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# Theoretical Investigations on the Weak Nonbonded C=S...CH<sub>2</sub> Interactions: Chalcogen-Bonded Complexes With Singlet Carbene as an Electron Donor

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**ABSTRACT:** In this article, we explored the noncovalent bonding interactions between O=C=S, S=C=S, F<sub>2</sub>C=S, Cl<sub>2</sub>C=S, and singlet carbene. Six chalcogen-bonded complexes were obtained. It is found that all the vibrational frequencies of C=S bond presented a red shift character. Interaction energy, topology property of the electron density and its Laplacian, and the donor-acceptor interaction have been investigated. All these results show that there exists a weak nonbonded interaction between the chalcogen bond donor and CH<sub>2</sub>. An energy decomposition analysis was performed to disclose that the electrostatic interaction is the main stabilized factor in these nonbonded complexes. © 2010 Wiley Periodicals, Inc. *Int J Quantum Chem* 111: 3881–3887, 2011

**Key words:** chalcogen-bonded; carbene; electrostatic interaction;  $\sigma$ -hole; electrostatic potential

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## 1. Introduction

Noncovalent bonding interactions play a key role in crystal engineering, molecular recognition, and biological processes [1–3]. Although the most important noncovalent forces are hydro-

gen bonding interactions [4], halogen-bonded interactions have been the subject of many theoretical and experimental investigations [5–11]. The reason why halogen-bonded complexes can be formed is a confusing question for a long time because both the halogen atom and the electron donor are negatively charged. Recently, Politzer and coworkers [12–15] studied the electrostatic potentials of halogen-containing molecules, and

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they show that the halogen atoms bound to carbon often have a region of positive potential along the direction of C–Hal bond directed toward the electron donor. They call this region “ $\sigma$ -hole,” and it has also been termed “the electro-positive crown” by Auffinger et al. [16]. Similarly, Politzer [17–19] pointed out that group IV atoms (S, O, Se, and Te) and group V atoms (N, P, As, and Ti) also have electropositive regions at their outermost ends. It means that group IV atoms can also form noncovalent complexes with electron donors. Wang et al. [20] named this noncovalent bonding as the chalcogen bond, which is borrowed from the definitions of the halogen bond and the hydrogen bond.

Noncovalent chalcogen–chalcogen interactions are the most well-known chalcogen bonds [21–24]. Iwaoka et al. [21] have suggested that nonbonded S··O interactions may stabilize folded protein structures. Bleiholder et al. [22, 23] investigated 32 model systems to understand the intermolecular interactions between chalcogen centers. They are pairs of monomers of the composition (CH<sub>3</sub>)<sub>2</sub>X<sub>1</sub> (X<sub>1</sub>=O, S, Se, Te) as the donors and CH<sub>3</sub>X<sub>2</sub>Z (with X<sub>2</sub>=O, S, Se, Te and Z=Me, CN) as the acceptors. Sulfur- $\pi$  contacts are other important chalcogen bonds, which have been the subject of many theoretical studies due to the recognition of their importance in biological systems [25–27]. Sulfur- $\pi$  interactions were found to occur more frequently than originally thought as exemplified by database searches carried out by Reid et al. [28].

Carbene is a neutral compound featuring a divalent carbon atom and two nonbonded electrons in which methylene is the simplest one. Although carbenes are highly reactive species with short lifetimes, some stable carbenes are known at room temperature [29]. There are two types of carbenes: singlet and triplet carbenes. Because of presence of a free electron pair in the singlet carbene, hydrogen bond can be formed with singlet carbene as an electron donor [4]. Li et al. [30, 31] have calculated a great many of halogen-bonded and lithium-bonded complexes and concluded that they could form stable noncovalent complexes. Just saying this, chalcogen-bonded complexes may be formed with singlet carbene as an electron donor.

In this article, we employ quantum chemical calculations to study several chalcogen-bonded complexes with singlet carbene as an electron donor. The compounds that offer chalcogen atoms

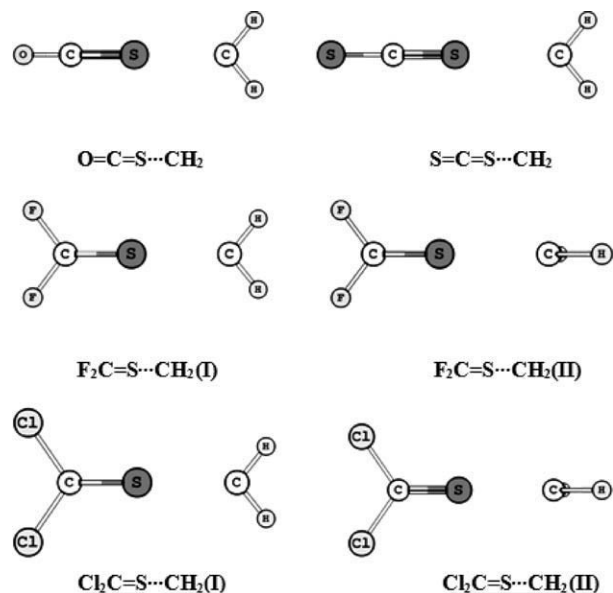
are O=C=S, S=C=S, F<sub>2</sub>C=S, and Cl<sub>2</sub>C=S. This series of compounds has been verified to form stable chalcogen-bonded complexes with Cl<sup>−</sup> [20]. We also performed natural bond orbital (NBO) and atoms in molecules (AIM) analyses to confirm the existence of chalcogen bond. Finally, an energy decomposition analysis was performed to disclose the nature of such chalcogen-bonded complexes with singlet carbene as an electron donor. We believe that our study can enrich the knowledge on chalcogen bonding interactions.

## 2. Computational Details

The complexes of CH<sub>2</sub> with O=C=S, S=C=S, F<sub>2</sub>C=S, and Cl<sub>2</sub>C=S have been optimized at the MP2/6-311++G(3df,2p) level [13]. Vibrational frequencies were calculated at the same level. Dunning’s [32] correlation consistent basis sets (aug-cc-PVDZ, aug-cc-PVTZ, aug-cc-PVQZ) were used to perform single point calculations by MP2 and CCSD(T) methods. The basis set superposition error (BSSE) was corrected for all calculations by using the counterpoise method proposed by Boys and Bernardi [33].

The MP2 level interaction energy at the basis set limit [ $E_{\text{MP2}(\text{limit})}$ ] was estimated by the method of Helgaker et al. [34] from the calculated MP2 interaction energies using the aug-cc-PVTZ and aug-cc-PVQZ basis sets. In the method of Helgaker et al., the calculated MP2 interaction energies with the Dunning’s correlation consistent basis sets were fitted to the form  $a + bX^{-3}$  (where  $X$  is 3 for aug-cc-PVTZ and 4 for aug-cc-PVQZ). The  $E_{\text{MP2}(\text{limit})}$  was then estimated by extrapolation. The CCSD(T) level interaction energy at the basis set limit [ $E_{\text{CCSD(T)}(\text{limit})}$ ] was estimated as the sum of the estimated  $E_{\text{MP2}(\text{limit})}$  and CCSD(T) correction term  $\Delta\text{CCSD(T)}$  (the difference between the calculated CCSD(T) and MP2 level energies using aug-cc-PVDZ basis set). All these calculations were performed by using the Gaussian 03 program package [35].

The bonding characteristic of the S··CH<sub>2</sub> contact was analyzed by using AIM theory [36]. AIM analysis was performed with AIMAll software package [37] using the MP2/6-311++G(3df,2p) wave functions as input. We also performed NBO analysis by using the MP2/6-311++G(3df,2p) geometries, the Hartree–Fock (HF) densities at the same basis set, and NBO3.1 program in Gaussian



**FIGURE 1.** Optimized geometries of the six chalcogen-bonded complexes.

03 [38]. Energy decomposition analysis has been carried out at the PBE/TZ2P level with ADF program to explore the bonding nature of the chalcogen-bonded complexes [39].

### 3. Results and Discussion

#### 3.1. GEOMETRICAL PARAMETERS AND VIBRATIONAL FREQUENCIES

We have optimized the structures of the chalcogen-bonded complexes  $O=C=S\cdots CH_2$ ,  $S=C=S\cdots CH_2$ ,  $F_2C=S\cdots CH_2$ , and  $Cl_2C=S\cdots CH_2$ . The structures of the complexes can be seen from Figure 1. For  $O=C=S\cdots CH_2$  and  $S=C=S\cdots CH_2$ , only

one stable point was obtained for each complex. For  $F_2C=S\cdots CH_2$  and  $Cl_2C=S\cdots CH_2$ , we have acquired four optimized geometries. Because there are two different molecule surfaces in these complexes,  $F_2C=S(Cl_2C=S)$  can be at the same plane with the plane of  $CH_2$  or be perpendicular with that of  $CH_2$ . The former geometries were defined as Type I, and the latter ones were named Type II. Some selected geometrical parameters and vibrational frequencies of the six complexes were given in Table I. It is noted from Table I that the two structures of  $Cl_2C=S\cdots CH_2$  and one  $F_2C=S\cdots CH_2$  structure are transition states (only one imaginary frequency). It is not strange because Wang et al. [20] have obtained similar structures for  $H_2C=S\cdots Cl^-$  and  $F_2C=S\cdots Cl^-$  complexes. One can see from Table I that  $d_{(S\cdots CH_2)}$  is smaller than the sum of the van der Waals radii of S and C ( $\sim 3.5$  Å). But the difference between them is smaller than other nonbonded complexes, which shows the weak nonbonding character of the  $C=S\cdots CH_2$  interactions.

Table I shows that all the values of  $r_{(C=S)}$  increase compared with those in the monomers. Furthermore, the frequency analysis reveals that all  $C=S\cdots CH_2$  complexes present a red shifting character. This result agrees with the empirical correlation, which states that bond elongation indicates red shift and bond contraction means blue shift.

#### 3.2. INTERACTION ENERGIES

Calculated intermolecular interaction energies for the six chalcogen-bonded complexes are summarized in Table II. Vibrational zero-point energies (ZPE) for the dimers and monomers are calculated in the MP2/6-311++G(3df,2p) level.  $\Delta ZPE$  is the variation of ZPE between the chalcogen-bonded

**TABLE I** Optimized geometries (Å), frequencies ( $cm^{-1}$ ), and number of imaginary frequencies ( $N_{img}$ ) of the six chalcogen-bonded complexes.

Complexes	$r_{(C=S)}$	$d_{(S\cdots CH_2)}$	Frequencies (C=S)	$N_{img}$
OCS...CH <sub>2</sub>	1.5594 ( <b>1.5571</b> )	3.3891	symm:891.2 ( <b>900.6</b> ), asy:2096.6 ( <b>2111.0</b> )	0
SCS...CH <sub>2</sub>	1.5549 ( <b>1.5542</b> )	3.4441	symm:680.3 ( <b>684.8</b> ), asy:1626.1 ( <b>1635.9</b> )	0
F <sub>2</sub> CS...CH <sub>2</sub> (I)	1.5879 ( <b>1.5870</b> )	3.4623	symm:803.9 ( <b>811.8</b> ), asy: 1404.6 ( <b>1415.6</b> )	1
F <sub>2</sub> CS...CH <sub>2</sub> (II)	1.5882 ( <b>1.5870</b> )	3.4211	symm:803.3 ( <b>811.8</b> ), asy: 1404.6 ( <b>1415.6</b> )	0
Cl <sub>2</sub> CS...CH <sub>2</sub> (I)	1.5993 ( <b>1.5989</b> )	3.4506	symm:516.7 ( <b>523.2</b> ), asy: 1176.5 ( <b>1186.3</b> )	1
Cl <sub>2</sub> CS...CH <sub>2</sub> (II)	1.6002 ( <b>1.5989</b> )	3.4002	symm:516.7 ( <b>523.2</b> ), asy: 1174.3 ( <b>1186.3</b> )	1

Numbers in bold are those of the corresponding monomers.

**TABLE II**  
Calculated MP2 and CCSD(T) interaction energies for the six chalcogen-bonded complexes.

Methods	OCS...CH <sub>2</sub>	SCS...CH <sub>2</sub>	F <sub>2</sub> C=S...CH <sub>2</sub> (I)	F <sub>2</sub> C=S...CH <sub>2</sub> (II)	Cl <sub>2</sub> C=S...CH <sub>2</sub> (I)	Cl <sub>2</sub> C=S...CH <sub>2</sub> (II)
MP2/6-311++G(3df,2p)	-1.13	-0.96	-0.73	-0.77	-0.69	-0.76
MP2/aug-cc-PVDZ	-1.68	-1.48	-1.20	-1.30	-1.17	-1.29
MP2/aug-cc-PVTZ	-1.88	-1.63	-1.27	-1.37	-1.25	-1.37
MP2/aug-cc-PVQZ	-1.99	-1.73	-1.37	-1.47	-1.35	-1.47
CCSD(T)/aug-cc-PVDZ	-1.51	-1.31	-1.11	-1.19	-1.06	-1.16
$E_{\text{MP2}(\text{limit})}$	-2.07	-1.80	-1.44	-1.54	-1.42	-1.54
$\Delta\text{CCSD(T)}$	0.17	0.17	0.09	0.11	0.11	0.13
$E_{\text{CCSD(T)}(\text{limit})}$	-1.90	-1.63	-1.35	-1.43	-1.31	-1.41
$\Delta\text{ZPE}$	0.64	0.56	0.44	0.49	0.43	0.47
$D_0$	-1.26	-1.07	-0.91	-0.94	-0.88	-0.94

Energy in kcal/mol. BSSE was corrected by the counterpoise method. Geometries was optimized in MP2/6-311++G(3df,2p) level.  $E_{\text{MP2}(\text{limit})}$  was estimated using the method of Helgaker from the calculated MP2 interaction energies with aug-cc-PVTZ and aug-cc-PVQZ.  $\Delta\text{CCSD(T)} = E_{\text{CCSD(T)aug-cc-PVDZ}} - E_{\text{MP2aug-cc-PVDZ}}$ .  $E_{\text{CCSD(T)}(\text{limit})} = E_{\text{MP2}(\text{limit})} - \Delta\text{CCSD(T)}$ .  $\Delta\text{ZPE}$  is the change of vibrational ZPE by formation of chalcogen-bonded complexes at MP2/6-311++G(3df,2p) level.  $D_0$  is the interaction energy calculated by the sum of  $E_{\text{CCSD(T)}(\text{limit})}$  and  $\Delta\text{ZPE}$ .

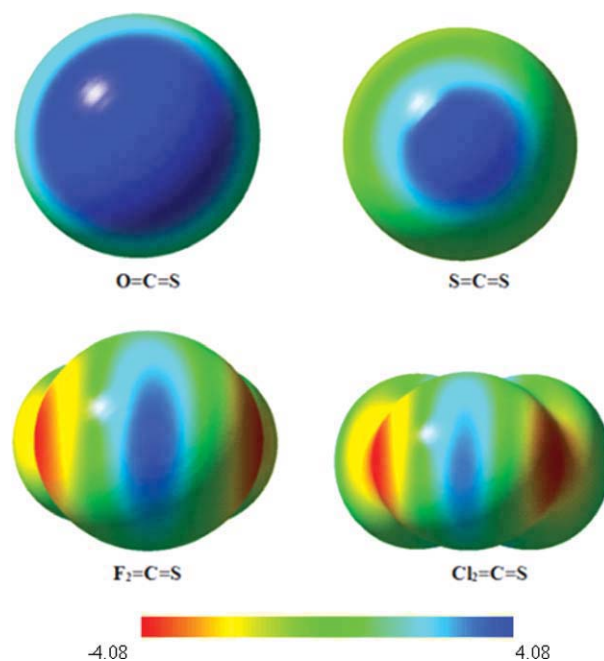
complexes and the monomers. The MP2 method overestimates the attraction compared with CCSD(T), which shows that electron correlation beyond MP2 is important. The estimated  $E_{\text{CCSD(T)}(\text{limit})}$  values for the six chalcogen-bonded complexes are from -1.31 to -1.90 kcal/mol. The interaction energies  $D_0$  were calculated by the sum of  $E_{\text{CCSD(T)}(\text{limit})}$  and  $\Delta\text{ZPE}$ . F<sub>2</sub>C=S is more stabilized by CH<sub>2</sub> than Cl<sub>2</sub>C=S, for fluorine has stronger electron withdrawn ability than chlorine. It is noted that the interaction energy in the F<sub>2</sub>C=S...CH<sub>2</sub>(II) complex is calculated to be -0.95 kcal/mol, which is larger than that in the F<sub>2</sub>C=S...CH<sub>2</sub>(I) complex. Similar result can be found between Cl<sub>2</sub>C=S...CH<sub>2</sub>(I) and Cl<sub>2</sub>C=S...CH<sub>2</sub>(II).

The existence of the chalcogen bond is due to the positive  $\sigma$ -hole in the chalcogen atom. We also calculated the electrostatic potential of O=C=S, S=C=S, F<sub>2</sub>C=S, and Cl<sub>2</sub>C=S at the MP2/6-311++G(3df,2p) level, which was showed in Figure 2. From Figure 2 one can see that the  $\sigma$ -hole becomes larger and more positive in the order of O=C=S > S=C=S > F<sub>2</sub>C=S > Cl<sub>2</sub>C=S. It is evident that this order is consistent with that of interaction energy. This result shows that the C=S...CH<sub>2</sub> interactions are mainly stabilized by electrostatic interactions.

### 3.3. AIM ANALYSIS

AIM theory is based on a topological analysis of the electron charge density and its Laplacian, which has been successfully applied in characterizing hydrogen bonds and halogen bonds of dif-

ferent strengths in a wide variety of molecular complexes [40–42]. We calculated the topological properties of the six chalcogen-bonded complexes using the MP2/6-311++G(3df,2p) densities under



**FIGURE 2.** Computed electrostatic potentials at MP2/6-311++G(3df,2p) level on the 0.004-au molecular surface of O=C=S, S=C=S, F<sub>2</sub>C=S, and Cl<sub>2</sub>C=S. The sulfur atoms are facing to the readers. The units of electrostatic potential are kcal/mol. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE III**  
The topology properties in the BCP of C=S...CH<sub>2</sub> interactions in the six chalcogen-bonded complexes.

Complexes	$\rho_b$	Laplacian	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\varepsilon$
OCS...CH <sub>2</sub>	0.0080	0.0239	-0.0049	-0.0049	0.0338	0.0000
SCS...CH <sub>2</sub>	0.0073	0.0220	-0.0045	-0.0045	0.0310	0.0013
F <sub>2</sub> CS...CH <sub>2</sub> (I)	0.0070	0.0211	-0.0045	-0.0040	0.0296	0.1224
F <sub>2</sub> CS...CH <sub>2</sub> (II)	0.0075	0.0228	-0.0049	-0.0043	0.0320	0.1242
Cl <sub>2</sub> CS...CH <sub>2</sub> (I)	0.0072	0.0217	-0.0046	-0.0041	0.0304	0.1420
Cl <sub>2</sub> CS...CH <sub>2</sub> (II)	0.0079	0.0238	-0.0051	-0.0045	0.0339	0.1471

All units are atomic units.

the MP2/6-311++G(3df,2p) geometries. The corresponding results were shown in Table III. Popelier has developed eight criteria for the existence of hydrogen bond. There are two most important ones among them: the electron density ( $\rho_b$ ) at the bond critical point (BCP) should range from 0.002 to 0.035 au, and the Laplacian of the electron density should range from 0.024 to 0.139. Wang et al. [20, 41] have proved that these criteria can also be applied to halogen bond and chalcogen bond. One can see from Table III that the  $\rho_b$  criteria are satisfied for all the six chalcogen-bonded complexes, and the Laplacian is close to the upper limit. It has proven that  $\rho_b$  is related to the bond strength, but our results seem to be against this law. The S=C=S...CH<sub>2</sub> complex has larger interaction energy than that of F<sub>2</sub>C=S...CH<sub>2</sub>(II) and Cl<sub>2</sub>C=S...CH<sub>2</sub>(II), but its  $\rho_b$  is smaller. Similar results were also found in the latter NBO analysis.

The Laplacian is the sum of the eigenvalues  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ . The two negative eigenvalues of the Hessian matrix of electron density ( $\lambda_1$  and  $\lambda_2$ ) measure the degree of contraction of  $\rho$  perpendicular to the bond toward the critical point, whereas the positive eigenvalue ( $\lambda_3$ ) measures the degree of contraction parallel to the bond and from the BCP toward each of the neighboring nuclei. According to the theory of Bader, which states that the Laplacian values of closed-shell interactions are positive, the six chalcogen-bonded complexes are all typically closed-shell interactions. The ellipticity,  $\varepsilon$ , which is defined as  $\lambda_1/\lambda_2-1$ , provides a measure of not only the  $\pi$  character of a bond but also the bond stability. It is noticed from Table III that the ellipticities of O=C=S...CH<sub>2</sub> and S=C=S...CH<sub>2</sub> complexes is significantly smaller than the others, which is consistent with the interaction energy order.

### 3.4. NBO ANALYSIS

We have performed NBO analysis at the HF/6-311++G(3df,2p) level using the MP2/6-311++G(3df,2p) geometry. Bleiholder et al. [22, 23] investigated the nature of chalcogen-chalcogen interactions and found that the charge transfer mainly occurs between the lone pair of the chalcogen bond donor and the antibonding orbital of C-Chal bond. Wang et al. [20] concluded that for the C=S...Cl<sup>-</sup> interactions, the lone pairs of Cl<sup>-</sup> had interactions with the C=S antibonding  $\sigma^*$  and  $\pi^*$  orbitals. Similar results have been found in our study, which were shown in Table IV. The second-order perturbation stabilization energy,  $\Delta E^2$ , can be used to evaluate the charge transfer between the chalcogen bond donor and chalcogen bond acceptor.

One can see from Table IV that there exists a charge transfer between the lone pair of CH<sub>2</sub> and the antibonding  $\sigma^*$  C=S orbital. NBO analysis did not give any stabilized interactions between the

**TABLE IV**  
Second-order perturbation stabilization energies of donor-acceptor interactions in the six chalcogen-bonded complexes.

Complexes	Donor	Acceptor	$\Delta E^2$
OCS...CH <sub>2</sub>	LP(C)	BD*(1)C=S	2.89
SCS...CH <sub>2</sub>	LP(C)	BD*(1)C=S	2.33
F <sub>2</sub> CS...CH <sub>2</sub> (I)	LP(C)	BD*(1)C=S	2.21
F <sub>2</sub> CS...CH <sub>2</sub> (II)	LP(C)	BD*(1)C=S	2.45
Cl <sub>2</sub> CS...CH <sub>2</sub> (I)	LP(C)	BD*(1)C=S	2.06
Cl <sub>2</sub> CS...CH <sub>2</sub> (II)	LP(C)	BD*(1)C=S	2.35

$\Delta E^2$  are in kcal/mol. LP(C) denotes the lone pairs in CH<sub>2</sub>, and BD\*(1)C=S denotes the antibonding  $\sigma^*$  C=S bond.

**TABLE V**  
**Decomposition of the interaction energies in the six chalcogen-bonded complexes.**

Complexes	$\Delta E_{\text{int}}$	$E_{\text{Pauli}}$	$E_{\text{elst}}$	$E_{\text{oi}}$
OCS...CH <sub>2</sub>	-1.76	2.79	-3.06	-1.49
SCS...CH <sub>2</sub>	-1.39	2.42	-2.51	-1.30
F <sub>2</sub> CS...CH <sub>2</sub> (I)	-0.88	2.21	-2.04	-1.05
F <sub>2</sub> CS...CH <sub>2</sub> (II)	-1.17	2.52	-2.33	-1.36
Cl <sub>2</sub> CS...CH <sub>2</sub> (I)	-0.84	2.32	-1.92	-1.24
Cl <sub>2</sub> CS...CH <sub>2</sub> (II)	-1.25	2.74	-2.28	-1.71

The interaction energies are in kcal/mol.  $\Delta E_{\text{int}} = E_{\text{Pauli}} + E_{\text{elst}} + E_{\text{oi}}$ .

lone pair and the antibonding  $\pi^*$  C=S orbital, which is different from the C=S...Cl interactions. This is because that the lone pair of CH<sub>2</sub> is perpendicular to the antibonding  $\pi^*$  C=S orbital. It is also noted that there is not a correlation between the stabilization energy terms in Table IV and the interaction energy terms in Table II. This indicates that charge transfer is not the only contribution to stabilize the chalcogen-bonded complex. To find out the nature of C=S...CH<sub>2</sub> interactions, an energy decomposition analysis must be carried out.

### 3.5. ENERGY DECOMPOSITION ANALYSIS

To reveal the nature of the C=S...CH<sub>2</sub> interactions, we performed a fragment-based energy decomposition analysis for the interaction energies. They were decomposed into three parts: electrostatic interaction energy ( $E_{\text{elst}}$ ), Pauli repulsion energy ( $E_{\text{Pauli}}$ ), and orbital interaction energy ( $E_{\text{oi}}$ ). The results are presented in Table V. The  $E_{\text{elst}}$  and  $E_{\text{oi}}$  terms are negative, showing a positive contribution to the stability of the complexes, whereas the  $E_{\text{Pauli}}$  value is positive. The contribution of  $E_{\text{elst}}$  to  $E_{\text{total}}$  is larger than  $E_{\text{oi}}$  in all complexes, and the  $E_{\text{elst}}$  order is the same as that of binding energy. We can conclude that the C=S...CH<sub>2</sub> interactions are mainly stabilized by electrostatic interactions, which is in accordance with the result of electrostatic potential.

## 4. Conclusion

In this article, we explored the noncovalent bonding interactions between O=C=S, S=C=S, F<sub>2</sub>C=S, Cl<sub>2</sub>C=S, and singlet carbene. Six chalcogen-bonded complexes were obtained. It is found that all the vibrational frequencies of C=S bond

presented a red shift character. We carried out AIM and NBO analyses for these complexes. All these results show that there exists a weak nonbonded interaction between the chalcogen bond donor and CH<sub>2</sub>. An energy decomposition analysis was performed to disclose that the electrostatic interaction is the main stabilized factor in these nonbonded complexes.

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