

Chalcogen Bonds in Small-Organic Molecule Compounds Derived from the Cambridge Structural Database (CSD)

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Abstract

Growing interest in non-covalent interactions involving chalcogen atoms has been ascribed to their importance in crystal engineering, molecular recognition and macromolecular edifices. The present study is dealing with chalcogen bonds involving divalent Sulphur, Selenium and Tellurium atoms, acting as sigma-hole donors, in small-molecule compounds using the Cambridge Structural Database (CSD) in conjunction with *ab initio* calculations. Results derived from CSD surveys and computational study revealed that nucleophiles formed complexes with the chalcogen-bond donors R₁-X-R₂ (X = S, Se or Te). The main forces stabilizing the complexes were chalcogen bonds, enhanced by dispersion interactions. Complexation pattern and energetics show that nucleophile bonding at divalent S, Se and Te atoms is a relatively strong and directed interaction. The bond consists of a charge transfer from a nucleophile atom lone pair to an X-R₁ or X-R₂ antibonding orbital.

Keywords

Chalcogen Bond, CSD, *Ab Initio* Calculation, Interaction Geometry, Interaction Energy

1. Introduction

There are numerous computational studies reporting on interactions of divalent chalcogen atoms (acting as σ -hole bond donors), mostly in small-inorganic molecule compounds (Pal, D. & Chakrabarti, P., 2001 [1]; Politzer, P. *et al.*, 2007

[2]; Bleiholder, C. *et al.*, 2006 [3]; Clark, T. *et al.*, 2007 [4]; Ramos, L. A. *et al.*, 2010 [5]; Politzer, P. *et al.*, 2010 [6]; Politzer, P. *et al.*, 2013 [7]; Politzer, P. & Murray, J. S., 2013 [8]; Politzer, P. *et al.*, 2014 [9]; Pandiyan, B. V. *et al.*, 2016 [10]; Zabardasti, A. *et al.*, 2017 [11]; Bauza, A. & Frontera A., 2018 [12]; 2019 [13]; 2020 [14]). Computational studies also showed that positive electrostatic potentials as well as σ -hole interactions are strongly affected by the environment of the covalently bonded chalcogen atom (Murray *et al.*, 2007 [15]; Murray & Politzer, 2011 [16]; Politzer & Murray, 2017 [17]).

To understand the intermolecular interaction between chalcogen atoms (O, S, Se, Te) quantum chemistry calculations using some model systems have been performed. Previous investigation on the intermolecular interactions between two molecules containing elements of group VI showed that the chalcogen-chalcogen interaction dominates and hydrogen bonding plays only a minor role in aggregates with heavier atoms (Bleiholder, C. *et al.*, 2006 [3]). The strength of the chalcogen interaction increased steadily from oxygen via sulphur to selenium and peaked around 6 kcal/mol for tellurium. The bond strength also increased when adding an electron withdrawing substituent such as the cyanide group CN.

However, experimental data supporting chalcogen-bonded complexes are rare and scarce (Goettel, J. T. & Gerken, M., 2016 [18]; Karjalainen, M. M. *et al.*, 2016 [19]). Analysis of consistent experimental data dealing with chalcogen interactions in organic molecules may be crucial due to their nature, importance and implications in the chemical, biological and medicinal areas. Theoretical study in addition to the data analysis is useful to provide a better understanding of the interaction and to guide its application in a wide variety of fields, like crystal engineering and drug design. The present study aims at using crystallographic data derived from the Cambridge Structural Database (CSD) to investigate on σ -hole interactions in small-organic molecule compounds containing divalent chalcogen atoms in conjunction with *ab initio* calculations in order to provide consistent insights into the nature of chalcogen bonding at divalent S, Se and Te atoms acting as σ -hole bond donors. This is of some interest as previous studies of inorganic chalcogen-bonded complexes reported that the chalcogen bond was a relatively strong and nearly linear interaction. They also showed the dependence of the interaction strength on the environment of chalcogen atoms [15] [16] [17].

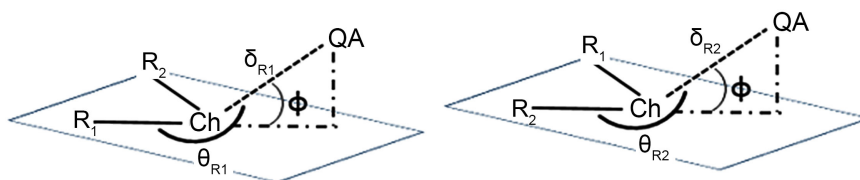
2. Materials and Methods

2.1. CSD Analysis

Work CSD version 5.41 plus November 2019 update was used to perform the analysis of sulfur, selenium and tellurium compounds, this version contains a total of 1,034,174 structural entries. The CSD-System program ConQuest (Bruno *et al.*, 2002 [20]) was used to question the database substructure searches to match selenium containing systems, as well as relevant non-bonded

interactions. The following secondary search criteria were employed: 1) atomic coordinates present in the entry; 2) error-free after CSD evaluation; 3) no disorder in the crystal structure; 4) no polymeric (catena) bonding; 5) no powder studies; 6) crystallographic R-factor < 0.10; 7) only organic structures (according to standard CSD definitions). Any specific variations of these criteria are noted in the text. In the results and discussion section, atoms and groups will be referred to by their coordination number as a superscript, with N³, for example, denoting a three-coordinate nitrogen atom. The CSD-System program Mercury (Macrae *et al.*, 2006 [21], 2008 [22]) was used for structure visualization, while numerical analysis of geometrical data retrieved by ConQuest was carried out using the Data Analysis Module implemented within Mercury (Sykes *et al.*, 2011 [23]).

The geometrical parameters δ (intermolecular distance) and θ (angle) of the chalcogen interaction are defined according to **Scheme 1**. The differences between sums of van der Waals radii of interacting atoms ($r_{\text{Ch}} + r_{\text{QA}}$) and distances δ represent the “normalized” distances Δ (Wood *et al.*, 2008 [24]). The values of van der Waals radii reported by Bondi *et al.* (1964) [25] were used for calculations.



Scheme 1. Ch = chalcogen atom S, Se or Te; R₁, R₂ = substituents as illustrated in **Table 1**; QA = nucleophile; θ = interaction angle; δ = interaction distance.

2.2. Computational Study

The second-order Moller-Plesset perturbation theory MP2 and the density functional theories B3LYP and B3PW91 at basis set 6-311G (3df,2p) were used for calculations, when investigating on S- and Se-containing chalcogen bond donors. Only HF/ chemical model was used for Te chalcogen donors containing Te atoms.

We use Equations (1) and (2) (Murray *et al.*, 2011 [26]; Lundemba S. *et al.*, 2020 [27]) to perform electrostatic potential (V) in the space around a chalcogen-bond donor, written in atomic units (au), and interaction energy (E_{int}) between a chalcogen donor and an acceptor, respectively. Energies E_{int} are energy minima at 0 K. Large basis sets are used to minimize the problem of correction for the basis set superposition error (Grimme S., 2006 [28]; Politzer P. *et al.*, 2013 [7]).

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (1)$$

$$E_{\text{int}} = E_{\text{complex}} - (E_{\text{donor}} + E_{\text{acceptor}}) \quad (2)$$

Figure 1 reports examples of molecular models of chalcogen bond used for *ab initio* calculations.

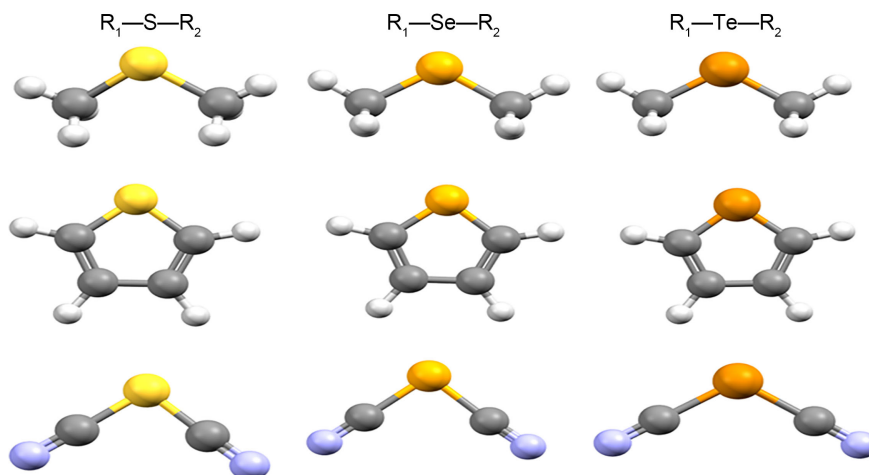


Figure 1. Molecular models of chalcogen-bond donors derived from CSD used for *ab initio* calculation.

3. Results and Discussion

3.1. CSD Surveys

3.1.1. Frequency of Occurrence (FoO)

CSD analysis reveals that many organic compounds containing divalent chalcogen atoms R_1-X-R_2 ($X = S, Se$ or Te) interact with various nucleophile atoms (QA) like N, O, F, P, S, Cl, As, Se, Br, Sb, Te or I. Occurrence frequencies of molecular fragments containing divalent chalcogens R_1-X-R_2 ($X = S, Se$ or Te) involved in interactions with σ -hole acceptors are listed in **Table 1(a)-(c)**.

Table 1. Number (N_f) and occurrence frequency (FoO in %) of fragments forming intermolecular chalcogen-bonds.

(a) R_1-S-R_2			
R_1	R_2	N_f	FoO
C	C	13,943	70.77
N	S	1801	9.14
C	S	1550	7.86
C	N	624	3.17
N	N	623	3.16
S	S	440	2.23
C	P	81	0.41
	Other	638	3.24
	Total	19,700	

(b) R ₁ -Se-R ₂			
R ₁	R ₂	N _f	FoO
C	C	1318	49.49
C	Se	436	16.37
N	N	252	9.46
N	Se	192	7.21
C	N	142	5.33
N	S	111	4.16
Se	Se	80	3.00
	Other	132	4.96
	Total	2663	

(c) R ₁ -Te-R ₂			
R ₁	R ₂	N _f	FoO
C	C	379	42.78
C	Te	203	22.91
N	N	108	12.19
Te	Te	59	6.66
S	S	27	3.05
C	N	27	3.05
C	S	21	2.37
	Other	62	6.99
	Total	886	

According to those results shows, C, C-X compounds represent the **most important group** forming intermolecular interactions. It is noteworthy that the hybridization of carbon atoms affects the frequency of occurrence. Analysis of the carbon atom **hybridization** reveals that the occurrence frequency increases in the sequence $X-C_{sp} < X-C_{sp^3} < X-C_{sp^2}$.

3.1.2. Interaction Geometry

Figure 2 shows the propensity of the nucleophile bonding at chalcogen atoms, mainly along the extensions of the covalent bonds X-R.

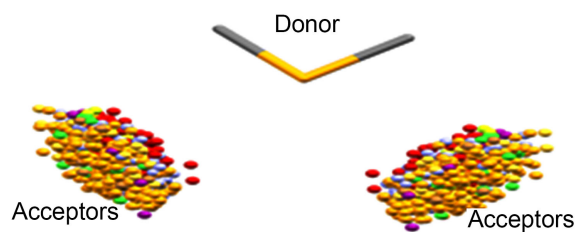


Figure 2. Intermolecular interactions of the C, C-S chalcogen bond donor with nucleophiles.

It can be seen that nucleophiles mostly interact with chalcogen atoms of the σ -hole donors R_1-X-R_2 along the extension of the X-R covalent bond.

The geometrical parameters θ and δ as described in scheme 1 as well as the length of the chalcogen interaction Δ are summarized in **Table 2**.

Table 2. Values of the geometrical parameters θ , δ and Δ of the chalcogen interaction.

Geometry	S complexes	Se complexes	Te complexes
θ ($^\circ$)	[162 - 175]	[162 - 178]	[165 - 174]
δ (\AA)	[2.900 - 3.541]	[2.701 - 3.652]	[2.659 - 3.960]
Δ (\AA)	[0.052 - 0.512]	[0.090 - 1.017]	[0.160 - 0.951]

The results in **Table 2** report mean bond angles $\theta > 160^\circ$, which support nearly linear interactions (Politzer *et al.* 2013 [7]) as illustrated by the pattern of O bonding at S atom in **Figure 3**.

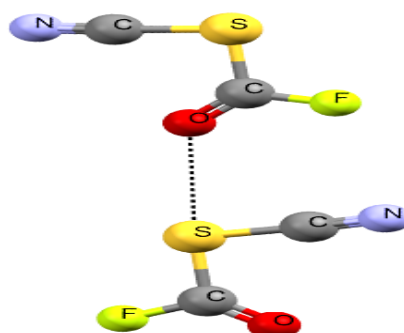


Figure 3. Bond pattern of S-bonded complex.

Nucleophile atom bonding at chalcogen atom with such θ values is one of main σ -hole bond characteristics (Politzer *et al.* 2009 [29], 2013 [7]).

Geometric data also show that mean interaction distances δ and lengths Δ have values less than the sums of van der Waals radii of the interacting atoms, demonstrating that the chalcogen interactions are relatively strong. Comparison of bond Δ values reveals that the ability of chalcogen atoms to interact with nucleophiles increases in the sequence $S < Se < Te$ for a similar environment.

3.2. *Ab Initio* Calculations

3.2.1. Molecular Electrostatic Potential (MEP) and Lowest Molecular Orbital (LUMO) of Chalcogen Bond Donor

The lowest molecular orbital (LUMO) of chalcogen bond donors shows a typical pattern depicted in **Figure 5** for $NC-X-CN$ ($X = S, Se$ and Te), while **Figure 4** illustrates calculated molecular electrostatic potential surfaces.

As it can be seen, the patterns of MEP and LUMO predict a directional bonding of nucleophiles at divalent chalcogen atoms. Indeed, MEP in **Figure 4** features two positive regions, which are located on the chalcogen atoms, and consequently, allow electrostatic interactions with nucleophiles.

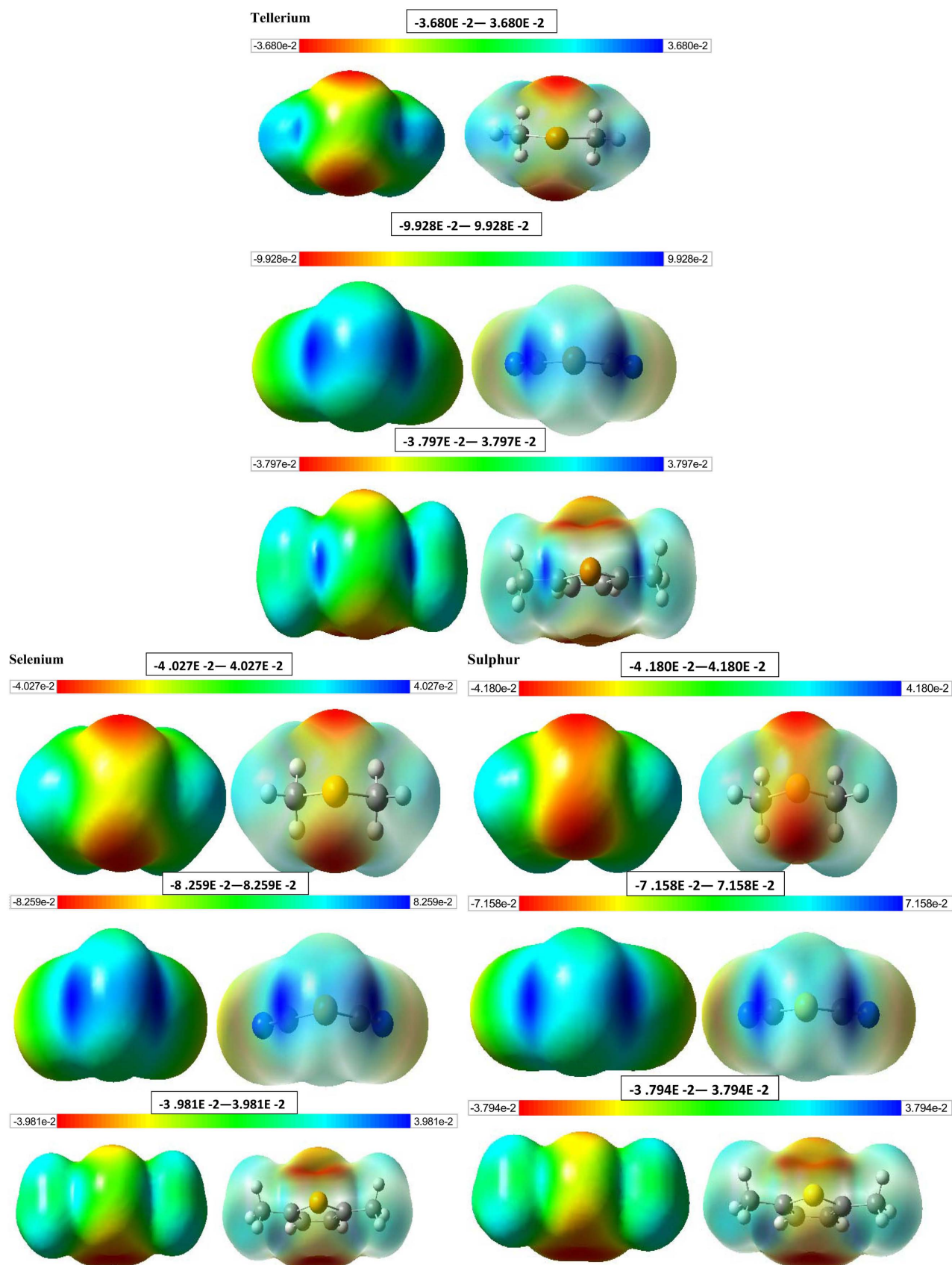


Figure 4. Molecular electrostatic potential surfaces calculated for typical chalcogen S, Se and Te bond donor.

It is noteworthy that positive region are more or less broad depending on the environment of the chalcogen atom. Values of the most positive electrostatic potential ($V_{S,max}$) calculated for some examples of chalcogen bond donors are listed in **Table 3**.

Table 3. Values of $V_{S,max}$.

R_1-X-R_2 σ -hole Donor	$V_{S,max}$ (kcal·mol ⁻¹)		
	X = S	X = Se	X = Te
H ₃ C-X-CH ₃	3.92	5.99	17.77
C ₆ H ₅ X	8.30	12.81	22.19
NC-X-CN	44.48	51.13	61.66

$V_{S,max}$ values show that the magnitude of the most positive electrostatic potential depends on chalcogen bond donor and substituents R_1 and R_2 , enhanced by electron withdrawing substituents as previously reported by Murray *et al.* (2009 [30], 2014 [31]) and Politzer *et al.* (2007 [2], 2013 [7], 2017 [17]). It increases in the sequence S < Se < Te for similar chalcogen environments. One may then expect an electrostatic interaction between chalcogen-bond donors and nucleophiles (Politzer *et al.* 2017 [17]).

The lowest molecular orbital (LUMO) of chalcogen bond donors shows a typical pattern depicted in **Figure 5** for NC-X-CN (X = S, Se and Te).

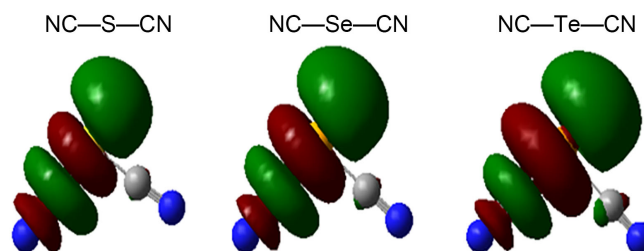


Figure 5. LUMO's examples for chalcogen-bond donors: CN-S-CN, CN-Se-CN and CN-Te-CN.

Interestingly, the lowest unoccupied molecular orbital also lies along extension of the covalent bond X-R like MEP does. Thus, both MEP and LUMO of chalcogen-bond donor predict directional bonding of nucleophiles at divalent chalcogen atoms as previously reported (Pal *et al.* 2001 [1]; Lundemba *et al.* 2020 [27]).

3.2.2. Interaction Energetics

Values of interaction energy (E_{int}) calculated using different theories are listed in **Table 4**.

Energy values are negative demonstrating attractive interactions between chalcogen donors and acceptors. Energies calculated with MP2 have values close to those calculated using B3LYP with dispersion correction, but markedly different to those without dispersion correction. That finding reveals that disper-

sion forces play an important role in stabilizing chalcogen-bonded complexes. E_{int} depends on chalcogen atoms and their environments similarly to bond length (Δ) and $V_{s,max}$. It increases according to $V_{s,max}$ in the sequence S < Se for interactions involving σ -hole donors containing S and Se divalent atoms.

Table 4. Values of E_{int} (kcal·mol⁻¹), θ (°), δ (Å) and number of imaginary frequencies (N_i).

Methods	AMOREA		KUYRIF		VAMPEF		FITLID		
	S	Se	S	Se	S	Se	S	Se	
B3LYP/6-311G (3df, 2p)	N_v	1	0	1	0	0	1	0	0
	E_{int}	-9.80	-11.04	-5.13	-11.10	-4.39	-5.23	-2.85	-3.06
	δ	3.21	3.23	3.37	3.16	3.35	3.43	4.21	4.17
	θ	177	172	171	172	163	167	164	161
B3LYP-D3/6-311G (3df, 2p)	N_f	1	1	0	0	0	0	0	0
	E_{int}	-17.47	-19.36	-20.46	-28.27	-23.94	-30.66	-13.07	-15.54
	δ	3.13	3.15	3.23	3.05	3.17	2.95	3.87	4.06
	θ	174	170	169	173	170	176	154	144
B3LYP-D3BJ/6-311G (3df, 2p)	N_f	1	1	0	0	0	0	2	2
	E_{int}	-18.15	-20.37	-21.34	-32.49	-27.36	-39.85	-14.09	-16.86
	δ	3.06	3.08	3.09	2.91	3.07	2.51	3.74	3.76
	θ	171	171	172	173	169	177	154	152
MP2/6-311G (3df, 2p)	E_{int}	-19.93	-21.24	-25.10	-34.66	-36.22	-62.50	-15.59	--
	δ	3.01	3.05	2.98	2.82	2.89	2.26	3.47	--
	θ	172	168	171	173	171	171	159	--

Table 5 reports results of NBO analysis for some chalcogen-bonded complexes.

Table 5. Charge transfer and stabilizing energy $E^{(2)}$ of chalcogen interactions.

R ₁ -S-R ₂ Complex	Chalcogen interaction	$E^{(2)}$ (kJ·mol ⁻¹)				
		B3LYP	B3LYP-D3	BJ	B3LYP-D3BJ	MP2
(NC) ₂ S-NH ₃	LP(1) N2→BD*(1) S1-C7	20.29	21.46	23.01	25.82	
(NC) ₂ S-O(CH ₃) ₂	LP(1) O6→BD*(1) S1-C2	8.87	10.71	11.59	14.64	
(NC) ₂ S-NCH	LP(1) N8→BD*(1) S1-C2	8.16	7.78	9.50	11.72	
R ₁ -Se-R ₂ Complex	Chalcogen interaction	$E^{(2)}$ (kJ·mol ⁻¹)				
		B3LYP	B3LYP-D3	BJ	B3LYP-D3BJ	MP2
(NC) ₂ Se-NH ₃	LP(1) O6→BD*(1) S1-C2	38.58	40.84	42.76	49.12	
(NC) ₂ Se-O(CH ₃) ₂	LP(1) O6→BD*(1) S1-C2	16.28	19.29	20.75	25.36	
(NC) ₂ Se-NCH	LP(1) N8→BD*(1) S1-C2	15.06	14.23	17.36	20.75	

According to the results reported in **Table 4**. The chalcogen-bond consists of charge transfer (CT) from a nucleophile lone pair (LP) acting as σ -hole bond acceptor to an antibonding orbital (BD*) X-R of the chalcogen bond donor (Guo *et al.* 2015 [32]). Furthermore, orbital contributions $E^{(2)}$ associated with electron delocalisation between depend on chalcogen atoms increasing as expected in the sequence S < Se.

4. Conclusions

We investigated on the chalcogen bonding at divalent S, Se and Te atoms in organic molecules, based on CSD analysis in conjunction with *ab initio* calculations using some chemical models. The work aimed to enable a better understanding of the interaction nature, geometry and strength. Several conclusions can be drawn from the results obtained:

1) CSD surveys showed that nucleophile atoms N, O, F, P, Cl, As, Se, Te and I interacted with the divalent chalcogen atoms. A significant frequency of occurrence (FoO) was found for 7 subgroups with (C; C), (C, N) and (N, N) as the most common σ -hole bond donors and the FoO decreasing in the sequence (C; C) > (N, N) > (C, N).

2) FoO and geometry were dependent on the R₁ and R₂ substituents. Values of the Δ interaction distance ranged from -0.052 \AA to -0.512 \AA for sulphur, from -0.086 \AA to -1.017 \AA for selenium and from -0.160 \AA to -0.951 \AA for tellurium, while those of the angle θ were close to 170° suggesting an attractive and nearly linear chalcogen interaction.

3) *Ab initio* calculations showed that the most positive electrostatic potential surfaces ($V_{s,\max}$) were located on chalcogens (S, Se; Te) in the extensions X-R₁ and X-R₂ bonds predicting directional and electrostatic interactions between the chalcogen atoms X and lone pairs of nucleophile atoms. LUMO orbitals of donors, with energy values decreasing in the sequence Te > Se > S, were involved in interactions nucleophiles.

4) All values of the interaction energy E_{int} were negative confirming the attractive nature of interaction. Comparison of E_{int} values calculated with the different quantum mechanical methods suggested that dispersion interactions played an important role in stabilizing σ -hole-bonded complexes. NBO analysis revealed that the chalcogen interactions consisted of transfer of charge from a nucleophile lone pair to an X-R₁ and X-R₂ antibonding orbital.

The present study provides a reliable contribution to the structural chemistry of chalcogen-bonded complexes. The relatively marked strength of the chalcogen bond and its characteristic directionality should guide the use of divalent S, Se and Te atoms in varied application areas like crystal engineering, drug design and supramolecular chemistry.

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Conflicts of Interest

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

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