Computational and Theoretical Chemistry 976 (2011) 83–87

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Is a $H_{m-1}X$ ($X = O, S, Se, m = 1; X = N, m = 2; X = C, m = 3$) radical a better proton donor than $H_mX–H$ in hydrogen bonding?

Qing-Zhong Li *, Hui Kou, Ran Li, Wen-Zuo Li, Jian-Bo Cheng

The Laboratory of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, PR China

ARTICLE INFO

Article history:
Received 19 June 2011
Received in revised form 2 August 2011
Accepted 4 August 2011
Available online 18 August 2011

Keywords:
Hydrogen bond
Radicals
Red shift
NBO
AIM

ABSTRACT

Quantum chemical calculations have been performed for $H_mX–H\cdots NH_3$ and $H_{m-1}X–H\cdots NH_3$ ($X = O, S, Se, m = 1; X = N, m = 2; X = C, m = 3$) complexes at the MP2, QCISD, and CCSD(T) levels with aug-cc-pVTZ basis set. The result shows that the methyl radical can also act as the proton donor besides the proton acceptor in formation of hydrogen bond. Furthermore, it is facile to provide protons when it interacts with NH_3. The ability of donating protons is larger for the C–H in the methyl radical than for the C–H in methane. The radicals provide the proton in order of C–H < N–H < O–H and Se–H < S–H < O–H. The complexes have also been analyzed with natural bond orbital (NBO) and atoms in molecules (AIM).

1. Introduction

Now hydrogen bond has been attracting attention from researchers due to its extensive applications in chemistry and biology [1–3]. Although conventional hydrogen bonds are still focus of ongoing research, interest in hydrogen bonds has been transferred to unconventional hydrogen bonds. Single-electron hydrogen bond is one kind of unconventional hydrogen bonds, in which the electron donor is a single electron in radicals [4]. Radicals are important species in atmospheric chemistry, combustion, plasma environments, inter-stellar clouds, and biochemistry [5]. For examples, the reactions of C_2H_5 with O, O_3, and NO_3 have been investigated in a discharge flow reactor at room temperature and it was thought that there is an intermediately formed, chemically activated ethoxy radical [6]. The reaction of HOCO radical with CH_3 and ClO radicals has been examined using the coupled cluster method to locate and optimize the critical points on the ground-state potential energy surface [7]. Electron affinities and electronic structures of o-, m-, and p-hydroxyphenoxyl radicals have been studied with a combined low-temperature photoelectron spectroscopy and ab initio calculations [8]. Thus hydrogen bonds involving radicals have attracted increasing interest recently.

Methyl radical is a simple prototype for a wide class of organic radicals which play a key role as an intermediate in the field of chemistry and biochemistry, thus it is often taken as an electron donor in single-electron hydrogen bonds. The $H_3C\cdots HF$ complex has been detected in the reaction of methane with F_2 in low-temperature noble gases with spectroscopic methods [9]. Wang et al. [4] investigated the single-electron hydrogen bond in $H_3C\cdots HF$ and $H_3C\cdots C_2H_2$ complexes with theoretical calculations and thought that it exhibits similar properties with conventional hydrogen bonds, such as a red shift of X–H stretch vibration. The finite temperature effect on the hyperfine coupling constant has been considered in $H_3C\cdots H_2O$ [10] and $CH_3\cdots HF$ [11] complexes. In a previous paper, we studied influence of substitution, hybridization, and solvent on the properties of single-electron hydrogen bond in $H_3C\cdots H_2O$ complex and the results showed that it is similar to that in conventional hydrogen bonds [12]. It has been demonstrated that single-electron hydrogen bonds display synergetic effects with other types of hydrogen bonds in $H_3C\cdots HCN\cdots HCN$ and $H_3C\cdots HNC\cdots HNC$ complexes [13]. It has been shown that the methyl radical forms a covalent-bonded complex with HCN and HNC besides a hydrogen-bonded complex [14]. In the study of hydrogen bonds involving methyl radical, it is often to put the methyl radical as the electron donor. However, it is seldom to take the methyl radical as the proton donor.

Radicals involving oxygen have also been focus of research due to their great importance in atmospheric and biological sciences. The hydroxyl radical plays an important role in eliminating some greenhouse gases such as methane and ozone [15]. It can form hydrogen-bonded complexes with HCOOH [16], H_2O [17], and H_2S [18]. $H_2O\cdots HO$ complex is more stable than $H_2O\cdots HS$ one [19]. The hydroxyl radical forms two isomers with H_2O: one with HO as the proton donor and one with OH as the electron donor

---

* Corresponding author. Tel./fax: +86 535 6902063.
E-mail address: liqingzhong1990@sina.com (Q.-Z. Li).

2210-271X/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.comptc.2011.08.007

[20]. It is concluded that OH is a stronger hydrogen bond donor but a weaker hydrogen bond acceptor than H_2O [17].

Due to the presence of one or more unpaired electrons, radicals are often very reactive and have short lifetime, which makes it difficult to conduct experiments. However, theoretical methods have unique advantages in studying the formation mechanism, structure, stability, reactivity, spectroscopy, and dynamics of radicals.

In this paper, the hydrogen-bonded complexes with NH_3 as the electron donor and with H_3C, H_2N, HO, HS, HSe radicals as the proton donor have been studied with quantum chemical calculations. For comparison, the corresponding complexes with the closed-shell molecules as the proton donor have also been analyzed. The following questions are answered: (1) can H_3C be a proton donor in formation of hydrogen bond? (2) is H_3C a better proton donor than CH_4? (3) the factor of determining the ability of donating proton of the radicals. The electronic structures, infrared spectra, and interaction energy in these complexes are analyzed in detail. These complexes have also been analyzed with natural bond orbital (NBO) and atoms in molecules (AIM).

2. Theoretical methods

Calculations were performed using the Gaussian09 program [21]. The structures of $H_mX–H\cdots NH_3$ and $H_{m-1}X–H\cdots NH_3$ (X = O, S, Se, $m = 1$; X = N, $m = 2$; X = C, $m = 3$) complexes and their monomers have been optimized at the MP2 and QCISD levels with aug-cc-pVTZ basis set. Then harmonic vibrational frequency was calculated at the same levels to confirm the stability of the complexes. All frequencies in the complexes are real. The interaction energy was calculated with the formulas of $\Delta E = E_{AB} - (E_A + E_B)$, where E_{AB} is the energy of the complex AB and E_A and E_B are the energies of the monomers. A single energy calculation was also performed at the CCSD(T)/aug-cc-pVTZ level on the QCISD/aug-cc-pVTZ geometries. The interaction energy was corrected for the basis set superposition error (BSSE), which was estimated with counterpoise (CP) method proposed by Boys and Bernardi [22]. The natural bond orbital (NBO) analyses were carried out at the HF/aug-cc-pVTZ level on the QCISD/aug-cc-pVTZ geometry using the NBO package [23] included in the Gaussian 09 suite of programs. The atoms in molecules (AIM) calculations were performed for critical points in these complexes at the QCISD/aug-cc-pVTZ level using the AIM2000 program [24].

3. Results and discussion

3.1. Geometries

It has been demonstrated that it is necessary to use sufficiently flexible basis sets, such as 6-311++G(2df,2p), to get reliable interaction energies for the open-shell hydrogen bonds [25]. In H_3C–ClF complex, the Cl–F stretch vibration suffers a reverse shift with different theoretical methods [26]. Thus, the $H_mX–H\cdots NH_3$ and $H_{m-1}X–H\cdots NH_3$ (X = O, S, Se, $m = 1$; X = N, $m = 2$; X = C, $m = 3$) complexes were calculated at the MP2 and QCISD levels with a big basis set of aug-cc-pVTZ. Fig. 1 shows the optimized structures of both types of complexes at the MP2/aug-cc-pVTZ level. The binding distance and bond angle of hydrogen bond in the complexes are presented in Table 1.

The calculation method brings out a negligible effect on the bond angle. The bond angle in $H_{m-1}X–H\cdots NH_3$ complex is a little larger than that in $H_mX–H\cdots NH_3$ complex (X = O, S, Se, $m = 1$; X = N, $m = 2$; X = C, $m = 3$), while it is equal in both C–H complexes. In the radical complex, the bond angle amounts to 180° in most complexes, while it is 172° in $HN–H\cdots NH_3$ complex.

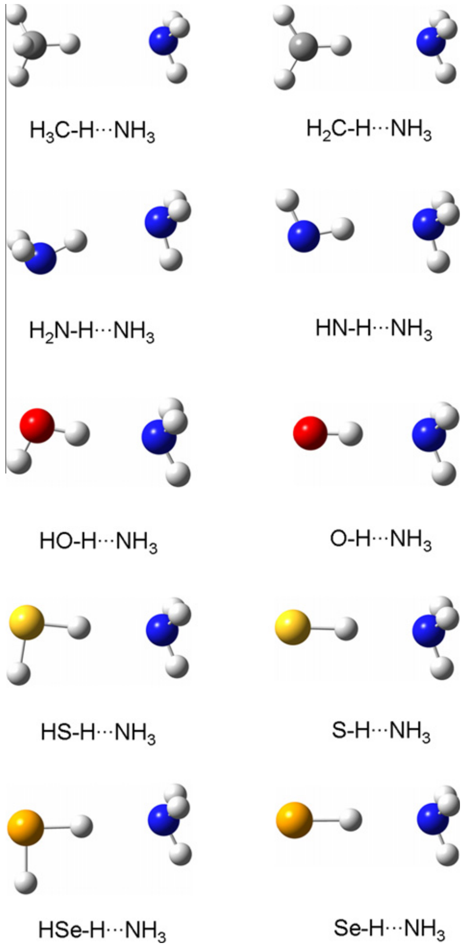

Fig. 1. The optimized structures of $H_mX–H\cdots NH_3$ and $H_{m-1}X–H\cdots NH_3$ (X = O, S, Se, $m = 1$; X = N, $m = 2$; X = C, $m = 3$) complexes at the MP2/aug-cc-pVTZ level.

One can see that the binding distance suffers a big effect from the calculation method. The binding distance is larger 0.025–0.111 Å at the QCISD level than at the MP2 level. The enhancing effect of QCISD method on the binding distance is prominent for the $H_mX–H\cdots NH_3$ complex. For $H_{m-1}X–H\cdots NH_3$ complex, the effect of calculation method becomes larger for the element of the same family from top to bottom but becomes smaller for the element of the same period from left to right. For $H_mX–H\cdots NH_3$ complex, the same effect is observed for the element of the same family from top to bottom and a small effect is found for the element of the same period from left to right.

At the QCISD level, the binding distance in $H_{m-1}X–H\cdots NH_3$ complex is calculated to be 1.9–2.6 Å, which is smaller than the sum of the van der Waals radii for the H and N atoms (about 2.6 Å). This confirms that the $H_{m-1}X–H\cdots NH_3$ complex is stable. Relative to the $H_mX–H\cdots NH_3$ complex, the binding distance in the $H_{m-1}X–H\cdots NH_3$ complex has a great shortening. The largest shortening of the binding distance is found in $H_2C–H\cdots NH_3$ complex (−0.119 Å), while the smallest one is observed in $Se–H\cdots NH_3$ complex (−0.020 Å). A similar change is also found at the MP2 level.

Table 2 presents the change of X–H bond in both types of complexes at the MP2 and QCISD levels. As expected, the X–H bond is elongated in all complexes. The elongation at the QCISD level is smaller than the MP2 one. The difference between both levels in the X–H bond elongation becomes larger with the increase of X atomic number. The elongation of X–H bond suffers a different