

A theoretical study on structure, stability and effects of substituents on intermolecular interaction of complexes of CH_3OCHX_2 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$) with 1CO_2 and $1\text{H}_2\text{O}$

Nghiên cứu lý thuyết về cấu trúc, độ bền và ảnh hưởng của các nhóm thế đến tương tác hình thành trong phức giữa CH_3OCHX_2 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$) với 1CO_2 và $1\text{H}_2\text{O}$

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Abstract

Intermolecular interactions between CH_3OCHX_2 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$) with carbon dioxide (CO_2) and water (H_2O) were theoretically investigated using high-level *ab initio* methods. The addition of an H_2O molecule to the $\text{CH}_3\text{OCHX}_2 \cdots \text{CO}_2$ complex enhances the stability of ternary complexes. This finding supports the increase of solubility of CH_3OCHX_2 in supercritical CO_2 with the presence of H_2O . The binding energies corrected both ZPE and BSSE of $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots 1\text{H}_2\text{O}$ complexes at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) range from $-21.2 \text{ kJ.mol}^{-1}$ to $-31.8 \text{ kJ.mol}^{-1}$. Especially, the effect of halogen substitution on the $\text{CH}_3\text{OCH}_3 \cdots 1\text{CO}_2 \cdots 1\text{H}_2\text{O}$ complexes was examined to compare with that in $\text{CH}_3\text{OCH}_3 \cdots 1\text{CO}_2$ complexes. It is noteworthy that the substitution of two H atoms by both di-halogen atoms and di-methyl groups induces a stabilization enhancement of the formed complexes, in which the later ones lead to a higher magnitude. AIM and NBO results demonstrate that intermolecular interactions are weakly noncovalent interactions. The $\text{C} \cdots \text{O}$ tetrel bond and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond together play crucial roles in stabilizing complexes when $\text{X} = \text{H}, \text{CH}_3$. For $\text{X} = \text{F}, \text{Cl}, \text{Br}$, the $\text{C}-\text{H} \cdots \text{O}$ hydrogen bond plays the main role among multiple weak noncovalent interactions in strengthening the complex stability.

Keywords: Dimethyl ether; carbon dioxide; water; tetrel bond; hydrogen bond.

Tóm tắt

Tương tác liên phân tử giữa CH_3OCHX_2 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CH}_3$) với 1CO_2 và $1\text{H}_2\text{O}$ đã được nghiên cứu bằng phương pháp tính từ đầu ở mức lý thuyết cao. Sự bổ sung một phân tử H_2O vào phức $\text{CH}_3\text{OCHX}_2 \cdots \text{CO}_2$ giúp tăng cường tính ổn định của phức chất tạo thành. Kết quả này chứng minh việc tăng khả năng hòa tan của CH_3OCHX_2 trong dung môi CO_2 siêu tới hạn với sự có mặt của H_2O . Năng lượng tương tác đã hiệu chỉnh ZPE và BSSE của các phức

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$\text{CH}_3\text{OCHX}_2\cdots\text{ICO}_2\cdots\text{H}_2\text{O}$ tại MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) nằm trong khoảng từ $-21,2 \text{ kJ}\cdot\text{mol}^{-1}$ đến $-31,8 \text{ kJ}\cdot\text{mol}^{-1}$. Trong đó, ảnh hưởng của sự thế halogen lên các phức $\text{CH}_3\text{OCH}_3\cdots\text{ICO}_2\cdots\text{H}_2\text{O}$ đã được nghiên cứu và so sánh với sự ảnh hưởng trên các phức $\text{CH}_3\text{OCH}_3\cdots\text{ICO}_2$. Đáng chú ý, sự thay thế hai nguyên tử hydro bởi hai nguyên tử halogen và hai nhóm methyl đã làm bền các phức tạo thành, trong đó sự thay thế hai nhóm methyl tạo ra phức bền hơn so với thế hai nguyên tử halogen. Kết quả phân tích AIM và NBO đã cho thấy rằng tương tác giữa các phân tử là tương tác yếu không cộng hóa trị. Liên kết tetrel $\text{C}\cdots\text{O}$ và liên kết hydro $\text{O}-\text{H}\cdots\text{O}$ cùng nhau đóng vai trò quan trọng trong việc ổn định các phức chất khi $\text{X} = \text{H}, \text{CH}_3$. Đối với $\text{X} = \text{F}, \text{Cl}, \text{Br}$, liên kết hydro $\text{C}-\text{H}\cdots\text{O}$ đóng vai trò chính trong việc tăng cường độ bền của phức.

Từ khóa: Dimethyl ether; carbon dioxide; nước; liên kết tetrel; liên kết hydro.

1. Introduction

Carbon dioxide (CO_2) is recognized as the main agent among a variety of greenhouse gases, but it is also known for large volumes and wide application in the food processing industry (freezing, cooling, gas packaging), and beverage carbonation. Supercritical carbon dioxide (scCO_2) is an important commercial and industrial solvent that is used in many fields including the separation and extraction processes, synthesis of nano-oxide, polymer, and pharmaceutical industries [1,2,3]. However, scCO_2 remains limited in the ability to solvate polar and high-molecular-weight compounds. Thus, many efforts have been made to find out the interacting species and effective thermodynamic reaction conditions aiming to enhance the solubility in scCO_2 . Fluorocarbons, fluoropolymers, and carbonyl-based compounds are previously considered as CO_2 -philic functional groups [4,5,6]. While high cost and toxicity are the limitations of the first two compounds, carbonyl-based compounds have been paid much attention thanks to their simple synthesis process and lower cost. Efforts for enhanced applicability of scCO_2 with the use of CO_2 -philes have been pursued *via* series of experimental and theoretical works [7,8,9,10,11,12].

From the theoretical viewpoint, it is important to elucidate the interactions, stability, and structures of complexes between organic compounds and CO_2 with/without H_2O at the molecular level. The mechanism of CO_2 capture could also be understood *via* the investigation

into CO_2 complexes in which the intrinsic strength of the noncovalent interactions between CO_2 and adsorbents is determined as a key to demanded captured abilities. Furthermore, a systematic theoretical investigation into complexes between organic compounds and CO_2 with/without H_2O at the molecular level could give information for solvent-solute and solvent-cosolvent interactions in systems involving CO_2 . Recently, series of theoretical investigations on the interactions of CO_2 with functional organic compounds including CH_3OCH_3 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3SOCH_3 , CH_3SSCH_3 , $\text{CH}_3\text{COCHX}_2$, $\text{CHX}=\text{CHX}$, XCHZ ($\text{X} = \text{CH}_3, \text{H}, \text{F}, \text{Cl}, \text{Br}$; $\text{Z} = \text{O}, \text{S}$) have been investigated [13,14,15,16], in which these complexes are mainly stabilized by $\text{C}\cdots\text{O}$ tetrel bond and an additional role of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond.

Dimethyl ether (DME) is a liquified gas and recognized as an potential alternative fuel, and also an organic extraction solvent for biomass applications [17,18]. The $\text{DME}\cdots\text{CO}_2$ complexes were performed both experimentally and theoretically on their structures, and intermolecular interactions [13,19,20,21]. Kim et al. reported that the weak hydrogen bond contributes a considerable amount to the stabilization energy of $\text{DME}\cdots\text{CO}_2$ complexes [21]. A theoretical work by Trung *et al.* previously pointed out the importance of the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond in stabilizing $\text{DME}\cdots\text{CO}_2$ complexes, and also discovered the effects of dihalogenated- and dimethyl-substitutions on the stability and characteristics

of the complexes with 1 CO₂ molecule [22]. It is shown that the halogen substituents leads to a decrease in the strength of CH₃OCHX₂⋯1CO₂ complex by 1.4-2.6 kJ.mol⁻¹ while that of two methyl groups leads to an enhancement of 1.8 kJ.mol⁻¹ in complexation energy at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p).

The addition of polar compounds, typically alcohols or water to the scCO₂ solvent, was recognized as a method to increase substantially the solubility of scCO₂ with regards to big polar solutes [23,24,25]. An investigation of complexes CH₃OCHX₂ ⋯1CO₂ with the presence of 1H₂O at molecular level will reveal the changes of structures, stability and intermolecular interactions formed between these molecules. In addition, the cooperativity energy (E_{coop}) in ternary complexes will be determined whether it is positive or negative effect. The negative value of E_{coop} indicates the positive cooperativity effect, and three components interact mutually to stabilize the corresponding complexes; and *vice versa*. To the best of our knowledge, there is no theoretical and experimental information of CH₃OCHX₂ ⋯1CO₂⋯1H₂O complexes (X = H, CH₃, F, Cl, Br) existed. Thus, in this work, we carry out the quantum calculations on the complexes of CH₃OCHX₂ (X = H, CH₃, F, Cl, Br) with 1CO₂ and 1H₂O to investigate the geometrical structures, the properties and role of intermolecular interactions in complex stabilization when existing the presence of water into the CH₃OCHX₂⋯CO₂ complexes.

2. Computational methodology

All geometries of investigated complexes and monomers were optimized using the MP2 Moller-Plesset perturbation method and in combination with the 6-311++G(2d,2p) Pople basis set. The harmonic vibrational frequencies were subsequently calculated at the same level of theory to specify the equilibrium structures and to estimate the zero-point energy (ZPE).

The counterpoise correction for the basis set superposition error (BSSE) was applied to get better electronic energy. The single-point and BSSE calculations were performed at the MP2/aug-cc-pVTZ level of theory with geometries obtained at MP2/6-311++G(2d,2p).

The binding energy of each complex was determined following the supramolecular method, as the difference between the total energy of complex and the sum of total energies of isolated monomers.[26] The characteristics of intermolecular interactions formed in considered complexes are analyzed based on the atoms in molecules theory (AIM). The AIM calculations were performed at MP2/6-311++G(2d,2p) using AIM2000 software.[27] Selected parameters at bond critical point (BCP) such as electron density ($\rho(rc)$), Laplacian ($\nabla^2\rho(rc)$), and total electron energy density ($H(rc)$) and topographical graphs are used to determine the existence and properties of intermolecular interactions formed between CH₃COCHX₂, CO₂ and H₂O. The individual energies of hydrogen bonds (E_{HB}) were calculated based on the formula of Espinosa-Molins-Lecomte $E_{HB} = 0.5V(r)$ [28,29] at MP2/6-311++G(2d,2p). The natural bond orbital (NBO) theory using NBO 5.G software was applied to analyze the electron density transfer (EDT) and the second-order perturbation energy ($E^{(2)}$) [30]. All quantum chemical calculations were performed by Gaussian 09 package [31].

3. Results and discussion

3.1. Structures and stability of CH₃OCHX₂⋯1CO₂⋯1H₂O complexes

The stable structures of complexes formed by interactions between CH₃OCHX₂ with 1CO₂ and 1H₂O are denoted as DME-X (Figure 1), where X = H, CH₃, F, Cl, Br. Figure 1 shows that the distances of the C⋯O and O⋯H contacts are in the ranges of 1.842-2.893 Å and

1.866-2.633 Å, respectively; which are smaller than the sum of van der Waals radii of the two atoms involving interactions (being 3.55 and 2.72 Å for the corresponding pairs of C and O, O and H atoms). These results indicate that the intermolecular interactions between CH_3OCHX_2 and CO_2 and H_2O are weak interactions which belong to the tetrel and the hydrogen bonds.

All found structures of $\text{CH}_3\text{OCHX}_2 \cdots \text{CO}_2 \cdots \text{H}_2\text{O}$ complexes are stabilized by a $\text{C} \cdots \text{O}$ tetrel bond between CH_3OCHX_2 and CO_2 , a $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond between H_2O and CO_2 moieties (except for DME- CH_3) and a $\text{C}-\text{H} \cdots \text{O}$ hydrogen bond between CH_3OCHX_2 and H_2O . Three components in these complexes interact mutually to form cage structures, which may

result in the positive cooperative effect between noncovalent interactions formed.

Table 1 presents the binding energies (BE) and cooperative energy (E_{coop}) of complexes $\text{CH}_3\text{OCHX}_2 \cdots \text{CO}_2 \cdots \text{H}_2\text{O}$ at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) level of theory. All investigated complexes are stable with BE^* with ZPE and BSSE corrections ranging from -21.2 to -31.8 $\text{kJ}\cdot\text{mol}^{-1}$. A similar overall trend of complex stability is observed in both cases, with and without the BSSE correction. However, BE values are more negative, from -26.7 $\text{kJ}\cdot\text{mol}^{-1}$ to -39.5 $\text{kJ}\cdot\text{mol}^{-1}$, compared to the BE^* . The BSSE amount of about 5.5-11.2 $\text{kJ}\cdot\text{mol}^{-1}$ indicates its large contribution to the complex stability. Therefore, only the BE^* with ZPE and BSSE are used in the following discussions.

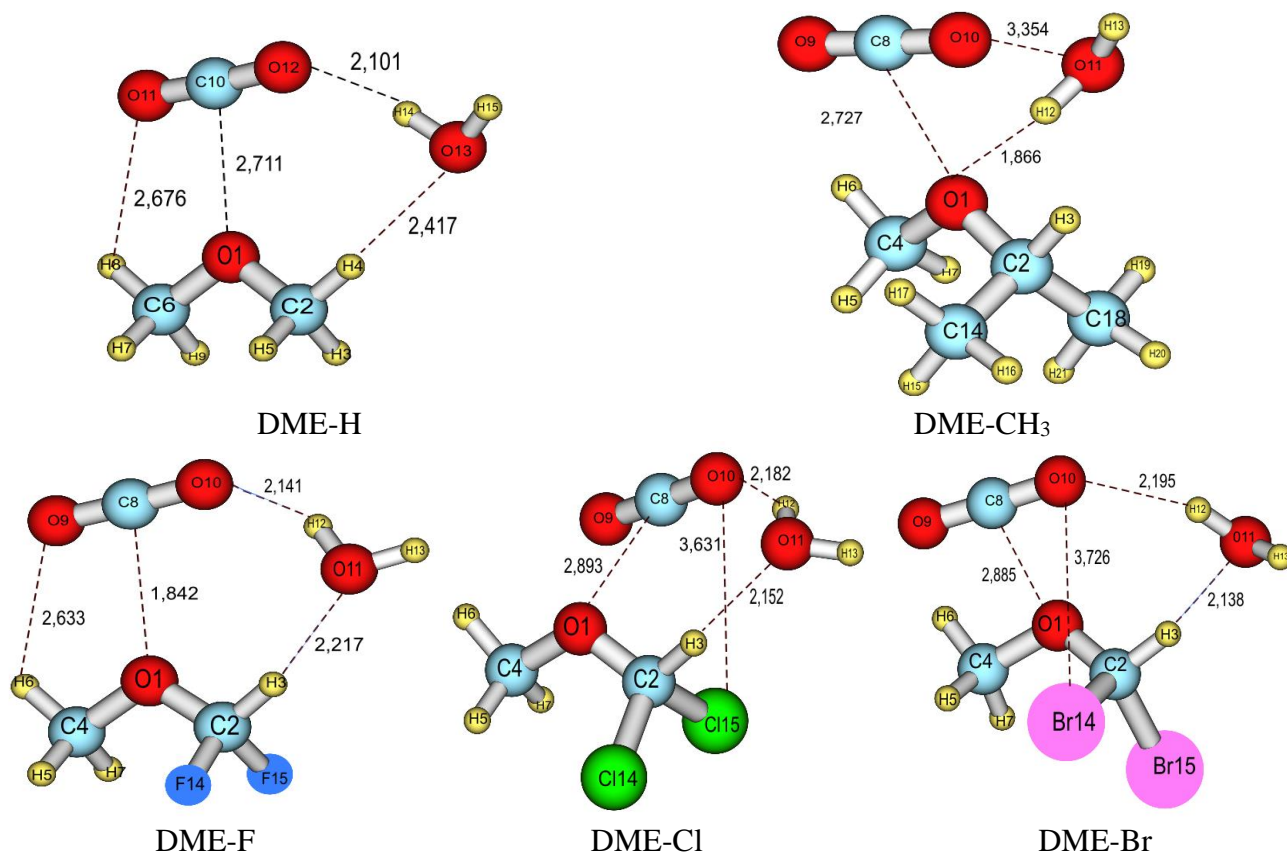


Figure 1. The most stable structures of complexes $\text{CH}_3\text{OCHX}_2 \cdots \text{CO}_2 \cdots \text{H}_2\text{O}$ ($\text{X} = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$)

Accordingly, the stability of complexes $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2\cdots\text{1H}_2\text{O}$ is increased in the order of substituents: $\text{H} \sim \text{F} < \text{Cl} < \text{Br} < \text{CH}_3$. The BE^* of $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2\cdots\text{1H}_2\text{O}$ is more negative than that of the corresponding binary $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2$ [22], demonstrating that the addition of water into the $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2$ leads to the enhancement in stability of the ternary complexes. Explicitly, for the complex

Table 1. Binding energy (BE) and cooperative energy (E_{coop}) of complexes $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2\cdots\text{1H}_2\text{O}$ (X = H, CH₃, F, Cl, Br)

Complexes	BE	BE*	E_{coop}
DME-H	-26.7	-21.2	-7.5
DME-CH ₃	-39.5	-31.8	-3.5
DME-F	-27.5	-21.5	-5.4
DME-Cl	-32.2	-24.9	-5.2
DME-Br	-37.3	-26.1	-3.3

All values in $\text{kJ}\cdot\text{mol}^{-1}$

(*) BE included BSSE correction

To evaluate the cooperative effect of intermolecular interactions formed, we also calculated the E_{coop} of ternary complexes, as shown in Table 1. The cooperative energies of $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2\cdots\text{1H}_2\text{O}$ complexes at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) are negative and vary from -3.3 to -7.5 $\text{kJ}\cdot\text{mol}^{-1}$. These results indicate that intermolecular interactions work together to enhance the complex stability, as predicted. This finding also helps explain the stability enhancement of dihalogen-derivative complexes where the positive cooperativity effect is dominant, as compared to the electron-withdrawing one of halogen groups.

of DME, a greater increase in BE^* is found for the addition of a H_2O molecule, that ranges from -13.3 to -21.2 $\text{kJ}\cdot\text{mol}^{-1}$. Remarkably, the halogen substituents in the ternary complexes with the presence of H_2O lead to a slight increase in the complex strength, which is inverse to the results observed in the binary $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2$ [22].

cooperative energy (E_{coop}) of complexes

3.2. AIM and NBO analyses of intermolecular interactions

We now discuss in more details the role and nature of intermolecular interactions formed between monomers, by using AIM and NBO theory. The selected parameters at BCPs from AIM results are collected in Table 2. The topological graphs of complexes $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2\cdots\text{1H}_2\text{O}$ (Figure 2) demonstrate the simultaneous existence of the $\text{C}\cdots\text{O}$ tetrel bond between CH_3OCHX_2 and CO_2 molecule; the $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bond between CO_2 and H_2O (except the DME-CH₃); and the $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bond between CH_3OCHX_2 and H_2O one. Furthermore, it also appears a connection between Cl/Br halogen atoms and CO_2 moiety through the $\text{Cl/Br}\cdots\text{O}_{\text{CO}_2}$ halogen bond.

Table 2. Selected parameters at BCPs taken from AIM results at MP2/6-311++G(2d,2p) of $\text{CH}_3\text{OCHX}_2\cdots\text{1CO}_2\cdots\text{1H}_2\text{O}$ (X = H, CH₃, F, Cl, Br, CH₃)

Complex	Interaction	$\rho(\mathbf{r})$ (au)	$\nabla^2\rho(\mathbf{r})$ (au)	$\mathbf{H}(\mathbf{r})$ (au)	E_{HB} ($\text{kJ}\cdot\text{mol}^{-1}$)
DME-H	O1 \cdots C10	0.0129	0.053	0.001	N/A
	C2-H4 \cdots O13	0.0093	0.033	0.001	-8.2
	O13-H14 \cdots O12	0.0138	0.059	0.002	-13.5
	C6-H8 \cdots O11	0.0062	0.025	0.001	-5.6

DME-CH ₃	O1...C8	0.0131	0.053	0.001	N/A
	O1...H12-O11	0.0306	0.100	-0.001	-34.6
	O11...O10	0.0050	0.021	0.001	N/A
DME-F	O1...C8	0.0098	0.041	0.001	N/A
	C2-H3...O11	0.0144	0.052	0.001	-13.1
	O11-H12...O10	0.0129	0.056	0.002	-12.6
	C4-H6...O9	0.0066	0.025	0.001	-5.7
DME-Cl	O1...C8	0.0097	0.038	0.001	N/A
	C2-H3...O11	0.0172	0.060	0.001	-16.0
	O11-H12...O10	0.0119	0.051	0.002	-11.5
	Cl15...O10	0.0045	0.018	0.001	N/A
DME-Br	O1...C8	0.0098	0.039	0.001	N/A
	C2-H3...O11	0.0179	0.061	0.001	-16.7
	O11-H12...O10	0.0116	0.050	0.002	-11.2
	Br14...O10	0.0048	0.018	0.001	N/A

The calculated values of $\rho(r)$ at BCPs of O...C tetrel bonds, O-H...O and C-H...O hydrogen bonds, Cl/Br...O and O...O chalcogen bonds lie in the range of 0.0097-0.0131 au, 0.0116-0.0306 au, 0.0062-0.0179 au, 0.0045-0.0048 au, and 0.0050 au, respectively. Combined with the positive values of $\nabla^2\rho(r)$ and $H(r)$ (cf. Table 2), it is suggested that all intermolecular interactions of complexes with the substituents are weakly noncovalent interactions.[32]

The $\rho(r)$ value at BCPs of C8(10)...O1 tetrel bonds in complexes DME-X is increased as order Cl < Br \approx F < H < CH₃, as observed in complexes between CH₃OCHX₂ and 1CO₂ [22]. The $\rho(r)$ value of O1...C8 tetrel bond in DME-H and DME-CH₃ is greater than that in the remaining complexes. Thus, the halogen substitution results in the weakening of C...O

tetrel bond, while the di-methyl substitution into the DME leads to an increase in the strength of this interaction. The stability of the O-H...O hydrogen bond in two previous complexes is also higher than the corresponding in complexes substituted halogen which is described through the $\rho(r)$ and E_{HB} values (cf. Table 2). The effect of halogen substitution leads to not only the weakening of O1...C8, but also the stronger C-H...O hydrogen bond by 5-9 kJ.mol⁻¹. In addition, it exists the C-Cl/Br...O halogen bond in DME-Cl/Br complexes. Combined with the AIM results, the DME-H/CH₃ is mainly stabilized by the O-H...O hydrogen bond and C...O tetrel bond while C-H...O plays the main role in the TCH-DME-F/Cl/Br among multiple weak noncovalent interactions.

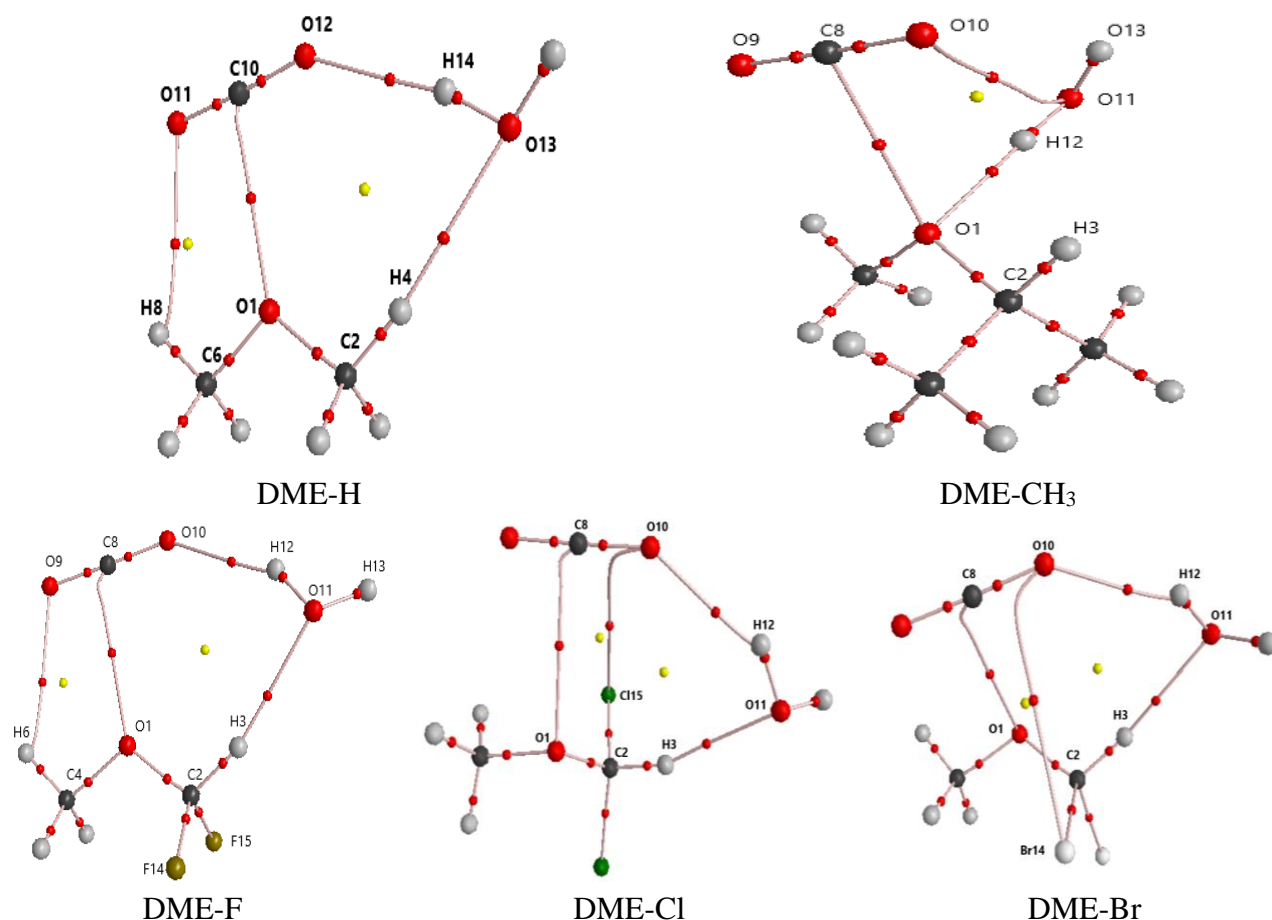


Figure 2. Topological graph of $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots 1\text{H}_2\text{O}$ complexes at MP2/6-311++G(2d,2p) (X = H, CH₃, F, Cl, Br)

The NBO analyses are performed at MP2/6-311++G(2d,2p) to determine the orbital interactions in the $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots 1\text{H}_2\text{O}$ complexes, as shown in Table 3. The EDT values of the CH_3OCHX_2 component in DME-H and DME-CH₃ are positive in the range of 0.0031-0.0248 e, while those of DME-F/Cl/Br are negative from -0.0069 to 0.0049 e. It is in good agreement with the electron-withdrawing effect of halogen atoms in DME-F/Cl/Br and

the electron releasing one of the methyl groups in DME-CH₃. In general, the orbital interactions $n(\text{O}) \rightarrow \pi^*(\text{C}=\text{O})$, $n(\text{O}) \rightarrow \sigma^*(\text{O}-\text{H})$ and $n(\text{O}) \rightarrow \sigma^*(\text{C}-\text{H})$ represent the $\text{C} \cdots \text{O}$ tetrel, $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds. The $n(\text{Cl}/\text{Br}) \rightarrow \sigma^*(\text{C}=\text{O})$ delocalization proves the interactions between Cl/Br with the $\text{C}=\text{O}$ group of CO_2 and plays an additional role in the complex stabilization.

Table 3. EDT and $E^{(2)}$ for $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots 1\text{H}_2\text{O}$ (X = H, CH₃, F, Cl, Br) at MP2/6-311++G(2d,2p) level of theory

Complex	EDT/e	Delocalization	$E^{(2)}/\text{kJ}\cdot\text{mol}^{-1}$
DME-H	0.0031 ^(a)	$n(\text{O}1) \rightarrow \pi^*(\text{C}10=\text{O}11)$	10.4
	-0.0035 ^(b)	$n(\text{O}12) \rightarrow \sigma^*(\text{O}13-\text{H}14)$	7.3
	0.0004 ^(c)	$n(\text{O}13) \rightarrow \sigma^*(\text{C}2-\text{H}4)$	5.2
DME-CH ₃	0.0248 ^(a)	$n(\text{O}1) \rightarrow \pi^*(\text{C}8=\text{O}9)$	2.9
	-0.0041 ^(b)	$n(\text{O}1) \rightarrow \pi^*(\text{C}8=\text{O}10)$	2.6
	-0.0207 ^(c)	$n(\text{O}1) \rightarrow \sigma^*(\text{O}11-\text{H}12)$	42.5

DME-F	-0.0049 ^(a)	n(O1) → π*(C8=O9)	5.7
	-0.0001 ^(b)	n(O10) → σ*(O11-H12)	7.9
	0.0050 ^(c)	n(O11) → σ*(C2-H3)	14.9
DME-Cl		n(O1) → π*(C8=O9)	5.6
	-0.0055 ^(a)	n(Cl15) → π*(C8=O9)	1.3
	-0.0032 ^(b)	n(O10) → σ*(O11-H12)	3.9
	0.0087 ^(c)	n(O11) → σ*(C2-H3)	16.4
		n(O11) → σ*(C2-Cl14)	0.7
DME-Br		n(O1) → π*(C8=O9)	5.6
	-0.0069 ^(a)	n(Br14) → π*(C8=O9)	1.4
	-0.0032 ^(b)	n(O10) → σ*(O11-H12)	3.4
	0.0101 ^(c)	n(O11) → σ*(C2-H3)	17.1
		n(O11) → σ*(C2-Br15)	0.9

(a), (b), (c) are EDT values of CH₃OCHX₂, CO₂, and H₂O, respectively.

The E⁽²⁾ values of (O)→π*(C=O) and n(O)→σ*(O-H) delocalizations are higher than those of n(O)→σ*(C-H) indicating the important role of C···O tetrel bond and O-H···O hydrogen bond in DME-H/CH₃ complexes. Especially, the E⁽²⁾ value of the O-H···O hydrogen bond in DME-CH₃ is the highest, of 42 kJ.mol⁻¹ demonstrating the great electron-releasing effect of methyl groups as compared to the corresponding value of 7.3 kJ.mol⁻¹ in complexes of dimethyl ether. The stabilization energy of n(O)→σ*(C-H) in DME-F/Cl/Br ranges from 14.9 to 17.1 kJ.mol⁻¹ which is higher than that of n(O)→σ*(O-H) and n(O)→π*(C=O) (about 3.9-7.9 kJ.mol⁻¹ and 5.6 kJ.mol⁻¹, respectively). It confirms the important role of C-H···O in halogen-derivative complexes.

The changes in bond length (Δr), and stretching vibrational frequency (Δν) of C/O-H-involved hydrogen bonds are collected in Table 4. The C-H···O in complexes DME-

H/CH₃ belong to the blue-shifting hydrogen bond, which is described through a shortened bond length of C-H of 0.0009-0.0010 Å and an increase of stretching vibrational frequency of 18.9-24.9 cm⁻¹. In contrast, the O-H···O hydrogen bonds in all complexes CH₃OCHX₂···1CO₂···1H₂O are red-shifted of 30.9-229.1 cm⁻¹ and an increase in bond length of O-H about 0.0021-0.0110 Å, as compared to those in isolated monomers. As observed in Table 4, an elongation of the O(C)-H bond length and a decrease in its corresponding stretching frequency is determined by an increase in the electron density at the σ*(O(C)-H) orbital of 0.0005-0.0028 e. For the C-H blue-shifting hydrogen bond, the contraction of the C-H bond length and the increase in its stretching vibrational frequency is controlled by the electron density's decrease in the σ*(C-H) anti-orbital and the enhancement of s-character of C hybrid orbital upon complexation.

Table 4. Changes of C(O)-H (Δr, in Å) bond length and stretching frequency (Δν(C/O-H), in cm⁻¹) of C-H and O-H bonds involved in hydrogen bond

Complex	Interaction	Δr (Å)	Δν (cm ⁻¹)	Δσ*(C(O)-H) (e)	Δ%s(C(O)) (%)
DME-H	C2-H4···O13	-0.0009	18.9	0.0007	0.92
	O13-H14···O12	0.0025	-37.4	0.0028	1.30
DME-CH ₃	O11-H12···O1	0.0110	-229.1	0.0233	3.01

DME-F	C2-H3...O11	-0.0010	24.9	-0.0012	1.38
	O11-H12...O10	0.0021	-30.9	0.0021	1.21
	C4-H6...O9	0.0001	0.4	0.0005	0.14
DME-Cl	C2-H3...O11	0.0008	1.3	-0.0010	1.87
	O11-H12...O10	0.0024	-33.7	0.0016	1.00
DME-Br	C2-H3...O11	0.0013	-6.4	0.0000	2.06
	O11-H12...O10	0.0024	-33.9	0.0014	0.93

4. Conclusion

A theoretical investigation into interactions of CH_3OCHX_2 ($X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$) with CO_2 and H_2O using high-level *ab initio* methods was carried out to explore the stability, properties, and effect of substituents to the complexes formed. For $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots \text{H}_2\text{O}$, the binding energy corrected ZPE+BSSE at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) level of theory ranges from -21.2 to -31.8 $\text{kJ}\cdot\text{mol}^{-1}$, and their stability is increased as the order of substituents as $\text{H} \sim \text{F} < \text{Cl} < \text{Br} < \text{CH}_3$. In general, halogenated and methyl substituents lead to the stability enhancement of the complexes formed.

The addition of H_2O into the dimer $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2$ helps to increase the stability of ternary complexes formed, in which the complex of DME exhibits the greatest increase of $\sim 8 \text{ kJ}\cdot\text{mol}^{-1}$. The positive effect of cooperativity is found in all $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots \text{H}_2\text{O}$ complexes ($X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$) with the E_{coop} lying from -3.3 to -7.5 $\text{kJ}\cdot\text{mol}^{-1}$ at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p).

Going from the binary $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2$ to the ternary $\text{CH}_3\text{OCHX}_2 \cdots 1\text{CO}_2 \cdots \text{H}_2\text{O}$, the C...O tetrel bond remains to be the dominant interaction, accompanying with the O-H...O hydrogen bond, when $X = \text{H}, \text{CH}_3$. For $X = \text{F}, \text{Cl},$ and Br , both mentioned interactions are weaker than those when $X = \text{H}, \text{CH}_3$, and the C-H...O hydrogen bond plays the main role in the **DME-F/Cl/Br** among multiple weak noncovalent interactions.

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