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Nghiên cứu ảnh hưởng của nhóm thế đến tương tác và độ bền của phức giữa CO_2 và CH_3OCHX_2 ($X = H, F, Cl, Br, CH_3$)

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TÓM TẮT

Cấu trúc, độ bền và ảnh hưởng của nhóm thế đến phức giữa CH_3OCHX_2 và CO_2 được nghiên cứu bằng phương pháp tính từ đầu *ab initio*. Năng lượng tương tác hiệu chỉnh ZPE và BSSE tại mức lý thuyết MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) của các phức có giá trị khoảng từ -2,8 $kJ.mol^{-1}$ đến -15,1 $kJ.mol^{-1}$. Đáng chú ý, sự thế 2 nguyên tử H bằng 2 nguyên tử halogen làm giảm độ bền của phức khoảng 1,4-2,6 $kJ.mol^{-1}$, trong khi đó, sự thế 2 nhóm $-CH_3$ làm tăng độ bền của phức khoảng 1,8 $kJ.mol^{-1}$. Độ bền của các phức thế halogen $CH_3OCHX_2\cdots 1CO_2$ có xu hướng tăng khi nhóm thế thay đổi từ F, đến Cl và đến Br. Kết quả phân tích AIM và NBO cho thấy các tương tác hình thành đều là tương tác yếu không cộng hóa trị, trong đó liên kết tetrel C···O đóng vai trò quyết định đến sự làm bền phức. Ngoài ra, kết quả phân tích SAPT2+ cho thấy sự đóng góp đáng kể của năng lượng tương tác tĩnh điện so với các hợp phần phân tán và cảm ứng khi hình thành phức.

Từ khóa: *Dimethyl ether, carbon dioxide, liên kết tetrel, liên kết hydro.*

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TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Effects of substituents on intermolecular interaction and stability of complexes of CO_2 and CH_3OCHX_2 ($X = H, F, Cl, Br, CH_3$)

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ABSTRACT

The structures, stability and effect of substituents on the complexes of CH_3OCHX_2 with CO_2 were examined by *ab initio* quantum calculations. The interaction energies corrected both ZPE and BSSE at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) range from -2.8 $kJ.mol^{-1}$ to -15.1 $kJ.mol^{-1}$. It is remarkable that the substitution of two H atoms by di-halogen ones leads to a decrease of 1.4-2.6 $kJ.mol^{-1}$ in energy while that by two methyl groups induces a stabilization enhancement of 1.8 $kJ.mol^{-1}$. The stability of $CH_3OCHX_2 \cdots 1CO_2$ di-halogenated derivatives tends to increase from X = F *via* Cl and to Br. AIM and NBO results indicate that intermolecular interactions are weakly noncovalent interactions, and the C···O tetrel bond plays the crucial role in stabilizing complexes. In addition, SAPT2+ analysis shows a significant contribution of the attractive electrostatic component as compared to the dispersion and induction one in complex stabilization.

Keywords: *Dimethyl ether, carbon dioxide, tetrel bond, hydrogen bond.*

1. INTRODUCTION

Nowadays, supercritical carbon dioxide ($scCO_2$) is used in many fields including the separation and extraction processes, synthesis of nano-oxide, polymer and copolymer and even cosmetic and pharmaceutical industries.[1-4] These applications are developed relying on the preeminent physicochemical properties of $scCO_2$ such as low cost, non-toxic and environmentally friendly.[5-7] Although $scCO_2$ provides great economic efficiency, it exists limitations in the ability to solvate polar compounds and high-molecular-weight ones. Many efforts have been done to find the enhancing applicability of $scCO_2$ through the use of "CO_2-philes".[8-10] Therefore, in order to improve the efficiency of using $scCO_2$ solvents and find the CO_2-philic materials, it is necessary to elucidate the factors affecting the solubility of organic compounds in $scCO_2$ solvent as well as understand the nature of intermolecular interactions. Recently, series of computational studies on the interactions between CO_2 and simple organic compounds such as CH_3OCH_3, CH_3OH, C_2H_5OH, CH_3SOCH_3, CH_3SSCH_3, CH_3COCHX_2, CHX=CHX, XCHZ ($X = CH_3$, H, F, Cl, Br; Z = O, S) have been investigated.[11-16] In which, these complexes are mainly stabilized by C···O tetrel bond and an additional role of C-H···O hydrogen bond.

Dimethyl ether (DME) is known as a low cost, popular solvent and has been used in variety of fuel applications.[17] Some experimental

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and theoretical studies on structure and characteristic of intermolecular interactions of DME···CO_2 complexes were carrie dout.[11,13,18,19] The previous study showed that the weak hydrogen bond contributes a considerable amount of stabilization energy of DME···CO_2 complexes.[19] However, according to the result reported by Trung *et al*.,[13] there is no hydrogen bond in DME···CO_2 system. Therefore, the presence of hydrogen bond in complex of DME with CO_2 has not revealed yet. Besides, the effects of halogenated- and methyl- substitution on the stability and characteristics of complexes between CO_2 and CH_3COCHX_2 and CH_3SZCHX_2 (Z=O, S; X=H, F, Cl, Br, CH_3) were examined,[14,15] but these influences on DME···CO_2 complexes have not been investigated yet. Thus, in this work, we set out the quantum calculations on the complexes of CH_3OCHX_2 (X=H, F, Cl, Br, CH_3) with CO_2 at the molecular level to investigate the geometrical structures, the properties and role of intermolecular interactions in complex stabilization.

2. COMPUTATIONAL METHODS

The optimized calculations for CH_3OCHX_2···1CO_2 complexes and isolated monomers were carried out using the second-other Moller-Plesset perturbation (MP2) in conjunction with 6-311++G(2d,2p) basis set. The vibrational frequency was calculated at the same level of theory to find the local minimum on the potential energy surface, and to estimate the zero-point energy (ZPE). The total electronic energies and basis set superposition error (BSSE) were calculated at MP2/aug-cc-pVTZ with geometries obtained at MP2/6-311++G(2d,2p). The interaction energies were quantitively determined following the supramolecular method[20] as shown:

$$\Delta E = E_{complex} - \sum E_{monomer}$$

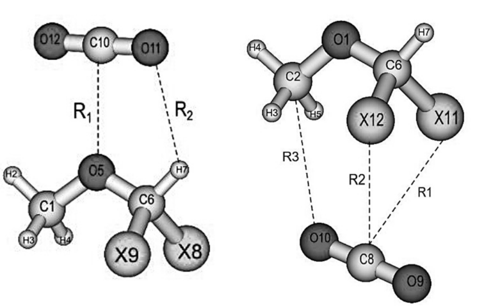
The properties of intermolecular interactions are characterized through selected parameters at bond critical point (BCP) such as electron density (ρ(rc)), Laplacian ($\nabla^2\rho(rc)$), and total electron energy density (H(rc)) using atoms in molecules theory (AIM). The AIM calculations were performed at MP2/6-311++G(2d,2p) using AIM2000 software.[21] NBO analysis using NBO 5.G software was carried out to analyze electron density transfer and second order perturbation energy ($E^{(2)}$).[22] Proton affinity (PA) at O of CH_3OCHX_2 monomers and deprotonation enthalpy (DPE) of C-H bonds involving hydrogen bond were estimated at MP2/6-311++g(2d,2p) level of theory. All quantum calculations mentioned above were executed with the Gaussian 09 package.[23]

SAPT2+ analysis were carried out by PSI4 software[24] to determine the contribution of energetic components into the stabilization energy. The interaction energy of the complexes is analyzed into physical components including exchange (E_{exch}), electrostatic (E_{elst}), induction (E_{ind}) and dispersion term (E_{disp}).

3. RESULTS AND DISCUSSION

3.1. Structure and stability

Stable structures formed by interactions of CH_3OCHX_2 (X = H, F, Cl, Br, CH_3) with CO_2 are presented in Figure 1, denoted by **D1-X** and **D2-X** where **X** = H, F, Cl, Br, CH_3. The intermolecular distances of studied complexes are listed in Table 1.



D1-X **D2-X**

Figure 1. Stable structures of CH_3OCHX_2···1CO_2 complexes

From Figure 1, CH_3OCHX_2···1CO_2 complexes are stabilized by intermolecular contacts including C···O, C−H···O and X···O (X = F, Cl, Br) interactions. For **D1-X** complexes, all C···O distances are in the range of 2.66-

2.75 Å, considerably shorter than sum of van der Waals radii of two relevant atoms (3.22 Å). This gives the first evidence for the formation of C···O tetrel bond. The symmetry of **D2-H** is C_{2V} and consistent with result of previous study.[11] The O···H distances in **D1-Cl** and **D1-Br** are 2.69 Å and 2.72 Å, respectively, shorter than or very close to sum of van der Waals radii of relevant atoms (2.72 Å) while those in the remaining complexes are longer ranging from 2.78 Å to 2.96 Å. For **D2-X**, all C···X (F, Cl, Br) distances range from 3.00 to 3.60 Å, slightly shorter or close to the sum of van der Waals radii of two corresponding atoms (3.17-3.55 Å), indicating the formation of C···X (X=F, Cl, Br) interactions.

Table 1. Intermolecular distances (Å) of CH_3OCHX_2···$1CO_2$ complexes

D1-X					
X	**H**	**F**	**Cl**	**Br**	**CH_3**
R_1	2.69	2.75	2.73	2.73	2.66
R_2	2.96	2.85	2.72	2.69	2.78
D2-X					
X	**H**	**F**	**Cl**	**Br**	**CH_3**
R_1	3.10	3.00	3.47	3.60	-
R_2	3.20	3.00	3.47	3.60	-
R_3	3.09	3.40	3.38	3.36	-

The interaction energies corrected ZPE and both ZPE+BSSE of studied complexes at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) are summarized in Table 2. The correlation in interaction energies **D1-X** and **D2-X** structures are described in Figure 2. In general, all values of the interaction energies are negative, indicating that the reactions between CH_3OCHX_2 and $1CO_2$ are favorable thermodynamics. Indeed, the interaction energies range from -4.5 kJ.mol^{-1} to -18.3 kJ.mol^{-1} with only ZPE correction and from -2.8 kJ.mol^{-1} to -15.1 kJ.mol^{-1} with both ZPE and BSSE corrections (*cf.* Table 1). A similar trend for the interaction energies with and without BSSE correction is observed. Consequently, only the interaction energies corrected ZPE+ BSSE are used in the following discussions.

Table 2. Interaction energies corrected ZPE (ΔE) and ZPE+BSSE (ΔE*)

	ΔE	**ΔE***		**ΔE**	**ΔE***
D1-H	-15.7	-13.3	**D2-H**	-4.5	-2.8
D1-F	-13.4	-10.7	**D2-F**	-10.8	-8.1
D1-Cl	-14.7	-11.7	**D2-Cl**	-12.7	-9.8
D1-Br	-16.4	-11.9	**D2-Br**	-16.1	-10.4
D1-CH_3	-18.3	-15.1			

All values are in kJ.mol^{-1}

With the same substituents, the interaction energies of **D1-X** complexes are more negative than those of **D2-X**, implying that the former geometries are energetic-favored than the later ones. Thus, CO_2 counterpart favors to locate around O atom of DME to form the stable structures. For **D1-X** system, **ΔE*** has negative value ranging from -10.7 kJ.mol^{-1} to -15.1 kJ.mol^{-1} and its magnitude increases in order: **D1-F < D1-Cl < D1-Br < D1-H < D1-CH_3**, indicating that the strength of complexes also increases in this order. Furthermore, **D1-H** complex represents an interaction energy of -13.3 kJ.mol^{-1}, in well agreement with the value of -13.7 kJ.mol^{-1} at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ.[13] Moreover, Ginderen *et al.*[11] also reported **D1-H** as the global minimum structure of CH_3OCH_3···CO_2 system with an interaction energy (without BSSE) of -15.58 kJ.mol^{-1}, completely consistent with the calculated value of -15.7 kJ.mol^{-1} in this work (*cf.* Table 1). The substitution of two H atoms by two halogens leads to a decrease in the strength of CH_3OCHX_2···$1CO_2$ 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. The effect of substituents on the complex stability is consistent with the results of halogenated- and methyl- substitutions on complexes of acetone and CO_2.[14]

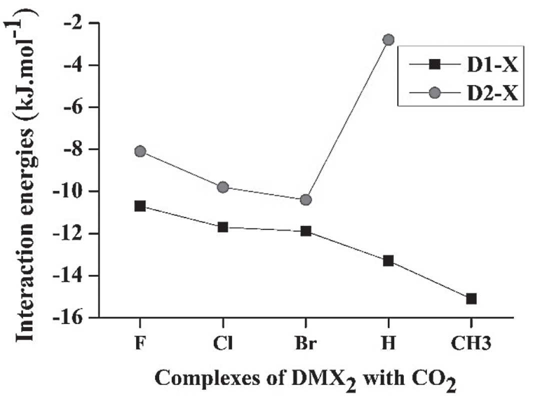


Figure 2. The difference in interaction energies (with ZPE and BSSE) of CH_3OCHX_2···$1CO_2$ complexes

For **D2-X** complexes, the stability of di-halogenated derivatives is significantly higher than that of DME which increases in order: **D2-H < D2-F < D2-Cl < D2-Br**. From geometric structure of **D2-X** complexes, they are stabilized by two C···X interactions and an additional cooperation of the C−H···O interactions, except **D2-H** with only two weak hydrogen bonds. The fact is that the electronegativity decreases from F *via* Cl to Br. Therefore, the C···X interactions (X = F, Cl, Br) existed in **D2-X** complexes are predicted to be electrostatic in nature.

The interaction capacity of CO_2 with CH_3OCHX_2 are significantly stronger than that of C_2H_6, C_2H_4 and CH_3SCH_3 by 7.7-12.1, 8.4-10.2 and 0.8-5.2 kJ.mol^{-1}; respectively.[12, 16, 25] Moreover, for the same halogenated-substitution, the complexes of CO_2 and CH_3OCHX_2 are also more stable than the corresponding XHC=CHX ones by 4.1-4.5 kJ.mol^{-1}.[12] Therefore, CH_3OCHX_2 is predicted to be an effective functional group in aiming of CO_2 capture.

3.2. SAPT analysis

SAPT2+ analysis for **D1** complexes is performed to better understand the nature and role of each energetic component into the total stabilization energy of CH_3OCHX_2···$1CO_2$ complexes. The contribution percentages of different energetic components including electrostatic, induction and dispersion of **D1-X** energetic-favored complexes are described in Figure 3.

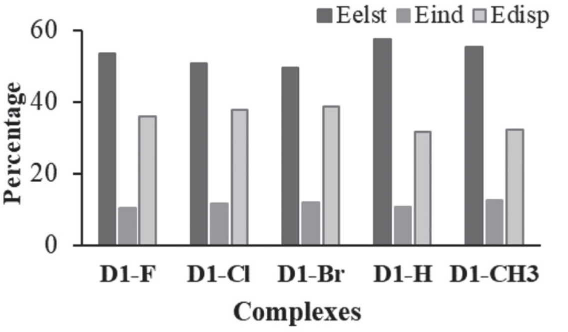


Figure 3. Contributions (%) of physical energetic terms

It is showed that the attractive electrostatic term mainly contributed to the stabilization of CH_3OCHX_2···$1CO_2$ system as compared to dispersion and induction ones. In particularly, the contribution of electrostatic attraction component ranges from 49.5% to 57.4%, considerably larger than that of two remaining counterparts, which is roughly 31.8% - 38.6% for dispersion and 10.5% - 12.5% for induction one. For the halogenated-substituted derivatives, the percentage of attractive electrostatic term is decreased in going from -F *via* -Cl to -Br, while that of dispersion is slightly increased in this order. The interaction energies taken from SAPT2+ approach are estimated from -13.2 kJ.mol^{-1} to -18.0 kJ.mol^{-1}, which the magnitude increases in order F < Cl < Br < H < CH_3 and consistent with those derived from supramolecular theory.

For **D2-X** complexes, the contributions of electrostatic, induction and dispersion terms are about 18.4 - 42.1%, 8.3 - 19.1% and 41.6 - 62.4%, respectively. Going from **D1-X** to **D2-X**, there is a change of the main contribution component, which is going from electrostatic to dispersion one, respectively.

3.3. An AIM analysis

The molecular graphs of CH_3OCHX_2···$1CO_2$ complexes according to AIM approach are shown in Figure 4 (Red points denote the BCPs).

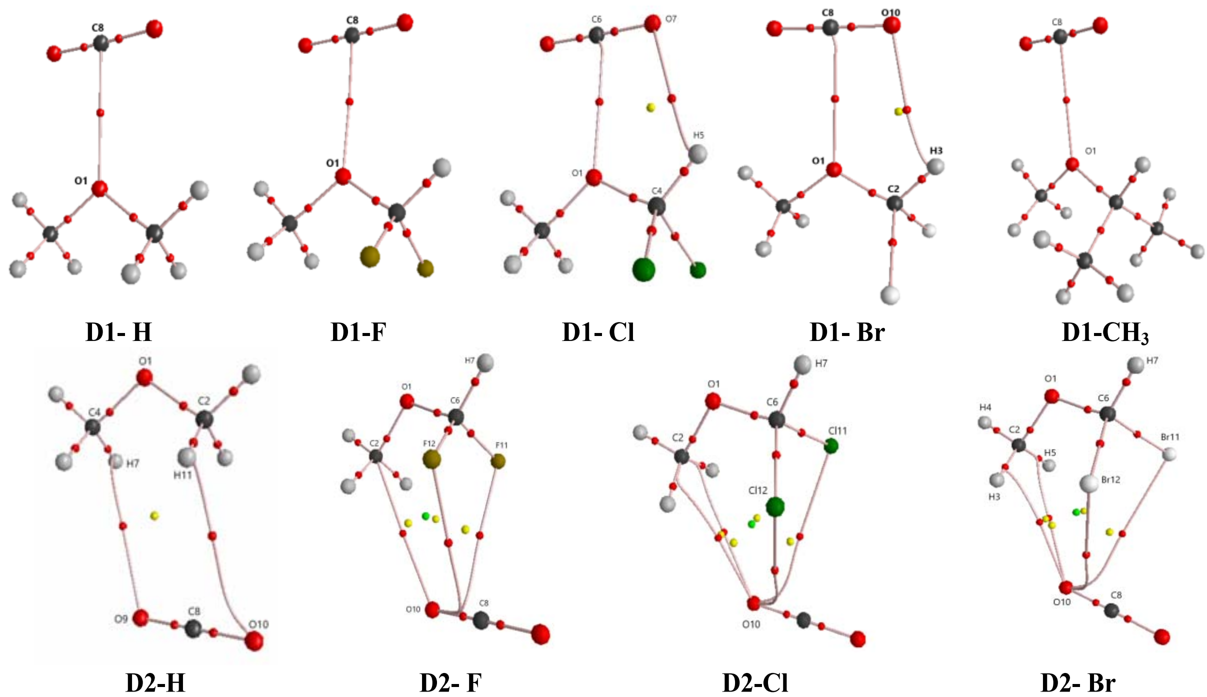


Figure 4. Topological of $CH_3OCHX_2\cdots 1CO_2$ complexes (X = H, F, Cl, Br, CH_3)

The existence of BCPs between the contacts of the two molecules, demonstrating the formation of intermolecular interactions (*cf*. Figure 4). The selected features at BCPs of intermolecular interactions are collected in Table 3 to investigate the properties of intermolecular interactions. In general, the electron density, Laplacian and total electron energy density at BCPs of all interactions formed are in the range of 0.0032-0.0144 au, 0.0128-0.0589 au and 0.0007-0.0020 au, respectively; indicating that they are weakly non-covalent interactions.[26-28]

The proton affinity at O site and deprotonated enthalpy of the C−H involved C−H···O hydrogen bond of isolated monomers are summarized in Table 4 to further investigate the effect of substituents.

Table 3. Selected parameters (au) of $CH_3OCHX_2\cdots 1CO_2$ complexes (X = H, F, Cl, Br, CH_3)

D1	Contact	ρ(rc)	$\nabla^2\rho$(rc)	H(rc)	D2	Contact	ρ(rc)	$\nabla^2\rho$(rc)	H(rc)
H	O1···C8	0.0135	0.0589	0.0020	**H**	C2−H11···O10	0.0038	0.0155	0.0010
F	O1···C8	0.0117	0.0527	0.0020		C4−H7···O9	0.0032	0.0128	0.0007
Cl	O1···C6	0.0121	0.0540	0.0020	**F**	F11(12)···O10	0.0058	0.0306	0.0017
	C4−H6···O7	0.0056	0.0247	0.0011		C2···O10	0.0042	0.0177	0.0010
Br	O1···C8	0.0121	0.0538	0.0020	**Cl**	Cl11(12)···O10	0.0049	0.0183	0.0009
	C2−H3···O10	0.0060	0.0255	0.0011		O10···C2	0.0045	0.0191	0.0011
CH_3	O1···C8	0.0144	0.0614	0.0019	**Br**	Br11(12)···O10	0.0049	0.0169	0.0008
						C2−H3···O10	0.0046	0.0198	0.0011

For **D1-X** complexes, the ρ(rc) values at BCPs of O···C tetrel bonds are enhanced in order of **D1-F** < **D1-Cl** ≈ **D1-Br** < **D1-H** < **D1-CH$_3$**. This means that the O···C tetrel bond becomes stronger in **D1-CH$_3$** and weaker in halogenated derivatives, as compared to that in CH_3OCH_3···$1CO_2$ complex. This change is explained based on the gas phase basicity at the O site increases as followed: CH_3OCHF_2<CH_3OCHCl_2<CH_3OCHBr_2<CH_3OCH_3<$CH_3OCH(CH_3)_2$ (*cf.* Table 4). Furthermore, the DPE values of isolated monomers show that the polarization of the C−H bond increases in the sequence CH_3 ≈ H < F < Cl < Br. This result is confirmed by the existence of C−H···O hydrogen bond in **D1-Cl** and **D1-Br** and no hydrogen bond formed in the remaining complexes. Taking into account the strength of C−H···O hydrogen bond, its ρ(rc) value at BCP in **D1-Br** is slightly higher than that in **D1-Cl**. Combined AIM results and energetic parameters, CH_3OCHX_2···$1CO_2$ complexes are mainly stabilized by the C···O tetrel bond and an additional role of C−H···O hydrogen bond. Regarding **D2-X** complexes, it is existed the O···X (F, Cl, Br) interactions in which are slightly reinforced from Br *via* Cl to F. These interactions are predicted to be electrostatic in nature due to the electronegativity of halogenated atoms also decreases in the same order.

The substitution of halogen and methyl group leads to a significant change in the strength of intermolecular interactions and stability of complexes. It is explained by the electron density withdrawing effect of halogenated groups, which causes a decrease electron density at O site and the largest decrement belongs to F-substituted derivative, followed by -Cl and finally, by -Br one. In contrast, the presence of -CH_3 groups instead of -H atoms results in a slight enhancement of the electron density at the O site as compared to CH_3OCH_3.

Table 4. PA at O atom and DPE of C-H bond of CH_3OCHX_2 (in $kJ.mol^{-1}$)

Monomers	PA	DPE
CH_3OCH_3	788.3	1728.9
CH_3OCHF_2	700.2	1694.1
CH_3OCHCl_2	714.8	1607.5
CH_3OCHBr_2	718.2	1576.5
$CH_3OCH(CH_3)_2$	826.3	1725.8

3.4. An NBO analysis

The charge transfer and the formation of intermolecular orbital interactions upon complexation are examined at MP2/6-311++G(2d,2p). The electron density transfer (EDT, m*e*) and second-order perturbation energy ($E^{(2)}$, $kJ.mol^{-1}$) are gathered in Table 5.

The existence of intermolecular interactions is confirmed by means of EDT from Lp(O) and σ(C−H) orbitals to π*(C=O) and σ*(C−H) anti-bonding orbitals. The EDT values of CH_3OCHX_2 are positive in range of 0.4-6.0 m*e*, implying that electron density transfers from DME and its derivatives to CO_2 monomer. The EDT value of the halogenated-substituted complexes is smaller than that of the remaining ones due to the electron withdrawing effect of halogen atoms.

Generally, the second-order energies of orbital interactions in **D1-X** complexes are considerably higher than those of in **D2-X** ones supporting that CH_3OCHX_2···$1CO_2$ complexes favor **D1** geometry. The $E^{(2)}$ values of Lp(O)→π*(C=O) delocalization in **D1-X** complexes range from -8.6 to -12.5 $kJ.mol^{-1}$, significantly larger than those of Lp(O)→σ*(C−H) by 8.3-11.5 $kJ.mol^{-1}$. This result confirms the dominant role of the former interactions as compared to the later. For **D2-X** complexes, the $E^{(2)}$ of Lp(X)→π*(C=O) (X = F, Cl, Br) is roughly 1.5−1.8 $kJ.mol^{-1}$, which is the main interactions of these complexes.

Table 5. EDT and $E^{(2)}$ for $CH_3OCHX_2\cdots1CO_2$ complexes

	EDT*	Orbital interaction	$E^{(2)}$
D1-H	6.0	Lp(O1)→π*(C8=O9)	11.3
D1-F	2.7	Lp(O1)→π*(C8=O9)	8.6
		Lp(O10)→σ*(C2−H3)	1.0
D1-Cl	2.3	Lp(O1)→π*(C6=O8)	8.8
		Lp(O7)→σ*(C4−H5)	0.7
D1-Br	1.9	Lp(O1)→π*(C8=O9)	8.7
		Lp(O10)→σ*(C2−H3)	0.5
D1-CH_3	4.5	Lp(O1)→π*(C8=O10)	12.5
		Lp(O10)→σ*(C2−H3)	0.3
D2-H	0.4	σ(C2−H12)→π*(C8=O10)	0.2
D2-F	3.1	Lp(F11)→π*(C8=O9)	1.8
		Lp(F12)→ π*(C8=O9)	1.8
		Lp(O10)→σ*(C2−H4)	0.3
D2-Cl	3.4	Lp(Cl11)→π*(C8=O9)	1.8
		Lp(Cl12)→π*(C8=O9)	1.8
		Lp(O10)→σ*(C2−H3)	0.2
		Lp(O10)→σ*(C2−H5)	0.2
D2-Br	3.2	Lp(Br11)→π*(C8=O9)	1.7
		Lp(Br12)→π*(C8=O9)	1.7
		Lp(O10)→σ*(C2−H3)	0.5
		Lp(O10)→σ*(C2−H5)	0.3

* the EDT values of CH_3OCHX_2 monomers

4. CONCLUSIONS

The interactions of CO_2 with CH_3OCHX_2 (X = H, F, Cl, Br, CH_3) induce nine stable complexes on the potential surfaces with two geometries including **D1-X** and **D2-X** at MP2/6-311++G(2d,2p). The interaction energies with both ZPE and BSSE of these complexes range from -2.8 kJ.mol^{-1} to -15.1 kJ.mol^{-1} at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) level of theory. SAPT2+ results indicate that the attractive electrostatic energy is the main contribution overcoming dispersion and induction energetic components in stabilizing the complexes.

D1-X is found to be energetic-favored structure as compared to **D2-X** one. The halogenated-substituted derivatives cause a decrease in the complex strength while methyl-substituted one leads to a stabilization enhancement, which is described in order F < Cl < Br < H < CH_3. The C···O tetrel bond plays the main contribution into the stability of complexes with the complement of C−H···O hydrogen bond, and all intermolecular interactions are weakly non-covalent interactions.

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