Effect of methyl group on the cooperativity of CH···O blue-shifted hydrogen bond in HCHO–HCHO–HCHO cyclic complex

Qingzhong Li [a,*], Haiping Liu [b], Xiulin An [a], Baoan Gong [a], Jianbo Cheng [a]

[a] Science and Engineering College of Chemistry and Biology, Yantai University, Yantai 264005, China
[b] Department of Basic Agriculture, Hebei North Academy, Zhangjiakou 075131, China

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The effect of methyl group on the cooperativity of CH···O blue-shifted hydrogen bond in HCHO–HCHO–HCHO cyclic complex has been studied with quantum chemical calculations at the MP2/6-31+G(d,p) level. We report herein the optimized geometries of the stable structures, their vibrational frequencies, NMR chemical shifts, stabilization energies, and binding energies. The cooperativity of CH···O blue-shifted hydrogen bond varies from −0.57 kcal/mol in triformaldehyde through −0.65 kcal/mol in trimethyltri-formaldehyde to −0.79 kcal/mol in trifluorotriformaldehyde. The result indicates that the methyl group has a little enhancing effect on the cooperativity of CH···O blue-shifted hydrogen bond in the cyclic complex. A negative nonadditivity of methyl group is evaluated in enhancing the cooperativity of three CH···O blue-shifted hydrogen bonds. In the formation of the CH···O blue-shifted hydrogen bond, the methyl group in the proton-acceptor plays a positive contribution, whereas that in the proton-donor plays a negative contribution.

1. Introduction

Hydrogen bonds are of great importance in stabilizing biomolecular structures [1–3], modulating specificity and speed of enzymatic reactions [4,5], and constructing supramolecular structures [6,7]. At most cases, these functions of hydrogen bonds are achieved through hydrogen-bonding cooperativity [8]. The cooperativity of hydrogen bond is present when more than two hydrogen bonds are formed among molecules simultaneously.

When X–H stretching vibration moves to low frequency upon formation of an X–H···Y hydrogen bond, such hydrogen bond is classified as red-shifting hydrogen bond; otherwise, it is classified as blue-shifted hydrogen bond [9]. Studies on the cooperativity of hydrogen bond have been performed mainly for the red-shifting hydrogen bonds [10–14]. In large degree, polarization induced in each subunit by the presence of its H-bonding partner is responsible for the cooperativity of hydrogen bond [12]. However, the cooperativity of blue-shifted hydrogen bond is not intensively investigated. Kar and Scheiner compared the cooperativity of CH···O blue-shifted hydrogen bond in chain $(FCHO)_{2-5}$ cluster and OH···O red-shifting hydrogen bond in chain $(H_2O)_{2-5}$ cluster with quantum chemical calculations and thought that the cooperativity in the former is smaller than that in the latter [12].

Recently, we studied the role of methyl groups in both proton-acceptor and proton-donor of dimethyl sulfoxide (DMSO)-methanol complex in the formation of O···HO hydrogen bond using excess infrared spectroscopy, nuclear magnetic resonance spectroscopy, and ab initio methods [15]. It was found that the methyl group in DMSO is electron-donating, whereas that in methanol is electron-withdrawing, both making a positive contribution to the strength of hydrogen bonding. In this paper, we will study the role of methyl group in the cooperativity of CH···O blue-shifted hydrogen bond. The CH···O blue-shifted hydrogen bond has been evaluated in HCHO dimer and trimer [16,17]. On basis of the structure of cyclic triformaldehyde, we constructed some target supermolecules and answered three questions. The first one is what role methyl group plays in the cooperativity of CH···O blue-shifted hydrogen bond? The second one is if a nonadditivity among methyl groups is present in affecting the cooperativity of CH···O blue-shifted hydrogen bond? The third one is what role methyl group plays in influencing the strength of CH···O blue-shifted hydrogen bond?

2. Molecular models and computational methods

First, a cyclic structure containing three HCHO molecules was designed to form three CH···O hydrogen bonds (Fig. 1). In the cyclic structure, three CH···O hydrogen bonds are same. The geometry optimization for the initial structure was carried out at the MP2/6-31+G(d) level. And then three H atoms not participating in the

* Corresponding author. Tel./fax: +86 535 6902063.
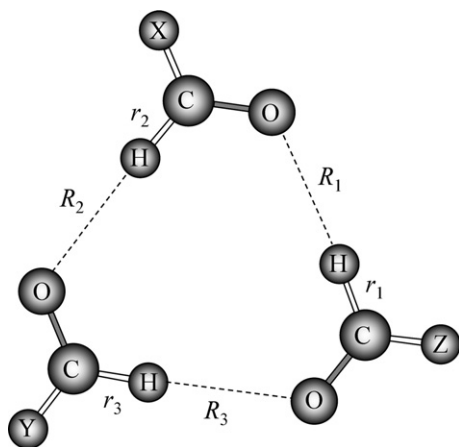E-mail address: lqz02@mails.tsinghua.edu.cn (Q. Li).

Fig. 1. Sketch map of XCHO–YCHO–ZCHO cyclic cluster involving three CH···O hydrogen bonds. X = Y = Z = H (F and Me).

formation of the CH···O hydrogen bond in the cyclic triformalde-hyde (TF) were replaced with three F atoms and three methyl groups, respectively. Followed by another cycle of geometry optimization at the same level, two optimized structures of trifluorotriformaldehyde and trimethyltriformaldehyde were obtained. Harmonic vibrational frequencies were also computed using the same method to confirm that these structures are local minima on the energy surfaces. Finally, the MP2/6-31+G(d,p) method was adopted to optimize all the structures obtained at the MP2/6-31+G(d) level for obtaining the geometric parameters and interaction energies. The MP2/6-31+G(d,p) method had been used for describing the cooperativity of blue-shifted hydrogen bonds in chain $(HCHO)_{2-5}$ and $(FCHO)_{2-5}$ clusters [12]. There have been a number of papers that studied the issue of the sensitivity of H-bond cooperativity to basis set [12,18]. The results indicated that this sensitivity is surprisingly low. Meanwhile, the basis set superposition error (BSSE) correction was also estimated using the counterpoise method of Boys and Bernardi [19] at the MP2/6-31+G(d,p) level for obtaining accurate binding energy.

The NBO analyses were carried out on the MP2/6-31+G(d,p) wave functions using the NBO package included in the Gaussian 03 suite of programs [20]. NMR chemical shifts were computed by using the gauge-including atomic orbital approach [21] at the MP2/6-31+G(d,p) level. All calculations were performed with Gaussian 03 program [22].

3. Results and discussion

Fig. 1 shows the sketch map of the cyclic structure of XCHO–YCHO–ZCHO studied in this paper, where X, Y, and Z denote H atom, F atom, or methyl group (Me). When X = Y = Z = H, F, and Me, respectively, the cyclic structure is abbreviated as TF (triformaldehyde), TFTF (trifluorotriformaldehyde), and TMTF (trimethyltriformaldehyde), respectively. When X = Me and Y = Z = H, the cyclic structure is denoted as MMTF (monomethyl triformaldehyde). When X = Y = Me and Z = H, the cyclic structure is represented with BMTF (bimethyltriformaldehyde). In Fig. 1, R is binding distance of the CH···O interaction and r is bond length of the C–H covalent bond. Some important parameters of these structures are listed in Tables 1 and 2.

3.1. Role of methyl group in hydrogen-bonding cooperativity

Structures of TF, TFTF, and TMTF cyclic clusters have C_{3h} symmetry, thus three CH···O hydrogen bonds in each cluster are same.

Table 1
Interaction energies (ΔE), bond length differences (Δr), binding distances (R), frequency shifts ($\Delta \nu$), stabilization energies (E), and chemical shifts (δ) in three complexes (TF, TFTF, and TMTF) calculated at the MP2/6-31+G(d,p) level

Parameters	TF	TFTF	TMTF
ΔE^a (kcal/mol)	−1.98(−1.41)	−2.40(−1.60)	−2.06(−1.40)
$\Delta E_{coop}{}^b$ (kcal/mol)	−0.57	−0.79	−0.65
Δr(C–H)^c (Å)	−0.0037	−0.0019	−0.0046
R(H···O) (Å)	2.3587	2.3138	2.3574
$\Delta \nu$(C–H)^d (cm^{-1})	50	38	70
E^e (kcal/mol)	2.46	3.13	2.94
δ(H)^f (ppm)	−0.9/1.6	−1.0/1.1	−0.7/1.7
δ(O)^f (ppm)	2.8/−4.8	7.3/0.0	5.7/−1.8

^{a} ΔE in the trimers was corrected with BSSE. BSSE in TF, TFTF, and TMTF is 1.64, 1.88, and 2.25 kcal/mol, respectively. Data in parentheses are the interaction energy of the corresponding dimer obtained at the same level. The dimers have two same CH···O contacts and their averages were shown [16,26,27].
^{b} $\Delta E_{coop} = \Delta E_{trimer} - \Delta E_{dimer}$.
^{c} Bond length of C–H covalent bond in the respective monomer is 1.0948, 1.0874, and 1.0996 Å, respectively.
^{d} Asymmetrical stretching frequency.
^{e} E is stabilization energy due to the $n(O) \to \sigma$(C–H) orbital interaction in the CH···O interaction.
^{f} Isotopic/anisotropic chemical shifts.

Table 2
Total interaction energies (ΔE_{trimer}) and binding distances (R) in three complexes (MMTF, BMTF, and TMTF) calculated at the MP2/6-31+G(d,p) level

Parameters	MMTF	BMTF	TMTF
ΔE_{trimer} (kcal/mol)	−6.05	−6.13	−6.18
$\Delta \Delta E$ (kcal/mol)	−0.11	−0.19	−0.24
R_1(H···O) (Å)	2.3292	2.3321	2.3574
R_2(H···O) (Å)	2.3847	2.3569	2.3574
R_3(H···O) (Å)	2.3559	2.3839	2.3574

Note: $\Delta \Delta E$ was calculated with the formula of $\Delta \Delta E = \Delta E_{trimer}(n) - \Delta E_{trimer}$(TF), where n is number of methyl group in the cyclic clusters. ΔE_{trimer}(TF) is −5.94 kcal/mol.

The interaction energies (ΔE) given in Table 1 were calculated with the formula of $\Delta E = (E_{trimer} - 3E_{monomer})/3$. The ΔE values in Table 1 were corrected with BSSE. The ΔE of the CH···O interaction in TF is −1.98 kcal/mol, which is larger in magnitude than that of the CH···O interaction between DMSO and water molecules (−1.64 kcal/mol at the MP2/6-311++G(d,p) level) [23]. This result is attributed mainly to the bigger acidity of the C–H proton in HCHO molecule. As three H atoms not participating in the CH···O interaction in TF are substituted with F atoms, the ΔE of the CH···O interaction in TFTF increases in magnitude by as much as 21%. This substituent effect is similar to that of CH···O red-shifting hydrogen bond in C_2H_2–H_2O complex [24]. Similar result is found in TMTF when three H atoms not participating in the CH···O interaction in TF are substituted with methyl groups. This demonstrates that the methyl group plays a positive contribution to the strength of CH···O interaction, which is reverse to that in C_2H_2–H_2O–H_2O cyclic complex [25]. The interaction energy in TMTF is smaller in magnitude than that in TFTM. The result indicates that the strength enhancement of the CH···O hydrogen bond due to the presence of methyl group is smaller than that from F atom.

Interaction energy is a most reliable means of evaluating the cooperativity of hydrogen bond. When the cooperativity of hydrogen bond in polymer is studied with interaction energy, it is crucial to choose a proper reference. Usually, the interaction energy in the similar dimer is selected as such a reference. For HCHO dimer, however, there are different conformations. To make a comparison with the trimers, the dimers having two same CH···O hydrogen bonds [16,26,27] were selected and optimized at the same method. The ΔE_{dimer} values given in Table 1 are their average. The ΔE_{dimer} value is −1.41, −1.60, and −1.40 kcal/mol for HCHO dimer, FCHO