpies of ***cdH***$^+$ and ***d*** structures would be much higher (858 and 874 kJ mol^{-1}, respectively). Conversely, both HC(=X)–CH=CH–CTeH (X = O, S) compounds, for which the ***d*** form is the most stable neutral structure, would behave as oxygen or sulfur bases in the gas phase, with corresponding PAs of 852 and 856 kJ mol^{-1}, respectively. There is good agreement between the B3LYP/6-311+G(3df,2p) and G2(MP2) calculated values, although the former systematically exceed the latter by 8 kJ mol^{-1} on average.

In summary, if only the most stable neutral conformer were present in the gas phase, the selenium compounds would behave as selenium bases, while the corresponding Te-containing analogues would behave as oxygen and sulfur bases. In this respect the experimental measurement of the PAs of the

Table 6. Proton affinities[a] [kJ mol^{-1}] associated with two different protonation processes.

	X = O, Y = Se		X = S, Y = Se		X = O, Y = Te		X = S, Y = Te	
Process	B3LYP	G2(MP2)	B3LYP	G2(MP2)	B3LYP	G2(MP2)	B3LYP	G2(MP2)
a → ***aH***$^+$	**823**	**812**	**854**	**844**	848	838	876	867
d → ***cdH***$^+$	858	847	874	866	**852**	**846**	**856**	**845**

[a] Bold type denotes the PA associated with the most stable neutral species.

selenium bases would provide a useful information on the relative stability of the neutral conformers, since ***a***-type species, according to our estimates, should have a much lower intrinsic basicity than ***d***-type structures.

For protonation processes leading to ***cdH***$^+$ structures, the values in Table 6 show that the intrinsic basicity of the O or the S atom depends only slightly on the nature of the chalcogen atom Y, and the largest difference is 18 kJ mol^{-1}. However, quite unexpectedly, the intrinsic basicity of the ***d*** forms of Se compounds is larger than that of the corresponding Te-containing analogues, in spite of the fact that the donor ability of the O and S atoms of the latter should be greater due to the lower electronegativity of Te relative to Se. This can be explained by the fact that the chalcogen – chalcogen interaction is particularly strong for Te-containing compounds, and the relative decrease in its strength on protonation is also greater for Te compounds. In fact, on going from **OSe*d*** to **OSe*cdH***$^+$ the Se ⋯ O distance increases by 0.154 Å, while on going from **OTe*d*** to **OTe*cdH***$^+$ this increase (0.351 Å) is more than twice as large. In any case, our results indicate that, as was found before for carbonyl and thiocarbonyl compounds,[28] sulfur compounds are stronger bases than oxygen compounds.

Gas-phase acidities: The structures of the anions formed by loss of a proton attached to a chalcogen atom are also included in Figure 1 and Figure 2. Their total and relative energies are listed in Table 1, and the corresponding acidities are summarized in Table 7. Neutral conformers ***a*** – ***c*** yield a common anion (conformer **XY**$^-$(**1**)) upon deprotonation, although due to the repulsion between the electron pairs of X and Y, the two conformers **XY**$^-$(**2**) and **XY**$^-$(**3**) are systematically more stable by 32 – 40 kJ mol^{-1} (see Table 1). Conformers **XY**$^-$(**2**) and **XY**$^-$(**3**) can be viewed as the result of an internal rotation of the −CHX and −CHY groups of **XY**$^-$(**1**), respectively. For Se compounds, these processes involve significant activation barriers (X = O: 73 and X = S: 104 for **XY**$^-$(**1**) → **XY**$^-$(**2**); X = O: 123 and X = S: 149 kJ mol^{-1} for **XY**$^-$(**1**) → **XY**$^-$(**3**); see Table 1). Similar values were obtained for the corresponding Te-containing compounds (see Table 1).

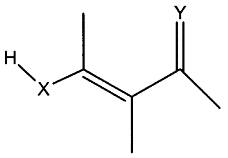
Alternatively, **XY**$^-$(**2**) and **XY**$^-$(**3**) can also be formed by a direct deprotonation of the neutral conformers ***e*** – ***h***, but these neutral forms are higher in energy (7 – 56 kJ mol^{-1})[10] than the corresponding global minimum (***a*** or ***d***).

Table 7. Gas-phase acidities[a] [kJ mol^{-1}].

X = O, Y = Se	X = S, Y = Se	X = O, Y = Te	X = S, Y = Te
1391	1375	1399	1355

[a] Values obtained at the B3LYP/6 – 311 + G(3df,2p) level for deprotonation of the most stable neutral species.

Hence, we can conclude that, under normal experimental conditions, only the conformer **XY**$^-$(**1**) should be observed. However, since for Se compounds the most stable neutral conformer (***a*** type) is stabilized by an X−H ⋯ Se (X = O, S) IHB, which is lost in the deprotonation process, these compounds should exhibit a lower intrinsic acidity than expected in the absence of this IHB.



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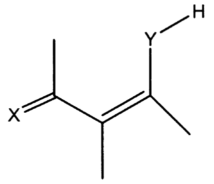

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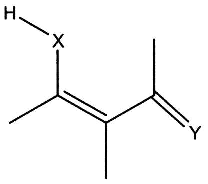

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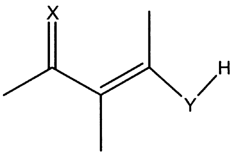

h

X = O, S
Y = Se, Te

For Te compounds the situation is different, since the most stable neutral conformer is stabilized by an $\mathrm{X}\cdots\mathrm{Te}^{*}_{\mathrm{YH}}\mathrm{H}$ chalcogen – chalcogen interaction. The X ⋯ Te distances in the anion show that on deprotonation the chalcogen – chalcogen interaction becomes repulsive rather than attractive. This is confirmed by the fact that in the anion no X ⋯ Te bcp is found. Furthermore, analysis of the X ⋯ Te interaction in terms of electrostatic and dative contributions shows that the latter disappear while the former become repulsive. This implies that all these compounds will also exhibit a lower acidity than expected in the absence of these chalcogen – chalcogen interactions.

As it was also found for the proton affinities, the calculated acidities do not depend much on the nature of the chalcogen atom Y involved. However, the sulfur compounds are systematically stronger acids in the gas phase than the oxygen-containing analogues.

Conclusion

Our results show that selenovinylaldehyde and selenovinylthioaldehyde should behave as Se bases in the gas phase, because the most stable neutral conformer is stabilized by an

X–H···Se (X = O, S) IHB. In contrast the corresponding Te-containing analogues behave as oxygen or sulfur bases, because the most stable conformer is stabilized by typical X···Y–H chalcogen–chalcogen interactions. Nevertheless, for all Se and Te compounds the ***cdH***$^+$ protonated conformer, which exhibits an X···YH chalcogen–chalcogen dative bond, is more stable than those stabilized by X–H···Y (***aH***$^+$) or X···H–Y (***bH***$^+$) IHBs. Owing to the high tautomerization barriers between ***aH***$^+$ and ***cdH***$^+$ structures for Se compounds, only the former should be observed in the gas phase under normal experimental conditions. The presence of chalcogen–chalcogen interactions or IHBs is responsible for the low basicity of these species, since all these interactions become weaker in the protonated forms. Similarly, all of them are weaker acids than expected, because deprotonation results in an anion that is significantly destabilized relative to the neutral compound. Loss of a proton from the X–H or Y–H groups is a much more favorable process than from the C–H groups. Therefore, for Se compounds the deprotonation process implies the disappearance of the X–H···Se (X = O, S) IHB present in the most stable neutral conformer, while for Te-containing compounds the stabilizing X···Y–H chalcogen–chalcogen interaction present in the most stable neutral conformer becomes repulsive in the corresponding anion.

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