

COMPUTATIONAL INVESTIGATION OF THE CH₃XC=S...S (X = H, HO, HS, PH₂, CH₃) BONDING TYPE

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The CH₃XC=S...S (X = H, HO, HS, PH₂, CH₃) bonding types are investigated using the second order Møller-Plesset perturbation approximation with the cc-pVDZ basis set. Electrostatic density potential maps of CH₃XC=S (X = H, HO, HS, PH₂, CH₃) are generated at the MP2/cc-pVDZ level of theory. The interaction energy and topological property are theoretically encompassed for the five complexes. Electrostatic density potential maps of five monomers are generated for the determination of attractive interaction sites. There are different misshaped electron clouds. The red-shifting character is obtained for the CH₃XC=S...S (X = H, HO, HS, PH₂) interaction. For all complexes the S...S bonds are typical closed-shell interactions, and the topological properties of the S...S bond fall short of three criteria for the existence of the hydrogen bond. Theoretical values are in very good agreement with the experimental results.

Keywords: MP2, interaction energy, topological property analysis.

INTRODUCTION

The halogen bond plays an important role in biomolecular systems and has been investigated mostly in [1-6]. Being similar to the nature of the halogen bond, the X-Chal...Y bonding type has been also examined in recent years [7-11]. Wang and co-workers proved that the X = S...Cl⁻¹ bonding type and the halogen bond had similar qualities [12]. As the X = S...Cl⁻¹ bonding type, the existence of the CH₃XC=S...S bonding type was verified in the crystal structure [13]. Furthermore, no theoretical study has been reported on the CH₃XC=S...S bonding type. In the X = S...Cl⁻¹ bonding type, an interesting question is whether there is the effect of one atom replacing the halogen ion. In addition, it is not known whether the CH₃XC=S...S bonding type exists in biological systems or not. Discrepancies between the experimental and theoretical studies demonstrate the need for further studies of the CH₃XC=S...S bonding type. The atoms in molecules (AIM) theory [14] is not only a real object that can be obtained computationally using the electron density as a starting point, but also can provide quantities for a researcher to extract chemical information from the topological property of the electron charge density and its Laplacian. The AIM theory has already been successfully applied to understand conventional hydrogen bonds [15, 16]. In addition, recent publications [17, 18] have also shown that the AIM theory is a powerful tool to analyze the bonding nature. The present study is intended to examine theoretically the CH₃XC=S...S (X = H, HO, HS, PH₂, CH₃) bonding type according to the AIM method. The work introduces a detailed operation on the interaction energies and topological property for the CH₃XC=S...S bonding type. We hope that insights provided herein will assist experimental

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and theoretical workers in their efforts to study the $\text{CH}_3\text{XC}=\text{S}\dots\text{S}$ ($\text{X} = \text{H}, \text{HO}, \text{HS}, \text{PH}_2, \text{CH}_3$) bonding type in biomolecular systems and crystal engineering.

COMPUTATIONAL APPROACHES

Equilibrium geometries of monomers and complexes are fully optimized with the correlation-consistent polarized valence double-zeta basis sets (cc-pVDZ) [19] at the second-order Møller-Plesset (MP2) level [20] using the Gaussian 03 program package [21]. Harmonic frequencies of optimized geometries are calculated at the same level to confirm the equilibrium geometries that correspond to energy minima. Based on the equilibrium geometries, the electrostatic density potentials are computed at the MP2/cc-pVDZ level of theory, and the interaction energies are calculated at the MP2/cc-pVTZ level of theory. The basis set superposition error (BSSE) was calculated using the counterpoise (CP) method of Boys and Bernardi [22]. The bonding characteristics of the C=S and S...S bonds in this investigation are analyzed in terms of AIM theory. The AIM analysis was performed using the MP2/cc-pVDZ calculated equilibrium geometries.

RESULTS AND DISCUSSION

Equilibrium Geometry, Vibrational Frequency, and Interaction Energies. Table 1 summarizes the structures of monomers and complexes at the MP2/cc-pVDZ level of theory.

Table 1 shows that C=S and C–C bonds in the complexes $\text{CH}_3\text{XC}=\text{S}\dots\text{S}$ ($\text{X} = \text{H}, \text{HO}, \text{HS}, \text{PH}_2$) are elongated. However, C=S and C–C bonds are not distinctive in the $(\text{CH}_3)_2\text{C}=\text{S}\dots\text{S}$ complex and the corresponding monomer, which illustrates that the sulfur atom has no influence on the $(\text{CH}_3)_2\text{C}=\text{S}$ molecule. It is obvious that C=S bond values agree very well with the experimental values. Comparing with experimental data, S...S distances are elongated, but the discrepancies between the experimental and theoretical studies are minor. In addition, the corresponding harmonic vibrational frequencies are also given in Table 1. The frequency analysis reveals the red-shifting character of the $\text{CH}_3\text{XC}=\text{S}\dots\text{S}$ ($\text{X} = \text{H}, \text{HO}, \text{HS}, \text{PH}_2$) interaction, whereas the ignorable blue-shift has been obtained for the $(\text{CH}_3)_2\text{C}=\text{S}\dots\text{S}$ complex. The frequency analysis illustrates deeply that the frequency shift of molecule complexation is relative to the bond length change. Additionally, as for the five complexes, there are true minima (all real frequencies) on their respective potential energy surfaces.

In addition, the electrostatic potential maps of five corresponding monomers $\text{CH}_3\text{XC}=\text{S}$ ($\text{X} = \text{H}, \text{HO}, \text{HS}, \text{PH}_2, \text{CH}_3$) are shown in Fig. 1. It is proved that different misshaped electron clouds in 3D five monomers result in different properties. Because of the relatively strong electronegativity of the sulfur atom in the C=S bond, a large electron density is conferred on

TABLE 1. Optimized Geometries (angstroms and degrees), Frequencies (inverse centimeters), Number of Imaginary Frequencies (N_{img}) of Five Complexes and Corresponding Monomers

Complexes	Interaction	$R_{\text{C}=\text{S}}$	$R_{\text{S}\dots\text{X}}$	$\angle\text{CSX}$	Freq(C=S)	N_{img}
$\text{CH}_3\text{HCS}\dots\text{S}$	S...S	1.6307	4.0459	179.83	1195.3	0
CH_3HCS		1.6302			1196.4	0
$\text{CH}_3\text{HOCS}\dots\text{S}$	S...S	1.6340	4.0720	176.99	1493.2	0
CH_3HOCS		1.6336			1493.8	0
$\text{CH}_3\text{HSCS}\dots\text{S}$	S...S	1.6399	3.9859	177.80	1287.3	0
CH_3HSCS		1.6395			1288.1	0
$\text{CH}_3\text{PH}_2\text{CS}\dots\text{S}$	S...S	1.6404	3.9957	179.41	1268.8	0
$\text{CH}_3\text{PH}_2\text{CS}$		1.6401			1269.5	0
$(\text{CH}_3)_2\text{CS}\dots\text{S}$	S...S	1.6380	4.0472	180.00	1333.4	0
$(\text{CH}_3)_2\text{CS}$		1.6380			1333.2	0
	S...S	1.642 [13]	3.432 [13]	162.8 [13]		

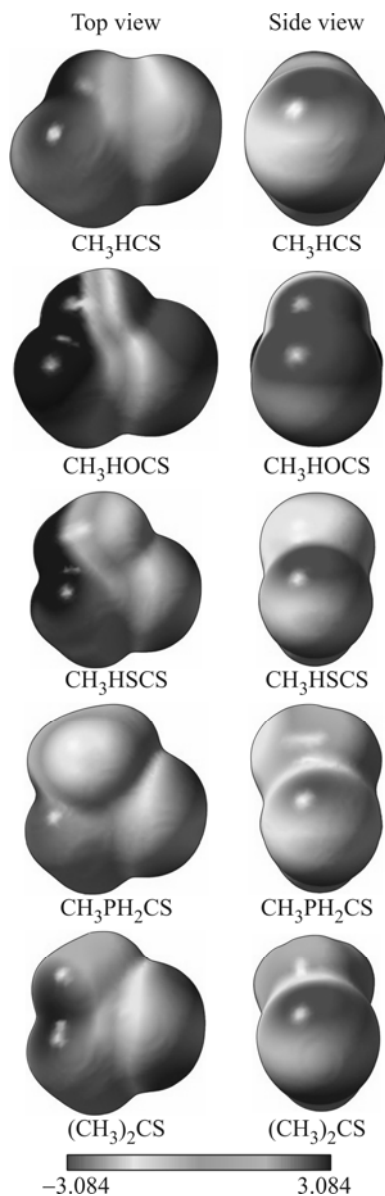


Fig. 1. Electrostatic potentials of five monomers $\text{CH}_3\text{XC}=\text{S}$ ($\text{X} = \text{H}, \text{HO}, \text{HS}, \text{PH}_2, \text{CH}_3$) computed at the MP2/cc-pVDZ theory level with a scale of -3.084 kcal/mol to 3.084 kcal/mol.

the sulfur atom of the C=S bond. Evidently, this is provided by the MEP map (Fig. 1). The MEP plot indicates a positive electrostatic potential (shown in black). Around the sulfur atom, regions of a negative electrostatic potential (shown in grey) are noticeable, with the strongest negative potential being in the immediate vicinity of the sulfur atom of the C=S bond. On the one hand, positive and negative electrostatic potentials are stronger in $\text{CH}_3\text{HOC}=\text{S}$ than in the other monomers, which implies that the positive charge atom should point in the direction of the strong negative potential on the sulfur atom of the C=S bond. On the other hand, there is a negative potential in the region of the oxygen atom of the H–O bond in $\text{CH}_3\text{HOC}=\text{S}$.

Interaction energies ΔE_1 , BSSE, counterpoise corrected interaction energies ΔE_1^{CP} are calculated at the MP2/cc-pVDZ level of theory for the five complexes (Table 2). At the same time, interaction potentials ΔE_2 at the MP2/ cc-pVTZ

TABLE 2. Interaction Energies ΔE , BSSE, Interaction Energies Corrected for BSSE ΔE^{CP} of the Complexes at 298.15 K*

Complexes	ΔE_1	BSSE	ΔE_1^{CP}	ΔE_2
CH ₃ HCS...S	-0.22	0.30	0.08	-0.34
CH ₃ HOCS...S	-0.14	0.31	0.17	-0.28
CH ₃ HSCS...S	-0.27	0.33	0.06	-0.41
CH ₃ PH ₂ CS...S	-0.28	0.33	0.05	-0.42
(CH ₃) ₂ CS...S	-0.19	0.32	0.13	-0.34

*All values are in kcal/mol.

TABLE 3. Density (ρ), Density Laplacian ($\nabla^2\rho$), Eigenvalues of the Hessian Matrix ($\lambda_1, \lambda_2, \lambda_3$), and Ellipticity (ϵ) at the Bond Critical Points of Five Complexes at the MP2/cc-pVDZ level of theory*

Complexes	Interaction	ρ^a	$\nabla^2\rho^b$	ϵ^c	λ_1	λ_2	λ_3
CH ₃ HCS...S	C=S	0.22220	0.3545	0.1126	-0.2210	-0.1987	0.7742
	S...S	0.00342	0.0091	0.0703	-0.0017	-0.0016	0.0124
CH ₃ HOCS...S	C=S	0.21581	0.4909	0.1411	-0.2072	-0.1816	0.8797
	S...S	0.00317	0.0087	0.0208	-0.0015	-0.0015	0.0117
CH ₃ HSCS...S	C=S	0.21487	0.3973	0.1082	-0.2015	-0.1818	0.7806
	S...S	0.00370	0.0101	0.0454	-0.0018	-0.0017	0.0136
CH ₃ PH ₂ CS...S	C=S	0.21780	0.3228	0.1092	-0.2090	-0.1884	0.7202
	S...S	0.00369	0.0100	0.0688	-0.0018	-0.0017	0.0135
(CH ₃) ₂ CS...S	C=S	0.21996	0.3486	0.1401	-0.2179	-0.1911	0.7576
	S...S	0.00340	0.0091	0.0623	-0.0017	-0.0016	0.0124

*All units are atomic units.

^aElectron charge density at the bond critical points.

^bLaplacian of the electron density at the bond critical points.

^cThe ellipticity at bond critical point.

level of theory are also presented in Table 2. It is obvious that the BSSE is overestimated by the counterpoise method [23-26]. However, the MP2/ cc-pVTZ level of theory is free of BSSE and computationally feasible for the complexes studied here. All of the interaction potentials show that the strongest bond is formed between CH₃PH₂C=S and the sulfur atom, which is -0.42 kcal/mol. All in all, the substitution of methyl and other radicals (H, HO, HS, PH₂, CH₃) causes a negligible effect on the CH₃XC=S...S (X = H, HO, HS, PH₂, CH₃) bonding type comparing to the study reported in the literature [12].

AIM Analysis. AIM theory is a very important tool in analyzing the bonding nature [14]. Moreover, AIM theory based on a topological analysis of the electron charge density with its Laplacian at the bond critical points (BCPs) correlating to the hydrogen bond strength, has frequently been applied to study noncovalent bonds [14, 27]. Based on AIM theory, Popelier built a set of criteria for the assessment of hydrogen bond interaction [27]. Hydrogen bonding was evidenced to exist in a bond path, an interatomic surface, and BCP between the donor hydrogen nucleus and the acceptor. In addition, the electron density (ρ) at these BCPs should range from 0.002 au to 0.035 au, and the Laplacian of the electron density ($\Delta^2\rho$) should range from 0.024 au to 0.139 au. In the present work, the topological properties of these bonds have been examined in five complexes. The electron density (ρ) of BCPs of some bonds are showed for all complexes in Table 3.

It is obvious that the values of the electron density for C=S in five complexes are much larger than the proposed range for the H-bond, which reflects that the bonds are stronger than the hydrogen bond. However, the electron density (ρ) values for S...S are within the proposed range of 0.002 au to 0.035 au for the hydrogen bond. It has been proven that ρ is

related to the bond strength [28]. The value of ρ is much higher for the C=S bonds than those of the S...S bonds and similar to the S...S bonds in five complexes. In addition, three λ_1 , λ_2 , and λ_3 values are three ordered ($\lambda_1 < \lambda_2 < \lambda_3$) eigenvalues for the diagonalization of the Hessian of the Laplacian of the electron density of BCP. The two negative eigenvalues of the Hessian matrix of electron density λ_1 and λ_2 measure the degree of contraction of ρ perpendicular to the bond toward the critical point, and the positive eigenvalue (λ_3) measures the degree of contraction parallel to the bond and from the BCP toward each of the neighboring nuclei. The Laplacian $\Delta^2\rho$ is the sum of λ_1 , λ_2 , and λ_3 eigenvalues. Bader pointed out that for closed-shell interactions (ionic bonds, hydrogen bonds, and van der Waals interactions), the $\Delta^2\rho$ value is positive. For shared interactions the Laplacian is negative [14]. According to Table 3, in all complexes, S...S bonds are typical closed-shell interactions. However, the positive values of $\Delta^2\rho$ go too far the proposed range of 0.024 au to 0.139 au for the hydrogen bond. Evidently, the topological properties of the S...S bond fall short of three criteria for the existence of the hydrogen bond. Moreover, the ellipticity ε is defined as $\lambda_1/\lambda_2 - 1$ and measures the extent to which the charge is preferentially accumulated. On the one hand, the ellipticity provides a measure of not only the π character of a bond, but also the bond stability.

CONCLUSIONS

This work investigated the geometries, interaction energies, and the topological property of the $\text{CH}_3\text{XC}=\text{S}\dots\text{S}$ (X = H, HO, HS, PH_2 , CH_3) bonding type. According to the study, the X = S...S bonding type is different from the X = S... Cl^{-1} bonding type in the charge transfer. The red-shifting character has been obtained for the $\text{CH}_3\text{XC}=\text{S}\dots\text{S}$ (X = H, HO, HS, PH_2) interaction. In all complexes, S...S are typical closed-shell interactions and the topological properties of the S...S bond fall short of three criteria for the existence of the hydrogen bond. In addition, theoretical and experimental results are in agreement with each other. It is hoped that the insights provided herein will assist experimental workers in their efforts to reopen the S...S bond in biological systems.

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