

Hydrogen Bonds of C=S, C=Se and C=Te with C-H in Small-Organic Molecule Compounds Derived from the Cambridge Structural Database (CSD)

Dikima D. Bibelayi¹, Albert S. Lundemba¹, Philippe V. Tsalu², Pitchouna I. Kilunga¹, Jules M. Tshishimbi¹, Zéphirin G. Yav^{1*}

¹Department of Chemistry, University of Kinshasa, Kinshasa, The Democratic Republic of Congo

²Austrian Institute of Technology, Vienna, Austria

Email: *zgyav@yahoo.fr

How to cite this paper: Bibelayi, D.D., Lundemba, A.S., Tsalu, P.V., Kilunga, P.I., Tshishimbi, J.M. and Yav, Z.G. (2022) Hydrogen Bonds of C=S, C=Se and C=Te with C-H in Small-Organic Molecule Compounds Derived from the Cambridge Structural Database (CSD). *Crystal Structure Theory and Applications*, 11, 1-22.

<https://doi.org/10.4236/csta.2022.111001>

Received: October 13, 2021

Accepted: December 20, 2021

Published: December 23, 2021

Copyright © 2022 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Considerable interest in hydrogen bonding involving chalcogen has been growing since the IUPAC committee has redefined hydrogen bonding. Not only the focus is on unconventional acceptors, but also on donors not discussed before. It has been mentioned in previous studies that the proton of the H-C group could be involved in hydrogen bonding, but with conventional acceptors. In this study, we explored the ability of hydrogen bond formation of Se, S and Te acceptors with the H-C donor using Cambridge Structural Database in conjunction with *Ab Initio* calculations. In the CSD, there are respectively 256, 6249 and 11 R₁,R₂-C=Se, R₁,R₂-C=S and R₁,R₂-C=Te structures that form hydrogen bonds, in which the N,N groups are majority. Except for C=S acceptor which can form a hydrogen bond with its C, C group, both C=Se and C=Te acceptors could form a hydrogen bond only with N,C and N,N groups. CSD analysis shows very similar *d* (norm) around -0.04 Å, while DFT-calculated interaction for N,C and N,N groups are also similar. Both interaction distances derived from CSD analysis and DFT-calculated interaction energies demonstrate that the acceptors form stable complexes with H-CF₃. Besides hydrogen bonds, dispersion interactions are forces stabilizing the complexes since their contribution can reach 50%. Analysis of intra-molecular geometries and *Ab Initio* partial charges show that this bonding stems from resonance induced C^{δ+}=X^{δ-} dipoles. In many respects, both C=Se, C=S and C=Te are similar to C=S, with similar *d* (norm) and calculated interaction strengths.

Keywords

Hydrogen Bond, Cambridge Structural Database Survey, Frequency of Occurrence (FoO), *Ab Initio* Calculation, Interaction Geometry and Energy

1. Introduction

Selenium, sulphur and tellurium, of respectively atomic numbers 34, 16 and 52 are chalcogens and share properties with oxygen and polonium, all of which have six valence electrons, although oxygen is sometimes excluded from the collective term “chalcogen”. The importance of chalcogen is known and has been demonstrated [1]-[8]. Significant interest in hydrogen bonding involving chalcogen has been growing since the IUPAC committee has redefined hydrogen bonding. Not only the focus is on unconventional acceptors, but also on donors not discussed before. It has been mentioned in previous studies [9] [10] that the proton of the H-C group could be involved in hydrogen bonding, but with conventional acceptors.

Hydrogen bonding of divalent chalcogens compounds has also been studied computationally [11] [12] [13].

Due to the importance of both inorganic and organic chalcogens, we are embarking on a series of studies of the structural chemistry of small-molecule Se, S and Te compounds, with an emphasis on their intermolecular interactions in crystal structures. In this paper, we report a general survey of both three chalcogens in small-molecule crystal structures, before examining the ability of them to accept H-C hydrogen bonds in $[(\text{NH}_2)_2\text{-C}=\text{X}]$, $[(\text{NH}_2)\text{-C}=\text{C}=\text{X}]$, and $[(\text{C})_2\text{-C}=\text{X}]$ models. This work builds on earlier studies of the hydrogen-bonding ability of analogous C=Se and C=S acceptors with O-H and N-H donors [14]. Surveys and analyses of the Cambridge Structural Database [15] [16] have been used in conjunction with *Ab Initio* and DFT calculations of model systems using Gaussian 09 [17] to probe hydrogen bonding in terms of structure, energetics and electrostatics.

2. Methodology

2.1 CSD Analysis

We performed the CSD analysis using an analogous approach to that outlined elsewhere [14] using CSD version 5.41 (November 2019) including the November data update, which has a total of 1,034,174 structural entries. Geometric parameters (d distance, ρ , ϕ and θ angles) for intermolecular interactions between H-bond acceptors (C=Se/S/Te) and donors (QA) were performed according to **Figure 1**.

In addition, we calculated the van der Waals normalized hydrogen-bond distances d (norm) to explore the bond-strength bond-length relationship according to the Equation (1):

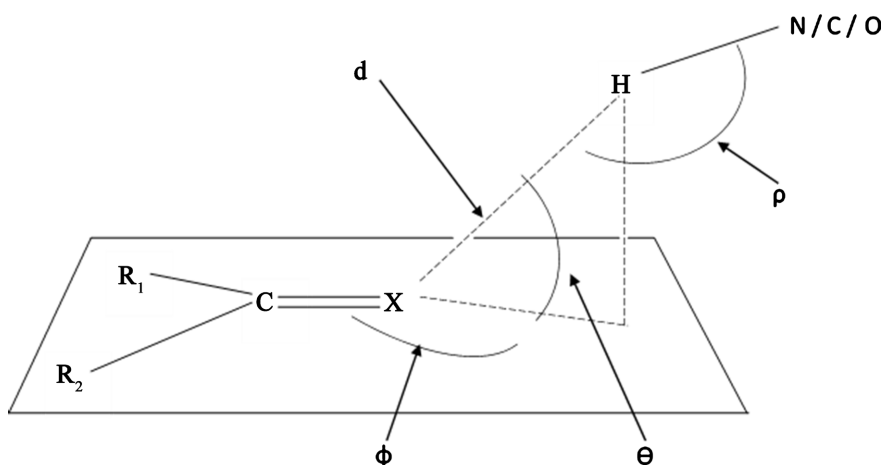


Figure 1. Schematic illustration of electron delocalisation in N,R-C=X (R = C or N; X=S, Se or Te) systems.

$$d(\text{norm}) = d - \text{vdW}(\text{H}) - \text{vdW}(\text{X}) \quad (1)$$

where d is the hydrogen bond distance, H and X are respectively the hydrogen and acceptor atoms, $\text{vdW}(\text{H})$ and $\text{vdW}(\text{X})$ are the van der Waals radii of the H and acceptor atoms respectively.

2.2. Computational Studies

To complement the database results, a series of calculations were carried out with the density-functional theory (DFT) method using Gaussian 09 [17]. The B3LYP [18] [19] [20] three-parameter hybrid functional and the B3LYP augmented with the D3 dispersion correction [21] were used with the basis set of 6-311++G(3df,2p). Use of this large basis set should minimize the problem of correction for the basis set superposition error [22] [23] [24]. Both approaches were used to calculate atomic partial charges, molecular electrostatic potentials and energies of interaction, but also to perform NBO analysis.

The electrostatic potential $V(r)$ in the space around a molecule, created by the electrons and nuclei at any point r , was calculated according to the Equation (2), written in atomic units, a.u.:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (2)$$

Z_A and $\rho(r)$ are, respectively, the charge on nucleus A located at distance R and the electronic density of the molecule. $|R_A - r|$ and $|r' - r|$ respectively represent the nucleus distance from r , the distance of each electronic charge increment $\rho(r') dr'$ from r .

Interaction energies were calculated for the interactions of trifluoro-methane molecules with the hydrogen bonding acceptors $R_1, R_2\text{-C=X}$, where $R = \text{CH}_3\text{CH}_2$ or NHCH_3 according to equation (3), as difference between the energy of the complex (E_{complex}) and the sum of the energies of the isolated h-bond donor (E_{donor}) and acceptor (E_{acceptor}) using optimised geometries:

$$E_{\text{int}} = E_{\text{complex}} - (E_{\text{donor}} + E_{\text{acceptor}}) \quad (3)$$

E_{complex} , E_{donor} , and E_{acceptor} are the energy minima at 0 K.

Vibrational analysis was also performed calculated with all DFT levels of theory to determine true minima and saddle points of different orders.

3. Initial Survey of Se Compounds in the CSD

We start with a brief overview of compounds containing the three chalcogens X (X = Se/S/Te) of CSD. The complete CSD (all inputs, without secondary filters applied) contains 13,787/208,565/5221 compounds of Se/S/Te which, 5692 (41.29%)/94421 (45.27%)/2858 (54.74%) are organic and, 8095 (58.71%)/114,144 (54.73%)/2363 (45.26%) are metallo-organic complexes respectively. When the secondary search criteria of Section 2.1 are applied, the total falls to 8625/128,636/3397 structures containing Se/S/Te which 4248 (49.25%)/68,890 (53.55%)/2052 (60.41%) are organic and 4377 (50.75%)/59,746 (46.45%)/1345 (39.59%) are organometallic. Among the Se/S/Te compounds that are classified as organic, we find respectively 7352/121,426/2874 independent selenium, sulphur and tellurium atoms (some structures contain X atoms in an environment of more than one coordination): 957 (22.53%)/10,818 (15.68%)/71(3.46%) structures are mono-coordinates Se (Se¹)/S (S¹)/Te (Te¹), 2840 (66.85%)/32,951 (47.83%)/582 (28.36%) Se²/S²/Te², 422 (9.93%)/5089 (7.39%)/369 (17.98%) Se³/S³/Te³, 226 (5.32%)/25,393 (36.86%)/ 687 (33.48%) Se⁴/S⁴/Te⁴, 24 (0.56%)/19 (0.03%)/174 (8.48%), Se⁵/S⁵/Te⁵, 31 (0.73%)/ 134 (0.19%)/258 (12.57%), Se⁶/S⁶/Te⁶, 0 (0.0%)/0 (0.0%)/11 (0.54%) Se⁷/S⁷/Te⁷ and one (0.0%)/1 (0.02%)/8 (0.39%) are, Se⁸/S⁸/Te⁸. Both three chalcogens can exist in -2, +2, +4, and +6 oxidation states, and the highest coordination type is taken from the highest of these states.

There are 890/10,348/38 structures containing 1254/14,226/49 fragments of Z = Se/S/Te in the CSD, where Z = any atom attached to the acceptor, (67/470/33 others structures have negatively charged mono-coordinated Se, S and Te atoms of the Z-Se-/Z-S-/Z-Te-type). In the Z = X subset, 420 (33.49%)/11,298 (79.42%)/14 (28.57%) fragments are C=Se, C=S and C=Te respectively, 808 (64.43%)/2843 (19.98%)/23 (46.94%) are P=Se, P=S and P=Te respectively, and in the 26 (2.07%)/85 (0.60%)/12 (24.49%) remaining Se/S/Te fragments, Z = Si, S, As or Te.

In the present work, we are concerned with organo-selenium (ii) compounds and therefore, we concentrate on those compounds featuring mono-coordinate Se atoms in C=Se/S/Te bonds. Preliminary analysis using *ConQuest* showed that the Se acceptors in the C=Se/S/Te subsets routinely form hydrogen bonds with N-H, O-H and C-H donors.

4. Intramolecular Geometry of the Systems R₁,R₂-C=Se, R₁,R₂-C=S and R₁,R₂-C=Te

In CSD there are 15 different combinations of R₁ and R₂ bonded to C=Se. There are 21 and 3 respectively for C=S and C=Te. For C=Se, 7 combinations have N

substituents, we can count 9 and 3 for C=S and C=Te respectively. The vast majority of these combinations have three-coordinate nitrogen atoms (N^3), however, only two combinations (N^3 with N^3 and N^3 with C) are common to all three chalcogens. The average bond lengths for these subgroups are collected in **Tables 1-3** together with the data for $R_1 = C$, and $R_2 = C$.

Tables 1-3 generally show that the average lengths of the C=X and C-N bonds vary with the R_1 and R_2 substituents, and also with the hybridization of the carbon atom. This tendency is also presented by C=O acceptors [25] [26]. The length of the C=X bond increases in the sequence $C^4, C^4-C=X < N^3, C^4-C=X < N^3, C^3-C=X < N^3, N^3-C=X$. The average C-N bond is longer for N,N-C=X than for

Table 1. Mean bond lengths d (in Å) for subgroups of R_1, R_2 in $R_1, R_2-C=Se$ systems with standard deviations in parentheses. N_f is the number of fragments contributing to the average.

$R_1, R_2-C=Se$				
R_1	R_2	N_f	C=Se	C-N
N	N	261	1.841 (0.022)	1.352 (0.018)
N^3	N^3	252	1.841 (0.022)	1.352 (0.018)
N	C	97	1.830 (0.018)	1.323 (0.025)
N^3	C^3	71	1.832 (0.017)	1.322 (0.026)
N^3	C^4	23	1.819 (0.019)	1.329 (0.016)
C	C	3	1.796 (0.026)	–
C^3	C^3	2	1.808 (0.024)	–
C^4	C^4	1	1.773	–

Table 2. Mean bond lengths d (in Å) for subgroups of R_1, R_2 in $R_1, R_2-C=S$ systems with standard deviations in parentheses. N_f is the number of fragments contributing to the average.

$R_1, R_2-C=S$				
R_1	R_2	N_f	C=S	C-N
N	N	5994	1.678 (0.014)	1.352 (0.015)
N^3	N^3	5743	1.677 (0.014)	1.352 (0.015)
N	C	1602	1.662 (0.021)	1.341 (0.027)
N^3	C^3	1010	1.666 (0.019)	1.344 (0.028)
N^3	C^4	553	1.656 (0.021)	1.336 (0.022)
N^2	C^3	32	1.675 (0.018)	1.342 (0.028)
C	C	183	1.665 (0.036)	–
C^3	C^3	123	1.673 (0.029)	–
C^3	C^4	46	1.660 (0.038)	–
C^4	C^4	14	1.607 (0.020)	–

Table 3. Mean bond lengths d (in Å) for subgroups of R_1, R_2 in $R_1, R_2-C=Te$ systems with standard deviations in parentheses. N_f is the number of fragments contributing to the average.

$R_1, R_2-C=Te$				
R_1	R_2	N_f	C=Te	C-N
N	N	10	2.070 (0.012)	1.358 (0.009)
N ³	N ³	10	2.070 (0.012)	1.358 (0.009)
N	C	3	2.056 (0.018)	1.316 (0.007)
N ³	C ³	2	2.062 (0.008)	1.313 (0.006)
N ³	C ⁴	1	2.045	1.322
C	C	-	-	-

N,C-C=X, consistent with the data for the C=O and C=S analogues [26] and as expected from the resonance model.

In relation with our earlier work [14] and the previous studies by Allen [25] and Blessing [27], we analyzed the variations in bond length within the N,N-C=X subset by plotting $d(C-N)$ vs $d(C=Se)$, $d(C=S)$ and $d(C=Te)$ in Figures 2-4 respectively. Negative correlations between the two variables are observed, but with lower correlation coefficients of -0.672 ; -0.704 ; and -0.593 respectively for selenium, sulphur and tellurium, compared to -0.752 and -0.771 reported by Allen [25] for ureas and thioureas respectively, but higher than the value of -0.645 [14] for selenoureas.

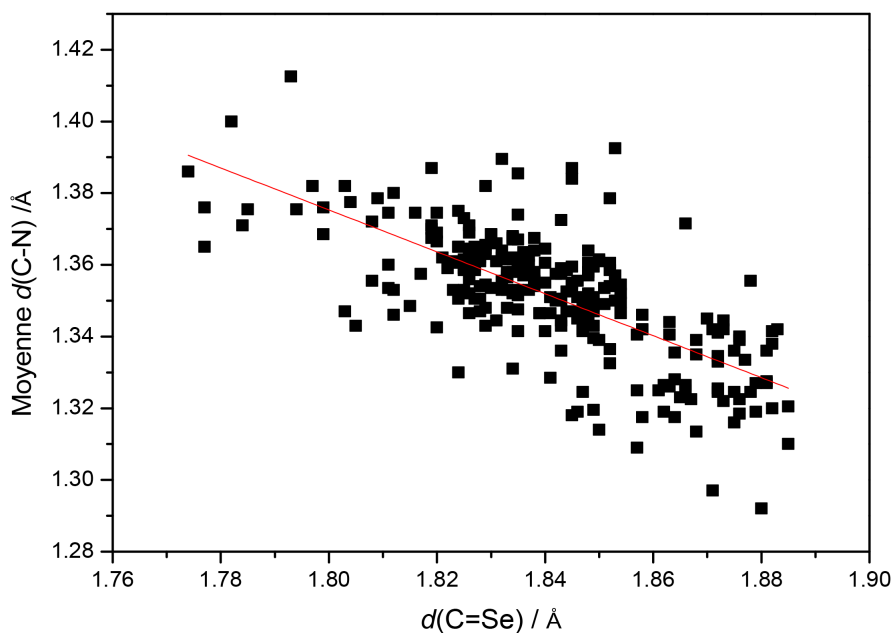


Figure 2. Plot of the average C-N bond length [AVE(C-N)] (Å) vs. the C=Se bond length (Å) in selenoureas in the CSD. The line indicates a linear fit showing a correlation coefficient of -0.672 , indicating some approximate relationship between the two quantities.

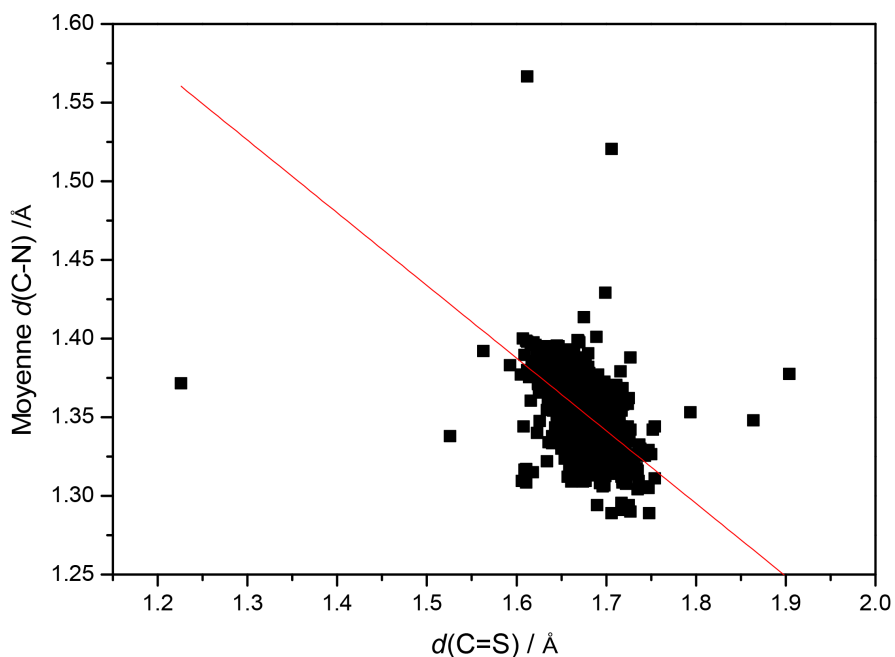


Figure 3. Plot of the average C–N bond length [AVE(C–N)] (Å) vs. the C=S bond length (Å) in thioureas in the CSD. The line indicates a linear fit showing a correlation coefficient of -0.704 , indicating some approximate relationship between the two quantities.

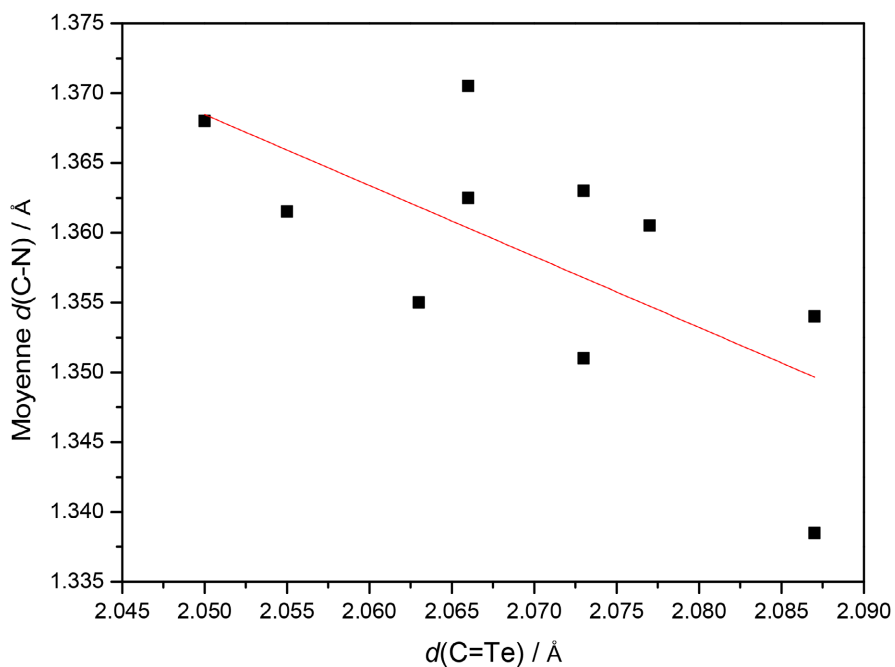


Figure 4. Plot of the average C–N bond length [AVE(C–N)] (Å) vs. the C=Te bond length (Å) in telluroreas in the CSD. The line indicates a linear fit showing a correlation coefficient of -0.593 , indicating some approximate relationship between the two quantities.

5. CSD Analyses of Hydrogen Bonding in C=X Acceptors

5.1. Occurrence of Hydrogen Bonds Involving C=S, C=Se and C=Te

An initial survey in the CSD showed that there are 7146 compounds $R_1, R_2-C=S$,

with R_1 and R_2 assigned as any type of atom (X), which formed hydrogen bonds with OH, NH or CH donors, and 6249 of these compounds formed hydrogen bonds with C-H. In all cases, one or both of R_1 , R_2 are three-coordinate nitrogen atoms. The overall frequency of occurrence (FoO) of hydrogen bond formation by C=S in CSD is 89.3% since we found 8002 structures in which a hydrogen bond to S could have been formed. The separate probability values for the structures of thioureas and thioamides, in which a hydrogen bond to S could have been formed, are quite different at 92.9% and 85.3% respectively. Of the 856 sulphur structures, where a hydrogen bond C=S...H is not formed, the available H donors bind to stronger acceptors in some cases, such as carbonyl and hydroxyl oxygen, in some others sulphur is involved in other types of interactions.

Furthermore, the equivalent frequencies of occurrence of hydrogen bond formation of the C=O analogues (urea and amide) were determined using CSD version 5.41 with an R-factor limit of 0.05. This resulted in overall FoO values of 94.3% and 94.8% respectively for the urea and amide analogues of C=O. Although these values are almost the same as those obtained for the C=Se compounds and less than of C=Te compounds, they should not be taken as an indication of the relative strengths of hydrogen bonds.

The CSD survey also showed that 278 compounds $R_1, R_2-C=Se$, with R_1 and R_2 assigned as any type of atom (X), formed hydrogen bonds with O-H, N-H and C-H donors, while there are 256 which formed with C-H donors. In all cases, one or both of R_1 , R_2 are three-coordinate nitrogen atoms. In a separate search, we found 300 crystal structures that also contained O-H, N-H or C-H donors, *i.e.*, structures in which a hydrogen bond to Se could have been formed. Thus, the overall occurrence frequency (FoO) of hydrogen bond formation by C=Se in CSD is 92.6%. The separate probability values for the structures of selenoureas and selenoamides, in which a hydrogen bond to Se could have been formed, are quite similar at 92.0% and 90.8% respectively. These results confirm that C=Se is an efficient hydrogen bond acceptor when Se is activated by resonance effects. Of the 22 selenium structures where a hydrogen bond C=Se...H does not form, the majority of available H donors bind to stronger acceptors, such as carbonyl and hydroxyl oxygen, or selenium is involved in other types of interactions.

Interestingly, there are 11 compounds $R_1, R_2-C=Te$, with R_1 and R_2 assigned as any type of atom (X) in CSD that have formed hydrogen bonds with O-H, N-H or C-H donors. All 11 compounds formed hydrogen bonds with C-H. One or both of R_1 , R_2 are three-coordinate nitrogen atoms. Crystal structures also containing OH, NH or CH donors in which a hydrogen bond to Te could have been formed are 11. Thus, the overall occurrence frequency (Fo) of hydrogen bond formation by C=Te in CSD is of 100%. The separate probability values for tellurourea and telluroamide structures, in which a hydrogen bond to Te could have been formed, are 100% and 100% respectively.

In the present work, we are concerned with hydrogen-bonding of C-H donors at the monovalent chalcogen atoms, since those bonds report marked values of

FoO. A similar study of the hydrogen-bonding of O-H and N-H donors will be reported shortly.

5.2. Hydrogen Bond Geometry

Tables 4-6 give geometric data for intermolecular hydrogen bonds with the acceptors C=Se, C=S and C=Te for C-H donors on the basis of the parameters defined in Figure 1. For comparison, the tables also report data for O-H and N-H.

Table 4. Mean geometry for hydrogen bonds from C-H, N-H and O-H donors to S acceptors in $R_1, R_2-C=S$ systems. N_f is the number hydrogen bonds, while the parameters and the parameters d , ρ , φ and θ are defined in Figure 3. All distances are in Å, while angles are in °. Mean values are presented with estimate standard deviations in parentheses.

R_1	R_2	Donor	N_f	d	$d(C=S)$	ρ	φ	θ
$\rho \geq 90^\circ$								
X	X	C	14,435	2.87 (0.10)	1.67 (0.02)	145 (16)	120 (27)	37 (24)
		N	6030	2.50 (0.17)	1.68 (0.02)	157 (15)	108 (12)	25 (22)
		O	760	2.40 (0.20)	1.69 (0.02)	156 (17)	103 (13)	37 (24)
$\rho \geq 120^\circ$								
X	X	C	13,477	2.87 (0.10)	1.67 (0.02)	147 (14)	119 (27)	37 (24)
		N	5873	2.49 (0.16)	1.68 (0.02)	158 (14)	107 (12)	25 (22)
		O	722	2.38 (0.17)	1.69 (0.02)	159 (14)	103 (13)	37 (24)
N	N	C	7850	2.86 (0.10)	1.68 (0.02)	147 (14)	119 (27)	38 (24)
		N	4834	2.49 (0.16)	1.69 (0.02)	159 (13)	108 (11)	25 (22)
		O	495	2.37 (0.17)	1.69 (0.02)	158 (14)	103 (12)	37 (23)
N^3	N^3	C	7468	2.86 (0.10)	1.68 (0.02)	147 (14)	119 (27)	38 (24)
		N	4691	2.49 (0.16)	1.69 (0.02)	159 (13)	108 (11)	25 (22)
		O	477	2.37 (0.17)	1.69 (0.02)	158 (14)	103 (12)	37 (23)
N	C	C	2132	2.87 (0.10)	1.66 (0.02)	146 (14)	119 (25)	37 (23)
		N	510	2.52 (0.16)	1.67 (0.02)	156 (15)	108 (12)	26 (22)
		O	65	2.37 (0.16)	1.68 (0.02)	159 (13)	103 (12)	37 (25)
N^3	C	C	2076	2.87 (0.10)	1.66 (0.02)	146 (14)	119 (25)	37 (23)
		N	506	2.52 (0.16)	1.67 (0.02)	156 (15)	109 (12)	26 (22)
		O	56	2.36 (0.19)	1.68 (0.02)	160 (12)	104 (10)	37 (25)
C	C	C	228	2.87 (0.10)	1.67 (0.03)	148 (15)	119 (27)	35 (23)
		N	27	2.45 (0.23)	1.69 (0.02)	156 (15)	104 (14)	31 (23)
		O	17	2.39 (0.19)	1.67 (0.02)	158 (18)	104 (17)	26 (20)
C^3	C^3	C	164	2.86 (0.10)	1.68 (0.03)	147 (15)	119 (27)	34 (23)
		N	24	2.45 (0.22)	1.69 (0.02)	156 (15)	104 (14)	32 (24)
		O	17	2.39 (0.19)	1.67 (0.02)	158 (18)	104 (17)	26 (20)

Table 5. Mean geometry for hydrogen bonds from C-H, N-H and O-H donors to Se acceptors in $R_1, R_2-C=Se$ systems. N_f is the number hydrogen bonds, while the parameters and the parameters d , ρ , φ and θ are defined in **Figure 3**. All distances are in Å, while angles are in °. Mean values are presented with estimate standard deviations in parentheses.

R_1	R_2	Donor	N_f	d	$d(C=Se)$	ρ	φ	θ
$\rho \geq 90^\circ$								
X	X	C	678	2.96 (0.09)	1.84 (0.02)	147 (16)	118 (27)	37 (24)
		N	250	2.65 (0.18)	1.86 (0.02)	152 (17)	103 (13)	34 (24)
		O	17	2.48 (0.19)	1.83 (0.02)	158 (17)	97 (8)	41 (25)
$\rho \geq 120^\circ$								
X	X	C	637	2.96 (0.10)	1.84 (0.02)	149 (14)	116 (26)	37 (23)
		N	236	2.63 (0.16)	1.86 (0.02)	154 (14)	103 (13)	33 (24)
		O	16	2.45 (0.15)	1.83 (0.02)	161 (11)	97 (8)	42 (26)
N^3	N^3	C	394	2.95 (0.10)	1.84 (0.02)	148 (14)	117 (26)	37 (24)
		N	172	2.64 (0.17)	1.86 (0.02)	155 (13)	101 (12)	37 (24)
		O	8	2.45 (0.11)	1.84 (0.02)	161 (5)	97 (10)	46 (24)
N	C	C	147	2.98 (0.09)	1.83 (0.02)	151 (15)	114 (25)	37 (24)
		N	53	2.60 (0.13)	1.84 (0.02)	152 (17)	107 (15)	26 (23)
		O	6	2.47 (0.20)	1.83 (0.02)	159 (18)	97 (8)	47 (24)
N^3	C	C	135	2.98 (0.09)	1.83 (0.02)	150 (15)	115 (25)	37 (24)
		N	53	2.60 (0.13)	1.84 (0.02)	152 (17)	107 (15)	26 (23)
		O	6	2.47 (0.20)	1.83 (0.02)	159 (18)	97 (8)	47 (24)

Table 6. Mean geometry for hydrogen bonds from C-H, N-H and O-H donors to Te acceptors in $R_1, R_2-C=Te$ systems. N_f is the number hydrogen bonds, while the parameters and the parameters d , ρ , φ and θ are defined in **Figure 3**. All distances are in Å, while angles are in °. Mean values are presented with estimate standard deviations in parentheses.

R_1	R_2	Donor	N_f	d	$d(C=Te)$	ρ	φ	θ
$\rho \geq 90^\circ$								
X	X	C	25	3.12 (0.13)	2.06 (0.02)	149 (15)	118 (26)	31 (22)
		N	-	-	-	-	-	-
		O	-	-	-	-	-	-
$\rho \geq 120^\circ$								
X	X	C	24	3.12 (0.13)	2.06 (0.02)	150 (14)	116 (25)	32 (22)
		N	-	-	-	-	-	-
		O	-	-	-	-	-	-
N	N	C	15	3.12 (0.14)	2.07 (0.01)	154 (12)	117 (24)	27 (23)
		N	-	-	-	-	-	-
		O	-	-	-	-	-	-
N^3	N^3	C	15	3.12 (0.14)	2.07 (0.01)	154 (12)	117 (24)	27 (23)

Continued

		N	-	-	-	-	-	-
		O	-	-	-	-	-	-
N	C	C	5	3.10 (0.16)	2.06 (0.01)	146 (19)	105 (18)	50 (19)
		N	-	-	-	-	-	-
		O	-	-	-	-	-	-
N ³	C	C	5	3.10 (0.16)	2.06 (0.01)	146 (19)	105 (18)	50 (19)
		N	-	-	-	-	-	-
		O	-	-	-	-	-	-

The first three rows of **Tables 4-6** show hydrogen bonds for all angles ρ , while the rest of the tables only consider those structures where $\rho \geq 120.0^\circ$, which is the recommended limit given by Wood [28]. Since the vast majority of the structures shown in these tables are those with N³ (three-coordinate N) and bonded to C-H donors, where the hydrogen bond angle $\rho \geq 120.0^\circ$, the following analysis and discussion are limited to those hydrogen bonds.

We can note that C=Se and C=S could form hydrogen bonds with O-H, N-H and C-H donors, but C=Te could form only with C-H donors. The average hydrogen bond distance (d) of C=Te acceptors in **Table 6** is approximately 0.16 Å and 0.25 Å longer than that of C=Se and C=S acceptors in **Table 4** and **Table 5** respectively, which is consistent with the larger van der Waals (vdW) radii of Te (2.06 Å) with respect to S (1.80 Å) and Se (1.90 Å) [29]. There is no significant difference between the hydrogen bond distances (d) observed in subgroups (N³, N³), and the subgroups (N³, C) for all acceptors. However, there is some indication that the hydrogen bond distances for CH...X interactions are longer than their NH...X and OH...X counterparts up to 0.33 Å and 0.51 Å respectively for selenium, 0.38 Å and 0.49 Å for sulphur. This situation has also been observed in previous studies of the C=S acceptor [25] [26] and C=Se acceptor [14]. This is an indication that the differences between the interaction energies between N-H and C-H donors could be greater than those between O-H and N-H donors.

An earlier comparative analysis of C = O and C = S acceptors [26] used standard van der Waals hydrogen bond distances, *i.e.*

$$d(\text{norm}) = d(\text{H bond}) - \text{vdW}(\text{H}) - \text{vdW}(\text{X}),$$

where X represents the acceptor atom (O or S) and vdW (X) is the vdW radius of this atom. The value of 1.10 Å determined by Rowland and Taylor [30] was used for vdW (H), while the values of 1.52 Å for vdW (O) and 1.80 Å for vdW (S) were taken from Bondi [29]. For hydrogen bonds from NH with oxygen O of ureido and sulphur S of thioureido, a large and homogeneous subgroup for both acceptors, $d(\text{norm})$ values were -0.692 Å and -0.449 Å for the acceptors C = O and C = S respectively, which clearly indicates that the hydrogen bonds formed with C = O are much stronger compared to those with C = S. Calculation of $d(\text{norm})$ using the d values of 2.95 Å for the Se...HC bonds of selenoureido, of 2.86 Å for the S...HC bonds of thio-

ureido and of 3.12 Å for the Te...HC bonds of telluroureido from **Tables 4-6**, vdW (S) = 1.80 Å [29], vdW (Se) = 1.90 Å [29] and vdW (H) = 1.10 Å [30], $d(\text{norm})$ gives -0.05 Å, -0.04 Å and -0.04 Å respectively for Se...HC, S...HC and Te...HC which values are lower than the values of -0.44 Å and -0.45 Å respectively for Se...HO and S...HO [14] [26]. Thus, we can deduce that the stabilization energy of both three acceptors C=X...H bonds should be similar with the CH donor.

The angular directionality parameters (ρ , φ and θ , **Figure 1**) for the C=X acceptors show remarkably similar mean values to each other. Thus, the angle on the donor atom of H is completely linear (ρ tends towards 180°). This is an expected behaviour for hydrogen bonds [28].

In addition, the tendency for the hydrogen bond donor vector (C-H) to approach X in the plane of the >C=X group is typical. The θ values in **Tables 4-6** show mean deviations of coplanarity around 37 (23)°, 37 (24)° and 32 (22)° respectively. The most interesting angle is φ , the angle at which the hydrogen atom approaches with respect to the C=X bond, for which the mean values of 116 (26)°, 119 (27)° and 116 (25)° are obtained for Se, S and Te acceptors respectively. These values, for the N-H and O-H donors, are slightly upper than those 103 (13)° and 97 (8) for selenium and than 107 (12)° and 103 (13)° for sulphur in **Table 4** and **Table 5**, and all of these values can be attributed to interactions between $\text{H}^{\delta+}$ and the lone pairs on the atoms of Se, S and Te. The finding that hydrogen bonding at C=Te acceptors shows directional properties like hydrogen bonding at C=Se and C=S, should also make Te atoms versatile tools to directing and controlling the structure of molecular systems, with consequences for the use in crystal engineering [9] [31] [32] [33] and its integration in pharmaceutical agents [34] [35] [36].

Furthermore, we note that intramolecular hydrogen bonds of acceptors N-C=Se, N-C=S and N-C=Te are formed in 216, 4533 and 9 structures respectively, with very variable geometries. Structures forming 5 to 8 membered hydrogen bond rings are observed. For these structures, the distances Se...H, S...H and Te...H vary from from 2.32 to 3.10 Å, 1.85 to 3.00 Å and from 2.75 to 3.25 Å respectively, but the hydrogen bond angles are significantly distorted from the intermolecular normal values discussed above by the constraints of ring formation: ρ values are in the ranges 79° - 174°, 76° - 178° and 86° - 156°, φ in the ranges 54° - 116°, 44° - 173° and 58° - 92° and θ in the ranges 0° - 30°, 0° - 83° and 1° - 62° respectively for Se, S and Te.

5.3. Hydrogen Bond Coordination

In the earlier comparative study by Allen [25], it was found that C=S and C=O normally accept one or two hydrogen bonds, but on rare occasions C=S accepts up to six hydrogen bonds, then C=O accepts up to five. This analysis was performed on all of the hydrogen bonds formed by the C=S or C=O acceptors at that time, and included both intramolecular and intermolecular hydrogen bonds. We performed a similar hydrogen bond coordination analysis of C=Se acceptors

[14] and we saw that the coordination values 1 (66.3%) and 2 (25.5%) were the norm, while the maximum hydrogen bond coordination observed for C=Se was 3. The hydrogen bond coordination analysis performed for Se and S acceptors with C-H, N-H and O-H donors shows that these chalcogens can form up to eight and nine bonds respectively for Se and S.

6. Computational Results

6.1. Atomic Point Charges and Molecular Electrostatic Potential of Systems $R_1, R_2-C=X$

Table 7 reports the Mulliken and NBO partial charges on the O atom in formaldehyde, formamide and urea and on the Se and S atoms in their Se and S analogues, calculated using a variety of different methods, as described in section 2.2. **Table 8** gives the Mulliken and NBO partial charges of Te.

The data in **Table 7** show the expected trends in the electronegativity induced by the resonance in O, Se and S. The negative partial charge of the O atom increases due to the resonance moving from formaldehyde to formamide, then to

Table 7. Mulliken and NBO atomic partial charges on O, S and Se in $R_1, R_2-C=X$ ($X=O, S$ or Se) calculated using various levels of theory.

R_1	R_2	$q(O)$		$q(S)$		$q(Se)$	
		Mulliken	NBO	Mulliken	NBO	Mulliken	NBO
HF/6-311++G(3df,2p)							
H	H	-0.634	-0.579	-0.162	0.047	0.039	0.119
NH ₂	H	-0.787	-0.700	-0.452	-0.229	-0.237	-0.214
NH ₂	NH ₂	-0.946	-0.765	-0.501	-0.364	-0.366	-0.356
MP2/6-311++G(3df,2p)							
H	H	-0.634	-0.590	-0.168	0.033	0.036	0.105
NH ₂	H	-0.783	-0.713	-0.441	-0.213	-0.215	-0.182
NH ₂	NH ₂	-0.933	-0.774	-0.478	-0.331	-0.342	-0.316
B3PW91/6-311++G(3df,2p)							
H	H	-0.499	-0.497	-0.121	0.085	0.033	0.155
NH ₂	H	-0.651	-0.608	-0.408	-0.138	-0.228	-0.106
NH ₂	NH ₂	-0.804	-0.670	-0.459	-0.264	-0.399	-0.256
B3LYP/6-311++G(3df,2p)							
H	H	-0.472	-0.501	-0.119	0.086	0.038	0.152
NH ₂	H	-0.625	-0.612	-0.398	-0.136	-0.209	-0.106
NH ₂	NH ₂	-0.778	-0.674	-0.456	-0.261	-0.385	-0.255
NH(CH ₃)	NH(CH ₃)	-0.763	-0.675	-0.443	-0.266	-0.414	-0.259

Table 8. Mulliken and NBO atomic partial charges on Te in R₁R₂-C=Te calculated using various levels of theory.

		q (Te)	
R ₁	R ₂	Mulliken	NBO
HF/3-21G			
CH ₃	CH ₃	+0.157	+0.085
CH ₃	NH ₂	-0.118	-0.245
NH ₂	NH ₂	-0.179	-0.316
HF/3-21G*			
CH ₃	CH ₃	-0.009	+0.110
CH ₃	NH ₂	-0.229	-0.212
NH ₂	NH ₂	-0.301	-0.319
B3LYP/3-21G			
CH ₃	CH ₃	+0.162	+0.143
CH ₃	NH ₂	-0.027	-0.100
NH ₂	NH ₂	-0.146	-0.248
MP2/3-21G			
CH ₃	CH ₃	+0.165	+0.096
CH ₃	NH ₂	-0.048	-0.168
NH ₂	NH ₂	-0.152	-0.288

urea, with both four theoretical levels and methods of calculating the partial charges, giving comparable results and trends. For Se and S with R₁ and R₂ as H atoms, the partial charges of the two atoms are quite small, in agreement with the similar electronegativities of Se, S and C. When we move to thioformamide and selenoformamide, then to thiourea and to selenourea, both Se and S have significant negative partial charges. These results and values are comparable to those previously reported for O and S by Allen [25] and for urea, thiourea and selenourea by Moudgil [37].

As for Te, the data in **Table 8** show the same expected trend of electronegativity induced by resonance on Te. Indeed, the partial charge of Te tends more and more towards the negative when R₁ and R₂ move from C and C to N and N via C and N.

As shown by the above results, the Mulliken partial charges have lower values than the general NBO loads in **Table 7**, while in **Table 8**, the NBO partial charges have lower values than the Mulliken partial charges. This behaviour reflects the different approaches to obtaining atomic charges in each method. Indeed, all the methods of calculating the atomic charge are necessarily arbitrary, since it is not a quantum mechanical observable. There is then no rigorous physical basis for assigning charges to atoms in molecules, because assigning a single

positive or negative value to each atom implicitly assumes that the charge distributions are spherical symmetrical [24].

The electrostatic potential has then been suggested as a significant representation of the electrostatic effects of molecular charge distribution [13].

Figure 5 shows the molecular electrostatic potential (MEP) for acetone, acetamide, urea and their selenium, sulphur and tellurium analogues. All molecules containing O exhibit a significant region of negative electrostatic potential, where the O atom will accept hydrogen bonds. For the Se, S and Te analogues, this region becomes more evident when the C atom bonded to the chalcogen has an N atom as a substituent. As previously reported for C=S [26], a marked fall-off in the negative charge density around Se and Te is observed in $(\text{CH}_3, \text{CH}_3)\text{-C=Se}$ and $(\text{CH}_3, \text{CH}_3)\text{-C=Te}$, and explains the lack of hydrogen bonds to C=Se and C=Te in crystal structures when carbon bound to chalcogen has C as substituents. MEPs for selenourea, thiourea and, more clearly, for telluourea also show a zone of positive electrostatic potential associated with the Se, S and Te atoms, which is directed outward along the C=Se, C=S and C=Te bonds suggesting the ability of chalcogen atoms to form both hydrogen bonds and positive hole-based bonds similar to sigma-hole interactions [24] [38] [39]. It was also found in chalcogen bonding in divalent Se, S and Te compounds [40] [41] [42] [43].

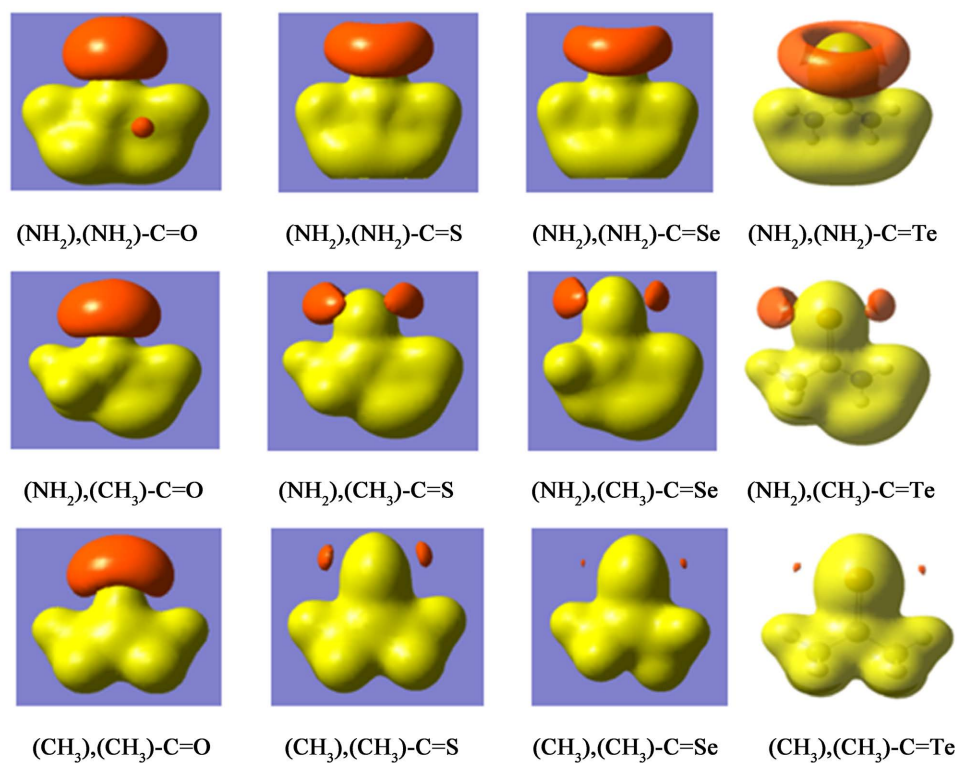


Figure 5. Molecular electrostatic potential (MEP) for acetone, acetamide and urea and their sulphur, selenium and tellurium analogues calculated using HF/6-311++G(3df,2p) for O, S, Se and B3LYP/3-21G for Te. Isovalue 0.04 u.a. Positive regions are in yellow, while negative regions are in orange.

6.2. Interaction Energies of Hydrogen Bonds to C=X Acceptors

DFT calculations were performed to determine the geometry and energy of interaction with trifluoro-methane as donors according to the scheme shown in **Figure 6**. The number of vibration frequencies (N_v) shows that all the complexes were true minima ($N_v = 0$).

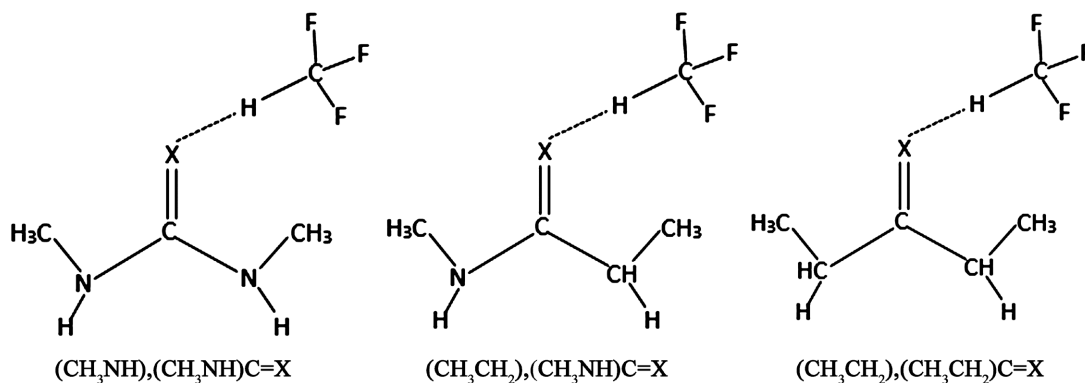


Figure 6. Model systems used for calculating hydrogen bond interaction energies of C=X acceptors with trifluoromethane.

Structural information from the CSD and electrostatic data from *Ab Initio* calculations suggest that the N-substituted C=Se acceptors should have hydrogen bond interaction strengths comparable to the corresponding C=S acceptors. **Table 9** and **Table 10** report the geometries and interaction energies (as defined in **Figure 1** and **Figure 6**) of the complexes $(\text{NHCH}_3, \text{NHCH}_3)\text{-C=Se}\cdots\text{H-CF}_3$ (**I1**), $(\text{NHCH}_3, \text{CH}_3\text{CH}_2)\text{-C=Se}\cdots\text{H-CF}_3$ (**I2**), $(\text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2)\text{-C=Se}\cdots\text{H-CF}_3$ (**I3**), $(\text{NHCH}_3, \text{NHCH}_3)\text{-C=S}\cdots\text{H-CF}_3$ (**II1**), $(\text{NHCH}_3, \text{CH}_3\text{CH}_2)\text{-C=S}\cdots\text{H-CF}_3$ (**II2**) and $(\text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2)\text{-C=S}\cdots\text{H-CF}_3$ (**II3**) calculated with both B3LYP (EintB3LYP) and B3LYP-3D (EintB3LYP-3D). We were unable to calculate the interaction energies of the acceptor Te due to the failure of calculations.

The methyl groups of the substituents were placed *cis* at the Y-H \cdots X interaction to avoid an interaction between the N-H and the donor molecule, after which all three systems were able to relax completely.

The results of **Table 9** and **Table 10** show that the interaction strength C=Se

Table 9. Values of total interaction energy (E_{int}) and geometric parameters d , φ and ρ for C-H \cdots Se=C hydrogen bonds in N,N-, N,C- and C,C-disubstituted systems, as calculated using B3LYP/6-311++G(3df,2p) and B3LYP-GD3/6-311++G(3df,2p).

		C-H \cdots Se=C							
R ₁	R ₂	B3LYP/6-311++G(3df,2p)				B3LYP-GD3/6-311++G(3df,2p)			
		d (Å)	φ (°)	ρ (°)	E (kJ/mol)	d (Å)	φ (°)	ρ (°)	E (kJ/mol)
NH(CH ₃)	NH(CH ₃)	2.86	89	158	-14.30	2.88	73	146	-27.76
NH(CH ₃)	CH ₃ CH ₂	2.89	118	166	-12.16	2.82	113	165	-22.37
CH ₃ CH ₂	CH ₃ CH ₂	2.98	105	162	-9.81	2.89	99	161	-20.45

Table 10. Values of total interaction energy (E_{int}) and geometric parameters d , φ and ρ for C–H...S=C hydrogen bonds in N,N-, N,C- and C,C-disubstituted systems, as calculated using B3LYP/6-311++G(3df,2p) and B3LYP-GD3/6-311++G(3df,2p).

		C–H...S=C							
R_1	R_2	B3LYP/6-311++G(3df,2p)				B3LYP-GD3/6-311++G(3df,2p)			
		d (Å)	φ (°)	ρ (°)	E (kJ/mol)	d (Å)	φ (°)	ρ (°)	E (kJ/mol)
NH(CH ₃)	NH(CH ₃)	2.75	77	145	-14.29	2.75	77	145	-27.04
NH(CH ₃)	CH ₃ CH ₂	2.76	123	167	-12.55	2.67	118	165	-22.32
CH ₃ CH ₂	CH ₃ CH ₂	2.83	109	163	-5.20	2.77	102	162	-16.71

is very similar to that C=S for systems (NHCH₃NHCH₃)-C=X...H-CF₃ and (NHCH₃,CH₃CH₂)-C=X...H-CF₃; and clearly shows that C=Se and C=S can form stabilizing hydrogen bonds. Indeed, values of -14.30 kJ/mole (EintB3LYP) and -27.76 kJ/mole (EintB3LYP-3D) of C=Se for the NN groups are similar with values of -14.29 kJ/mole (EintB3LYP) and -27.04 kJ/mole (EintB3LYP-3D) of C=S respectively, and those of -12.16 kJ/mole (EintB3LYP) and -22.37 kJ/mole (EintB3LYP-3D) of C=Se for the NC groups are similar with values of -12.55 kJ/mole (EintB3LYP) and -22.32 kJ/mole (EintB3LYP-3D) of C=S respectively.

As for the systems (CH₃CH₂,CH₃CH₂)-C=X...H-CF₃, we notice the difference in interaction strength for the two acceptors C=Se and C=S, values of -9.81 kJ/mole (EintB3LYP) and -20.45 kJ/mole (EintB3LYP-3D) of C=Se are different from -5.20 kJ/mole (EintB3LYP) and -16.71 kJ/mole (EintB3LYP-3D) of C=S respectively.

The geometries parameters (d , φ and ρ) obtained in the DFT calculations much well with the trends observed in CSD (Table 4 and Table 5), but we can note a difference by 30° - 40° on φ angle for N,N groups. For example, an φ angle of 117 (26)° was found while the corresponding in calculation gives 89° for selenium acceptor.

The results of these Table 9 and Table 10 also show that the calculated energies follow the expected trend of the hydrogen bond strength already established on the basis of the geometry analysis of the structures in the CSD and are consistent with the partial charges and MEP of the groups C=Se and C=S substituted. Indeed, the trend of the interaction energies agrees well with that of CSD d (norm). One can expect from analysis of d (norm) values of three chalcogens that C=Te should be of comparable strength than C=Se.

Furthermore, insights into the nature of interaction involved in the complex formation can be provided by NBO interaction analysis. Table 11 and Table 12 report NBO interactions with values of the associated second order perturbation energies $E^{(2)}$ for C=Se and C=S respectively.

It appears from those Tables that all hydrogen bonds consist of charge transfer (CT) from a selenium or sulphur lone pair (LP) acting as hydrogen bond acceptor to a H-C antibonding orbital (BD*) of the hydrogen bond donor.

Table 11. NBO perturbation energy $E^{(2)}$ for C=Se...H-CF₃ complexes calculated with B3LYP/6-311++G(3df,2p) and B3LYP-GD3/6-311++G(3df,2p).

Complex	B3LYP/6-311++G(3df,2p)		B3LYP-GD3/6-311++G(3df,2p)	
	Acceptor HB	$E^{(2)}$	Acceptor HB	$E^{(2)}$
(I1)	LP(2) Se14 → BD*(1) C15-H16	4.10	LP(2) Se14 → BD*(1) C15-H16	2.85
	LP(2) F17 → BD*(1) C6-H9	0.50	LP(2) F17 → BD*(1) C6-H9	0.79
(I2)	LP(2) Se15 → BD*(1) H16-C17	16.19	LP(2) Se15 → BD*(1) H16-C17	21.13
	LP(2) F18 → BD*(1) C4-H7	0.21	LP(2) F20 → BD*(1) C4-H6	0.79
(I3)	LP(2) Se16 → BD*(1) C17-H18	15.02	LP(2) Se16 → BD*(1) C17-H18	19.25
	LP(2) F21 → BD*(1) C5-H7	0.71	LP(2) F21 → BD*(1) C5-H7	1.67

Table 12. NBO perturbation energy $E^{(2)}$ for C=S...H-CF₃(CH₃CH₂,CH₃CH₂)-C=X...H-CF₃ calculated with B3LYP/6-311++G(3df,2p) and B3LYP-GD3/6-311++G(3df,2p).

Complex	B3LYP/6-311++G(3df,2p)		B3LYP-GD3/6-311++G(3df,2p)	
	AcceptorHB	$E^{(2)}$	AcceptorHB	$E^{(2)}$
(II1)	LP(1) S19 → BD*(1) C14-H15	2.89	LP(1) S19 → BD*(1) C14-H15	0.69
	LP(2) F16 → BD*(1) C6-H9	0.67	LP(2) F16 → BD*(1) C6-H9	0.16
(II2)	LP(2) S20 → BD*(1) H15-C16	14.69	LP(2) S20 → BD*(1) H15-C16	19.20
	LP(2) F17 → BD*(1) C4-H7	0.25	LP(2) F17 → BD*(1) C4-H7	0.75
(II3)	LP(2) S21 → BD*(1) C16-H17	13.81	LP(2) S21 → BD*(1) C16-H17	17.99
	LP(2) F20 → BD*(1) C5-H7	0.63	LP(2) F20 → BD*(1) C5-H7	1.67

For C=Se acceptor, $E^{(2)}$ values range from 4.10 to 16.19 kJ·mol⁻¹ for B3LYP and from 2.85 to 21.13 kJ·mol⁻¹ for B3LYP-D3 depending on the hydrogen-bond donor and substituents bonded to carbon in C=X acceptors. Those calculated for C=S acceptor with B3LYP and B3LYP-D3 respectively vary from 2.89 to 14.69 kJ·mol⁻¹, and from 2.05 to 19.20 kJ·mol⁻¹.

7. Conclusions

The present study investigated the ability of C=Se, C=S and C=Te acceptors to form hydrogen bonds with C-H hydrogen bond donors using CSD analysis in conjunction with computational methods. Following relevant conclusions can be drawn:

- There are respectively 256, 6249 and 11R₁,R₂,-C=Se, R₁,R₂,-C=S and R₁,R₂,-C=Te structures in CSD that form hydrogen bonds, in which the majority groups are N,N compounds. Except for the C=S acceptor which can form the hydrogen bond with its C,C group, both C=Se and C=Te could form a hydrogen bond only with N,C and N,N groups.
- C-H hydrogen-bond donors approach C=X acceptors at greater angles than their corresponding N-H and O-H donors, and the hydrogen bonding to C=X acceptors is highly directional, like to N-H and O-H donors.
- Partial charges and electrostatic potentials calculated for Te atoms in C=Te acceptors, as well as intramolecular geometries, suggest that the hydrogen bond

stems from the substituent groups inducing $C^{\delta+}=Te^{\delta-}$ dipole as occurs in hydrogen bonding C=Se and C=S acceptors.

- Molecular electrostatic potential surfaces calculated for C=Te acceptors show remarkably similar patterns to those for C=Se acceptors and C=S with a negative area and a positive hole suggesting the ability of chalcogen atoms to form both hydrogen bonds and positive hole-based bonds similar to sigma-hole.
- Both interaction distances derived from CSD analysis and DFT-calculated interaction energies demonstrate that the acceptors strongly interact with H-CF₃. Besides hydrogen bonds, dispersion interactions are forces stabilizing the complexes since their contribution can reach 50%.
- NBO interaction analysis shows that C=Se...H-C and C=S...H-C interactions are characterized by the transfer of charge from lone pair of the proton acceptor to the antibonding orbital of the C-H covalent bond.

Acknowledgements

Didi D. Bibelayi is grateful to the CCDC for material support, and to Gaussian Inc, Wallingford, CT for providing Gaussian 09 software package.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Araújo, E.B., Idalgo, E., Moraes, A.P.A. and Souza, F.A.G. (2009) Crystallization Kinetics and Thermal Properties of 20Li₂O-80TeO₂ Glass. *Materials Research Bulletin*, **44**, 1596-1600. <https://doi.org/10.1016/j.materresbull.2009.01.019>
- [2] Ferrarini, R.S., Princival, J.L., Comasseto, J.V. and Santos, D. (2008) A Concise Enantioselective Synthesis of (+)-endo-brevicommin Accomplished by a Tellurium/Metal Exchange Reaction. *Journal of the Brazilian Chemical Society*, **19**, 811-812. <https://doi.org/10.1590/S0103-50532008000500002>
- [3] Liu, Y., Wu, W. and Goddard, A. (2018) Tellurium: Fast Electrical and Atomic Transport along the Weak Interaction Direction. *Journal of the American Chemical Society*, **140**, 550-553. <https://doi.org/10.1021/jacs.7b09964>
- [4] Luo, Z. (2016) Selenourea: A Convenient Phasing Vehicle for Macromolecular X-Ray Crystal Structures. *Scientific Reports*, **6**, Article No. 37123. <https://doi.org/10.1038/srep37123>
- [5] Okumura, K. (1974) Photovoltaic Effects at the Interface between Amorphous Selenium and Organic Polymers. *Journal of Applied Physics*, **45**, 5317. <https://doi.org/10.1063/1.1663237>
- [6] Poborchii, V.V., Kolobov, A.V. and Tanaka, K. (1998) An *In Situ* Raman Study of Polarization-Dependent Photocrystallization in Amorphous Selenium Films. *Applied Physics Letters*, **72**, 1167-1169. <https://doi.org/10.1063/1.121002>
- [7] Qi, R. and Cheng, Y. (2019) Synthesis of Se Nanowires at Room Temperature Using Selenourea as Se Source. *Journal of Materials Science*, **31**, 5843-5847. <https://doi.org/10.1007/s10854-019-02616-y>
- [8] Vargas, F., Toledo, F.T. and Comasseto, J.V. (2010) N-Functionalized Organolithium

- Compounds via Tellurium/Lithium Exchange Reaction. *Journal of the Brazilian Chemical Society*, **21**, 2072-2078.
<https://doi.org/10.1590/S0103-50532010001100007>
- [9] Desiraju, G.R. (1996) The C-H...O Hydrogen Bond: Structural Implications and Supramolecular Design. *Accounts of Chemical Research*, **29**, 441-449.
<https://doi.org/10.1021/ar950135n>
- [10] Marques, M.P.M., Amorim da Costa, A.M. and Paulo, J.A. (2001) Evidence of C-H...O Hydrogen Bonds in Liquid 4-Ethoxybenzaldehyde by NMR and Vibrational Spectroscopies. *The Journal of Physical Chemistry A*, **105**, 5292-5217.
<https://doi.org/10.1021/jp0046041>
- [11] Madzhidov, T.I. and Chmutova, G.A. (2010) The Nature of Hydrogen Bonds with Divalent Selenium Compounds. *Journal of Molecular Structure: THEOCHEM*, **959**, 1-7. <https://doi.org/10.1016/j.theochem.2010.07.041>
- [12] Mishra, K.K., Singh, K., Gosh, P., Gosh, D. and Das, A. (2017) Nature of Selenium Hydrogen Bonding: Gas Phase Spectroscopy and Quantum Chemistry Calculations. *Physical Chemistry Chemical Physics*, **19**, 24179-24187.
<https://doi.org/10.1039/C7CP05265K>
- [13] Murray, J.S., Lane, P. and Politzer, P. (2009) Expansion of the σ -Hole Concept. *Journal of Molecular Modeling*, **15**, 723-729. <https://doi.org/10.1007/s00894-008-0386-9>
- [14] Bibelayi, D.D., Lundemba, A.S., Allen, F.H., Galek, P.T., Pradon, J., Reilly, A.M., Groom, C.R. and Yav, Z.G. (2016) Hydrogen Bonding at C = Se Acceptors in Seleno-Ureas, Seleno-Amides and Selones. *Acta Crystallographica Section B*, **72**, 317-325.
<https://doi.org/10.1107/S2052520616003644>
- [15] Groom, C.R. and Allen, F.H. (2014) The Cambridge Structural Database in Retrospect and Prospect. *Angewandte Chemie International Edition in English*, **53**, 662-671.
<https://doi.org/10.1002/anie.201306438>
- [16] Allen, F.H. (2002) The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising. *Acta Crystallographica Section B*, **58**, 380-388.
<https://doi.org/10.1107/S0108768102003890>
- [17] Frisch, M.J., *et al.* (2014) GAUSSIAN09. Gaussian Inc., Wallingford.
- [18] Becke, A.D. (1993) Density-Functional Thermochemistry. III. The Role of Exact Exchange. *The Journal of Chemical Physics*, **98**, 5648-5652.
<https://doi.org/10.1063/1.464913>
- [19] Lee, C., Yang, W. and Parr, R.G. (1988) Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Physical Review B*, **37**, 785-789. <https://doi.org/10.1103/PhysRevB.37.785>
- [20] Stephens, P.J., Devlin, F.J., Habalowski, C.F. and Frisch, M.J. (1994) *Ab Initio* Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *The Journal of Physical Chemistry*, **98**, 11623-11627.
<https://doi.org/10.1021/j100096a001>
- [21] Grimme, S.J. (2006) Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *Journal of Computational Chemistry*, **27**, 1787-1799. <https://doi.org/10.1002/jcc.20495>
- [22] Grimme, S., Anthony, J., Ehrlich, S. and Krieg, H. (2010) A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *The Journal of Chemical Physics*, **132**, Article ID: 154104.
<https://doi.org/10.1063/1.3382344>
- [23] Politzer, P., Murray, J.S. and Lane, P. (2007) σ -Hole Bonding and Hydrogen Bonding: Competitive Interactions. *International Journal of Quantum Chemistry*, **107**, 3046-3052.

- <https://doi.org/10.1002/qua.21419>
- [24] Politzer, P., Murray, J.S. and Clark, T. (2013) Halogen Bonding and Other σ -Hole Interactions: A Perspective. *Physical Chemistry Chemical Physics*, **15**, 11178. <https://doi.org/10.1039/c3cp00054k>
- [25] Allen, F.H., Bird, C.M., Rowland, R.S. and Raithby, P.R. (1997) Resonance-Induced Hydrogen Bonding at Sulphur Acceptors in $R_1R_2C=S$ and $R_1CS_2^-$ Systems. *Acta Crystallographica Section B*, **53**, 680-695. <https://doi.org/10.1107/S0108768197002656>
- [26] Wood, P.A., Pidcock, E. and Allen, F.H. (2008) Interaction Geometries and Energies of Hydrogen Bonds to C=O and C=S Acceptors: A Comparative Study. *Acta Crystallographica Section B*, **64**, 491-496. <https://doi.org/10.1107/S0108768108015437>
- [27] Blessing, R.H. (1983) Interdependence of Carbon-Nitrogen and Carbon-Oxygen Bond Lengths in Urea Structures and in Ureido Ring Structures. *Journal of the American Chemical Society*, **105**, 2776-2783. <https://doi.org/10.1021/ja00347a043>
- [28] Wood, P.A., Allen, F.H. and Pidcock, E. (2009) Hydrogen-Bond Directionality at the Donor H Atom—Analysis of Interaction Energies and Database Statistics. *CrystEngComm*, **11**, 1563-1571. <https://doi.org/10.1039/b902330e>
- [29] Bondi, A. (1964) van der Waals Volumes and Radii. *The Journal of Physical Chemistry*, **68**, 441-451. <https://doi.org/10.1021/j100785a001>
- [30] Rowland, R.S. and Taylor, R. (1996) Intermolecular Nonbonded Contact Distances in Organic Crystal Structures: Comparison with Distances Expected from van der Waals Radii. *The Journal of Physical Chemistry*, **100**, 7384-7391. <https://doi.org/10.1021/jp953141+>
- [31] Desiraju, G.R. (2002) Hydrogen Bridges in Crystal Engineering: Interactions without Borders. *Accounts of Chemical Research*, **35**, 565-573. <https://doi.org/10.1021/ar010054t>
- [32] Jin, L., Li, B., Cui, Z., Shang, J., Wang, Y., Shao, C., Pan, T., Ge, Y. and Qi, Z. (2019) Selenium Substitution-Induced Hydration Changes of Crown Ethers as Tools for Probing Water Interactions with Supramolecular Macrocycles in Aqueous Solutions. *The Journal of Physical Chemistry B*, **123**, 9692-9698. <https://doi.org/10.1021/acs.jpcc.9b09618>
- [33] Custelcean, R. (2008) Crystal Engineering with Urea and Thiourea Hydrogen-Bonding Groups. *Chemical Communications*, No. 3, 295-307. <https://doi.org/10.1039/B708921I>
- [34] Michael, H.A., Ibrahim, A., Zissimos, A.M., Zhao, Y.H., Comer, J. and Reynolds, D.P. (2002) Application of Hydrogen Bonding Calculations in Property Based Drug Design. *Drug Discovery Today*, **7**, 1056-1063. [https://doi.org/10.1016/S1359-6446\(02\)02478-9](https://doi.org/10.1016/S1359-6446(02)02478-9)
- [35] Uma, R.S.A., Subba, R.S., Chandra, S.R.G., Veera, N.R.M. and Naga, R.C. (2011) Synthesis, Spectral, and Antimicrobial Evaluation of Some New 8-membered Phosphorus Heterocyclic Compounds. *Medicinal Chemistry Research*, **20**, 962-967. <https://doi.org/10.1007/s00044-010-9425-z>
- [36] Kilembe, J.T., Lundemba, A.S., Bibelayi, D.D., Ndefi, G.M., Pradon, J. and Yav, Z.G. (2019) Docking of Human Heat Shock Protein 90 with Selenoderivatives of Geldanamycin. *Crystal Structure Theory and Applications*, **8**, 13-27. <https://doi.org/10.4236/csta.2019.82002>
- [37] Moudgil, R., Bharatam, P.V., Kaur, R. and Kaur, D. (2002) Theoretical Studies on Electron Delocalisation in Selenourea. *Journal of Chemical Sciences*, **114**, 223-230. <https://doi.org/10.1007/BF02704266>
- [38] Metrangolo, P., Neukirch, H., Pilati, T. and Resnati, G. (2005) Halogen Bonding Based Recognition Processes: A World Parallel to Hydrogen Bonding. *Accounts of Chemical*

- Research*, **38**, 386-395. <https://doi.org/10.1021/ar0400995>
- [39] Lundemba, A.S., Bibelayi, D.D., Wood, P.A., Pradon, J. and Yav, Z.G. (2020) σ -Hole Interactions in Small-Molecule Compounds Containing Divalent Sulphur Groups R1-S-R2. *Acta Crystallographica Section B*, **76**, 707-718. <https://doi.org/10.1107/S2052520620008598>
- [40] Bauza, A., Quinonero, D., Deya, P.M. and Frontera, A. (2013) Halogen Bonding versus Chalcogen and Pnicogen Bonding: A Combined Cambridge Structural Database and Theoretical Study. *CrystEngComm*, **15**, 3137-3144. <https://doi.org/10.1039/C2CE26741A>
- [41] Bleiholder, C., Werz, D.B., Koppel, H. and Gleiter, W. (2006) Theoretical Investigations on Chalcogen-Chalcogen Interactions: What Makes These Nonbonded Interactions Bonding? *Journal of the American Chemical Society*, **128**, 2666-2674. <https://doi.org/10.1021/ja056827g>
- [42] Bleiholder, C., Gleiter, W., Werz, D.B. and Koppel, H. (2007) Theoretical Investigations on Heteronuclear Chalcogen-Chalcogen Interactions: On the Nature of Weak Bonds between Chalcogen Centers. *Inorganic Chemistry*, **46**, 2249-2260. <https://doi.org/10.1021/ic062110y>
- [43] Garrett, G.E., Gibson, G.L., Straus, R.N., Seferos, D.S. and Taylor, M.S. (2015) Chalcogen Bonding in Solution: Interactions of Benzotelluradiazoles with Anionic and Uncharged Lewis Bases. *Journal of the American Chemical Society*, **137**, 4126-4133. <https://doi.org/10.1021/ja512183e>