Theoretical Studies on Pyrrole-HCN Complexes in Gas Phase and in Solution*

Shi Fu-Qiang Jiang Xiao-Ming Xu Zhi-Cheng An Jing-Yi Yu Jia-Yong
(*The Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101*)

Abstract The hydrogen bonds between the HCN and pyrrole were subjected to density functional theory (DFT) calculations using 6-311G(*d*, *p*) basis set. The structures and vibrational frequencies of the hydrogen-bonding complexes were computed at the B3LYP/6-311G(*d*, *p*) level. To obtain the accurate binding energies, single-point calculations were performed at the B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ level, respectively. After BSSE (basic set superposition error) correction by the counterpoise method, the interaction energies of the complexes between HCN and pyrrole are -25.10, -19.30 kJ·mol^{-1} at MP2 level, respectively. The calculations indicate that solvents enhance significantly the strength of hydrogen bond as shown by the decrease of the N···H distance and cause appreciable red shift of the H – N vibration mode. The solvent effect is obvious when dielectric constant ε is within 1.5 ~ 30.0 and is weak when ε exceeds 30.0.

Keywords: Density functional theory, BSSE, Dielectric constant

The study of hydrogen bonding interactions has generated substantial interest given its relevance in the field of chemistry and biology [1-3]. The pyrrole ring is especially important to model typical binding sites on proteins. For this reason, many studies have been devoted to the binding properties and non-covalent interactions of pyrrole derivatives with organic and inorganic molecules [4-5]. These interactions are mainly described as unconventional hydrogen bonds. In these complexes, the *p*-cloud of the pyrrole ring acts as the proton acceptor of the hydrogen bond. The possible existence of HCN-water isomer in which the hydrogen cyanide (HCN) acts as the proton acceptor has recently been investigated [6-8]. However, few studies have been done on the comparative study of HCN as proton donor and as proton acceptor in complexes. For further investigating the nature of hydrogen bond, a theoretical study was carried out to investigate π type hydrogen bond and N – H···N type hydrogen bond between HCN and pyrrole.

1 Computational methods

All calculations were carried out with the Gaussian 98[9] package. It has already been proven that the DFT method supplies excellent results in most hydrogen-bonding systems [10-13]. The Becke proposed hybrid (B3) together with the LYP correlation functional and the basis set 6-311G(*d*, *p*) was chosen for this work[14-15]. All the molecular complexes have been fully optimized without any constraint at the B3LYP/6-311G(*d*, *p*) level. Frequency analyses were performed to ensure that the stationary points are local minima. Basis set superposition error (BSSE) was calculated by applying the full Boys-Bernardi counterpoise (CP) correction technique [16].

$$\mathrm{BSSE} = E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{A}) + E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{B}) - E_{\mathrm{AB}}^{\mathrm{A}}(\mathrm{A}) - E_{\mathrm{AB}}^{\mathrm{B}}(\mathrm{B})$$

Where $E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{A})$ and $E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{B})$ are the total energies of the monomers in their respective complex geometries using the full basis set of the complex, whereas $E_{\mathrm{AB}}^{\mathrm{A}}(\mathrm{A})$ and $E_{\mathrm{AB}}^{\mathrm{B}}(\mathrm{B})$ are the total energies of the monomers calculated at their respective complex geometries but using only the monomer basis sets. The natural bond orbital (NBO) analysis was used to understand the nature of the intermolecular interactions. The solvent effect on the N – H···N type hydrogen bond was explored by the Onsager reaction model in self-consistent reaction field (SCRF) method.

2 Results and discussion

2.1 Geometry and energy

To examine the basis set effects on the accuracy of geometry optimization, we performed a series of comparative test calculations on pyrrole and HCN monomers. The effects of the

Received: April 16, 2004; Revised: June 17, 2004. Correspondent: Shi Fu-Qiang (E-mail: shifq1976@sohu.com; Tel: 010-64888165; Fax: 010-64879375). *The Project Supported by NKBRP (G19990225)

Table 1 Computed equilibrium bond lengths (nm), bond angles (degree) of pyrrole and HCN monomers at B3LYP level with different basis sets

Monomer		6-311G	6-311++G	6-311G(*d*, *p*)	6-311++G(*d*, *p*)	Exp[17-18]
Pyrrole	C1 – C2	0.1380	0.1381	0.1376	0.1377	0.1382
	C1 – N5	0.1386	0.1387	0.1374	0.1375	0.1370
	C2 – C3	0.1430	0.1431	0.1424	0.1425	0.1417
	C1 – H6	0.1075	0.1075	0.1078	0.1078	0.1076
	C2 – H7	0.1076	0.1077	0.1079	0.1079	0.1077
	N5 – H10	0.1003	0.1004	0.1006	0.1006	0.0996
	C1 – C2 – C3	107.6	107.6	107.4	107.4	107.4
	C2 – C1 – N5	107.5	107.5	107.7	107.7	107.7
	C1 – N5 – C4	109.7	109.7	109.8	109.8	109.8
	C1 – N5 – H10	125.2	125.2	125.1	125.1	125.1
	C2 – C1 – H6	131.0	131.0	131.1	131.1	130.8
	C1 – C2 – H7	125.9	125.8	125.7	125.7	125.5
HCN	N12 – C11	0.1161	0.1161	0.1149	0.1149	0.1153
	C11 – H13	0.1064	0.1064	0.1066	0.1067	0.1066

polarization functions and diffuse functions were investigated by calculating with 6-311G, 6-311++G, 6-311G(*d*, *p*), and 6-311++G(*d*, *p*) basis sets. The optimized geometrical parameters are shown in Table 1. As seen from Table 1, the equilibrium geometrical parameters of pyrrole and HCN calculated at B3LYP level with 6-311++G and 6-311++G(*d*, *p*) are close to the results computed with 6-311G and 6-311G(*d*, *p*), respectively, which shows that the diffuse functions have little effect on the equilibrium geometrical parameters of pyrrole and HCN molecules. Comparing with the 6-311G and 6-311++G, the calculated equilibrium geometrical parameters of pyrrole and HCN monomers with 6-311G(*d*, *p*) and 6-311++G(*d*, *p*) basis sets approximate well the experimental geometries, which shows that the polarization functions are necessary to optimize the geometrical parameters, so we use the 6-311G(*d*, *p*) basis set in following studies.

The optimized geometrical parameters of pyrrole-HCN complexes are shown in Fig. 1. The conformer A(C_s) is a C – H⋯ π complex. The HCN molecule acts as a proton donor and the pyrrole is a proton acceptor. The HCN is not perpendicular to the pyrrole molecule plane. The angle of C – H⋯pyrrole is 56° and the hydrogen bond distance is 0.2407 nm. The conformer B (C_{2v}) is a N – H⋯N complex and the hydrogen bond distance is 0.2176 nm. The hydrogen bond length of the N – H⋯N complex is shorter than that of C – H ⋯ π complex, because lone-pair electrons are more contracted than π electrons. Table 2 shows the interaction energies of the pyrrole-HCN complexes. ΔE_{cp} is the energy difference between the dimer and monomers with BSSE correction. The single-point energies are obtained at the 6-311G(*d*, *p*) geometry at the B3LYP and MP2 levels. Table 2 tells us that adding diffuse functions to 6-311G(*d*, *p*) basis set decreases the corresponding intermolecular interactions. ΔE_{cp} depends much on the computational methods. The values of ΔE_{cp} computed at the MP2 level is much larger than that computed at the B3LYP level, especially for A. The ΔE_{cp} of B computed using 6-311++G(*d*, *p*) and aug-cc-pVDZ basis sets at the B3LYP level is larger than that of A computed using the same levels, which is different with those obtained by the MP2

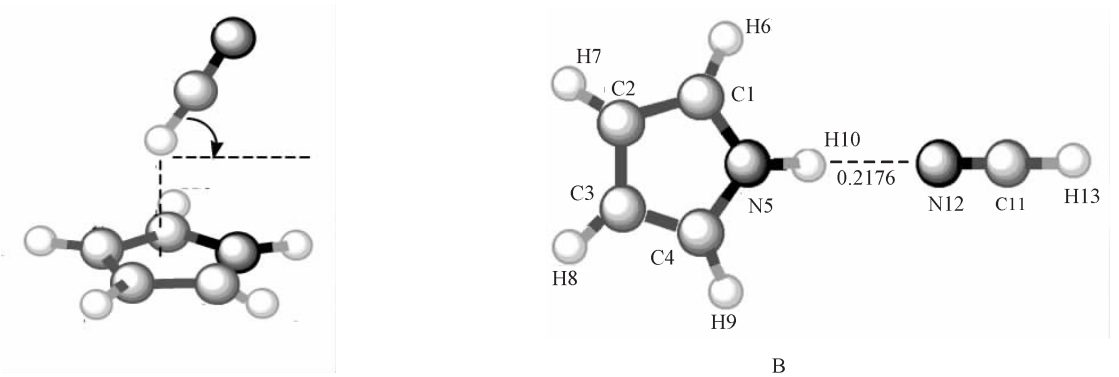

Fig. 1 Computed equilibrium structure of pyrrole-HCN complexes

Table 2 Interaction energies (ΔE_{cp}/kJ · mol^{-1}) of the complexes A and B

complex	B3LYP			MP2		
	6-311G(*d*, *p*)	6-311 + + G(*d*, *p*)	aug-cc-pVDZ	6-311G(*d*, *p*)	6-311 + + G(*d*, *p*)	aug-cc-pVDZ
A	– 16. 53	– 15. 32	– 14. 68	– 22. 35	– 22. 24	– 25. 10
B	– 16. 10	– 15. 42	– 16. 85	– 18. 33	– 18. 22	– 19. 30

method.

2. 2 Vibrational spectra

One of the most characteristic features of the hydrogen bonds is related to their vibrational spectrum. Table 3 shows the harmonic vibrational frequencies of the HCN in complexes A and B. We notice that the studied complexes are characterized by red shifts of C – H and N – H stretching vibrations. These effects are due to the weakening of the force constant for the C – H and N – H stretching modes, caused by the formation of H bond. The C – H and N – H stretching vibrations red shift by 82 and 75 cm^{-1}, respectively.

The infrared intensities might also shed light on the bonding pattern. In the studied complexes, the C – H and N – H vibrational intensities increase significantly.

2. 3 NBO analysis of the electronic structure

The formation of a hydrogen-bonded complex implies that a certain amount of electronic charge is transferred from proton acceptor to proton donor molecule. In addition, there is a rearrangement of electron density within each monomer. Table 4 lists the charge transfer (CT) of HCN molecule in complexes.

As shown in Table 4, the HCN acts as electron acceptor and the CT is – 14. 7 *me* in conformer A. The charge in HCN molecule is rearranged and the N12 atom gains 339. 9 *me*. The HCN acts as electron donor in conformer B and the total charge transfer is 10. 5 *me*.

On the basis of these NBO analyses, it can be concluded that the antibonding orbital of HCN molecule mainly interacts with the π-orbital of C1 – C2, C3 – C4 and C – H … π type H-bonding forms in conformer A. In conformer B, the main interaction exists between the lone pair electron of N12 and antibonding orbital of N5 – H10 (Table 5). The forming of hydrogen bonding between pyrrole and HCN is not a simple process. The primary effect is the charge transfer from the proton acceptor to the C – H antibonding orbital of proton donor and the charge rearranges in the whole proton donor molecule.

Table 3 Calculated harmonic vibrational frequencies (cm^{-1}) and IR intensities (km · mol^{-1})

	A		B	
	$\nu_{C(11)H(13)}$	*I*	$\nu_{N(5)H(10)}$	*I*
monomer	3458	62	3675	61
complex	3376	213	3600	451
$\Delta\nu$ or ΔI	– 82	151	– 75	390

Table 4 Charge transfer (*me*) and charge rearrangement

Conformer	CT[a]	$\Delta q_{H(13)}$[b]	$\Delta q_{C(11)}$	$\Delta q_{N(12)}$
A	– 14. 7	230. 8	94. 4	– 339. 9
B	10. 5	223. 7	143. 6	– 356. 8

[a]Charge transfer (CT) is defined as the sum of atomic charge changes on the proton acceptor molecule. [b] By convention positive values indicate a loss of charge and negative values a gain of charge.

2. 4 Solvent effect

Compared with the gas results, the solvent effects on the geometries, mullikin charge distribution, vibrational frequencies, dipole moments and interaction energies of conformer B were systematically explored with the Onsager reaction model in self-consistent reaction field (SCRF) technique with different dielectric constants of 1. 5, 3. 0, 5. 0, 7. 0, 10. 0, 20. 0, 30. 0, 40. 0, 50. 0 and 78. 5.

It is clear from the inspection of bond lengths given in Fig. 2 that solvent existing leads to decrease substantially the N12 … H10 distance and increase the N5 – H10 distance of N5 – H10 … N12 hydrogen bond. We considered that just for shortening the N12 … H10 distance and lengthening the N5 – H10 distance lead to a strengthening of the hydrogen bond interaction. For the loss of electron, the force constant of C11 – H13 decreases when the dielectric constant increases, which causes the distance of C11 –

Table 5 A part of calculated results at the B3LYP/6-311G (*d*, *p*) level by NBO analysis[a]

Complex	Donor NBO(i)	Acceptor NBO(j)	*E*/kJ · mol^{-1}
A	BD(2) C1 – C2	BD*(1)C11 – N12	0. 71
	BD(2)C1 – C2	BD*(1)C11 – H13	3. 35
	BD(2)C3 – C4	BD*(1)C11 – N12	0. 71
	BD(2)C3 – C4	BD*(1)C11 – H13	3. 47
	LP(1)N5	BD*(2)C11 – N12	0. 25
	BD*(2)C1 – C2	BD*(1)C11 – H13	0. 29
	BD*(2)C3 – C4	BD*(1)C11 – H13	0. 33
B	BD(1)C11 – H13	BD*(1)N5 – H10	0. 50
	BD(2)C11 – N12	BD*(1)N5 – H10	0. 21
	LP N12	BD*(1)N5 – H10	19. 41

[a] BD denotes bonding orbital; BD* denotes antibonding orbital; (1) and (2) denote σ-orbital and π-orbital respectively; LP denotes lone pair electron.

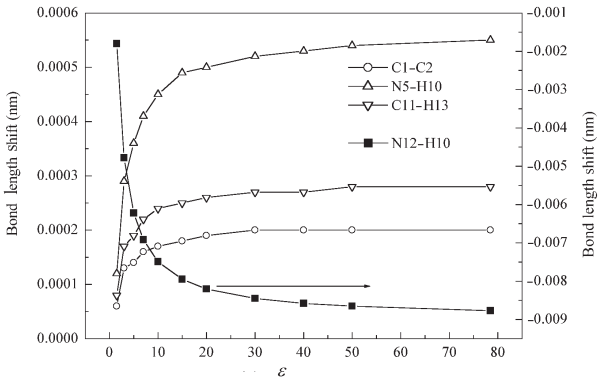

Fig. 2 Relationship between bond lengths and the dielectric constant of solvent

H13 increases. The bond length of C1 – C2 increases too.

Negative charge on N12 and positive charge on H10 atom increase, when ε increases (Fig. 3). It is well known that the chemical bond will have higher polarity and stability in the solvent with larger polarity. The total charge of HCN molecule diminishes when ε increases, indicating that the HCN molecule is a proton acceptor in the hydrogen bond of HCN-pyrrole complex.

Three characterized vibration frequencies $\nu_{\text{full-sysm}}$ (the full symmetrical stretching mode of pyrrole), $\nu_{\text{N5-H10}}$ (the stretching mode of N5 – H10) and $\nu_{\text{C11-H13}}$ (the stretching mode of C11 – H13) have been discussed, and the corresponding frequency shifts are labeled as $\Delta\nu_{\text{full-sysm}}$, $\Delta\nu_{\text{N5-H10}}$ and $\Delta\nu_{\text{C11-H13}}$.

Fig. 4 collects the frequency shifts of the characterized vibration mode in different solvents. As shown in Fig. 4, the $\Delta\nu_{\text{N5-H10}}$ has strong dependence on the dielectric constant ε, and the absolute value of its frequency shift is far larger than those of the other two. When ε is within 1.5 ~ 30.0, $\nu_{\text{N5-H10}}$ decreases sharply, but when ε exceeds 30.0, $\nu_{\text{N5-H10}}$ decreases very slowly. The trend of $\Delta\nu_{\text{C11-H13}}$ is similar to that of $\Delta\nu_{\text{N5-H10}}$. The $\Delta\nu_{\text{full-sysm}}$ shows very weak solvent effect and the absolute value of

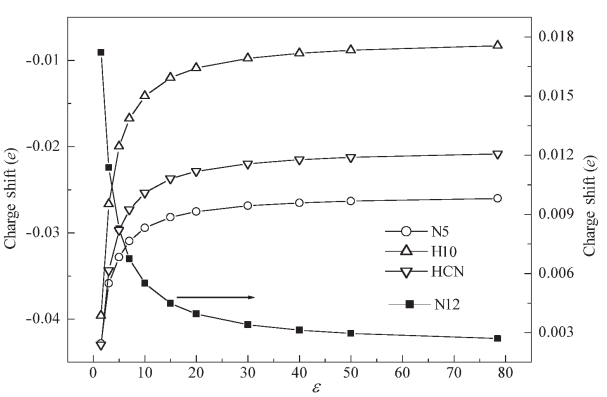

Fig. 3 Relationship between Mullikin charges and the dielectric constant of solvent

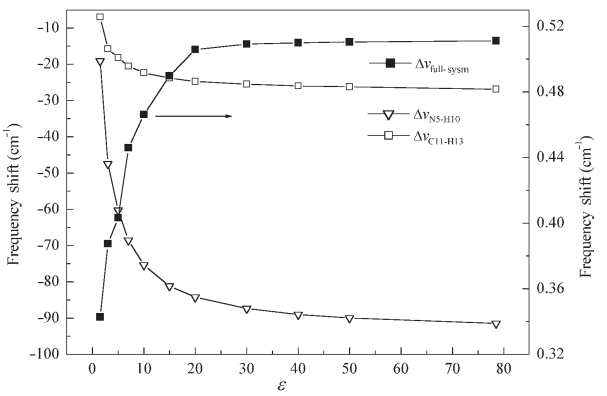

Fig. 4 Relationship between harmonic vibrational frequencies and the dielectric constant of solvent

$\Delta\nu_{\text{full-sysm}}$ is no more than 0.2 cm^{-1}.

As shown in Fig. 5, total energy decreases and dipole moment increases when ε increases, which shows that the interaction between HCN molecule and pyrrole molecule is strengthened.

3 Conclusions

Ab initio calculations at the B3LYP level with the 6-311G (*d*, *p*) basis set have been performed for investigating the equilibrium structures, vibrational spectra, and energies of pyrrole-HCN complexes. Accurate energies are obtained with the correlation consistent basis sets (aug-cc-pVDZ) at B3LYP and MP2 level. On the base of the NBO analysis, we confirmed that the hydrogen bonds have formed between the pyrrole and HCN molecules. The interaction are –25.10, –19.30 kJ · mol^{-1} computed at MP2 level, respectively. The solvents enhance significantly the strength of hydrogen bond. The solvent effect is obvious when ε is in 1.5 ~ 30.0 and is weak when ε exceeds 30.0.

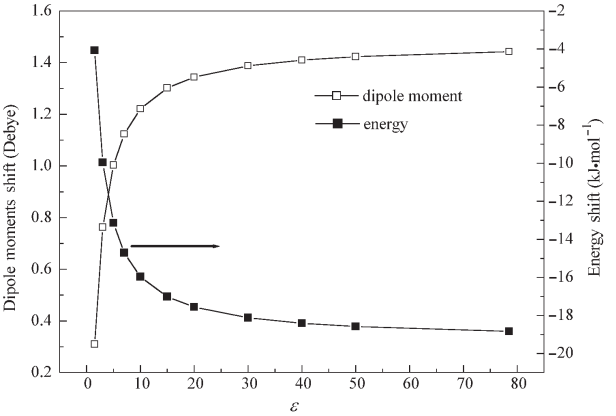

Fig. 5 Relationship between energies, dipole moments and dielectric constant of solvent

References

1 Jeffery, G. A. ; Saenger, W. Hydrogen bonding in biological structures. Berlin: Springer, 1991
2 Smith, D. A. Modeling the hydrogen bond. Vol. 569. Washington, DC: American Chemical Society, 1994
3 Scheiner, S. Hydrogen bonding: A theoretical perspective. New York: Oxford, 1997
4 Kawamata, K. ; Chowdhury, P. K. ; Ito, F. ; Sugawara, K. ; Nakanaga, T. *J. Phys. Chem. A,* **1998, 102**: 4788
5 Shi, F. Q. ; An, J. Y. ; Li, W. ; Zhao, S. ; Yu, J. Y. *Acta Chim. Sin.,* **2004, 62**: 1171 [史福强,安静仪,李 文,赵 澉,俞稼镛. 化学学报(*Huaxue Xuebao*),**2004, 62**: 1171]
6 Heikkila, A. ; Pettersson, M. ; Lundell, J. L. ; Khriachtchev, L. ; Rasanen, M. *J. Phys. Chem. A*, **1999, 103**: 2945
7 Rivelino, R. ; Canuto, S. *Chem. Phys. Lett.,* **2000, 322**: 207
8 Samuels, A. C. ; Jensen, J. O. ; Krishnan, P. N. ; Burke, L. A. *J. Mol. Struct.,* **1998, 427**: 199
9 Frisch, M. J. ; Trucks, G. W. ; Schlegel, H. B. *et al.* Gaussian 98, Revision A. 9. Pittsburgh, PA: Gaussian, Inc., 1998
10 Labanowsky, J. ; Andelzelm, J. Density functional methods in chemistry. New York: Springer, 1991
11 Tschinke, V. ; Ziegler, T. *Theor. Chim. Acta,* **1991, 81**: 651
12 Johnson, B. G. ; Gill, P. M. W. ; Pople, J. A. *J. Chem. Phys.,* **1993, 98**: 5612
13 Rablen, P. R. ; Lockman, J. W. ; Jorgensen, W. L. *J. Phys. Chem. A,* **1998, 102**: 3782
14 Becke, A. D. *J. Chem. Phys.,* **1993, 98**: 5648
15 Lee, C. ; Yang, W. ; Parr, R. G. *Phys. Rev. B,* **1998, 37**: 785
16 Boys, S. F. ; Bernardi, F. *Mol. Phys.,* **1970, 19**: 553
17 Herzberg, G. ; Huber, K. P. Molecular spectra and molecular structure. Ⅳ. Constants of diatomic molecules. New York: Van Nostrand, 1979
18 Domotor, G. ; Stacho, L. L. ; Ban, M. I. *J. Mol. Struct. (Theochem.),* **1998, 455**: 219

吡咯-HCN体系在气相及溶液中相互作用的理论研究*

史福强 姜小明 徐志成 安静仪 俞稼镛

(中国科学院理化技术研究所,北京 100101)

摘要 用量子化学B3LYP方法在6-311G(*d*, *p*)水平上优化了吡咯-HCN氢键复合物,通过振动频率分析确定了两个吡咯-HCN体系稳定构型. 为了得到更加精确的氢键作用能,采用相关一致基组aug-cc-pVDZ以及Boys和Bernardi的CP(counterpoise)校正方法消除基组重叠误差后得到C–H…π和N–H…N型复合物的氢键相互作用能. 为了确定B3LYP方法计算的相互作用能的可靠性,在MP2/aug-cc-pVDZ水平计算了复合物的氢键相互作用能,结果分别为–25.10和–19.30 kJ·mol^{-1}. 采用自然键轨道(NBO)分析考察了吡咯与HCN分子间轨道相互作用. 以自洽场理论(SCRF)中的Onsager模型研究了不同极性溶剂对吡咯-氰化氢体系N–H…N型氢键几何构型,频率位移,电荷分布以及相对能量的影响. 研究发现,当溶液的介电常数在1.5~30.0范围时,溶液作用十分显著,而当介电常数超过30.0以后,溶液作用已经达到了极限.

关键词: 密度泛函理论, 基组重叠误差, 介电常数

中图分类号: O641

2004-04-16收到初稿,2004-06-17收到修改稿. 联系人:史福强(E-mail: shifq1976@sohu.com; Tel: 010-64888165; Fax: 010-64879375). *国家重点基础研究发展规划项目(G19990225)资助