Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 12337–12347

polymer

www.elsevier.com/locate/polymer

Molecular modeling of the H-bonds in polyurethane with multiple donors and acceptors

Zhiyong Ren [a], Xiguo Zeng [b], Xiaozhen Yang [b,*], Dezhu Ma [a], Shaw Ling Hsu [c]

[a] *Henan Key Laboratory of Fine Chemicals, Zhengzhou 450002, People's Republic of China*
[b] *State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry of Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[c] *Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA*

Received 30 May 2005; received in revised form 4 October 2005; accepted 4 October 2005
Available online 3 November 2005

Abstract

The molecular mechanics (MM) method with COMPASS force field was used to study the H-bonds in polyurethane with carboxyl (PUc), which has multiple donors and acceptors. 2-Methyl-3-{[(methylamino)carbonyl]oxy}propanoic acid was used as the model molecule. It was found that the model PUc possesses four conformers with lowest energy. Considering six possible H-bond types such as OH···OC(OH) (Type I), OH···OH(CO) (Type II), OH···OC(NH) (Type III), NH···OC(OH) (Type IV), NH···OH(CO) (Type V), NH···OC(NH) (Type VI), in such system 192 H-bond complexes are simply expected. All the complexes were simulated in this modeling. Obtained total energies of the complexes were used to analyze the existence probability of each H-bonding configuration. The results show that for the six types of H-bonds, Types I (61%) and VI (37%) are the main H-bonding configurations in PUc, Types III and IV have the low probability (2%) and mostly coexist with other H-bond types, and Type II and V hardly exist.

Keywords: Polyurethanes; H-bond; Conformation

1. Introduction

H-bonds in polyurethanes (PU) or in their model molecules have been an active topic of research for many decades including using experimental methods: FTIR [1–11], NMR [12,13], Raman [14], X-ray [15,16], and simulation method: quantum mechanics (QM) [17–22]. Besides, molecular mechanics (MM) was also shown to be an effective method to study the H-bonds in PU in our previous study [23].

Segmented PU are a type of polymers, which consist of the alternating soft and hard segment units. It has been accepted that many of the unusual properties of these materials are primarily due to the two-phase structure, which is closely related to the relating H-bond [2,4]. PU with carboxyl (PUc), in which COOH is attached to the hard segment of PU, is an intermediate of water-borne polymer and a potential polymer for self-assembly based on its H-bond. It is also an ideal system to be used to study the complicated H-bond interactions. Therefore, investigations on the H-bonds in PUc have significance in both theory and applications. It is expected to be helpful for further understanding their function and for designing new polymer complexes.

Different from the conventional PU, PUc has two strong H-bond donors and multiple H-bond acceptors, which lead to much more complicated H-bond interactions. Previous studies mainly dealt with one (strong) H-bond donor system whether it is polyether based or polyester based, whether it is diol extended or diamine extended PU. Besides, many papers were also concerned with compounds with carboxylic group [24,25], however, they are also just one (strong) donor H-bond system although the carboxyl usually exists in the way of carboxylic dimer.

Though there are some simulation studies concerning the H-bonds in the two strong H-donor molecules such as vigabatrin amino acid [26], pyrrole-2-carboxylic acid [27], these studies did not concern the two-donor based H-bonds as a whole. Instead, only part of the H-bonds was studied, e.g. in pyrrole-2-carboxylic acid, which has both OH and NH, only OH was considered forming the H-bond. Obviously, it is very complicated to consider all the possible H-bonds formed by the two strong donors and acceptors.

One more H-bond donor and multiple H-bond acceptors in PUc lead to much more H-bond types. As far as only the hard

---

* Corresponding author. Tel.: +86 10 64887741; fax: +86 10 62521519.
E-mail address: yangx@pplas.icas.ac.cn (X. Yang).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.036

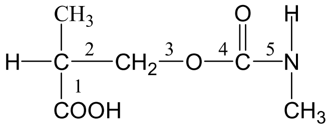
segment in PUc (Fig. 1) is concerned, there are still two strong donors including NH (urethane), OH (carboxyl) and five possible acceptors including carboxylic C=O, urethane C=O, hydroxylic O(H), urethane N (CO) and alkoxy O (CONH), which may form 10 different types of H-bonds. Since urethane N (CO) and alkoxy O (CONH) can form the H-bonds only in the special configurations [23], we consider only other three acceptors in the present work. We did not deal much with the weak H-bonds between CH and acceptors because it is not the main subject in the present paper although it indeed exists [28]. Even so (excluding weak H-bonds) there are still possible six different H-bond types in model hard segment (Figs. 2 and 3), which are considered to be formed between the OH group and carboxylic C=O group (Type I), hydroxylic O (from carboxyl) (Type II), urethane C=O group (Type III), as well as between NH and carboxylic C=O group (Type IV), hydroxylic O (from carboxyl) (Type V), urethane C=O group (Type VI). The first three types deal with the interactions between OH and the three acceptors while the last three types concern the interactions between NH and the same acceptors.

In addition, conformations and their relative probability based on one H-bond are also crucial to correctly analyze the H-bond characteristic and further assignment of their FTIR spectroscopy. However, FTIR is hard to recognize the H-bonds in various conformations, whereas molecular modeling provides a window to know about the configurations with H-bonds at atomistic level.

Hence in the present paper, MM method with COMPASS force field was used to study the H-bonds in PUc. The feasibility of MM calculation in such system was firstly verified using ab initio calculations. After the conformation analysis of the model molecule, we found four basic conformers of the model, and combining six types H-bonds we deduced 192 H-bond complexes in the modeling. Obtained total energy and H-bond energy was used to analyze the existence probability of each H-bonding configuration, and the strength of the six type H-bonds. The modeling results were also compared with FTIR experiments.

2. Molecular modeling

All molecular models were built on Silicon Graphics O_2 workstation using the program Cerius 2 version 3.8 developed by Molecular Simulations Incorporated (MSI). COMPASS [29] force field was used to optimize each model molecule. The high convergence option was adopted for the energy minimization of each model; the root mean square of force on each atom was controlled less than 0.001 kcal/mol/Å. The model PUc is 2-methyl-3-{[(methylamino) carbonyl]oxy}propanoic acid (Fig. 1), in which OH and NH were taken as the strong donors whereas the carboxylic C=O, urethane C=O and hydroxylic O were taken as the acceptors. This model contains both urethane and carboxylic groups, which can basically be used to represent PUc prepared from dimethylol propionic acid (DMPA) or dimethylol butanoic acid (DMBA) and diisocyanates [30].



$$H-\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}}\overset{2}{\underset{1}{—}}CH_2\overset{3}{—}O\overset{4}{—}\overset{\overset{O}{\|}}{C}\overset{5}{—}\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{N}}$$

Fig. 1. Model polyurethane with carboxyl (PUc) (2-methyl-3-{[(methylamino) carbonyl]oxy}propanoic acid).

Since the model PUc (Fig. 1) has five σ-bonds which may result in different conformers, in the present work, the Conformation Searching Model in Ceries 2 was used to search all the possible conformations and 36 conformers were found in the model molecule. Four of them with the lowest energy were used as the basic conformers (Fig. 4), which lead to 16 different H-bond pairs. Combining the six types of H-bonds with the 16 H-bond pairs, 192 different H-bond configurations (including the pair conformers, see Section 3 in details) can be formed. The 192 configurations include all the possible H-bonding interaction structures based on the six types of H-bonds with 32 configurations for each type of H-bond. The feasibility of using MM with COMPASS forced field was testified in our laboratory by ab initio calculations of QM with the Gaussian 03 sets programs [31] in MP2 method and the $6-31+G^*$ basis set, which has been widely used in the calculation of energy for small molecules [28,32]. We used the above two methods, respectively, to calculate the energy difference in the freely selected two same conformers (Fig. 5). These two conformers, also based on our model molecule (Fig. 1), are expected to have relatively big energy difference due to their obvious different conformer structure, so that we can have a better comparison by using QM and MM. The result in Table 1 shows that MM with COMPASS force field is suitable for the present study as the difference between the two methods QM and MM is less than 3% (Table 1). Then the MM calculation was used to deal with both the individual molecule and molecular complex in the 192 complexes.

For the individual molecule in a conformation, which can be a donor or an acceptor, the energy was obtained after being optimized; whereas for the H-bond complex, the two corresponding molecules were firstly located in a certain position where the H-bond donor atom, H and the acceptor atom are in line with a distance between the donor and the acceptor atom less than 3 Å before optimization. The energy of both the individual donor and acceptor molecule, and the energy of the complex were then obtained. According to classical mechanics, the association energy between two single molecules includes all non-bonded molecular interactions such as the Lennard–Jones interactions, the Coulombic interactions and H-bond interaction. However, for the molecules with functional groups such as NH and C=O in polyurethanes and nylon, the energy resulting from the first two is usually one magnitude smaller than that from H-bond, hence it becomes a routine way to take the association energy, i.e. the difference between the sum energy of both individual molecules and the energy of the complex, ΔE, as the H-bonding energy [17–19, 22]. Hence in the present study, we also take such ΔE as H-bonding energy ΔE_h. In addition, those with O(N)···O(N) length being or less than 3.2 Å and the O(N)–H···O(N) angle of

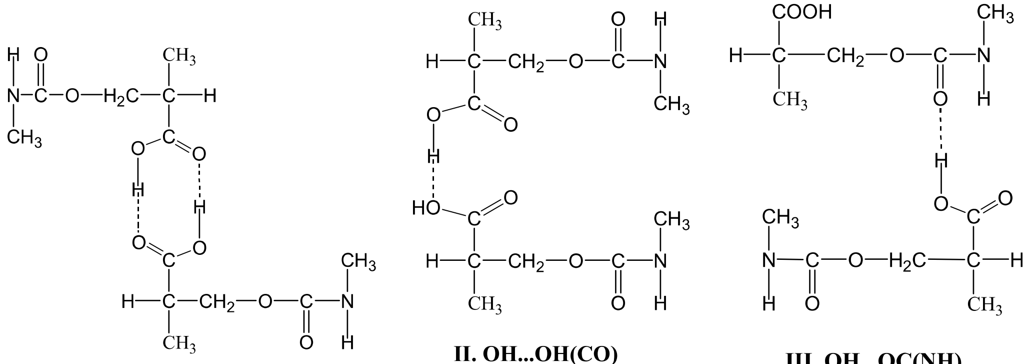

I. OH...OC(OH) **II. OH...OH(CO)** **III. OH...OC(NH)**

Fig. 2. Three possible H-bonds based on OH as donor in PUc.

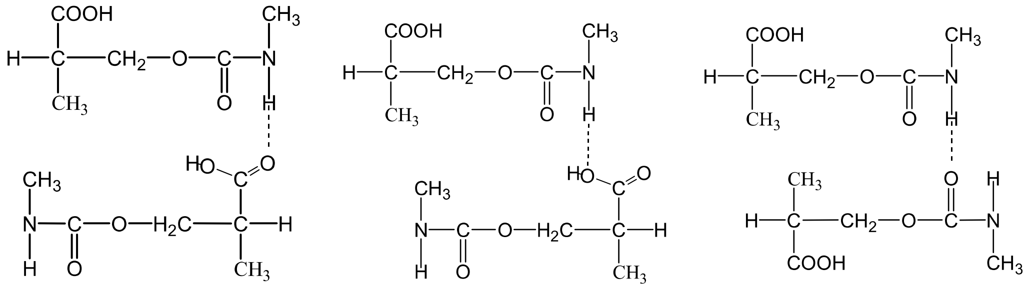

IV. NH...OC(OH) **V. NH...OH(CO)** **VI. NH...OC(NH)**

Fig. 3. Three possible H-bonds based on NH as donor in PUc.

above 130° were taken as the relative strong H-bonds, and those with C(H)···O(N) length being or less than 4.0 Å and C–H···O(N) angle of above 100° were take as the weak H-bonds [33].

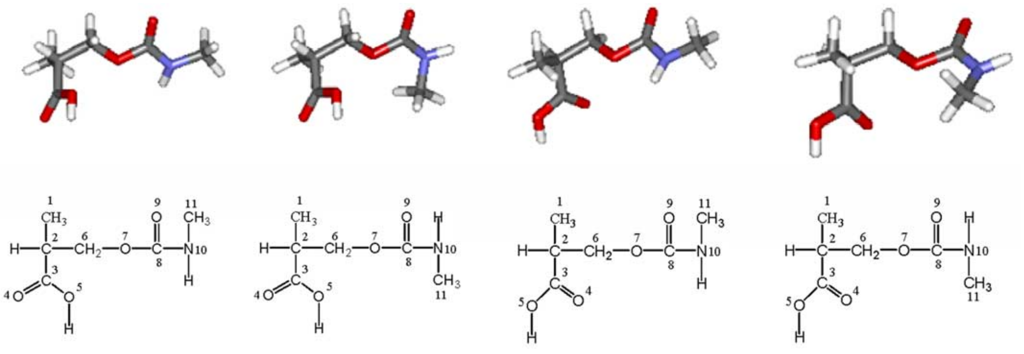
In order to calculate the probability of each H-bonded configuration, we firstly calculate the statistical weight factor $\sigma_{(i)}$ for each configuration by using Eq. (1), then calculate the partition function Z by using Eq. (2), and finally obtain the probability $P_{(i)}$ for each H-bonded complex by Eq. (3).

$$\sigma_{(i)} = \mathrm{e}^{-\Delta E_{\mathrm{c}}(i)/RT} \tag{1}$$

$$Z = \sum_i \mathrm{e}^{-\Delta E_{\mathrm{c}}(i)/RT} \tag{2}$$

$$P_{(i)} = \frac{\sigma_{(i)}}{Z} \tag{3}$$

Here $\Delta E_{\mathrm{c}}(i)$ is the energy difference between the energy in each H-bond configuration and the H-bond configuration with lowest energy in order to calculate probability (in our system, the lowest H-bond energy is −163.6551 kJ/mol/4.1851 in configuration $(\mathrm{B}+\mathrm{B})_{\mathrm{I}'}$, shown in Table 3, which is the one we


A **B** **C** **D**

E = -72.2876 kcal/mol **E = -72 3310 kcal/mol** **E = -72.0096 kcal/mol** **E = -72.0489 kcal/mol**

Fig. 4. Four conformers with lowest energies used as the basic conformers for further simulation.

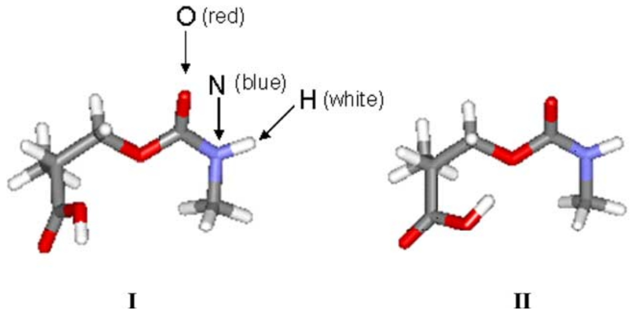


Fig. 5. Two conformers for validation of the energy difference between QM and MM in the present work.

select for the zero point energy. Note it is totally different from ΔE, the H-bonding energy mentioned above). Here R is 1.987×10^{-3} kcal/mol, T is taken 300 K (at about room temperature), hence RT is simply taken as 0.6 in order to make easier calculation. In the present paper, H-bonds coexisting with other H-bond also frequently used, here 'coexist' means the simultaneous occurrence of more than one H-bond type in a particular conformation.

3. Results and discussion

3.1. Feasibility of MM calculation for the H-bond in PUc

In the previous work, we have already shown that MM can be used to calculate the H-bond in the typical PU after QM and MM were used to make an energy comparison for the same models [23]. In the present work, two freely selected conformers in Fig. 5 based on the model molecule shown in Fig. 1 were also used in the energy calculation by means of both QM and MM, respectively. The result is shown in Table 1, where the energy differences calculated by the two methods are less than 3%. It obviously indicates that using MM in such system is reasonable.

3.2. The most probable conformers

The model PUc is not a rigid body, there are many conformers appearing. First of all we have to know those who are the most probable ones, which should be used in the interaction study. As mentioned in the last section, the model has five σ-bonds, thus the conformation searching model (rotation with a step of 10°) was used for searching the possible conformational states of each σ-bond. The result shows that for the five σ-bonds as labeled in Fig. 1, bond 1 and 5 has two conformational states (cis and trans), respectively, bond 2 and 3 has, respectively, three conformational states, while bond 4 has only one conformational state. As a result, the model PUc has total 36 conformers. Further analysis from the contour maps of conformational energies of the model shows that in the possible conformers only 29 conformers were found stabilized. The most stable conformers were found in Fig. 4. They are just four conformers for bond 1 and 5 being all combination in conformational states as cis/cis, cis/trans, trans/cis, and trans/trans. In the present study, they are labeled as A, B, C, and D conformer (Fig. 4). The detailed data are shown in Table 2. It shows when bond 4 is fixed, bond 2 and 3 being searched with variation of their torsion angles, torsion 2 and 3. The four conformers clearly possess the lowest conformational energies compared with those in their own kind of conformer. The torsion angle numbers in bracket are the actual angles after being optimized while the numbers without bracket are the angles directly from the contour map. In order to simplify the simulation process, further calculations were based on the four conformers in the present study.

Table 1
Energy comparison of the same model molecules (Fig. 5) calculated by QM and MM

Different methods	Energy difference[a] (kJ/mol/4.185)
Quantum mechanics (QM)	5.82
Molecular mechanics (MM)	5.67

[a] The error of the energy difference is less than 3%.

3.3. H-bonding configurations

In formation of H bonding configurations, people are likely to consider that the four conformers A, B, C and D shown in Fig. 4 would result in 16 pairs of H-bonded complexes, including A+A, A+B, B+A, A+C, C+A, A+D, D+A, B+B, B+C, C+B, B+D, D+B, C+C, C+D, D+C, D+D. Since each pair possibly contains the six types of H-bonds as shown in Figs. 2 and 3, the 16 pairs will contain 96 different H-bond complexes. In addition, because various H-bonding groups in the model are not in the central symmetric axis of the molecule, the formed pairs thus possess different conformations when one of the two parts in the pair rotates around H-bond. Here, this is recognized as 'pair conformation' [23]. Taking this pair conformation into account, if we simply define them as 'left' and 'right', there will exist two different pair conformations, therefore, the final total H-bond configuration number will be doubled. It amounts to 192 (with 32 complexes for each type of H-bond). In the present study, we calculated all the 192 possible H-bond configurations, which belong to the interactions between the hard segments of PUc.

Tables 3 and 4 list the possibility, length, energy and probability of the selected 64 H-bond complexes among the total 192, to show the most significant data and most commonly appeared H-bond type. Among them, H-bond $(A+A)_{I}$ stands for two A conformers forming a Type I H-bond complex. The footnote 'I' stands for the H-bond type; $(D+D)_{II}$ represents two D conformers forming a Type II H-bond complex. $(A+A)_{I'}$ stands for two A conformers forming another Type I H-bond complex as a pair conformation. Inside the table, 'turn to I' means that the expected H-bonds before optimization turn to Type I after optimization. 'With I', 'with IV', etc. show the H-bond types coexist with the Type I or Type IV H-bond. E_{total} means the total association energy of the H-bond complex; $\Delta E_{(\text{total})}$ is the total net association energy between a complex (may include all types of H-bonds if there are more than one type of H-bonds coexisting) and two single molecules; $\Delta E_{\text{h}}(\text{I})$

Table 2
Twenty-nine stabilized conformers produced by simultaneous optimizing bond 2 and 3 in the four main types of conformers shown in Fig. 4

Conformer A								
Torsion 2 (°)[a]	50(49.4)	50(53.5)	50(179.3)	160(162.4)	175(167.5)	300(−66.5)	300(−63.5)	300(−50.9)
Torsion 3 (°)	80(79.3)	180(−178.4)	260(−95.4)	175(179.7)	280(−72.3)	90(93.3)	175(176.1)	260(−91.0)
E (kJ/mol/4.185)	−71.4271	−71.6908	−69.8808	−70.2372	−69.7928	−70.5324	−72.2876	−70.4260
Conformer B								
Torsion 2 (°)	60(49.5)	60(53.3)	180(162.4)	180(167.2)	300(−63.1)	300(−66.6)	300(−52.0)	
Torsion 3 (°)	60(75.4)	180(−178.3)	180(179.9)	290(−72.8)	180(−178.6)	90(93.4)	260(−91.7)	
E (kJ/mol/4.185)	−71.3415	−71.7505	−70.1519	−69.7615	−72.3310	−70.3362	−70.7026	
Conformer C								
Torsion 2 (°)	60(57.4)	60(57.4)	180(175.73)	180(175.7)	180(−178.4)	300(−65.8)	300(60.0)	
Torsion 3 (°)	75(71.8)	180(178.0)	90(94.6)	180(178.2)	280(−74.7)	180(−177.3)	260(92.1)	
E (kJ/mol/4.185)	−71.0995	−71.4183	−70.2446	−71.6633	−71.5370	−72.0489	−70.7058	
Conformer D								
Torsion 2 (°)	60(60.0)	60(62.5)	180(175.7)	180(175.6)	180(−178.3)	300(−65.7)	300(−63.3)	
Torsion 3 (°)	75(73.6)	180(−178.7)	95(94.1)	180(178.0)	280(−74.5)	180(−177.4)	260(−92.6)	
E (kJ/mol/4.185)	−70.7209	−71.3475	−70.3536	−71.6418	−71.5694	−72.0096	−70.7197	

[a] Torsion 2 stands for the dihedral angle 1, 2, 6, 7 while torsion 3 represents the dihedral angle 2, 6, 7, 8 shown in Fig. 4.

Table 3
Energy and probability of 32 complexes in Type I H-bond

Initial configuration	H-bond O(N)···O(N)	H-bond angle O(N)···H–O(N)	E_{total} kJ/mol/4.185	$\Delta E_{(\mathrm{total})}$ kJ/mol/4.185	Prob. (%)
$(\mathrm{A+A})_{\mathrm{I}}$	2.692 (with IV, VI)	157.09	−161.403	−16.827	0.91
$(\mathrm{A+A})_{\mathrm{I'}}$	2.660/2.660 (with VI)	161.45/168.15	−160.822	−15.171	0.06
$(\mathrm{A+B})_{\mathrm{I}}$	2.675 (with IV)	167.34	−160.048	−15.429	0.10
$(\mathrm{A+B})_{\mathrm{I'}}$	2.685/2.652 (with VI)	168.11/154.81	−162.529	−17.910	5.95
$(\mathrm{B+A})_{\mathrm{I}}$	2.644 (with others)[a]	167.45	−159.686	−15.067	0.05
$(\mathrm{B+A})_{\mathrm{I'}}$	Same as $(\mathrm{A+B})_{\mathrm{I'}}$				
$(\mathrm{B+B})_{\mathrm{I}}$	2.681 (with others)[a]	174.01	−158.404	−13.742	0.01
$(\mathrm{B+B})_{\mathrm{I'}}$	2.684/2.684 (with VI)	166.86/159.56	−163.655	−18.993	38.86
$(\mathrm{A+C})_{\mathrm{I}}$	2.642 (with VI)	171.33	−163.278	−18.981	20.73
$(\mathrm{A+C})_{\mathrm{I'}}$	2.684/2.621 (with VI)	154.61/148.64	−163.443	−19.146	27.30
$(\mathrm{C+A})_{\mathrm{I}}$	2.673 (with IV)	157.25	−161.095	−16.798	0.55
$(\mathrm{C+A})_{\mathrm{I'}}$	Same as $(\mathrm{A+C})_{\mathrm{I'}}$				
$(\mathrm{C+C})_{\mathrm{I}}$	2.638 (with VI)	163.19	−161.996	−17.977	2.45
$(\mathrm{C+C})_{\mathrm{I'}}$	2.661/2.661	166.76/166.76	−158.192	14.173	∼0
$(\mathrm{A+D})_{\mathrm{I}}$	2.639 (with VI)	166.86	−160.705	−16.369	0.28
$(\mathrm{A+D})_{\mathrm{I'}}$	2.642/2.673 (with others)[a]	167.15/157.09	−160.840	−16.504	0.36
$(\mathrm{D+A})_{\mathrm{I}}$	2.681 (with IV)	163.56	−160.757	−16.4205	0.31
$(\mathrm{D+A})_{\mathrm{I'}}$	Same as $(\mathrm{A+D})_{\mathrm{I'}}$				
$(\mathrm{D+D})_{\mathrm{I}}$	2.682 (with VI)	175.70	−158.706	−14.608	0.01
$(\mathrm{D+D})_{\mathrm{I'}}$	2.660/2.660	166.33/166.33	−158.466	−14.368	0.01
$(\mathrm{B+C})_{\mathrm{I}}$	2.651 (with IV)	175.02	−159.997	−15.656	0.09
$(\mathrm{B+C})_{\mathrm{I'}}$	2.649/2.664 (with others)[a]	166.38/162.71	−158.997	−14.656	0.02
$(\mathrm{C+B})_{\mathrm{I}}$	2.656 (with others)[a]	152.48	−158.665	14.324	0.01
$(\mathrm{C+B})_{\mathrm{I'}}$	Same as $(\mathrm{B+C})_{\mathrm{I'}}$				
$(\mathrm{B+D})_{\mathrm{I}}$	2.656 (with others)[a]	172.84	−156.973	−12.593	∼0
$(\mathrm{B+D})_{\mathrm{I'}}$	2.650/2.661 (with others)[a]	166.77/163.66	−159.360	−7.490	0.03
$(\mathrm{D+B})_{\mathrm{I}}$	2.660 (with others)[a]	163.67	−158.572	−14.192	0.01
$(\mathrm{D+B})_{\mathrm{I'}}$	Same as $(\mathrm{B+D})_{\mathrm{I'}}$				
$(\mathrm{C+D})_{\mathrm{I}}$	2.662 (with VI)	170.65	−160.649	−16.5905	0.26
$(\mathrm{C+D})_{\mathrm{I'}}$	2.661/2.661	166.73/165.65	−158.317	−14.259	0.01
$(\mathrm{D+C})_{\mathrm{I}}$	2.671 (with others)[a]	173.18	−159.293	−15.235	0.03
$(\mathrm{D+C})_{\mathrm{I'}}$	Same as $(\mathrm{C+D})_{\mathrm{I'}}$				

[a] Including NH···N(H), NH···O(CO), CH···O(CO).

Table 4
Energy and probability of selected 32 complexes in Type II–VI H-bonds

Initial configuration	H-bond O(N)···O(N)	H-bond angle O(N)···H–O(N)	E_{total} kJ/mol/4.185	$\Delta E_{(total)}$ kJ/mol/4.185	Prob. (%)
$(B+A)_{II'}$	2.798 (with VI)	159.52	−157.633	−13.0144	–
$(A+B)_{II}$	2.730 (with others)[a]	166.22	−151.900	−7.281	–
$(D+D)_{II}$	2.835	156.10	−149.539	−5.441	–
$(D+C)_{II'}$	2.842	155.34	−149.504	−5.446	–
$(A+B)_{III}$	2.635 (with I)	177.22	−157.286	−12.667	–
$(A+C)_{III}$	2.612 (with IV)	156.30	−159.177	−14.880	0.02
$(A+C)_{III'}$	2.617[a]	174.55	−155.225	−10.928	–
$(C+A)_{III}$	2.623[a]	175.19	−155.036	−10.739	–
$(C+A)_{III'}$	2.621[a]	175.45	−155.123	−10.826	–
$(A+D)_{III}$	2.619 (with IV)	164.74	−159.015	−14.679	0.02
$(C+D)_{III}$	2.619 (with IV)	155.38	−157.986	−13.928	–
$(C+C)_{IV}$	2.990 (with III)	142.41	−158.227	−14.208	0.01
$(C+C)_{IV'}$	2.996/2.996 (with others)[a]	165.08/165.08	−159.956	−15.972	0.08
$(A+D)_{IV}$	2.981/2.936 (with others)[a]	157.60/144.99	−154.328	−9.992	–
$(A+D)_{IV'}$	3.014 (with I)	165.24	−160.830	−16.494	0.35
$(B+C)_{IV}$	2.923 (with III)	163.87	−158.890	−14.550	0.02
$(C+B)_{IV'}$	2.953/2.915 (with III)	163.91/152.51	−161.429	−17.088	0.95
$(C+D)_{IV'}$	2.926 (with I)	147.88	−158.542	−14.484	0.01
$(A+D)_{V}$	3.101[a]	147.18	−149.446		–
$(D+A)_{V'}$	Turn to III, IV		−159.504		0.04
$(B+D)_{V}$	Turn to I		−158.978		0.02
$(C+D)_{V'}$	Turn to I		−159.062		0.02
$(B+B)_{VI}$	2.909/2.909	168.70/172.76	−155.562	−10.900	–
$(C+A)_{VI}$	2.959 (with I)	152.88	−154.297	−10.000	–
$(A+D)_{VI'}$	2.910 (with IV)	171.48	−155.506	−11.170	–
$(D+D)_{VI'}$	2.910/2.910	169.72/169.00	−155.259	−11.162	–
$(B+C)_{VI}$	2.894 (with I)	152.11	−156.277	−11.936	–
$(C+B)_{VI'}$	2.948 (with IV)	142.75	156.622	−12.281	–
$(B+D)_{VI}$	2.907 (with I)	151.85	−156.162	−11.782	–
$(B+D)_{VI'}$	2.908/2.908	172.56/169.40	−155.547	−11.168	–
$(D+B)_{VI'}$	2.911/2.911	169.02/172.93	−155.321	−10.942	–
$(C+D)_{VI'}$	2.906 (with others)[a]	160.51	−154.813	−10.755	–

[a] With weak H-bonds.

or ΔE_h(VI)… means the Type I (or Type VI…) H-bond energy. *P* is probability (detailed is in next section).

Tables 3 and 4 show that only few H-bonds can be individually formed, whereas most of H-bonds coexist with other type of H-bonds. The coexisted H-bonds are either possibly another strong H-bonds like Type I–VI, or weak H-bonds whose donor is CH [33]. The coexisted H-bonds whose acceptor is N or ester O from urethane were also found. In addition, dimer can be formed in the Type I, IV and VI H-bonds. For Type I H-bond, the dimer is from two carboxylic acid molecules whereas for Type IV and VI, the dimers are from two same H-bonds too. Some dimers have the same H-bond length in their two H-bonds whereas some others have not. It can also be noted that some H-bond configurations can not actually exist, they would turn to other favorable types of H-bonds after being optimized, showing these types of H-bonds are not stable with high energy. Among all the H-bond configurations, the H-bond configuration $(B+B)_I$, has the lowest H-bond energy and highest probability (accounting for 38.86% of the total). Therefore, its H-bond can be used as the zero energy to calculate probability of each H-bond configuration.

Table 5
Average H-bond energy and length of six types of H-bonds in PUc

H-bond type	Type I HO···OC(OH)[a]	Type II HO···OH(CO)	Type III OH···OC(NH)	Type IV NH···OC(OH)	Type V NH···OH(CO)	Type VI NH···OC(NH)
Average H-bond length (Å)	2.661	2.838	2.620	2.959	3.101	2.909
H-bond energy (kJ/mol/4.185)	−7.141[b]	−5.443	∼−8.171∼−9.226	∼−4.500	∼−2.410	−5.519
Probability (%)[c]	61.40	0.00	0.38	1.63	0.00	36.51

[a] The H-bond length means the distance between two heavy atoms O···O or O···N.

[b] Dimer (1/2 type I H-bond energy).

[c] Other types of H-bonds including weak ones account for 0.08%.

3.4. The six types of H-bonds in PUc

As we mentioned above, the six types of H-bonds with each one having 32 configurations resulted in 192 H-bond configurations. In fact, after optimization, not each of them can lead to the expected complex. It varies. Obtained results from the calculation and the analysis for the 192 H-bond complexes are in turn mentioned according to the six types of H-bonds possibly formed in PUc. Their summary was listed in Table 5, which was discussed in detail in Section 3.5.

Type I H-bond can be formed in each of its own 32 initial complexes (Table 3). Among them, six initial complexes were found to be not existed, they turn to another complex after optimization. The other 26 Type I H-bonding complexes were found stable in certain minimums. Additionally, Type I H-bonding complexes can come from energy optimization of the other types of the complexes. Actually, 49 additional complexes were found from some initial structures of other types of H-bond complexes (including all other five H-bonding types) after optimization. They turned to Type I H-bond. Pure carboxylic dimer was found in Type I but most of Type I coexist with other types of H-bonds, mainly with Type IV and VI. It also possibly coexists with the H-bond with other acceptors such as N and ester O from urethane or other donor like CH. Fig. 6 shows two Type I H-bonds, in which both contain carboxylic dimer with one pure and another coexisting with a Type VI dimer. $(B+B)_{I'}$, in which there are one carboxylic dimer with one Type VI dimer shown in the left Fig. 6 leads to the H-bond with the lowest energy (−18.993 kcal/mol) among all the H-bond complexes and thus with the highest forming probability (38.86%). Besides $(B+B)_{I'}$, the high probability of two other complexes, $(A+C)_I$ and $(A+C)_I$ also exceed 20%. It can be noted that these three individual Type I H-bond all coexist with Type VI H-bond.

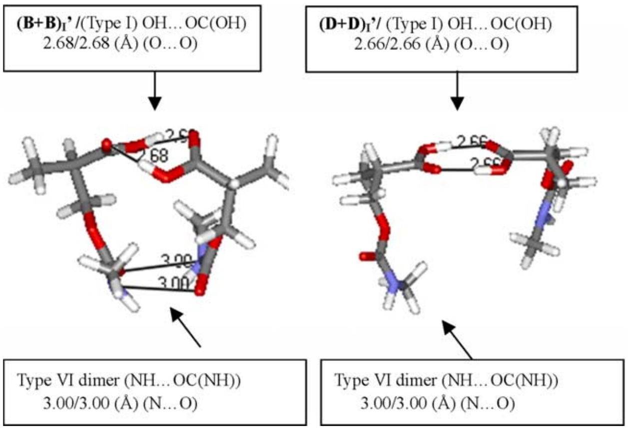


Fig. 6. Type I H-bond with and without other H-bonds; (A) $(B+B)_{I'}$ with a type VI dimer $\Delta E_h = -163.655$ kcal/mol; (B) without other H-bonds $\Delta E_h = -158.466$ kcal/mol.

These results show that Type I H-bond is easily formed, and H-bond dimer is its favorable way to exist. In addition, multiple H-bonds coexisting is another characteristic for Type I H-bond.

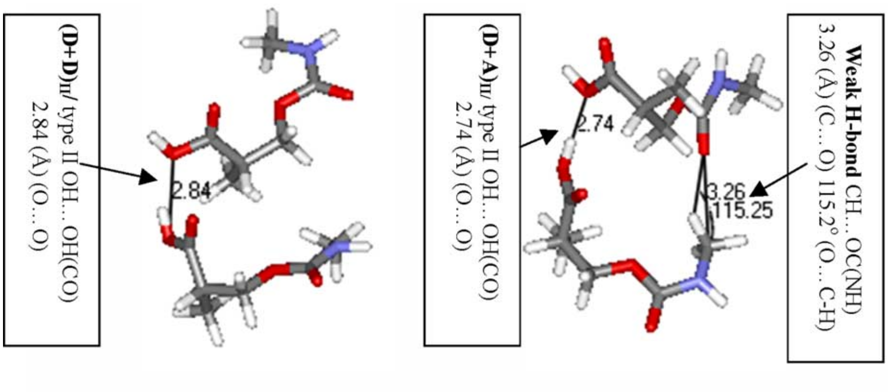
Type II H-bond can be formed in 18 complexes among its 32 initial ones, but only two exist in the individual Type II H-bond. Most of them coexist with either the strong H-bonds such as Type I, IV and VI or the weak H-bonds based on CH and OC(NH). The remaining 14 initial complexes turn to other types of H-bonds after being optimized, indicating Type II is not the favorite way to form H-bond for PUc. The configuration, energy and probability of four typical Type II H-bonds is shown in Table 4, among them two are able to exist independently while one coexists with Type VI and another turns to other type of H-bond. Their probability, however, is near zero as the H-bond energy is just around −5 kcal/mol. Fig. 7 shows two Type II H-bonds with and without a weak H-bond. Obviously weak H-bond affects energy of the strong H-bond as Fig. 7 shows. The energy of the pure Type II H-bond is 1.769 kcal/mol higher than that with weak H-bond, suggesting the energy of the weak H-bond based on CH and OC(NH) is at least 1 kcal/mol.

Type III H-bond exists in all its 32 possible complexes. However, none of them can exist individually. When one Type III exists, there is another H-bond coexisting with it. The coexisted H-bond can be either strong or weak H-bond. Among them, 18 coexist with weak H-bonds based on CH and OC(OH) whereas 12 coexist with strong H-bonds mainly with Type IV and I. In Table 4 were shown seven Type III H-bonds of its 32 H-bond complexes, four of the seven coexist with strong H-bonds including Type IV and I while three with weak H-bonds. Fig. 8 gives two examples to show Type III H-bond coexisting with either strong or weak H-bond. The formed eight-member ring is similar to the carboxylic dimer in Type I H-bond but the dimer consists of the different types of H-bonds. Since the total H-bond association energy is relatively high (higher than −14 kcal/mol), the probability for single Type III H-bond is only 0.2%.

Type IV H-bond exists in its 31 complexes, only one initial complex turns to another type after optimization. Among the 31 Type IV complexes, 21 coexist with strong H-bonds while 10 with weak H-bonds based on CH and OC(OH), therefore, Type IV always coexist with other type of H-bonds. Among the coexisted strong H-bonds, Type IV coexists more often with Type III. Table 4 shows the length, energy and probability of seven Type IV H-bond configurations selected from 32 of its kind. The highest probability of one single Type IV H-bond is 0.95%, showing Type IV is not the favorable H-bond in PUc.

Fig. 9 also gives two examples to show none of Type IV H-bond can separately exist although the coexisted H-bond concerns only a weak one. However, since the H-bond shown in the left of Fig. 9 contains only a very weak H-bond (3.93 Å between C and O) [33] besides two IV H-bonds, it is closer to take them as ‘pure’ Type IV H-bond.

Type V H-bond is different from other five types of H-bonds. Type V hardly exist, as most of the initial Type V H-bond complexes turn to other types of H-bonds, except one coexisting with weak H-bond. The selected results of Type V



A: (D+D)$_{II}$ without other H-bond
ΔE_h = - 5.411 kcal/mol

B: (D+A)$_{II}$ with weak H-bond CH…OC(NH)
ΔE_h = -7.180 kcal/mol

Fig. 7. Type II H-bond with and without other H-bond; (A) $(D+D)_{II}$ without other H-bond $\Delta E_h = -5.411$ kcal/mol; (B) $(D+A)_{II}$ with weak H-bond CH···OC(NH) $\Delta E_h = -7.180$ kcal/mol.

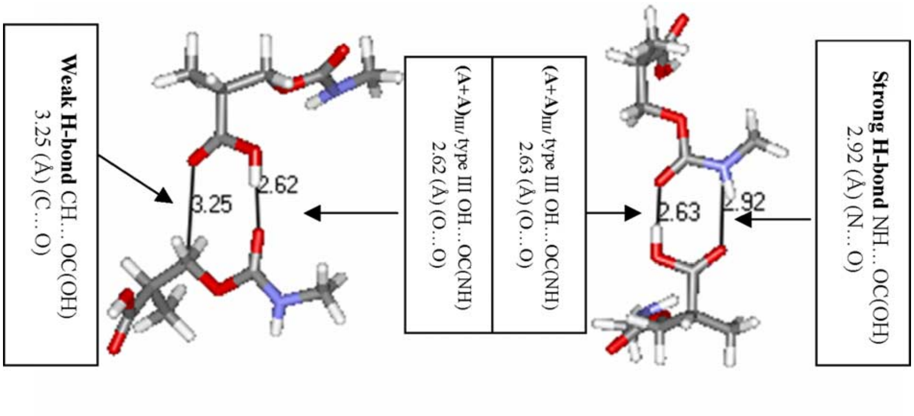
H-bond were shown in Table 4, suggesting that the hydroxylic O functions hardly as an acceptor. This is obviously due to the competition of other two strong H-bond acceptors, two carbonyls. Fig. 10 shows the only one Type V H-bond with which there are other two weak H-bonds. Type V itself is very weak as the H-bond length reaches 3.1 Å, near the upper limit of strong H-bond [33].

Type VI H-bond, though, appears in its all 32 complexes, only four dimers exist individually in Type VI H-bond, and in the cases of coexistence nine with strong H-bonds while 19 with weak H-bonds including CH···OC(OH) and CH···OC(NH). Table 4 shows the results for the 10 selected Type VI H-bond configurations (Fig. 11). Though Type VI H-bond is possible to form in various ways, yet the H-bond association energy is higher than −12 kcal/mol, leading to zero probability.

Fig. 12 shows the multiple H-bonds when three model molecules are put together. It can be seen that one acceptor can form the H-bonds with two donors, e.g. the carboxylic C=O forms the H-bond with two carboxylic OH in two COOH groups or the carboxylic C=O forms the H-bond with one carboxylic OH and with NH. This is another characteristic of PUc.

3.5. The overview of the six types of H-bonds in PUc

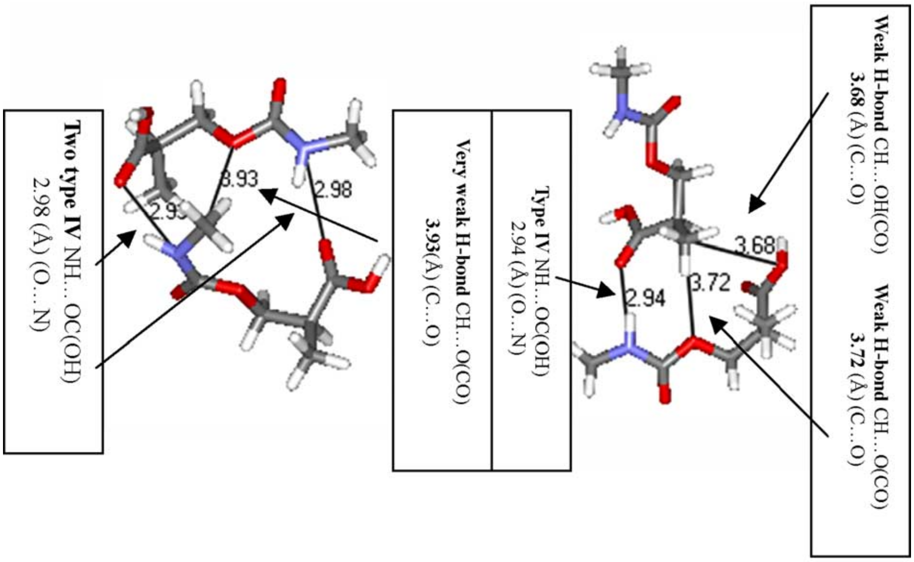
After examining the individual H-bonds from 192 H-bond configurations, it is possible now to get the average H-bond length, H-bond energy and probability for the six types of H-bonds. Table 5 lists the three results on average in each of the six types of H-bonds, based on the data analysis and summary from Tables 3 and 4. For a specific H-bond length, simple average were conducted to obtain the H-bond length for Types I, II and VI H-bonds, as pure H-bonds can be found in these three types. Since there is only one Type V H-bond available, we also take its length as the length of Type V H-bond. For other two types of H-bonds, Type III and IV, however, we adopted another way to get their average H-bond length since none of these two types of H-bonds can be found to exist in the pure state. For this purpose, we found their own zero energy in both Types III and IV H-bonds, respectively, and calculated the average H-bond length by Eqs. (1)–(3),



A: (A+A)$_{III}$ with weak H-bond
ΔE_h = -10.576 kcal/mol

B: (A+B)$_{III}$ with strong H-bond
ΔE_h = -12.667 kcal/mol

Fig. 8. Type III H-bond with weak or strong H-bond; (A) $(A+A)_{III}$ with weak H-bond $\Delta E_h = -10.576$ kcal/mol; (B) $(A+B)_{III}$ with strong H-bond $\Delta E_h = -12.667$ kcal/mol.



A: **$(A+D)_{IV}$ with two type IV and one very weak H-bond**
$\Delta E_h = -9.992$ kcal/mol

B: **$(C+A)_{IV}$ with one type IV and two weak H-bonds**
$\Delta E_h = -7.417$ kcal/mol

Fig. 9. Type IV H-bond with weak H-bond; (A) $(A+D)_{IV}$ with two type IV and one very weak H-bond $\Delta E_h = -9.992$ kcal/mol; (B) $(C+A)_{IV}$ with one type IV and two weak H-bonds $\Delta E_h = -7.417$ kcal/mol.

which is similar to the probability calculation for the 192 H-bonds shown in Tables 3 and 4.

There are also two ways to get the average H-bond energy for a specific H-bond since some H-bonds exist in the pure state while some coexist with other different types of H-bonds. For the pure H-bonds (same type), we present the average H-bond simply according to the average of the pure H-bonds. Such pure H-bonds can be found in Types I, II and VI. Whereas for the coexisted H-bonds, the H-bond energy directly from the calculation outcome may include the contribution from different H-bonds, therefore, the pure Type III, IV and V H-bonds energy should be calculated by deducting the energy of the coexisted one. According to our analysis for the weak H-bonds coexisting with Type IV H-bond (Fig. 9), we suppose the energy of weak H-bond is about 1.35 kcal/mol, hence we deduct 1.35 kcal/mol from the total energy shown in Fig. 9 for both Type IV H-bonds, and then take the average of the final result as the H-bond energy of Type IV H-bond. The average energy of Type V H-bond (Fig. 10) was also obtained in this way. For Type III H-bond shown in Fig. 8, however, we obtained the energy by deducting one weak and one Type IV H-bonds, respectively, to get two energy values. Since the two energy values have a big difference, we present the energy value just in the way of a scope (Table 5).

In order to get a close probability for each Type of H-bond, it is necessary to get the probability for each individual H-bond configuration (like $(A+A)_I$, $(B+B)_I$, etc.) in each type of H-bond. In Tables 3 and 4 were shown such a probability for each H-bond configuration of six types of H-bonds. However, since many H-bonds coexist with different types of H-bonds, the probability shown in Tables 3 and 4 represent the whole probability of the all coexisted H-bonds if the H-bond configuration consists of different type of H-bonds. Therefore, we firstly need to get the single H-bond probability by dividing the probability value shown in Tables 3 and 4. If the coexisted is two H-bonds, the probability is divided into half for each of them while if three H-bonds coexist, the probability was one third of it. Then the total probability for one type of H-bond was obtained by adding all the probability of the same type of H-bond, which lists in Table 5.

Although such a deduction in calculating energy and probability may not be very exact, as the two or three

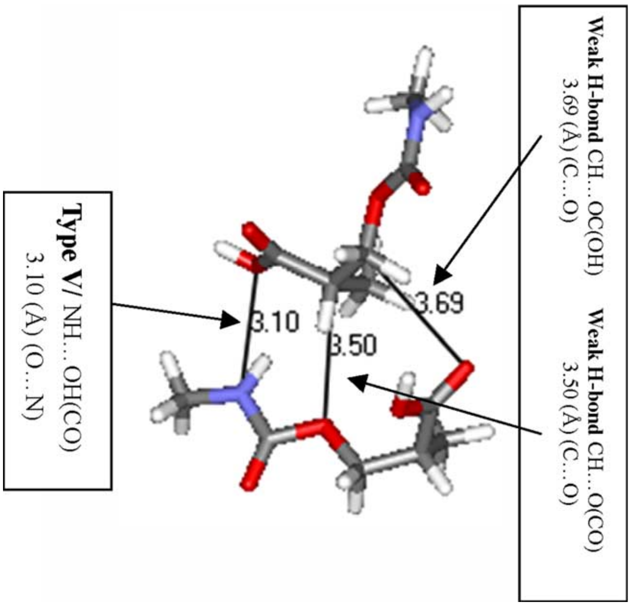
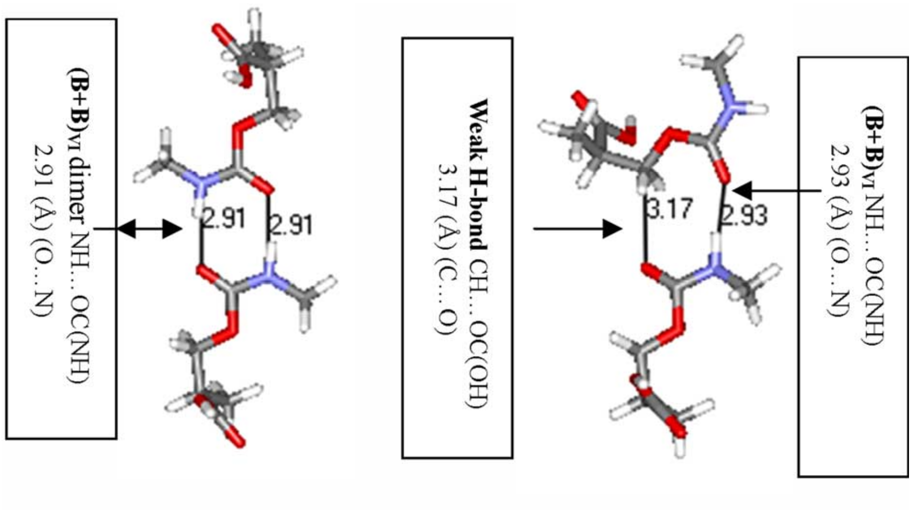


Fig. 10. Type V H-bond ($(A+D)_V$) with two weak H-bonds.



A: (B+B)$_{VI}$ with pure dimer

ΔE_h = -10.900 kcal/mol

B: (B+B)$_{VI}$' with one weak H-bond

ΔE_h = -7.733 kcal/mol

Fig. 11. Type VI H-bond with and without weak H-bond; (A) (B + B)$_{VI}$ with pure dimer $\Delta E_h = -10.900$ kcal/mol; (B): (B + B)$_{VI'}$ with one weak H-bond $\Delta E_h = -7.733$ kcal/mol.

H-bonds may not have the same probability, it is expected to have a closer H-bond energy and probability for a specific H-bond type, and to have a more reasonable estimation for the six types of H-bonds.

Table 5 clearly shows that the Types I and VI H-bonds are the main forms in PUc. The energy of Type I H-bond is obviously lower than that of Type II, IV, V and VI. The correlation between the H-bond length and energy for the same donor is also reasonable. The shorter the H-bond length, the lower the H-bond energy. In addition, it can be noted that although the energy of Type III H-bond (−8 to −9 kcal/mol) is lower than that of Type I (−7.141 kcal/mol), its probability is much lower. Since the probability is not from the bond energy here in Table 5 but the total energy of the configuration in Table 3. As mentioned in the last section, Type III H-bond cannot exist individually, but coexists mostly with weak H-bond. Type I H-bond not only exists individually but also forms dimer or coexists with the other Type H-bonds in most cases. Therefore, Type I H-bond has so higher population than that of Type III.

In fact, Types I (OH···OC(OH)) and VI (NH···OC(NH)) H-bonds are indeed the main H-bond form in PUc according to our FTIR results [30]. As we know, carboxylic dimer (Type I H-bond) is an extensive subject in many carboxylic compounds [33], whereas NH···O=C is also the most commonly existing H-bond in typical polyurethanes. When both Types I and VI coexist, the νC=O (from COOH) are in lower wavenumbers than that from urethane C=O, meanwhile, the H-bond resulting from NH···O=C becomes weak, suggesting Type I H-bond is stronger than Type VI [30], which is consistent with the H-bond energy value shown in Table 5.

It can also be seen from Table 5 that the H-bond length is shorter and the H-bond energy is lower when OH acts as the donor whereas the H-bond length is larger and the H-bond energy is higher when NH acts as the donor. When donor is the same, the H-bond formed by urethane C=O is stronger than that formed by carboxylic OH. The stronger C=O based H-bond also confirms that the assignment [30] of νC=O (from carboxylic dimer) in the lower wavenumber than NH based H-bond is reasonable.

Finally, we note that the H-bond length would become longer or shorter for a specific H-bond when it coexists with others, including forming a dimer. Such a change may vary with different H-bonds, such as strong or weak H-bonds. These are expected to relate to H-bond cooperative effect [20]. Since weak H-bond and cooperative effect are not the main objective in the present paper, we will publish such results separately.

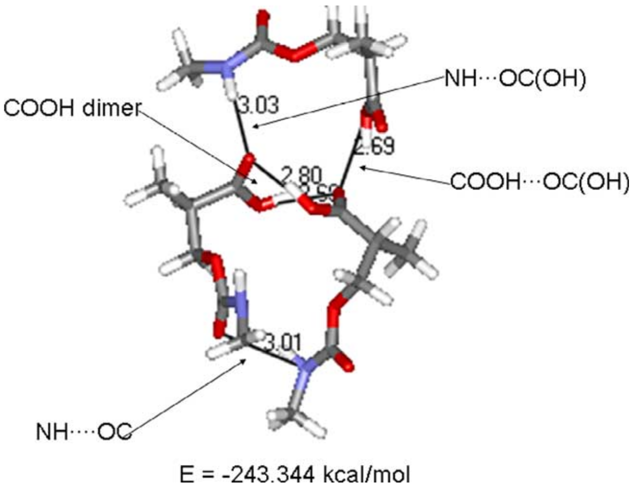


Fig. 12. Multiple H-bonds coexistence.

4. Conclusion

MM with COMPASS force filed has again been proved to be an efficient way in modeling of the H-bond interaction for PUc, which possesses the more complicated residual group with two donors and more acceptors. Six types of H-bond patterns possibly existed in PUc were systematically examined. The authors firstly in the conformational energy analysis of the model PUc molecule found A, B, C, D four conformers with the lowest energy. Then making a combination of them, taking the six ways of H-bonding and the pair-conformation into account, it resulted in 192 H-bonding complexes (the smallest basis). MM calculation was done for all the complexes on total energies and the association energies. It was found that the existence probabilities of H-bond Type I, III, IV and VI are 61.40, 0.38, 1.63 and 36.51%, respectively, whereas Type II and V hardly exist. In PUc, Types I and VI H-bond predominate and occupy 98% of all H-bonding complexes. Types III and IV take the rest of 2%. The bond length and the bond energy of the six types of H-bond were obtained.

Acknowledgements

This study has been supported by the National Nature Science Foundation (20474014, 20474073, 20274057), 863 High Technology Project, and the Special Funds for Major State Basic Research Project (2004CB720606).

References

[1] Sung CS, Schneider PNS. Macromolecules 1975;8:68–73.
[2] Srichatrapimuk VW, Cooper SL. J Macromol Sci Phys 1978;B15(2): 267–311.
[3] Brunette CM, Hsu LS, MacKnight WJ. Macromolecules 1982;15(1): 71–7.
[4] Teo LS, Chen CY, Kuo JF. Macromolecules 1997;20:1793–9.
[5] Coleman MM, Lee KH, Skrovanek DJ, Painter PC. Macromolecules 1986;19:2149–57.
[6] Wang FC, Feve M, Lam TM, Pascault J-P. J Polym Sci, Part B: Polym Phys 1994;32:1305–13.
[7] Luo N, Wang DN, Ying SK. Macromolecules 1997;30(15):4405–9.
[8] Matsunaga K, Oumi M, Tajima M, Yoshida Y. Nippon Kagaku Kaishi 2001;6:363–9.
[9] Furer VL. J Mol Struct 2000;520:117–23.
[10] McKiernan RL, Heintz AM, Hsu SL, Atkins EDT, Penelle J, Gido SP. Macromolecule 2002;35(18):6970–4.
[11] Kuan H-C, Ma C-CM, Chuang W-P, Su H-Y. J Polym Sci Part B: Polym Phys 2005;43(1):1–12.
[12] Eisenbach CD, Gronski W. Die Makromol Chem Rapid Commun 1983; 4(11):707–13.
[13] Deatz MJ, Fahey JE, Smith BD. J Phys Org Chem 2001;14:463–7.
[14] Romanova V, Begishev V, Karmanov V, Kondyurin A, Maitz MF. J Raman Spectrosc 2002;33(10):769–77.
[15] Born L, Crone J, Hespe H, Müller EH, Wolf KH. J Polym Sci, Polym Phy Ed 1984;22(2):163–73.
[16] Androsch R, Blackwell J, Chvalun SN, Festel G, Eisenbach CD. Acta Polym 1997;48(9):363–8.
[17] Bandekar J, Klima S. Spectrochim Acta 1992;48A(10):1363–70.
[18] Bandekar J, Okuzumi YJ. J Mol Struct (Theochem) 1993;281:113–22.
[19] Sun H. Macromolecules 1993;26:5924–36.
[20] Scheiner S. Hydrogen bonding, a theoretical prospective. New York, NY: Oxford University Press; 1997.
[21] Berry RJ, Wilson AL, Schwartz M. J Mol Struct (Theochem) 2000;496: 121–9.
[22] Yilgör E, Yilgör I, Yurtsever E. Polymer 2002;43:6551–9.
[23] Ren ZY, Ma DZ, Yang XZ. Polymer 2003;44:6419–25.
[24] MacKnight WJ, McKenna LW, Read BE, Stein RS. J Phys Chem 1968; 72(4):1122–6.
[25] Wolfs I, Desseyn HO. J Mol Struct (Theochem) 1996;360:81–97.
[26] Sadlej-Sosnowska N, Dobrowolski JC, Oziminski WP, Mazurek AP. J Phys Chem A 2002;106(44):10554–62.
[27] Dubis AT, Grabowski SJ, Romanowska DB, Misiaszek T, Leszczynski J. J Phys Chem A 2002;106(44):10613–21.
[28] Gu YL, Kar T, Scheiner S. J Am Chem Soc 1999;121:9411–22.
[29] Sun H. J Phys Chem B 1998;102:7338–64.
[30] Ren ZY, Wu HP, Ma JM, Ma DZ. Chin J Polym Sci 2004;22(3):225–30.
[31] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03, revision A.6. Pittsburgh, PA: Gaussian, Inc.; 2003.
[32] Zeng XG, Yang XZ. J Phys Chem Part B 2004;108:17384–92.
[33] Jeffrey GA. An introduction to hydrogen bonding. New York, NY: Oxford University Press; 1997.