

Ab initio and DFT studies of the interaction between carbonyl and thiocarbonyl groups: the role of S...O chalcogen bonds

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Abstract The chalcogen bonds formed between carbonyl bases ($\text{H}_2\text{C}=\text{O}$ and $\text{CH}_3\text{-}$ and Cl- derivatives) and carbon disulfide have been studied by density functional BLYP-D3 and ab initio CCSD(T) methods. The CCSD(T)/CBS calculated interaction energies between these molecules are moderate, ranging from -1.45 to -2.29 kcal mol⁻¹. The charge transfer occurs from the carbonyl base to CS_2 and is small. According to the AIM analysis, the molecules are bonded by S...O chalcogen bonds. In addition, weak van der Waals S...Cl and S...H interactions stabilize most of the systems. The same results can be extracted from the NBO calculations which reveal the nature of the interacting bonding and antibonding orbitals. For some of the carbonyl derivatives, other stable structures characterized by S...Cl bonds or $\text{CH}\cdots\text{C}$ hydrogen bonds are also predicted.

A SAPT decomposition of the interaction energies allows to conclude that the electrostatic energy is the predominant component in the stronger complexes and that the dispersion energy becomes more important in the weaker van der Waals complexes.

Keywords Chalcogen bonds · Carbonyl and thiocarbonyl groups · CCSD(T) · DFT

1 Introduction

An important class of noncovalent bonds is associated with the attraction between electronegative atoms. Depending on the nature of the bridging atoms [1–3], these interactions are commonly designed as halogen [4–9], chalcogen [10–16] or pnictogen [17–20] bonds. The attractive force has been attributed to an anisotropic distribution of electron density around the bridging X atom, characterized by a crown of positive electrostatic potential along the extension of the Y–X bond (σ -hole) or in areas perpendicular to it (π -hole) [6–8, 21, 22]. Let us remember that positive σ -holes often exist in conjugation with negative potentials in other portions of the atom surface; such atoms can interact electrostatically with both electrophiles and nucleophiles. The electrostatic interactions within these bonds are supplemented by charge transfer from the lone pair of the acceptor atom into the σ^* or π^* Y–X antibonding orbitals. The strength of the chalcogen bond depends on the properties of the σ -holes which can be characterized by their magnitude (V_{max}) and size [23]. In recent QM calculations, the remarkable ability of heteroboranes to form strong σ -hole interactions has been demonstrated [24, 25]. Phenyl-substituted thiaboranes have also been synthesized. The QM analysis of the crystal structure showed the dominant role

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of chalcogen bonding in the crystal packing of 2D/3D aromatics [26].

In the present work, the interaction between substituted carbonyl derivatives and carbon disulfide or, in other words, the interaction between a carbonyl and a thiocarbonyl base is investigated by theoretical methods. Various substituents on the C=O functional group (CH₃, H, Cl) are chosen in order to modulate the basicity of the carbonyls. It is important to mention that the S...O interaction has attracted the biggest attention owing to its significance in the biological activity of some sulfur-containing compounds revealing enzymatic activity [27–29]. Iwaoka et al. [30, 31] suggested that the S...O=C interactions control, to some extent, the protein folding and that these interactions depend on the nature of the carbonyl base involved [31, 32]. The importance of orientation has been outlined as well [31].

The role of the $\pi^*(\text{C}=\text{S})$ antibonding orbitals has been discussed in several works. In the complex between SO₂ and H₂C=S, for example, a charge transfer from a SO₂ oxygen lone pair to the $\pi^*(\text{C}=\text{S})$ antibonding orbital of H₂C=S has been predicted [33]. The potential interactions of the nitrile halides XNO₂ with NH₃ as electron donor in the σ - and π -hole regions have been investigated [34]. Let us notice that the interaction between carbon disulfide and Cl⁻, [35], HF [36], O, N, P, S bases [37], HOX (X = F, Cl, Br) [38] has been investigated by theoretical methods.

To the best of our knowledge, the interaction between carbonyl derivatives and SCS has not been investigated nor theoretically, nor experimentally. This work presents a study of the structure and stabilities of these complexes. Detailed AIM and NBO analysis along with the SAPT results allows to discuss and compare the nature of the interaction in the different systems.

2 Computational methods

The optimized geometries, vibrational harmonic frequencies and infrared intensities were calculated for the following eight carbonyl bases: H₂C=O; HClC=O; Cl₂C=O; Cl₃CHC=O; Cl₃CClC=O; (CCl₃)₂C=O; H₃CHC=O; and (CH₃)₂C=O. Full geometry optimization and calculations of vibrational properties were performed for the complexes of these carbonyl bases with SCS. The BLYP-D3 method [39] with the Def2TZVPP basis set [40, 41] was used in the calculations.

The DFT interaction energies were corrected for the basis set superposition error (BSSE) computed by the CP method [42]. The CCSD(T) complete basis set limit (CBS) interaction energies of the studied complexes were determined using a previously described scheme [43]:

$$\Delta E^{\text{CCSD(T)/CBS}} = \Delta E_{\text{CBS}}^{\text{MP2}} + \left(\Delta E^{\text{CCSD(T)} - \Delta E^{\text{MP2}}} \right)_{\text{aug-cc-pVDZ}}$$

where $\Delta E_{\text{CBS}}^{\text{MP2}}$ was approximated by MP2F12/cc-pVQZ-F12 [44].

For the isolated molecules, the critical points on the electrostatic potential surface ($V_{s,\text{max}}$ and $V_{s,\text{min}}$) were computed at the BLYP-D3/Def2TZVPP and HF/cc-pVDZ levels of theory using the WFA (wavefunction analysis) program [45].

A natural bond orbital (NBO) analysis provides a detailed insight into the charge transfer and the nature of the interacting orbitals in the molecular fragments. For isolated CS₂ and for the studied complexes, a NRT (natural resonance theory) analysis has been performed in order to find all possible resonance structures of these systems. Subsequently, a NBO analysis has been performed for this electronic structure of the complex, which has the largest resonance weight. The atomic charges, occupation of orbitals and the second-order interaction energies were calculated by the DFT method using the 5.0 version of the NBO program [46, 47].

The atoms-in-molecules (AIM) analysis [48] was used in order to characterize the intermolecular interactions in the molecular systems investigated in this work. The presence of a AIM bond critical point (BCP) between the centers of the monomers in the complexes supports the presence of attractive bonding interactions. Molecular surface electrostatic potential (ESP) was calculated in the isolated molecules at the HF/cc-pVDZ and BLYP-D3/Def2TZVPP levels of theory.

For all the complexes, the symmetry-adapted perturbation theory (SAPT) decomposition of the interaction energies was performed at the MP2/cc-pVTZ level of theory. All the computations were carried out with the Gaussian 09 [49], MOLPRO 2012 [50], Turbomole 6.6 [51] and Cuby4 [52] programs.

3 Results and discussion

The formation of S...O chalcogen bonds is a common feature of all the systems investigated in this work and will be discussed in part A. Other stable structures depending on the substituents implanted on the carbonyl bond will be discussed in parts B and C.

3.1 Chalcogen-bonded complexes

3.1.1 Structure and interaction energies

Figure 1 illustrates the structure of the complexes optimized at the BLYP-D3/Def2TZVPP level. Small variations of intramolecular bond lengths such as small elongations of

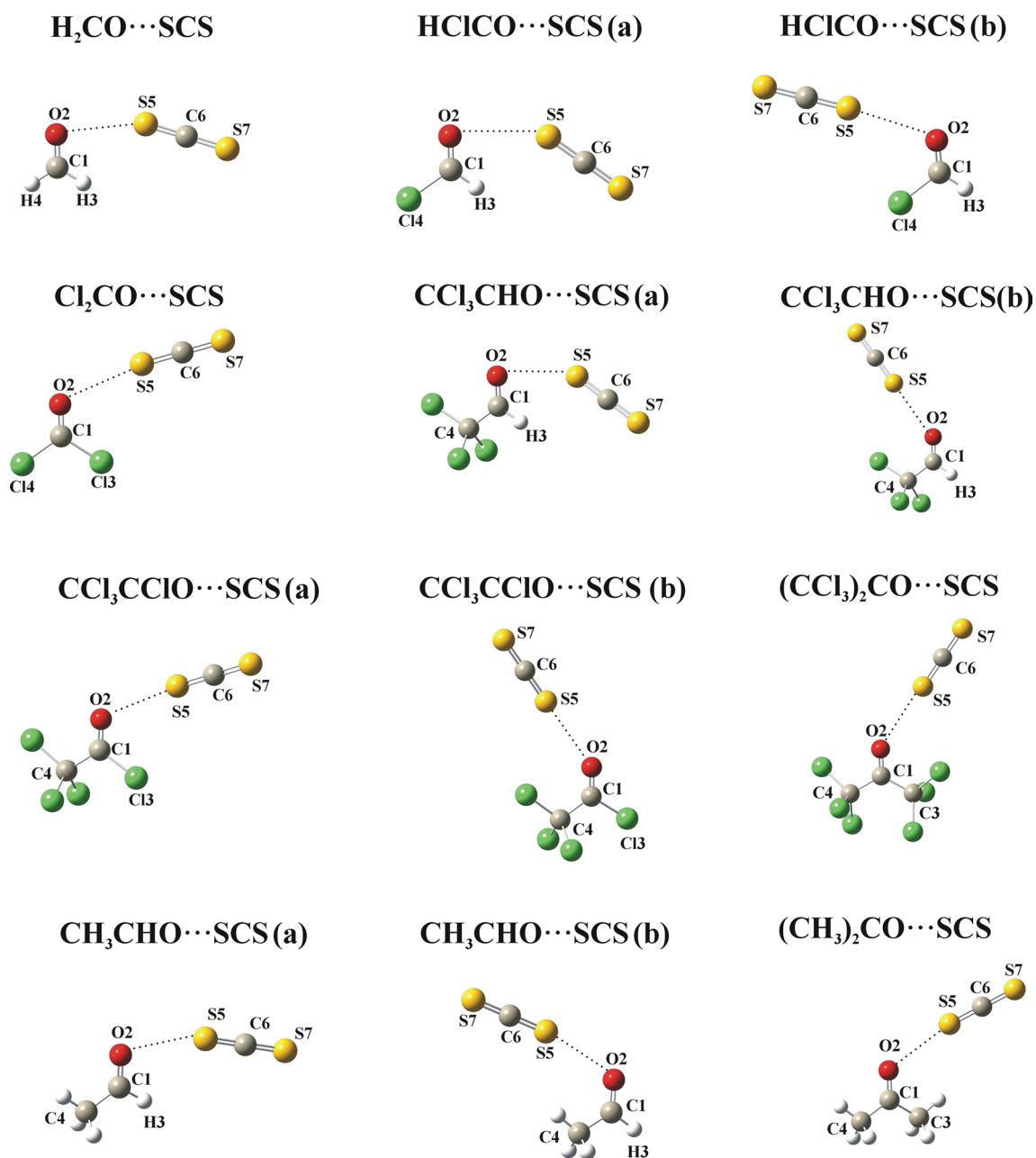


Fig. 1 Structures of the complexes between carbonyl bases and CS_2 optimized at the BLYP-D3/Def2TZVPP level of theory

the $\text{C}=\text{O}$ bond lengths between 0.9 and 1.5 mÅ are predicted for the carbonyl derivatives. These variations will no more be discussed hereafter, our work being focused on the changes occurring in the SCS molecule. Selected intermolecular parameters are indicated in Table 1. The SCS bond remains almost linear, the largest deviations from linearity being equal to 0.16° .

The complexes between SCS and CH_3CHO (a,b) or $(\text{CH}_3)_2\text{CO}$ are characterized by intermolecular $\text{S}\cdots\text{O}$ distances shorter than the sum on the van der Waals radii of O and S (3.32 Å) and can be considered as typical $\text{S}\cdots\text{O}$

chalcogen bonds. In the $\text{H}_2\text{C}=\text{S}\cdots\text{O}_2\text{S}$ complex, a similar distance of 3.198 Å has been predicted [33]. In contrast with the complexes between SCS and Cl^- [35], OH_2 [37] or OHX ($\text{X} = \text{Cl}, \text{Br}$) [38], in most of the systems investigated here, the $\text{C}=\text{S}\cdots\text{O}$ bond is not linear. This can be accounted for by other interaction than the $\text{S}\cdots\text{O}$ ones in the molecular fragments. The $\text{C1}=\text{O2}$ and $\text{S5}=\text{C6}$ bonds are coplanar, except for the systems bearing a CCl_3 group where the $\text{C1}-\text{O2}-\text{S5}-\text{C6}$ dihedral angle takes values between 5.7° and 8.4° . It must be noticed that the $\text{S}\cdots\text{H}$ distances predicted between 3.094 and 3.184 Å are larger than

Table 1 Intermolecular parameters (distances in Å, angles in degrees) in the complexes between substituted carbonyl bases and CS₂ calculated at the BLYP-D3/Def2TZVPP level of theory

System	R (O2...S5)	∠C=O...S5	R (S5...Y) ^a	∠C-O...S5=C
H ₂ CO...SCS	3.322	95.7	3.180	0.3
HCICO...SCS(a)	3.488	88.1	3.129	-0.3
HCICO...SCS(b)	3.412	114.5	3.954	-3.3
Cl ₂ CO...SCS	3.398	114.6	3.947	2.7
CCl ₃ CHO...SCS(a)	3.418	90.0	3.094	-1.3
CCl ₃ CHO...SCS(b)	3.347	141.5	3.828	6.7
CCl ₃ CCIO...SCS(a)	3.385	116.3	3.948	-8.4
CCl ₃ CCIO...SCS(b)	3.365	144.6	3.843	-6.9
(CCl ₃) ₂ CO...SCS	3.384	145.0	3.815	5.7
CH ₃ CHO...SCS(a)	3.273	97.9	3.184	-0.1
CH ₃ CHO...SCS(b)	3.280	119.3	3.160	-1.8
(CH ₃) ₂ CO...SCS	3.236	122.5	3.159	-4.8

^a Y designates the atom in the closest position to S5, excluding the O atom (Y=H or Cl; see Fig. 1)

Table 2 Interaction energies (ΔE , kcal mol⁻¹) of carbonyl bases complexed with CS₂ calculated at the CCSD(T)/CBS and BLYP-D3/Def2TZVPP levels of theory

System	CCSD(T)/CBS	BLYP-D3/Def2TZVPP
H ₂ CO...SCS	-1.82	-1.56 (0.26) ^a
HCICO...SCS(a)	-1.55	-1.37 (0.19)
HCICO...SCS(b)	-1.45	-1.15 (0.22)
Cl ₂ CO...SCS	-1.45	-1.16 (0.19)
CCl ₃ CHO...SCS(a)	-1.81	-1.60 (0.20)
CCl ₃ CHO...SCS(b)	-1.95	-1.51 (0.25)
CCl ₃ CCIO...SCS(a)	-1.54	-1.24 (0.20)
CCl ₃ CCIO...SCS(b)	-1.79	-1.35 (0.19)
(CCl ₃) ₂ CO...SCS	-1.96	-1.55 (0.22)
CH ₃ CHO...SCS(a)	-2.11	-1.76 (0.26)
CH ₃ CHO...SCS(b)	-2.04	-1.72(0.29)
(CH ₃) ₂ CO...SCS	-2.29	-1.91 (0.30)

^a The BSSE corrections are indicated in parentheses

the sum of the van der Waals radii of H and S (3.00 Å) and the S...Cl distances between 3.815 and 3.954 Å are larger than the sum of van der Waals radii of O and S (3.55 Å).

Table 2 reports the interaction energies calculated at the CCSD(T)/CBS and BLYP-D3/Def2TZVPP levels of theory. These results indicate that the interaction energies calculated at the CCSD(T)/CBS level are moderate, ranging from -1.45 to -2.29 kcal mol⁻¹. They are approximately 10–20 % lower at the BLYP-D3 level. As expected, electron-withdrawing substituents (Cl, CCl₃) decrease the interaction energies while the electron-donating substituent CH₃ increases the interaction strength. It is interesting to mention here that the binding energies calculated at the MP2/6-31G level of (CH₃)₂S₂ complexed with aliphatic ketones are of the same order of magnitude as those reported here [32].

Low binding energies were also reported for other SCS complexes, being -1.15 kcal mol⁻¹ for the SCS...OH₂ system (MP2/aug-cc-pVTZ level) [37] and -1.50 kcal mol⁻¹ for the SCS...OCIH system [38]. The binding energy is much higher when SCS interacts with a strong electron donor such as Cl⁻ (-10.59 kcal mol⁻¹) [35].

3.1.2 Electrostatic potential

It is known that chalcogen atoms may have an electropositive region at its outermost end. This means that the S atom can interact with electron donors such as carbonyl bases. The electrostatic potential ($V_{s,\min}$) of isolated CS₂ and some of the investigated carbonyl bases is illustrated in Fig. 2, and their values are reported in Table 3.

The calculated $V_{s,\max}$ for CS₂ is 16.0 kcal mol⁻¹ (HF/cc-pVDZ level) and 14.3 kcal/mol⁻¹ (BLYP-D3/Def2TZVPP). The $V_{s,\min}$ located on the S atoms around the σ -hole calculated at this last level is -1 kcal mol⁻¹. These values are lower than the value of 17.9 kcal mol⁻¹ ($V_{s,\max}$) and -2.2 kcal mol⁻¹ ($V_{s,\min}$) calculated at the MP2/aug-cc-pVTZ level [38]. Independently of the level of theory, these values are larger than those calculated for the majority of other sulfur-containing compounds. For example, $V_{s,\max}$ of F₂C=S is 12.6 kcal mol⁻¹. A larger value of 51.8 kcal mol⁻¹ is predicted for SF₄. However, the SF₄ complexes are stable only at low temperature.

The $V_{s,\min}$ values of the carbonyl bases vary between -21.2 and -42.2 kcal mol⁻¹. This indicates that substitution of hydrogen atoms by Cl or CCl₃ groups decreases the electrostatic potential while substitution by CH₃ groups increases it.

The largest values of the $V_{s,\min}$ are predicted for the strongest H₂C=O...SCS, CH₃CHO...SCS and (CH₃)₂CO...SCS complexes. For the other complexes, the

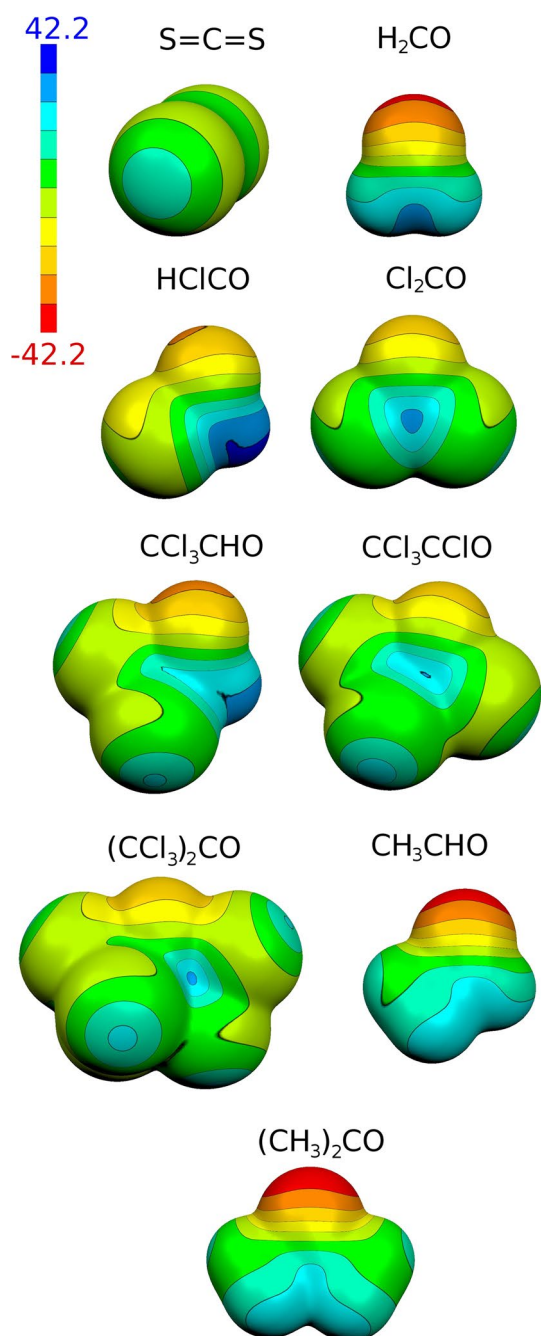


Fig. 2 Molecular surface of electrostatic potential (ESP, kcal/mol) of isolated SCS, H₂CO, HCICO, Cl₂CO, CCl₃CHO, CCl₃CCIO, (CCl₃)₂CO, CH₃CHO and (CH₃)₂CO computed on the 0.001 a.u. contour of the electrostatic density at the HF/cc-pVDZ level

stabilization energies are poorly correlated to the $V_{s,\min}$ values. As will be discussed in the next sections, this can be accounted for by the fact that the molecules are bonded together by other interactions than the S...O ones. The same remark also concerns the correlation between the interaction energies and the proton affinity (PA) of the carbonyl

Table 3 Electrostatic potentials $V_{s,\min}$ (in kcal mol⁻¹) on oxygen atoms for the isolated carbonyl bases calculated at the BLYP-D3/Def2TZVPP level of theory

Molecule	$V_{s,\min}$
H ₂ CO	-28.1
HCICO	-20.3
Cl ₂ CO	-16.7
CCl ₃ CHO	-22.4
CCl ₃ CCIO	-17.0
(CCl ₃) ₂ CO	-18.7
CH ₃ CHO	-32.6
(CH ₃) ₂ CO	-35.2

derivatives, even when the attack angle of the incoming proton is considered. (The PAs are given in S.I. Table S.1.) It must be noticed that correlations between binding energies and PAs have been calculated for halogen bonds involving ethers [53, 54] or carbonyl derivatives [55, 56], but in these systems, only one interaction site was detected.

3.1.3 AIM analysis

According to the AIM theory, two atoms are interacting with each other if their nuclei are linked by a line of maximal density named the bond path. Figure 3 indicates the presence of a bond critical point (BCP) in three selected complexes: CH₃CHO...SCS(a), CH₃CHO...SCS(b) and CCl₃CCIO...SCS(b). The electron density (ρ), the Laplacian of electron density ($\nabla^2\rho$) and the total electron energy (H) at the BCP of the studied complexes are collected in Table 4.

These calculations indicate that the H₂CO...SCS and CH₃CHO...SCS(a) complexes are stabilized only by S...O chalcogen bonds. In the case of the four complexes: HCICO...SCS(a), CCl₃CHO...SCS(a), CH₃CHO...SCS(b) and (CH₃)₂CO...SCS, the AIM analysis reveals additional stabilization interactions between the sulfur and hydrogen atoms (S...H). In the case of six other complexes: HCICO...SCS(b), Cl₂CO...SCS, CCl₃CHO...SCS(b), CCl₃CCIO...SCS(a), CCl₃CCIO...SCS(b) and (CCl₃)₂CO...SCS, additional S...Cl interactions have been detected.

According to the Popelier's criteria for hydrogen bonds, the electron density at the BCP ranges from 0.002 to 0.035 au, and the Laplacian of the electron density ranges from 0.024 to 0.139 au [57, 58]. As reported in Table 4, the S...H and S...Cl interactions do not fulfill the second criterion. Therefore, they cannot be classified as hydrogen or chalcogen bonds but as weak van der Waals interactions, in agreement with the corresponding intermolecular distances. It is worth mentioning that in all the complexes, except for

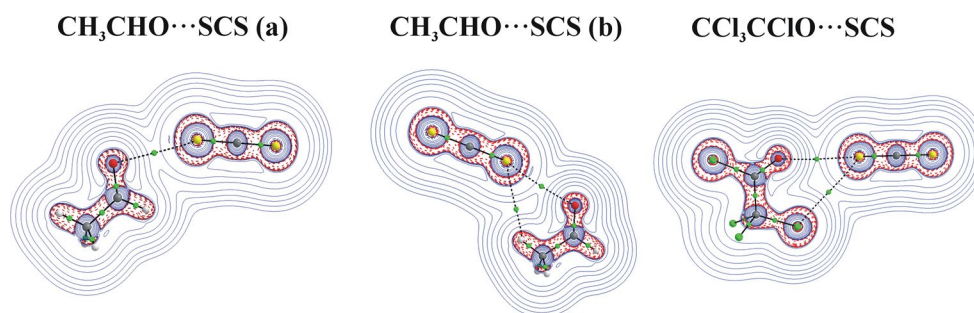


Fig. 3 Contour line diagram of the Laplacian of electron density of the $\text{CH}_3\text{CHO}\cdots\text{SCS}$ (a), $\text{CH}_3\text{CHO}\cdots\text{SCS}$ (b) and $\text{CCl}_3\text{CClO}\cdots\text{SCS}$ complexes (in the plane passing through the O, S and H or Cl atoms marked on the figure). The solid (blue) lines represent positive values

of the Laplacian, while the dashed (red) lines represent the negative values. Small green points represent the bond critical points (BCPs). The electron density description was obtained at the BLYP-D3/Def2TZVPP level

Table 4 Bond critical points (BCPs) properties: electron density ρ , Laplacian of electron density $\nabla^2\rho$ (both in atomic units) and total electron energy (H, kcal mol⁻¹). The electron density descriptions were obtained at the BLYP-D3/Def2TZVPP level

System	Interaction	ρ	$\nabla^2\rho$	H
$\text{H}_2\text{CO}\cdots\text{SCS}$	S...O	0.0064	0.0234	0.861
$\text{HCICO}\cdots\text{SCS}$ (a)	S...O	0.0047	0.0179	0.707
	S...H	0.0050	0.0165	0.560
$\text{HCICO}\cdots\text{SCS}$ (b)	S...O	0.0047	0.0181	0.748
	S...Cl	0.0034	0.0101	0.420
$\text{Cl}_2\text{CO}\cdots\text{SCS}$	S...O	0.0048	0.0186	0.771
	S...Cl	0.0034	0.0104	0.432
$\text{CCl}_3\text{CHO}\cdots\text{SCS}$ (a)	S...O	0.0054	0.0202	0.770
	S...H	0.0053	0.0175	0.577
$\text{CCl}_3\text{CHO}\cdots\text{SCS}$ (b)	S...O	0.0050	0.0205	0.849
	S...Cl	0.0041	0.0129	0.526
$\text{CCl}_3\text{CClO}\cdots\text{SCS}$ (a)	S...O	0.0049	0.0191	0.788
	S...Cl	0.0034	0.0103	0.430
$\text{CCl}_3\text{CClO}\cdots\text{SCS}$ (b)	S...O	0.0046	0.0195	0.826
	S...Cl	0.0040	0.0124	0.511
$(\text{CCl}_3)_2\text{CO}\cdots\text{SCS}$	S...O	0.0045	0.0188	0.795
	S...Cl	0.0042	0.0132	0.538
$\text{CH}_3\text{CHO}\cdots\text{SCS}$ (a)	S...O	0.0070	0.0256	0.924
$\text{CH}_3\text{CHO}\cdots\text{SCS}$ (b)	S...O	0.0066	0.0243	0.908
	S...H	0.0042	0.0126	0.468
$(\text{CH}_3)_2\text{CO}\cdots\text{SCS}$	S...O	0.0072	0.0266	0.970
	S...H	0.0041	0.0127	0.470

$\text{HCICO}\cdots\text{SCS}$ (a), the electron density (ρ), the Laplacian of the electron density ($\nabla^2\rho$) and the total electron energy (H) at the BCP are larger for the S...O interaction than for the S...H and S...Cl interactions. For the $\text{HCICO}\cdots\text{SCS}$ (a) complex, the electron density for the S...H interaction is nearly equal to that characterizing the S...O interaction. For this complex, the $\text{C}=\text{O}\cdots\text{S5}$ angle (88.1°) is the smallest,

the S5 atom being perpendicular to the $\text{C}=\text{O}$ bond. It can be concluded from the AIM analysis that the S...O chalcogen bond is the dominant stabilization interaction for most of the investigated complexes, but that additional van der Waals S...Cl or S...H interactions also contribute to the stability of the systems.

3.1.4 NBO analysis

Table 5 reports the charges on the C, S5 and S7 atoms along with the charge transfer taking place from the carbonyl bases to CS_2 . The charges on these atoms calculated by different methods are given in S.I. Table S.3. Let us notice that the charge on the C atom in isolated CS_2 calculated at the HF/aug-cc-PVTZ is $-0.2739e$ [38], much lower than the value of $-0.4506e$ obtained in the present work. The S and C atoms are characterized by the same electronegativity, and it may be rather surprising that our calculations predict in the isolated molecule large differences of charge on the C and S atoms. These differences can be accounted for by a large electronic delocalization within the molecule. Indeed, the NRT calculations show that in isolated $\text{S5}=\text{C}=\text{S7}$ (having a resonance weight of 54.7 %) there is a charge transfer from LP(1) S5 to $\sigma^*(\text{C}=\text{S7})$ and from LP(1)S7 to $\sigma^*(\text{C}=\text{S5})$ as well as a charge transfer from LP(2)S5 to $\pi^*(\text{C}=\text{S7})$ and from LP(2)S7 to $\pi^*(\text{C}=\text{S5})$. This delocalization results in occupation of the $\sigma^*(\text{C}=\text{S})$ and $\pi^*(\text{C}=\text{S})$ orbitals equal to 0.0242e and 0.5259e, respectively.

The results reported in Table 5 show that the charge transfer from the carbonyl base to CS_2 is small, ranging from 0.4 to 6.3 me and does not follow the order of stability of the systems. There is a flow of electrons from the S5 atom to the external S7 atom.

It is interesting to compare the results obtained from the AIM analysis and the NBO calculations. The second-order interaction energies are gathered in Table S.2 in S.I.

Table 5 NBO charges on the C, S5 and S7 atoms (e) and charge transfer (CT) from the carbonyl bases to S5=C6=S7 (me)

System	q(C6) ^a	q(S5) ^a	q(S7) ^a	CT
H ₂ CO...SCS	-0.4570	0.2401	0.2136	3.4
HCICO...SCS(a)	-0.4542	0.2238	0.2308	0.5
HCICO...SCS(b)	-0.4556	0.2441	0.2070	4.5
Cl ₂ CO...SCS	-0.4545	0.2382	0.2128	3.5
CCl ₃ CHO...SCS(a)	-0.4549	0.2308	0.2246	0.4
(CCl ₃)CHO...SCS(b)	-0.4779	0.2481	0.2059	3.5
(CCl ₃)ClCO...SCS(a)	-0.4546	0.2400	0.2112	3.5
(CCl ₃)ClCO...SCS(b)	-0.4556	0.2416	0.2117	2.3
(CCl ₃) ₂ CO...SCS	-0.4561	0.2446	0.2026	2.7
CH ₃ CHO...SCS(a)	-0.4582	0.2476	0.2066	4.0
CH ₃ CHO...SCS(b)	-0.4590	0.2490	0.2042	5.7
(CH ₃) ₂ CO...SCS	-0.4506	0.2552	0.1991	6.3

^a In isolated SCS, q(C) = -0.4506e, q(S) = 0.2254e

where E¹² and E²¹ refer, respectively, to electronic donation from the carbonyl base to CS₂ and in the reverse direction. Although the second-order energies are not strictly additive, these data indicate that in all the systems, except for HCICO...CS₂(a), E¹² > E²¹.

Both the AIM and NBO analyses reveal the existence of S5...O interactions and in some cases secondary S5...Cl or Cl...H interactions. Both methods reveal that the S5...O interaction is the stronger one, the E¹² energies varying between 0.11 and 0.74 kcal mol⁻¹. The only exception is the HCICO...SCS(a) complex where the charge transfer takes place to the S5 atom, resulting in a decrease in the positive charge on this atom (Table 5).

Both the AIM and NBO analyses indicate the presence of S...Cl interaction in the HCICO...SCS(b), Cl₂CO...SCS, CCl₃CHO...SCS(b), CCl₃ClO...SCS(a,b) systems and S...H interaction in the HCICO...SCS(b), CCl₃CHO...SCS(a), CH₃CHO...SCS(a,b) and (CH₃)₂...SCS systems.

Let us also notice that the NBO analysis shows that S...H interactions detected by the AIM analysis can be extended to σ*(CC), σ*(CO) and σ*(CCl) orbitals. The weak S...H interaction in the H₂CO...SCS and CH₃CHO...SCS(a) systems was not predicted by the AIM calculations, in contrast with the NBO calculations. Some discrepancies between

the AIM and NBO calculations have also been detected in the (XNO₂)₂ homodimers [59].

It may be argued that the charge transfer and second-order interaction energies are small (never exceeding 0.75 kcal mol⁻¹) and not significant. However, in most of the systems, there is a good agreement between the AIM and NBO results, which suggests that these small values are relevant.

There are some discrepancies between the literature data concerning the variation of the C=S distances resulting from the interaction with guest molecules. In the SCS...Cl⁻ system, the bonded C=S group contracts by 2.3 mÅ [35], while in the SCS...OCiH system, the bonded C=S group elongates by 3 mÅ [38]. In the chalcogen bond formed between Se=C=Se and water, the elongation of the free C=Se bond is larger (3 mÅ) than the elongation of the bonded C=Se group (1 mÅ) but a reverse trend is predicted when Se=C=Se interacts with electron donors such as PH₃ or H₂S [60]. These data indicate that the variation of the C=S distances induced by the interaction with electron donors is small. This is also the case for the present systems. The variation of the C=S5 and C=S7 bond lengths is indicated in Table 6 which also reports for the strongest complexes the variation of the σ*(C=S) and π*(C=S) populations of both C=S bonds.

It should be mentioned that a charge transfer from the LPs of the Cl⁻ anion to the σ*(C=S) and π*(C=S) has been predicted for the Cl⁻...SCS system, but the occupation of these antibonding orbitals has not been discussed [35].

These results show that the variations of the C=S5 distances are very small; this is tentatively explained by the fact that the increase in the σ*(C = 5) population is nearly compensated by the decrease in the π*(C = 5) population. In contrast, the increase in the C=S7 distances is significant and may result from the increase in both the σ*(C=S7) and π*(C=S7) populations.

3.1.5 SAPT decomposition of the energies

To evaluate the components of the interaction energies in the investigated complexes, a SAPT analysis has been

Table 6 Variation of the C=S5 and C=S7 distances (mÅ)^a and corresponding σ*(C=S) and π*(C=S) populations (me)^b

Systems	Δr(C=S5)	Δσ*(C=S5)	Δπ*(C=S5)	Δr(C=S7)	Δσ*(C=S7)	Δπ*(C=S7)
H ₂ CO...SCS	0.6	5.7	-6.3	1.5	1.0	6.4
CH ₃ CHO...SCS(a)	0.3	7.6	-10.2	2.3	1.3	9.3
CH ₃ CHO...SCS(b)	0.5	7.2	-9.4	2.6	1.2	9.7
(CH ₃) ₂ CO...SCS	0.3	7.4	-11.6	3.2	1.4	12.3

^a r(C=S) distance in isolated S=C=S is 1.5669 Å

^b σ*(C=S) occupation in isolated S=C=S is 0.0242e; π*(C=S) occupation in isolated S=C=S is 0.5259e

performed at the MP2/cc-pVTZ level of theory. The results are collected in Table 7.

The SAPT interaction energies are smaller than the CCSD(T) values and vary between -0.96 and -1.92 kcal mol $^{-1}$. These results indicate that the electrostatic term is the dominant attraction component, representing 51–52 % of the total energy for complexes characterized by typical S...O chalcogen bonds and between 39 and 46 % for the systems involving chlorinated bases. In contrast, the dispersion energy represents 39–43 % of the total energy for the stronger bases and increases to 48–56 % for the weaker bases. The induction effect is of the same order of magnitude in all the systems. The fact that dispersion forces contribute considerably to the bonding between chalcogen centers has been outlined in several dimethyl ether complexes [61, 62].

Table 7 SAPT (MP2/cc-pVTZ) interaction energies (E_{int} , kcal mol $^{-1}$) and their components: electrostatic $E(\text{elec})$, induction $E(\text{ind})$, dispersion $E(\text{disp})$ and exchange $E(\text{exch})$

System	E_{int}	$E(\text{elec})$	$E(\text{ind})$	$E(\text{disp})$	$E(\text{exch})$
H ₂ CO...SCS	-1.42	-1.68	-0.21	-1.35	1.82
HCICO...SCS(a)	-1.13	-1.28	-0.17	-1.34	1.66
HCICO...SCS(b)	-1.02	-1.06	-0.13	-1.26	1.43
Cl ₂ CO...SCS	-0.96	-1.00	-0.09	-1.34	1.46
CCl ₃ CHO...SCS(a)	-1.29	-1.45	-0.16	-1.59	1.90
CCl ₃ CHO...SCS(b)	-1.42	-1.40	-0.18	-1.62	1.78
CCl ₃ CCIO...SCS(a)	-1.06	-1.00	-0.10	-1.42	1.46
CCl ₃ CCIO...SCS(b)	-1.27	-1.13	-0.11	-1.59	1.56
(CCl ₃) ₂ CO...SCS	-1.39	-1.18	-0.13	-1.70	1.62
CH ₃ CHO...SCS(a)	-1.69	-1.92	-0.28	-1.51	2.01
CH ₃ CHO...SCS(b)	-1.68	-2.05	-0.33	-1.62	2.31
(CH ₃) ₂ CO...SCS	-1.92	-2.26	-0.41	-1.74	2.49

3.2 Structures stabilized by S...Cl interactions

Other stable structures characterized by S...Cl interactions have been predicted for chlorinated carbonyl bases, namely Cl₂CO, CCl₃CICO and (CCl₃)₂CO interacting with CS₂. The structures of these complexes are illustrated in Fig. 4.

In these structures, the C=O group is not involved in the interaction. The shortest Cl...S5 distances are: 3.848, 3.849 and 3.767 Å in the Cl₂CO...SCS, CCl₃CICO...SCS and (CCl₃)₂CO...SCS complexes, respectively. These distances are longer than the sum of the van der Waals radii of S and Cl (3.55 Å), indicating van der Waals interactions between these two atoms. The interaction energies are reported in Table 8. They are of the same order of magnitude as those calculated for the chalcogen-bonded complexes (Table 2). The NBO analysis indicates that in these complexes the charge transfer takes place from the carbonyl base to the CS₂ molecule. The values of the CT are: 2.5, 4.4 and 5.8 me in (CCl₃)₂CO...SCS, Cl₂CO...SCS and CCl₃CICO...SCS complexes, respectively.

The SAPT decomposition of the interaction energies is indicated in Table 9. As follows from these data, the dominant attraction component is the dispersion energy which represents about 70 % of the total attraction energy. The electrostatic component is equal to about 30 % of the total energy. The contribution of the induction energy is negligibly small. These results are in line with the data predicted for carbonyl complexes. For these systems, it was indeed concluded that the dispersion component of the energy predominates in van der Waals complexes.

3.3 Structures stabilized by CH...C hydrogen bonds

In the case of the four carbonyl bases bearing a CH group, other stable structures stabilized mainly by C-H...C hydrogen bonds are also predicted by our calculations. It is

Fig. 4 Structures of complexes between carbonyl bases and CS₂ stabilized by S...Cl interactions, optimized at the BLYP-D3/Def2TZVPP level of theory

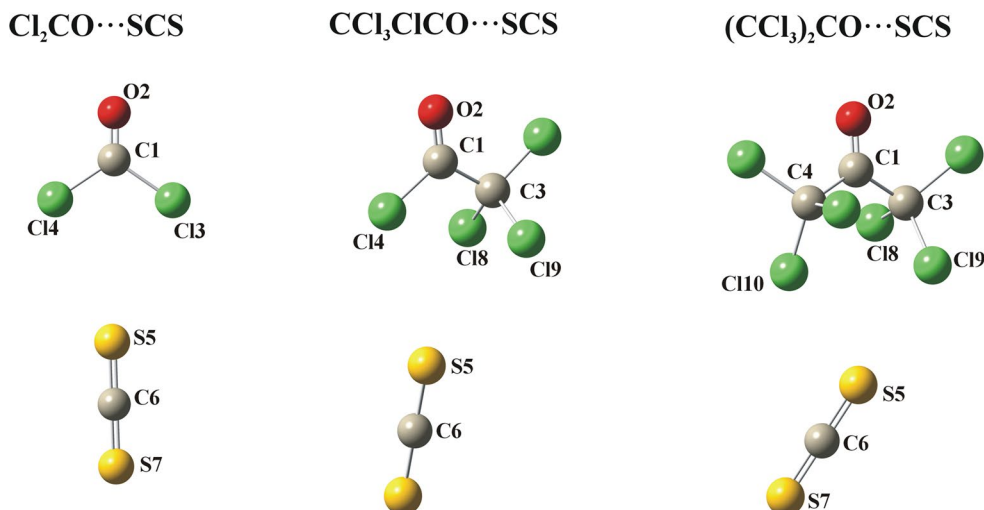


Table 8 Interaction energies (ΔE , kcal mol⁻¹) of CS₂ complexes with carbonyl bases stabilized by S...Cl interactions

	ΔE	ΔE_{corr}
	CCSD(T)	BLYP-D3/Def2TZVPP
Cl ₂ CO...SCS	-1.27	-1.04 (0.19) ^a
CCl ₃ CClO...SCS	-1.90	-1.61 (0.24)
(CCl ₃) ₂ CO...SCS	-2.17	-1.84 (0.24)

^a The values of BSSE corrections are in parentheses

Table 9 SAPT (MP2/cc-pVTZ) interaction energies (E_{int} , kcal mol⁻¹) and their components: electrostatic $E(\text{elec})$, induction $E(\text{ind})$, dispersion $E(\text{disp})$ and exchange $E(\text{exch})$ for the complexes investigated

System	E_{int}	$E(\text{elec})$	$E(\text{ind})$	$E(\text{disp})$	$E(\text{exch})$
Cl ₂ CO...SCS	-0.58	-0.55	-0.04	-1.33	1.34
CCl ₃ CClO...SCS	-0.89	-0.82	-0.05	-2.06	2.05
(CCl ₃) ₂ CO...SCS	-1.03	-1.1	-0.06	-2.36	2.49

important to mention here that with proton donors such as HF [36] or OHX (X = Cl, Br) [38], S...HF or S...HO hydrogen bonds nearly perpendicular to the S atom are formed. Owing to the weaker acidity of the CH bonds of the carbonyl bases as compared with the HF or OH acidities, these structures were not predicted by our calculations. The formation of these CH...C hydrogen bonds may find their origin in the large negative charge on the C atom ($\sim -0.45e$). Since the aim of this paper was mainly the discussion of the complexes stabilized by S...O chalcogen bonds, information on these complexes can be found in the S.I.

4 Conclusions

A theoretical study of interaction between carbonyl bases (H₂C=O and CH₃- and Cl-derivatives) and CS₂ has been carried out by means of DFT-BLYP-D3 and ab initio CCSD(T) methodologies. The main conclusions are the following:

1. The CCSD(T)CBS calculated interaction energies are moderate, ranging from -1.45 to -2.29 kcal mol⁻¹.
2. The electrostatic potential is very sensitive to the substituent implanted on the C=O group and varies between -21.2 kcal mol⁻¹ (for Cl₂C=O) and -42.2 kcal mol⁻¹ (for (CH₃)₂C=O).
3. The charge transfer occurs from the carbonyl to the thio-carbonyl base and is small, ranging from 0.4 to 6.3 me.
4. The AMI analysis reveals the presence of a BCP between the O and S atoms. As shown by this analysis, the complexes are stabilized not only by S...O chalcogen

bonds but also by weaker S...Cl or S...H interactions which are detected in most of the systems.

5. The results from NBO calculations provide further information on the nature of the bonding and antibonding orbitals and the second-order interaction energies.
6. The small variation of the C=S distances is tentatively assigned to the variation in occupation of the $\sigma^*(\text{C}=\text{S})$ and $\pi^*(\text{C}=\text{S})$ orbitals.
7. The SAPT decomposition of the interaction energies shows that in the stronger complexes, the electrostatic component of the energy predominates while in the weaker van der Waals complexes, the dispersion energy becomes predominant.
8. Other stable structures characterized by S...Cl interactions are predicted for the complexes between chlorinated ketones and CS₂. In these structures, the C=O group is not involved in the interaction, but the molecules are bonded together by two or three S...Cl intermolecular bonds. These systems have about the same stability as the C=O...S bonded systems.
9. Complexes between carbonyl bases bearing a CH group and CS₂ are also stabilized by CH...C hydrogen bonds. The interaction energies characterizing these systems are of the same order of magnitude as those predicted for the S...O chalcogen bonds.

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