

Investigation on Vibrational Spectra and Structures of 4-Mercaptopyridine Monomer and Its Dihydrate*

CHENG Jian-bo^{1,2}, XUE Wei-qing¹, ZHAO Bing^{1**}, ZHANG Gang³ and GONG Bao-an²

1. Key Laboratory for Supramolecular Structure and Material of Ministry of Education, Jilin University, Changchun 130012, P. R. China;
2. Science and Engineering College of Chemistry and Biology, Yantai University, Yantai 264005, P. R. China;
3. State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, P. R. China

Received Feb. 2, 2005

The optimized molecular structures and vibrational frequencies of 4-mercaptopyridine (4MPY) monomer and its dihydrate were studied by means of the density functional theory (DFT), *viz.* B3LYP method with the 6-311 + + G (*d,p*) basis set. On the basis of the calculations, the assignments of the vibrational spectra of the monomer and the dihydrate were performed, and so were investigated the changes in the structure and the vibrational spectrum of the dihydrate as well as the intermolecular force resulting in the formation of the dihydrate. The calculated results show that each of the water molecule planes is vertical to the pyridine ring plane in the dihydrate that is formed *via* the H-bonds between 4MPY and water molecules. Furthermore, the structure and the vibrational spectrum of 4MPY can be considerably affected by the water molecules.

Keywords 4MPY; Dihydrate; Vibrational spectra; DFT; Molecular structure

Article ID 1005-9040(2006)-01-090-04

Introduction

4-Mercaptopyridine (4MPY) has been always employed as a model molecule and a probe molecule for Raman spectra in many studies because of its special structure with two active groups and its excellent signal in a Raman spectrum. Therefore, 4MPY has been extensively investigated in solution and on metal substrates^[1–7]. 4MPY has many isomers^[1,4,8] and can form hydrates^[9] in solutions, but the vibrational spectra of the isomers and the hydrates are different from that of the monomer. Therefore, it is essential that the structures and the vibrational spectra of 4MPY monomer and its hydrates be investigated by using quantum chemistry methods. The density functional theory (DFT) is being widely used for the computation of molecular structures and vibrational frequencies^[10,11], especially for that of polyatomic molecules because of the inclusion of electron correlations and their efficiency which leads to the

computation of highly accurate and reliable theoretical fundamental vibrational frequencies, in addition to the modest computational expenses as compared to those of other sophisticated approaches such as the second-order Moller-Plesset (MP2) perturbation method. To the best of our knowledge, this is the first report on the structures and vibrational spectra of 4MPY and one of its dihydrates by using the DFT method as well as their optimized molecular structures and the vibrational frequencies. On the basis of the calculations, the assignments of the vibrational spectra were performed on the monomer and the dihydrate, and the changes in the structure and the vibrational spectrum of the dihydrate as well as the intermolecular force causing the formation of the dihydrate were investigated.

Computational Approaches

The DFT calculations were performed by using the GAUSSIAN 03 suite of programs on an SGI-3900 com-

* Supported by the National Natural Science Foundation of China (Nos. 20375014, 20473029 and 20573041), Program for Changjiang Scholars and Innovative Research Team in Chinese Universities, Program for New Century Excellent Talents in Chinese Universities and the Innovative Scholars of Jilin University (No. 2004CX035).

** To whom correspondence should be addressed. E-mail: zhaob@mail.jlu.edu.cn

puter system. The molecular structure of BPENB was fully optimized by employing the hybrid of the Beckes nonlocal three parameter exchange and correlation functional and the Lee-Yang-Parr correlation functional (B3LYP). The 6-311G + + (*d,p*) split valence-shell basis set augmented by *d* polarization functions on heavy atoms and *p* polarization functions on hydrogen atoms as well as diffuse functions for both hydrogen and heavy atoms was used.

Since 4MPY has a C—S single bond which will result in rotating-conformers, its structure was optimized with C_{2v} and C_s point group symmetry as well as the calculated frequency. On the basis of the stable conformer of 4MPY, the dihydrate was constructed and fully optimized without any symmetry constraint.

Results and Discussion

1 Geometrical Structures of 4MPY Monomer and Its Dihydrate

Because it possesses a C—S singlebond, 4MPY exhibits two possible conformations with C_{2v} or C_s point group symmetry, respectively. The computed results (by using the B3LYP/6-311 + + G(*d,p*) method) show that the conformer with C_{2v} symmetry is a transition state rather than a stable structure because it has an imaginary frequency, whereas the C_s symmetrical structure [Fig. 1(A)] is a stable conformer with all real frequencies. On the basis of the stable conformer of 4MPY, the dihydrate was constructed and fully optimized without any symmetry constraint. Because of the existence of a strong H-bond between the two water molecules, 4MPY and the two water molecules will form three possible dihydrates, which were computed at the B3LYP/6-311 + + G(*d,p*) level. The calculated results show that in the presented structure in Fig. 1(B), there is a larger influence of the water molecules on the spectrum and structure of 4MPY than those in the other two ones.

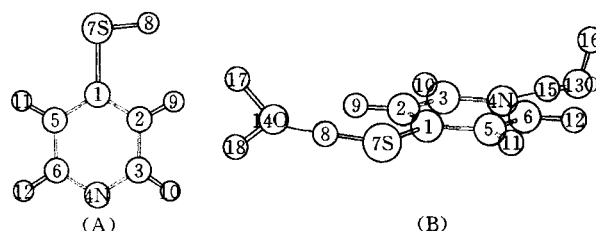


Fig. 1 Structures of the 4MPY monomer and a dihydrate.

Since this work aims at the influence of the water molecules on the spectrum and structure of 4MPY, only one structure [(Fig. 1(B))] is studied in detail and the other two structures are not shown here. Fig. 1(B) shows that the structure of the selected dihydrate is constructed by two kinds of H-bonds, $N\cdots H$ and $O\cdots H$, which are formed by two water molecules with the N atom of the pyridyl ring and the H atom of the SH moiety, respectively. Furthermore, each of the water molecule planes is vertical to the pyridine ring plane. The main bond lengths and bond angles of the 4MPY monomer and the dihydrate obtained with the B3LYP/6-311 + + G(*d,p*) method are listed in Table 1. From Table 1, one can find that the of H-bond length (0.1927 nm) $N\cdots H$ is 0.024 nm shorter than that of $O\cdots H$. This implies that the $N\cdots H$ H-bond strength is stronger than that of $O\cdots H$. Moreover, compared with those of the monomer, the bond-lengths and bond-angles of 4MPY in the dihydrate show some differences to an extent, of which the largest differences are 0.0004 nm and 0.53° , respectively. The difference between the S—H bond-length of the monomer and that of the dihydrate is 0.0004 nm, which is smaller than that between the S—H bond-length of the monomer and that of the dimer(0.016 nm). This can be explained by the fact that the $O\cdots H$ hydrogen bonding between the SH moiety and H_2O is weak. From the above discussion, we can see that the effect of the water molecules on the structure of 4MPY is considerable.

Table 1 The main bond-lengths and bond-angles of 4MPY monomer and its dihydrate

Monomer	Bond distance/nm		Bond angle/($^\circ$)				
	Monomer	Dihydrate	Monomer	Dihydrate	Monomer	Dihydrate	
C1—S7	0.1777	C1—S7	0.1773	A(1, 7, 8)	96.736	A(1, 7, 8)	96.615
S7—H8	0.1348	S7—H8	0.1352	A(2, 1, 7)	123.636	A(2, 1, 7)	123.208
C2—C1	0.1398	C2—C1	0.1400	A(2, 1, 5)	117.824	A(2, 1, 5)	117.896
C3—N4	1.336	C3—N4	0.1339	A(3, 4, 6)	116.586	A(3, 4, 6)	117.051
C6—N4	0.1337	C6—N4	0.1339	A(4, 6, 5)	124.168	A(4, 6, 5)	123.730
C2—C3	0.1392	C2—C3	0.1390	A(2, 3, 4)	124.186	A(2, 3, 4)	123.949
C5—C6	0.1391	C5—C6	0.1389	A(3, 2, 1)	118.607	A(3, 2, 1)	118.563
		O14—H8	0.2166	A(1, 5, 6)	118.628	A(1, 5, 6)	118.811
		N4—H15	0.1927				

2 Vibrational Spectra and Assignments

The computed vibrational frequencies of the main

modes of 4MPY and the dihydrate are listed in Table 2, while the calculated spectra of the monomer and the

Download English Version:

<https://daneshyari.com/en/article/1251522>

Download Persian Version:

<https://daneshyari.com/article/1251522>

[Daneshyari.com](https://daneshyari.com)