RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Remarkable effects of substitution on stability of complexes and origin of the C-H···O(N) hydrogen bonds formed between acetone's derivative and CO_2, XCN (X = F, Cl, Br)

Ho Quoc Dai[a], **Nguyen Ngoc Tri**[a], **Nguyen Thi Thu Trang**[b,c], **Nguyen Tien Trung**[a,*]

[a)] *Faculty of Chemistry, and Laboratory of Computational Chemistry, Quy Nhon University, Quy Nhon, Vietnam*

[b)] *Faculty of Science, Hai Phong University, Hai Phong, Vietnam*

[c)] *Faculty of Chemistry, Ha Noi National University of Education, Ha Noi, Vietnam*

(Abstract)

Interactions of the host molecules CH_3COCHR_2 (R = CH_3, H, F, Cl, Br) with the guest molecules CO_2 and FCN (X = F, Cl, Br) induce the significantly stable complexes with stabilization energies obtained at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p) level in the range of 9.2-14.5 kJ.mol^{-1} by considering for both ZPE and BSSE corrections. The CH_3COCHR_2···XCN complexes are found to be more stable than the corresponding CH_3COCHR_2···CO_2 ones. The overall stabilization energy is contributed by both the >C=O···C Lewis acid-base and C-H···O(N) hydrogen bonded interactions, in which the crucial role of the former is suggested. Remarkably, we propose a general rule to understand the origin of the C-H···O(N) hydrogen bonds on the basis of the polarization of a C-H bond of proton donor and the gas phase basicity of proton acceptor. In addition, the present work suggests that the >C=O group can be a valuable candidate in the design of CO_2-philic and adsorbent materials, and in the extraction of cyanide derivatives from the environment.

Keywords: blue-shifting hydrogen bond, acetone's substituted derivatives, proton affinity, deprotonation enthalpy

*Corresponding author: nguyentientrung@qnu.edu.vn

1. Introduction

Miscibility and dissolution of materials in liquid and supercritical CO_2 ($scCO_2$) have attracted much attention due to the advantage of CO_2 in industrial and chemical processes over the more conventional organic solvents, and in many potential applications of "green" chemistry [1]. Accordingly, during the last three decades, studies of the interaction between the organic and/or inorganic compounds and CO_2 have been carried out on a large scale not only in theory but also in experiment to rationalize the origin of interactions in order to be able to control solubility between macromolecules or colloidal particles and CO_2 [2,3,4]. Recently, direct sol-gel reactions in $scCO_2$ have been used in the synthesis of oxide nanomaterials, oligomers and polymers [5,6]. Nevertheless, due to a lack of polarity and dipole moment, $scCO_2$ is a poor solvent for most polar solutes and solvents. In this context, much effort has been dedicated to the enhancement in the applicability of CO_2 as a solvent through the use of "CO_2-philes" that can be incorporated into the structure of insoluble and poorly soluble materials, making them soluble in CO_2 at the soft temperatures and pressures [7]. Most of the available studies concentrated on the complexes of hydrocarbons and their fluorinated derivatives with CO_2, such as $CH_{4-n}F_n\cdots CO_2$, $C_2H_6\cdots(CO_2)_n$ and $C_2F_6\cdots(CO_2)_n$ (n=1-4) [8,9,10,11,12,13] and suggested that the fluor substitution increases the solubility of hydrocarbons in $scCO_2$. However, these fluorine-based CO_2-philes are less favorable both economically and environmentally. Therefore, it is necessary to develop novel CO_2-philic materials which are cheaper and more benign for human being. There is also a great interest in understanding the origin of the interactions between molecules and CO_2 at the molecular level in order to effectively use CO_2 in different purposes.

In the recent years, a large number of studies concerning the interaction of simple functionalized organic molecules, such as CH_3OH, CH_3CH_2OH [14,15,16], CH_3OCH_3, $CH_3OCH_2CH_2OCH_3$ [17,18,19], HCHO, CH_3CHO, CH_3COOCH_3, CH_3COOH [20,21,22,23] and XCHZ (X = CH_3, H, F, Cl, Br; Z = O, S) [24], with CO_2 have been performed by using the quantum chemical methods. The strength of these complexes has been assigned to a main contribution of the Lewis acid-base interaction and/or an additional contribution of the C-H···O hydrogen bonded interaction. However, the role of the C-H···O hydrogen bond in increasing solubility remains questionable. Additionally, for chemical origin, it can be expect that other model molecules possessing electron-deficient carbon atoms and electron-excess N atoms, such as FCN, ClCN and BrCN, would be potential candidates acting as Lewis acids and Lewis bases in the presence of carbonyl compounds. Despite the cyanides are not safe in solute-solvent processes, some of them are used in studies of intermolecular interactions [25]. Furthermore, the selection of these three cyanides interacting with carbonyl compounds is to understand the origin of interactions that may guide the use of substituted carbonyl polymer surfaces to adsorb and extract cyanide derivatives from the environment.

The hydrogen bond A-H···B is a weak non-covalent interaction whose significant importance is shown not only in chemistry, biochemistry but also in physics and medicine [26]. More noticeably, the existence of the C-H···O (N) hydrogen bonds has been revealed in protein, DNA, RNA,… Consequently, special attention has been paid to the C-H bond donors involved in hydrogen bond in the last decade [27,28,29]. Up to now, several hypotheses and models have been proposed to unravel the reasons for differences between the contraction and elongation, which are respectively accompanied by a blue shift and a red shift of stretching frequency, of A-H bond length upon complexation [30,31,32,33,34]. However, no general explanation has been formulated on the origin of blue shifting hydrogen bond. Most hypotheses were focused on explaining the origin of specific blue shifting hydrogen bond when the hydrogen bonded complexes are already formed. It might be more appropriate if one considers the origin of blue shifting hydrogen bond on the basis of inherent properties of isolated isomers that are proton donors and proton acceptors as reported in the literatures [24,32,34,35].

In this study we focus on interactions between the carbonyl compounds including acetone (CH_3COCH_3) and its doubly methylated and halogenated derivatives (CH_3COCHR_2, with R = CH_3, F, Cl, Br) with CO_2 and XCN (X = F, Cl, Br) in order to probe the existence and the role of the >C=O···C Lewis acid-base interaction along with the C-H···O(N) hydrogen bonded interactions on stabilization of the complexes examined. To the best of our knowledge, an investigation into these systems has not been reported in the literature. Another important purpose is how the durability of the complexes formed by the interactions of these compounds with CO_2 and XCN will be changed upon substitution. Remarkably, this work also aims at gaining the origin of the C-H···O(N) blue-shifting hydrogen bond on the basis of the polarizability of the C-H covalent bond and the gas phase basicity of the O and N atoms.

2. Computational Methodology

Geometry optimizations for monomers and complexes formed in the interactions of CH_3COCHR_2 (R = CH_3, H, F, Cl, Br) with CO_2 and XCN (X = F, Cl, Br) were carried out using the MP2/6-311++G(2d,2p) level of theory. Computations of the harmonic vibrational frequencies at the same level of theory were followed to ensure that the optimized structures were all energy minima on potential energy surfaces, and to estimate zero-point energy (ZPE). In order to avoid vibrational couplings between the CH_3 stretching modes of CH_3COCH_3 and $CH_3COCH(CH_3)_2$, the harmonic frequencies in both the monomers and relevant complexes were calculated by means of the deuterium isotope effect. Single point energy calculations were done in all cases at the CCSD(T)/6-311++G(3df,2pd) level based on the MP2/6-311++G(2d,2p) optimized geometries. Basis set superposition errors (BSSE) resulting from the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p) level were obtained using counterpoint procedure [36]. The interaction energies were derived as the difference in total energy between each complex and the sum of relevant monomers, corrected for ZPE only (ΔE) or for both ZPE and BSSE (ΔE^*). All of the calculations mentioned above were carried out using the Gaussian 09 program [37]. Topological parameters of the complexes were defined by AIM2000 software [38] based on Bader's Atoms in Molecules theory [39,40]. And finally, the electronic properties of the monomers and complexes were examined through a natural bond orbital (NBO) analysis using GenNBO 5.G program [41] at the MP2/6-311++G(2d,2p) level.

3. Results and discussion

3.1 Interactions of CO_2 with CH_3COCHR_2 (R = CH_3, H, F, Cl, Br)

Four stable shapes of complexes, which are denoted by **H1**, **H2**, **H3** and **H4**, and their interaction energies at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p) level are shown in Figure 1 and Table 1. Further evidences for existence of intermolecular contacts of complexes by means of AIM analysis are given in Figure S1 and Table S1 of Supplementary Information (SI). Indeed, as listed in Table S1, electron density and Laplacian values of bond critical points (BCP) of intermolecular contacts including O6···C11 and O12···H8 in **H1**, O6···C11 in **H2**, O6···C11 and O12···C5 in **H3**, and O12···H3(9) and O13···H4(10) in **H4** fall within the limitation criteria for the formation of weak interactions [40]. Accordingly, they are Lewis acid-base and hydrogen bonded interactions, both contributing to the strength of complexes examined.

As shown in Table 1, the interaction energies obtained are quite negative, and increase in the order **H1 < H2** ≈ **H3** < **H4**. This means that stability of the complexes reduces in the same order. The interaction energy of -10.3 $kJ.mol^{-1}$ with both ZPE and BSSE corrections for **H1** is between the values of -11.1 $kJ.mol^{-1}$ reported in ref. [42] at CCSD(T)/aug-cc-pVTZ and of -8.8 $kJ.mol^{-1}$ in ref. [43] at MP2/aug-cc-pVDZ. Notably, in this work, the interaction of CH_3COCH_3 with CO_2 induces **H3** less stable than **H1**, which is different from the results reported by Ruiz-Lopez *et al.* [44]. The authors carried out the calculations at MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ, and suggested that **H3** is more stable than **H1** with an average value of 1.0 $kJ.mol^{-1}$. Their predictions were obtained in the case of the interaction energies without taking BSSE correction into account since they asserted that a close BSSE value of 2.3 $kJ.mol^{-1}$ for both **H1** and **H3**. Our calculated BSSE values for these two structures at CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p) are 2.4 and 3.5 $kJ.mol^{-1}$. It is clear that the contribution of BSSE to the overall stabilization energy for **H3** is significantly larger than for **H1**. This leads to a larger magnitude in strength of **H1** compared to **H3** as estimated in Table 1.

In addition, to gain a more reliable evaluation, a higher level of theory (CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ) is used to obtain interaction energies which are -13.4, -12.3 $kJ.mol^{-1}$ for only ZPE correction, and -11.7, -9.5 $kJ.mol^{-1}$ for both ZPE and BSSE corrections in the cases of **H1** and **H3**, respectively. The results trustingly suggest that **H1** is more stable than **H3**, although their strengths are comparable when considering only ZPE correction (*cf.* Table 1). The present work also locates two new stable geometries denoted by **H2** and **H4** of the interaction between CH_3COCH_3 and CO_2, in which **H2** (-9.4 $kJ.mol^{-1}$) is negligibly more stable than **H3** (-9.2 $kJ.mol^{-1}$) when both ZPE and BSSE corrections are included.

Apart from the most stable **H1** structure in all the $CH_3COCH_3\cdots CO_2$ shapes, the presence of both Lewis acid-base and hydrogen bonded interactions in this structure and the demand to evaluate the solubility of carbonyl compounds in $scCO_2$ as well as to reveal the role of interactions contributing to the strength of formed complexes, we replaced two H atoms in a CH_3 group of CH_3COCH_3 by two CH_3, F, Cl and Br alike groups (denoted by CH_3COCHR_2, and considered as host molecules), and set out an investigation at the molecular level into their interactions with the CO_2 guest molecule. The most stable geometries of F, Cl and Br derivatives are virtually similar to **H1**. There is only a slight difference of the shape of complex in the case R = CH_3 (Figure 2). The selected parameters of the complexes are collected in Table 2. In general, all O···C and O···H contact distances are shorter or close to the sums of van der Waals radii of the two relevant atoms (3.22 Å for the former and 2.72 Å for the latter). They are indeed in the ranges of 2.85-2.94 Å for O···C contacts and 2.38-2.79 Å for O···H contacts. Consequently, it can be suggested roughly that these interactions are the >C=O···C (CO_2) Lewis acid-base type and the C-H···O hydrogen bond. An AIM analysis to lend further support for their existence and contribution to complex strength is given in Table S2 of SI.

All interaction energies are significantly negative, and range from -11.9 to -13.8 $kJ.mol^{-1}$ considering only ZPE and from -9.2 to -10.7 $kJ.mol^{-1}$ considering both ZPE and BSSE (*cf.* Table 2). These obtained results are consistent with the suggestion on larger magnitude in strength of carbonyl relative to fluorocarbons and other functionalized compounds in interacting with CO_2. Thus, at the MP2/aug-cc-pVDZ level, the interaction energies are in the range from -3.7 to -4.9 $kJ.mol^{-1}$ for the complexes of CO_2 with the hydrocarbons such as CH_4, C_2H_6, CF_4, C_2F_6; and from -2.4 to -7.8 $kJ.mol^{-1}$ for the complexes of CO_2 with $CH_{4-n}F_n$ (n = 0 ÷ 4) [9,11]. In our previous work, the complexes of CO_2 with carbonyl and thiocarbonyl compounds such as XCHZ (X = CH_3, H, F, Cl, Br; Z = O, S) possess the interaction energies (ΔE*) from -5.6 to -10.5 $kJ.mol^{-1}$ at CCSD(T)//aug-cc-pVTZ//MP2/aug-cc-pVTZ [24]. The fact that all interaction energies of these complexes are considerably more negative than that of the dimer of CO_2 [22,24] (ΔE* ≈ -5.5 $kJ.mol^{-1}$) suggests the $CH_3COCHR_2\cdots CO_2$ complexes more stable than the dimer. In another word, the compounds functionalized with the >C=O counterpart could be an effective approach in the design of CO_2-philic materials.

We now discuss in more detail the substitution effects on the contributing role of the interactions to the overall interaction energy in $CH_3COCHR_2\cdots CO_2$. Generally, association of CH_3COCHR_2 with CO_2 leads to a slight increase in interaction energy (including by both ZPE and BSSE corrections, *cf.* Table 2) in the order CH_3 < H ≈ Br < Cl < F. This is in accordance with a reported comment on the effect of substitution on the strength of complexes formed by halogenation of formaldehyde and acetaldehyde, and CO_2 [11,24]. To evaluate strength of the complexes investigated, we calculated the proton affinity (PA, using CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ) at the O site of the >C=O group and deprotonation enthalpy (DPE, using CCSD(T)/aug-cc-pVTZ//MP2/6-311++G(2d,2p)) of the C-H bond of the –CHR_2 group in the isolated CH_3COCHR_2 monomers. The obtained values are listed in Table 3. The polarization of C-H bond increases in the order CH_3 < H < F < Cl < Br, and the gas phase basicity at the O site increases in the order F < Cl < Br < H < CH_3. This is an evidence for withdrawing electron density from O atoms in halogenated compounds, causing a larger decrement in electron density at the O site in going from Br- *via* Cl- and F-substituted derivative. In contrast, a CH_3 substitution results in an enhancement of electron density at O site in $CH_3COCH(CH_3)_2$ compared to CH_3COCH_3. Accordingly, along with the strengthening order of interaction energy mentioned above, the total stabilization energy of complexes is contributed by both the >C=O···C (CO_2) Lewis acid-base interaction and the C-H···O hydrogen bond, in which the former predominates over the latter. This is in agreement with previous results on the additional contribution of the hydrogen bond in stabilizing complexes and enhancing solubility in scCO_2 [22,23,24]. In conclusion, the strength of CH_3COCHR_2···CO_2 complexes is gently increased when substituting two H atoms in a CH_3 group by two CH_3 groups of CH_3COCH_3, while it is slightly decreased with replacement by two halogen atoms (2F, 2Cl and 2Br). This is understood by an electron-donating effect of the CH_3 group and electron-withdrawing effect of halogen groups, which makes electron density at the O atom in the methylated monomer larger than in the halogenated monomers and acetone.

We continue investigation into characters of the C-H···O hydrogen bond in these complexes. Its formation results in a shortened C-H bond length of 0.00025-0.00084 Å, and a blue-shifted stretching frequency of 6.0-16.3 cm^{-1}, as compared to those in the relevant monomers (*cf.* Table 2). It is, however, remarkable that the C-H infrared intensity is reduced in the range of 2.1-10.1 $km.mol^{-1}$ for CH_3COCHR_2···CO_2, with R = CH_3, H, F, while it is enhanced by 10.6 and 14.8 $km.mol^{-1}$ for $CH_3COCHCl_2$···CO_2 and $CH_3COCHBr_2$···CO_2, respectively, in spite of a contraction of the C-H bond length and a blue shift of its stretching frequency. Nevertheless, this observation is consistent with our previously reported results [24,34]. With the all obtained results, we would suggest that the C-H···O blue shifting hydrogen bond, which partly contributes to the complex strength, is well present in the complexes examined. This finding is different from the Besnard's results [43,45] where they reported only the presence of Lewis acid-base interaction between electron donor being O atom of CH_3COCH_3 and electron acceptor being C atom of CO_2 for CH_3COCH_3···CO_2.

It should be noticed here that the general trend in magnitude of the C-H bond length contraction is in accordance with the magnitude order of polarity of the C-H bond in the isolated monomers. Thus, in going from F *via* Cl to Br, polarization magnitude of the C-H bond in the isolated monomers increases, and that is accompanied by a decrease in magnitude of the C-H bond length contraction and its stretching frequency enhancement when the complexes are formed (*cf.* Tables 2 and 3). This is not observed in the case of the CH_3 substitution group in the present work since the shape of $CH_3COCH(CH_3)_2\cdots CO_2$ complex differs from the remaining ones.

As reported by Joseph, Jemmis [33] and Szostak [46] there is a good correlation between NBO charge on H atom of proton donor involved in hydrogen bond and change of bond length and stretching frequency upon complexation. They suggested that the blue shifting hydrogen bond was more likely to occur for donors bearing smaller positive charges on H atom, and on the contrary the red shifting hydrogen bond occurred for molecules with larger positive charges on H atom. Our results further confirm this remark. Thus, the NBO charges at the MP2/6-311++G(2d,2p) level on the H atoms of –CHR_2 group in CH_3COCHR_2 monomers are calculated to be 0.216, 0.206, 0.139, 0.217 and 0.223 *e* for the substituted derivatives of H, CH_3, F, Cl and Br, respectively.

An NBO analysis at the MP2/6-311++G(2d,2p) level is performed to evaluate electron density transfer (EDT) between the host and the guest molecules, electron density in the σ*(C7-H8) antibonding orbitals, percentage of s-character at the C7(H8) hybrid orbitals and intermolecular hyperconjugation energies. Selected NBO results are given in Table S3 of SI. A positive EDT value implies electron transfer from the host to the guest molecules, and inversely for a negative value. Following complexation, there are electron density transfers from CH_3COCH_3 and $CH_3COCH(CH_3)_2$ to CO_2, while reverse transfers are observed for $CH_3COCHR_2\cdots CO_2$, with R = F, Cl and Br (*cf.* Table S3). This implies that the C7-H8···O12 hydrogen bonded interactions become stronger in going from CH_3 *via* H to F to Cl and finally to Br derivative. A slight increase of 0.12-0.66% in s-character percentage of the C7(H8) hybrid orbitals is obtained for all examined complexes. Such an enhancement of s-character contributes to the contraction of the C7-H8 bond. Remarkably, there is a different variation of the σ*(C7-H8) electron densities in the complexes as compared to that in the relevant monomers. They are indeed reduced by 0.0002-0.0003 *e* for $CH_3COCHR_2\cdots CO_2$, with R = F, Cl, Br, and are enhanced by 0.0004 *e* and 0.0009 *e* for $CH_3COCH(CH_3)_2\cdots CO_2$ and $CH_3COCH_3\cdots CO_2$, respectively. Therefore, a contraction of the C7-H8 bond along with a blue shift of its stretching frequency in the former ones arises from both a decrease in occupation of the σ*(C7-H8) orbital and an increase in s-character percentage of the

C7(H8) hybrid orbital, and in the latter ones due to an overriding enhancement of C7(H8) s-character relative to an increase of the σ*(C7-H8) electron density, following complexation.

In a word, the bond contraction and the frequency blue shift of a C-H bond involved in hydrogen bonded complexes depend on its polarization in the isolated monomer. In particular, the weaker the polarization of a C-H covalent bond acting as proton donor is, the stronger its distance contraction and frequency blue shift as a result of complex formation are, and *vice versa*.

3.2 Interactions of the guest molecules XCN (X = F, Cl, Br) with the host molecules CH_3COCHR_2 (R = H, CH_3, F, Cl, Br)

Interactions of CH_3COCHR_2 with XCN induce the stable shapes of complexes similar to that of $CH_3COCHR_2\cdots CO_2$ as shown in Figure 2. There is only a slight difference of the structures to be by replacing O12 and O13 atoms of CO_2 by N12 and X13 atoms of XCN, respectively, and their geometric shapes are presented in Figure S2 of SI. Some of typical data are tabulated in Table 4. Most of the contact distances O6···C11 and N12···H8(H17) are in turn in the range of 2.82-3.15 Å and 2.27-2.76 Å, shorter than or comparable to the sums of van der Waals radii of the two relevant atoms (3.22 Å and 2.75 Å for O···C and N···H respective contacts). Consequently, there is an existence of the >C=O···C Lewis acid-base and C-H···N hydrogen bonded interactions in $CH_3COCHR_2\cdots XCN$, in which the latter is quite weak. Further evidences for the existence and the stability of the mentioned interactions are provided by the results of AIM analysis given in Table S4 of SI.

All interaction energies of the complexes examined are significantly negative, more negative than those of $CH_3COCHR_2\cdots CO_2$. In particular, they are in the range from -11.1 to -14.5 $kJ.mol^{-1}$ for both ZPE and BSSE corrections, and from -13.5 to -18.7 $kJ.mol^{-1}$ for only ZPE correction (*cf.* Table 4). The obtained results suggest the larger magnitude in strength of $CH_3COCHR_2\cdots XCN$ relative to $CH_3COCHR_2\cdots CO_2$. In other words, replacement of the CO_2 by FCN or ClCN or BrCN guest molecule leads to an increase in strength of the formed complexes. Nevertheless, the variations in magnitude of their stabilization energies is not considerable, only about 1.0-1.5 $kJ.mol^{-1}$.

As shown in Table 4, the strength of the complexes of acetone and its substituted derivatives with FCN increases in the order F < H < Cl < CH_3 ≈ Br, and H < F < CH_3 < Cl < Br for ClCN and BrCN. The obtained results show that the stability of complexes is contributed by both the >C=O···C Lewis acid-base interaction and the C-H···N hydrogen bond since there are increases in both the C-H ($-CHR_2$) polarity and O-gas basicity in going from F *via* Cl to Br substituted derivative of CH_3COCHR_2 (*cf.* Table 3). Nevertheless, an enhanced contribution of the C-H···N hydrogen bond energy to the total stabilization energy should be suggested for the examined complexes, since CH_3COCH_3···XCN is in general less stable than CH_3COCHR_2···XCN (R = F, Cl, Br), in spite of the larger O-gas basicity of CH_3COCH_3. The considerable stability of $CH_3COCH(CH_3)_2$···FCN, which is close to the largest stability of $CH_3COCHBr_2$···FCN, might be mainly assigned to the >C=O···C Lewis acid-base interaction (due to the largest gas phase basicity at the O site and the largest electron-accepting capacity of FCN) and an additional cooperation of the two C-H···N hydrogen bonds. From the discussion on comparison of the complex strength, it indicates that the C-H···N hydrogen bond is more stable than the C-H···O hydrogen bond.

For the same host molecules, the stability of all CH_3COCHR_2···XCN complexes decreases in the order of the guest molecules from FCN *via* ClCN and to BrCN. This tendency is opposite to an increasing order of PA at N sites of the three guest molecules. Thus, PAs at the N sites in the guest molecules calculated at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p) level are 690.1, 733.9 and 747.5 kJ.mol^{-1} for FCN, ClCN and BrCN, respectively. Remarkably, at the N site of FCN our estimated PA of 690.1 kJ.mol^{-1} is very close to that of 690.3 kJ.mol^{-1} at the G2 level reported by Rossi *et al.* in ref. [47]. For explanation of this observation, a NBO analysis for the guest molecules is performed using the MP2/6-311++G(2d,2p) level. The NBO charge values at C atoms are estimated to be in turn 0.662, 0.163 and 0.072 *e* for FCN, ClCN and BrCN. This implies a decrease of the >C=O···C Lewis acid-base interaction in CH_3COCHR_2···XCN going from FCN to BrCN. The NBO analyses for monomers and their complexes (given in Table S5 of SI) indeed indicate an electron density transfer in decreasing order from the n(O) lone pairs of CH_3COCHR_2 to the π*(C≡N) orbital of XCN for each of

CH_3COCHR_2···XCN series in going from FCN to BrCN. Remarkably, an additional transfer of electron density from the n(O) lone pairs of CH_3COCHR_2 to the σ*(C-F) orbital of FCN is observed, following complexation. On the contrary, there is a slight increase in the stability of the C-H···N hydrogen bond from FCN to BrCN for each the host molecule (*cf.* Table S5). In summary, the crucial contribution to the overall stabilization energy in CH_3COCHR_2···XCN is predominated by the >C=O···C Lewis acid-base interaction, which overwhelms the C-H···N hydrogen bonded interaction. However, an enhanced role of the C-H···N hydrogen bond should be suggested for CH_3COCHR_2···XCN in going from FCN to BrCN.

As pointed out from Table 4, there is an enhancement of stabilization energy in each the CH_3COCHR_2···XCN relative to the corresponding CH_3COCHR_2···CO_2 series. This is due to the PA at all N sites in XCN larger than that at the O site in CO_2, and more noticeably the PA value is enhanced in the order of FCN to BrCN. Indeed, the PA at O atom of CO_2 is 541.6 kJ.mol^{-1} at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(3d,2p) level, which is significantly smaller than the PAs at N atoms of XCN. These results firmly indicate a larger magnitude in strength of the C-H···N relative to the C-H···O interaction in stabilizing the complexes. In brief, substitution of the two H atoms in a CH_3 group of CH_3COCH_3 by two R alike groups (R = CH_3, F, Cl, Br) results in an increase in strength of CH_3COCHR_2···XCN compared to CH_3COCH_3···XCN, while it negligibly affects the strength of CH_3COCHR_2···CO_2 relative to CH_3COCH_3···CO_2.

Following complexation, there are different changes of the C7-H8 bond length, its stretching frequency and infrared intensity in the examined complexes with respect to the relevant monomers. The C7-H8 bond lengths in CH_3COCHR_2···XCN (with R = H, CH_3, F) are slightly shortened by *ca.* 0.0001 Å, accompanied by increases of 8.0-17.5 cm^{-1} in the stretching frequency and decreases of 1.6-13.5 km.mol^{-1} in infrared intensity. In contrast, the interactions of CH_3COCHR_2 (with R = Cl, Br) with XCN lead to slight elongations (0.0001-0.0004 Å) of the C7-H8 bond length and tiny decrements (0.2-2.2 cm^{-1}) of its stretching frequency, along with enhancements (24.1-51.2 km.mol^{-1}) of corresponding infrared intensity, as compared to those in the relevant host derivatives. These characteristics point out that the C7-H8···N12 intermolecular interaction in the CH_3COCHR_2···XCN complexes belongs to the blue shifting hydrogen bond in the case of CH_3-, H- and F-substituted R host derivatives and the red shifting hydrogen bond in the case of Cl- and Br-substituted ones.

In the case of the alike substituted derivatives (R = CH_3, H or F) interacting with XCN, there is a tiny decrease in magnitude of the C7-H8 bond length shortening and its stretching frequency blue shift in going from F- to Br-substituted guest molecule. Going in the same order of the guest molecules, an increase in magnitude of the C7-H8 bond length elongation and its stretching frequency red shift is observed in each pairs of $CH_3COCHR_2\cdots XCN$ (R = Cl, Br) (*cf.* Table 4). These results are due to both an increase in gas phase basicity at N atoms from FCN to BrCN, and a stronger polarization of the C7-H8 bonds in the CH_3COCHR_2 (R = Cl, Br) relative to CH_3COCHR_2 (R = H, CH_3, F) host molecules (*cf.* Table 3). Accordingly, a stronger basicity of proton acceptor should lead to a weaker contraction of C-H bond acting as the proton donor and its weaker frequency blue shift, and *vice versa.* Thus, a red shift of C7-H8 stretching frequency is predicted in the case of $CH_3COCHR_2\cdots XCN$, with R = Cl, Br. In addition, as shown in Table 4, for each of XCN, there are a shortened-to-lengthened change of C7-H8 bond length and a blue-to-red shift of its stretching frequency in the examined complexes relative to the respective monomers. The obtained results should be firmly assigned to an increase in the polarity of C7-H8 covalent bond in going from CH_3 *via* H to F to Cl and finally to Br substituted derivative.

Consequently, *we would suggest that for the same proton acceptor the weaker the polarization of a C-H bond involved in the hydrogen bond is, the larger its bond contraction and frequency blue shift upon complexation are, and also for the same C-H proton donor, the weaker the gas phase basicity of the proton acceptor is, the larger its bond contraction and frequency blue shift are, and vice versa*. Thus, a similar trend of change in the C7-H8 bond length and its stretching frequency is also obtained for the $CH_3COCHR_2\cdots CO_2$ complexes. A contraction of the C7-H8 bond length and a blue shift of its stretching frequency are larger for each of $CH_3COCHR_2\cdots CO_2$ series than for each of $CH_3COCHR_2\cdots XCN$ series, respectively (*cf.* Tables 2 and 4). Generally, an electron density transfer from the XCN guest molecules to the CH_3COCHR_2 host molecules is predicted in the complexes examined, except for the two complexes $CH_3COCH_3\cdots FCN$ and $CH_3COCH(CH_3)_2\cdots FCN$ (*cf.* Table S5 of SI). This observation is similar to that obtained in the case of $CH_3COCHR_2\cdots CO_2$, in which electron density is transferred from CO_2 to CH_3COCHR_2 for $CH_3COCHR_2\cdots CO_2$ (R = F, Cl, Br), and a reverse tendency for $CH_3COCH_3\cdots CO_2$ and $CH_3COCH(CH_3)_2\cdots CO_2$. Upon complexation, there are electron density increases of 0.0001-0.0022 *e* in the σ*(C7-H8) orbitals and C7(H8) s-character percentage enhancements of 0.26-0.97% in $CH_3COCHR_2\cdots XCN$ (R = H, CH_3, F) with respective to the relevant monomers. As a result, the enhancement of C7(H8) s-character overcoming the increase in the occupation of the σ*(C7-H8) orbital plays a decisive role giving rise to the contraction and the blue shift of the C7-H8 stretching frequency. However, the elongation and the red shift of the C7-H8 stretching frequency in $CH_3COCHR_2\cdots XCN$ (R = Cl, Br) are determined by the significant increases of 0.0007-0.0019 *e* in population of the σ*(C7-H8) orbital predominating the increases of 1.23-1.53% in C7(H8) s-character percentage as a result of complexation. A large increase of electron density in the σ*(C7-H8) orbitals is due to the stronger interaction transferring electron density from n(N) and π(C≡N) orbitals of XCN to σ*(C7-H8) orbital of the host molecules, in going from F *via* Cl and to Br guest molecules (*cf.* Table S5). This observation differs from the case of $CH_3COCHR_2\cdots CO_2$ as discussed above.

4. Concluding Remarks

The significantly stable structures of the interactions between the CH_3COCHR_2 (R = H, CH_3, F, Cl, Br) host molecules with the CO_2 and XCN (X = F, Cl, Br) guest molecules were located on the potential energy surface at MP2/6-311++G(2d,2p). The stability of the $CH_3COCHR_2\cdots CO_2$ and $CH_3COCHR_2\cdots XCN$ complexes is contributed by a crucial role of the >C=O···C Lewis acid-base interaction and an additional cooperation of the C-H···O(N) hydrogen bonded interaction. The $CH_3COCHR_2\cdots XCN$ complexes are found to be more stable than the $CH_3COCHR_2\cdots CO_2$ ones, which is taken place from a stronger contribution of the C-H···N relative to C-H···O interaction to the overall stabilizing energy. Generally, the substitution of the two H atoms in a CH_3 group of CH_3COCH_3 by two R alike groups leads to an increase in the strength of $CH_3COCHR_2\cdots XCN$ relative to $CH_3COCH_3\cdots XCN$, while it negligibly affects the strength of $CH_3COCHR_2\cdots CO_2$ relative to $CH_3COCH_3\cdots CO_2$. It is noteworthy that FCN is the strongest Lewis acid among the four guest molecules. This revelation is assigned to an additional transfer of electron density from the n(O) lone pairs of CH_3COCHR_2 to the σ^*(C-F) orbital of FCN, which is not observed in the other cases, following complexation. The obtained results suggests that, for the same proton acceptor, the weaker the polarity of a C-H bond involved in the hydrogen bond is, the larger its bond contraction and frequency blue shift as a result of complexation are. Similarly, for the C-H same proton donor, the weaker the gas phase basicity of the proton acceptor is, the larger its bond contraction and frequency blue shift are, and *vice versa.*

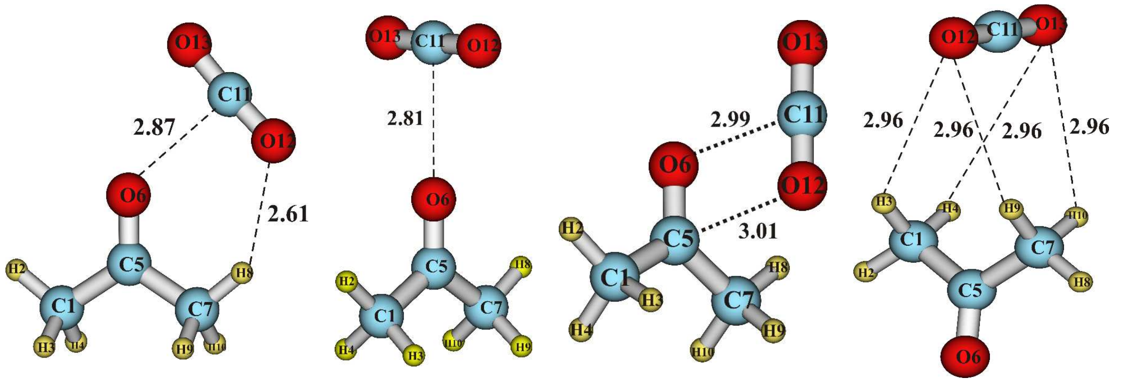
Acknowledgements

This research is funded by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03-2012.12. NTT thanks Prof. M. T. Nguyen for valuable discussion and Katholieke Universiteit Leuven for extending computational facilities.

FIGURE CAPTIONS

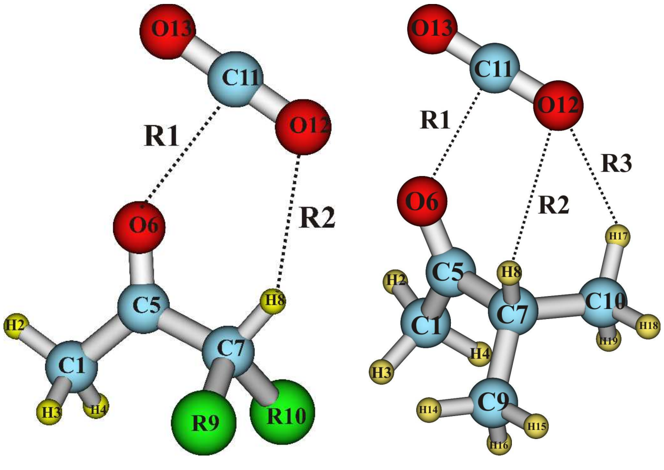
Figure 1. The stable complexes of interaction between CH_3COCH_3 and CO_2 (distances in Å).

Figure 2. The stable shapes of the complexes between CH_3COCHR_2 and CO_2 (with R = H, CH_3, F, Cl, Br).



H1 **H2** **H3** **H4**

Figure 1



CH_3COCHR_2···CO_2 $CH_3COCH(CH_3)_2$···CO_2

Figure 2

TABLE CAPTIONS

Table 1. Interaction energies (given in kJ.mol^{-1}) corrected for only ZPE, for both ZPE and BSSE, and BSSE of the complexes displayed in Figure 1.

Table 2. Interaction energies (kJ.mol^{-1}), BSSE (kJ.mol^{-1}), changes of the bond length (Δr, Å), stretching frequency (Δν, cm^{-1}) and infrared intensity (ΔI, km.mol^{-1}) of C7-H8 bond in the complexes relative to the relevant monomers.

Table 3. Deprotonation enthalpy of the C-H bond of $-CHR_2$ group, proton affinity at O site of >C=O group in the relevant monomers (all in kJ.mol^{-1}).

Table 4. Intermolecular contact distances (in Å), interaction energies (in kJ.mol^{-1}), and changes of the bond length (Δr, in Å), stretching frequency (Δν, in cm^{-1}) and infrared intensity (ΔI, in km.mol^{-1}) of C7-H8 bond in the complexes relative in respective monomers.

Table 1

	H1	**H2**	**H3**	**H4**
ΔE	-12.7	-11.3	-12.7	-4.7
BSSE	2.4	1.9	3.5	2.3
ΔE*	-10.3	-9.4	-9.2	-2.4

Table 2

	$CH_3COCHR_2\cdots CO_2$							
	R1	R2(3)	ΔE	BSSE	ΔE*	Δr(C_7H_8)	Δν(C_7H_8)	ΔI(C_7H_8)
R = H	2.87	2.61	-12.7	2.4	-10.4	-0.00025	10.9	-3.1
R = CH_3	2.85	2.77	-13.6	2.8	-10.7	-0.00054	14.1	-2.1
		$2.79^{b)}$				$-0.00054^{a)}$	$6.0^{a)}$	$-3.4^{a)}$
R = F	2.94	2.51	-11.9	2.8	-9.2	-0.00084	16.3	-10.1
R = Cl	2.92	2.40	-13.8	3.8	-10.1	-0.00068	15.0	10.6
R = Br	2.91	2.38	-13.8	2.4	-10.4	-0.00065	14.8	14.8

$^{a)}$*for the C10-H17 bond in* $CH_3COCH(CH_3)_2\cdots CO_2$, $^{b)}$*for the value of R3*

Table 3

	CH_3COCH_3	$CH_3COCH(CH_3)_2$	CH_3COCHF_2	$CH_3COCHCl_2$	$CH_3COCHBr_2$
DPE*	1704.6	1707.8	1669.9	1579.4	1558.4
PA	812.7	832.9	738.6	762.1	776.1

**Single point energy of the CH_3COCR_2 anions calculated at the respective geometry of isolated monomer without optimization*

Table 4

	$CH_3COCHR_2\cdots XCN$						
	R1	R2(3)	ΔE	ΔE*	$\Delta r(C_7H_8)$	$\Delta\nu(C_7H_8)$	$\Delta I(C_7H_8)$
R = H, X = F	2.84	2.57	-16.7	-13.9	-0.00013	10.0	-2.8
R = H, X = Cl	3.09	2.55	-15.1	-11.8	-0.00010	8.9	-1.7
R = H, X = Br	3.13	2.56	-13.5	-11.1	-0.00006	8.0	-2.0
R = CH_3, X = F	2.82	2.76	-17.9	-14.4	-0.00084	12.8	-1.6
		2.74			-0.00084$^{a)}$	9.1$^{a)}$	-5.7*
R = CH_3, X = Cl	3.06	2.74	-18.3	-12.4	-0.00082	12.2	-1.9
		2.76			-0.00080$^{a)}$	8.1$^{a)}$	-3.8*
R = CH_3, X = Br	3.11	2.71	-15.1	-11.9	-0.00081	12.0	-2.0
		2.76			-0.00080$^{a)}$	8.1$^{a)}$	-3.2*
R = F, X = F	2.89	2.46	-16.4	-13.0	-0.00090	17.5	-13.4
R = F, X = Cl	3.11	2.43	-16.0	-12.1	-0.00078	15.8	-13.5
R = F, X = Br	3.15	2.41	-14.8	-11.7	-0.00076	15.4	-13.4
R = Cl, X = F	2.87	2.33	-18.7	-14.1	0.00009	-0.2	24.1
R = Cl, X = Cl	3.08	2.29	-18.5	-13.3	0.00035	-0.4	40.1
R = Cl, X = Br	3.13	2.28	-17.4	-13.0	0.00038	-0.8	44.1
R = Br, X = F	2.87	2.31	-18.6	-14.5	0.00014	-1.2	42.9
R = Br, X = Cl	3.08	2.28	-18.4	-13.7	0.00038	-1.8	48.8
R = Br, X = Br	3.13	2.27	-17.3	-13.4	0.00040	-2.2	51.2

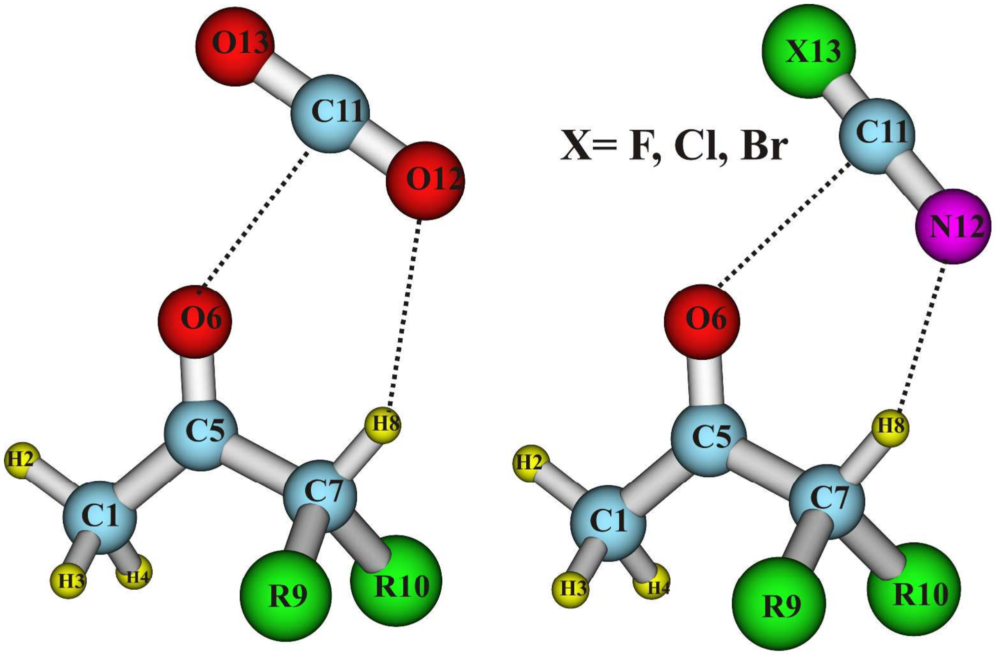
[a] *for the C10-H17 bond*

References:

---

(1) C. A. Eckert, B. L. Knutson and P. G. Debenedetii, *Nature,* 1996, **383**, 313-318.
(2) T. W. Zerda, B. Wiegand and J. Jonas, *J. Chem. Eng. Data.*, 1986, **31**, 274-277.
(3) J. Sadlej, J. Makarewicz and G. Chalasinski, *J. Chem. Phys.*, 1998, **109**, 3919-3928.
(4) A. J. Cox, T. A. Ford and L.Glasser, *J. Mol. Struct.*, 1994, **312**, 101-108.
(5) R. Sui, J. M. H. Lo and P. A. Charpentier, J. *Phys. Chem.* C, 2009, **113**, 21022-21028.
(6) Y. Wang, L. Hong, D. Tapriyal, I. C. Kim, I.-H Paik, J. M. Crosthwaite, A. D. Hamilton, M. C. Thies, E. J. Beckman, R. M. Enick and J. K. Johnson, *J. Phys. Chem. B*, 2009, **113**, 14971-14980.
(7) E. J. Beckman, *J. of Supercritical Fluids*, 2004, **28**, 121-191.
(8) A. Cece, S. H. Jureller, J. L. Kerschner and K. F. Moschner, *J. Phys. Chem.*, 1996, **100**, 7435-7439.
(9) P. Diep, K. D. Jordan, J. K. Johnson and E. J. Beckman, *J. Phys. Chem. A*, *1998*, **102**, 2231-2236.
(10) Y. K. Han and H. Y. Jeong, *J. Phys. Chem. A*, 1997, **101**, 5604-5604.
(11) P. Raveendran and S. L. Wallen, *J. Phys. Chem. B*, 2003, **107**, 1473-1477.
(12) C. R. Yonker and B. J. Palmer, *J. Phys. Chem. A*, 2001, **105**, 308-314.
(13) M. Tafazzoli and A. Khanlarkhani, *J. of Supercritical Fluids*, 2007, **40**, 40–49.
(14) J. M. Stubbs and J. I. Siepmanna, *J. Chem. Phys.*, 2004, **121**, 1525-1534.
(15) E. Dartois, K. Demyk, L. d'Hendecourt and P. Ehrenfreund, *Astron. Astrophys.*, 1999, **351**, 1066–1074.
(16) P. Lalanne, T. Tassaing, Y. Danten, F. Cansell and S. C. Tucker, *J. Phys. Chem. A*, 2004, **108**, 2617-2624.
(17) J. J. Newby, R. A. Peebles and S. A. Peebles, *J. Phys. Chem. A*, 2004, **108**, 11234-11240.
(18) K. H. Kim and Y. Kim, *J. Phys. Chem. A*, 2008, **112 (7)**, 1596-1603.
(19) P. V. Ginderen, W. A. Herrebout and B. J. van der Veken, *J. Phys. Chem. A*, 2003, **107**, 5391-5396.
(20) R. Rivelino, *J. Phys. Chem. A*, 2008, **112 (2)**, 161-165.
(21) M. A. Blatchford, P. Raveendran and S. L. Wallen, *J. Phys. Chem. A*, 2003, **107**, 10311-10323.
(22) P. Raveendran and S. L. Wallen, *J. Am. Chem. Soc.*, 2002, **124 (42)**, 12590-12599.
(23) P. Raveendran and S. L. Wallen, *J. Am. Chem. Soc.*, 2002, **124 (25)**, 7274-7275.
(24) N. T. Trung, N. P. Hung, T. T. Hue and M. T. Nguyen, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14033- 14042.
(25) E. Muchova, V. Spiro, P. Hobza and D. Nachtigallova, *Phys. Chem. Chem. Phys.,* 2006, **8**, 4866-4873.
(26) G. R. Desiraju and T. Steiner, *The weak hydrogen bond in structural chemistry and biology*. Oxford University Press: New York, 1999.
(27) X. Li, L. Liu and H. B. Schlegel, *J. Am. Chem. Soc.*, 2002, **124**, 9639-9647.
(28) K. S. Rutkowski, A. Karpfen, S. M. Melikova, W. A. Herrebout, A. Koll, P. Wolschann and B. van der Veken, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1551-1563.
(29) E. S. Kryachko, in: Grabowski S. J. (Ed.). *Hydrogen Bonding – New Insights.* Springer, Dordrecht, p.293, 2006.
(30) O. Donoso-Tauda, P. Jacque and J. C. Santos, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1552-1559.
(31) P. Hobza and Z. Havlas, *Chem. Rev.*, 2000, **100**, 4253-4264, and references here.
(32) I. V. Alabugin, M. Manoharan, S. Peabody and F.Weinhold, *J. Am. Chem. Soc.*, 2003, **125**, 5973-5987.
(33) J. Joseph and E. D. Jemmis, *J. Am. Chem. Soc.*, 2007, **129**, 4620-4632.
(34) N. T. Trung, T. T. Hue and M. T. Nguyen, *J. Chem. Phys. A*, 2009, **113**, 3245-3253.

(35) An Yong Li, *J. Chem. Phys.*, 2007, **126**, 154102-154113.
(36) S. F. Boys and F. Bernadi, *Mol. Phys.*, 1970, **19**, 553-566.
(37) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, *et al.* Gaussian 09 (version A.02), Inc., Wallingford CT, 2009.
(38) AIM 2000 designed by Friedrich Biegler-König, University of Applied Sciences, Bielefeld, Germany, 2000.
(39) R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893-928.
(40) P. Popelier, *Atoms in Molecules*, Pearson Education Ltd.: Essex, U.K., 2000.
(41) GenNBO 5.G, E. D. Glendening, J. K. Baderhoop, A. E. Read, J. E. Carpenter, J. A. Bohmann and F. Weinhold, Theoretical Chemistry Institue, University of Wisconsin Madison, WI, 1996-2001.
(42) N. T Trung and M. T. Nguyen, *Chem. Phys. Lett.*, 2013, **581**, 10-15.
(43) Y. Danten, T. Tassaing and M. Besnard, *J. Phys. Chem. A*, 2002, **106**, 11831-11840.
(44) M. Altarsha, F. Ingrosso and M. F. Ruiz-Lopez, *ChemPhysChem.*, 2012, **13**, 3397-3403.
(45) M. Besnard, M. I. Cabaco, S. Longelin, T. Tassaing and Y. Danten, *J. Phys. Chem. A*, 2007, **111**, 13371-13379.
(46) R. Szostak, *Chem. Phys. Lett.*, 2011, **516**, 166-170.
(47) F. Bernardi, F. Cacace, G. Occhiucci, A. Ricci and I. Rossi, *J. Phys. Chem. A*, 2000, **104**, 5545-5550.



What do the important factors affect C-H bond length change in C-H···O and C-H···N hydrogen bonds

383x292mm (300 x 300 DPI)