A THEORETICAL STUDY OF VIBRATIONAL SPECTROSCOPY OF SEGMENTED POLY(ETHERURETHANES)

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Introduction

Hydrogen bonding plays an essential role in determining overall properties of many natural and synthetic polymers. It is especially important in thermoplastic, segmented polyurethanes and polyureas(1,2). The extent of medium to strong competitive hydrogen bonding between urethane, urea, ester and ether groups is a major determining factor for the microphase separation and thermal and mechanical properties of these polymers.

Influence of the extent and the strength of hydrogen bonding on the mechanical properties of polyether and polyester based segmented polyurethanes and polyureas have previously been reported (1). In polyether based systems there exists hydrogen bonding both between urethane-urethane in the hard segments and urethane-ether groups in the hard and soft segments. Possible phase mixing and an eventual reduction in the mechanical properties and performance of these copolymers may be detected in close correlation with the extent of these interactions. Segmented polyureas show much higher tensile strength and modulus values when compared with polyurethanes of similar compositions(4,5). This is attributed to much stronger hydrogen bonding between urea groups when compared with urethanes. We also demonstrated that there is fairly strong hydrogen bonding interaction between urea and ether segments(6).

The standard technique of studying hydrogen-bonding between hard and soft segments in polymeric systems has been IR spectroscopy(7,8). The shifts in peak positions due to hydrogen-bonding can be used as qualitative measures of the existence and strength of such bonding. Additional information on the extent of the phase mixing due to hydrogen bonding between hard and soft segments can be obtained by dynamic mechanical thermal analysis (DMTA)(1,2).

In this work, we report a study of the formation of the hydrogen bonding in poly(etherurethanes) by carrying out quantum mechanical calculations of model compounds of methylcarbamate (urethane) (U), diethylether (E) and ethanol (A). As a first step, the potential energy surfaces of U-U, U-E and U-A pairs have been carefully searched with semi-empirical methods (AM1) for locating likely structures for the formation of hydrogen bonds. A recent similar study on characterization of hydrogen-bonded structures in urea has provided a reasonably large number of structures of varying stability (6,9). However, due to the presence of the methyl groups on nitrogen, a fewer number of likely structures have been found in our calculations. Majority of these structures forms a single hydrogen bond whereas some forms two bonds resulting in cyclic structures.

After this rough search is completed, more rigorous self-consistent-field (SCF) and density-functional-theory (DFT) methods are used to optimize the hydrogen-bonded structures. Within both methodologies, frequency calculations are carried out to obtain the vibrational spectra and zero-point-energy (ZPE) corrections. The intermolecular O-H distances and IR frequencies for O-H stretching are analyzed in order to compare the stability and strength of hydrogen bonds.

Quantum Mechanical Calculations

AM1 calculations are carried out with MOPAC7(10). Ab-initio and DFT results are obtained from Gaussian98(11). The electronic structures are obtained from optimization of all geometrical variables with the basis set of 6-311G**. DFT results are obtained from three-point hybrid method using the LYP correlation functional of Becke (12). ZPE is corrected by a factor of 0.85, vibrational frequencies are scaled by 0.895 and IR spectra are drawn by fitting Gaussian functions with half-widths of 100 cm^{-1}.

Results and Discussion

Urethane-Urethane interactions. In order to compare the strengths and characteristics of the hydrogen bonded pairs, we start with the pure urethane. The lowest energy structure of the dimer obtained from DFT results is given in Figure 1. In this unsymmetrical structure, only one hydrogen bond is formed and molecular planes of urethanes have a dihedral angle of 30°. The O·····H distance is 1.96 A and the relative stability with respect to two separate urethane molecules is around 30 kJ/mol. This value drops to 26 kJ/mol after the zero-point-energy (ZPE) correction. These results are in the range of the average hydrogen bonds (12-36 kJ/mol). Calculated IR spectrum of urethane shows the C=O stretching at 1733 cm^{-1} and N-H at 3397 cm^{-1}. Once the hydrogen bond is formed, the N-H stretching for the hydrogen bond is IR active and its frequency is 120 cm^{-1} lower. The inactive N-H stretching has the same frequency as the free urethane molecule. C=O stretching, interestingly, remains fairly unaffected by the formation of the hydrogen bond.

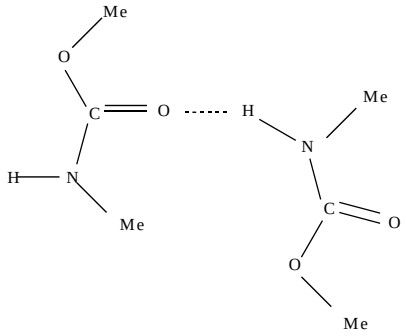


Figure 1. Minimum energy conformation for the hydrogen-bonded urethane dimer

A symmetrical structure is also found at only 0.5 kJ/mol higher than the above structure (Fig.2). The dihedral angle between molecular planes are also about 30°. Here two mutual hydrogen bonds are formed between hydrogen of N-H and carbonyl oxygen. The O·····H distances are 2.05 A well within the hydrogen bond range. N-H stretching of urethanes are now coupled into two symmetric and antisymmetric vibrations, The symmetric one is IR inactive and the frequency of the antisymmetric stretching is calculated to be at 3424 cm^{-1} which is 100 cm^{-1} lower than that of the free urethane.

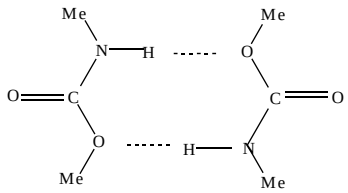


Figure 2. Symmetrical conformation for the hydrogen-bonded urethane dimer.

Geometry optimization within the DFT methodology of various other starting structures failed to give any other local minima.

Urethane-ether interactions. Only one minimum energy structure for methylcarbamate-diethylether pair has been found, which is given in Figure 3. Hydrogen bond is formed between the hydrogen of N-H and the oxygen of the ether. The bond distance is around 1.96 A, relative stability with respect to two monomers is 27 kJ/mol (23 kJ/mol with ZPE correction). IR frequency for the N-H stretching is calculated to be 270 cm^{-1} lower than the free urethane.

Urethane-alcohol interactions. Finally the interaction between methylcarbame (urethane) and ethanol has been studied. Since polyurethanes are obtained by the reaction of diisocyanates and diols, statistically it is possible to get (O–H) end-groups in these systems. As a result, ethanol is chosen to be a model compound to represent the OH end groups. A rough search within AM1 optimization has produced a number of local minima and from DFT three structures of hydrogen bonds have been observed. In the minimum energy conformation, N-H of urethane forms the hydrogen bond

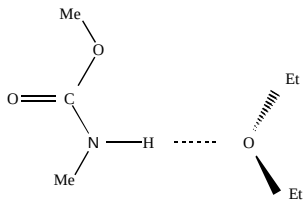


Figure 3. Minimum energy conformation of urethane-ether pair.

with the O-H of ethanol (Figure 4). The other two structures are stabilized due to the interaction between C=O of urethane and O-H of alcohol. They differ by the relative position of the O-H of alcohol and C-O-C group in the urethane. These two structures energetically lie very close to the global minimum (0.8-2.0 kJ/mol). In all cases the O·····H distances are 1.9 to 2.0 A. The relative stability of three conformations changes from 36-39 kJ/mol (ZPE corrected values are 1kJ/mol lower). Again a relatively large shift in N-H stretching is observed for the minimum energy conformation (165 cm^{-1}). In two higher laying structures, O-H of alcohol group absorbs at 100 cm^{-1} lower frequency compared to ethanol.

Overall results for the energetics and vibrational spectroscopy of three studied model hydrogen-bonded systems are summarized in Tables 1 and 2.

Table 1. Thermodynamic stability of hydrogen-bonded dimers (kJ/mol)

	SCF	SCF-ZPE	DFT	DFT-ZPE
U-U	21.9		29.8	
U-E	17.2		27.0	
U-A	22.7		38.0	

For the cases studied here, DFT results favor the formation of hydrogen bond compared to ab-initio methods. The strongest interactions are found in urethane-alcohol pair as expected. There are strong interactions between urethane monomers with at least two different conformers, however it is more surprising to see that urethane forms a fairly strong hydrogen bond with the ether group. We detect a single structure for this complex although it cannot be claimed that this search is exhaustive. In addition to that, the frequency analysis of that structure shows a small negative frequency pointing out that it corresponds to a first order saddle point. However, this negative frequency is most likely due to problems in the optimization since there are enough evidences to the existence of the hydrogen bonds such as the distance of the O·····H bond and the relative stability.

Table 2. Shifts in IR frequencies in hydrogen-bonded dimers relative to monomers (cm^{-1})

	N-H*	N-H	C=O*	C=O	O-H
U-U	-123	-5	-13	-2	
U-E	-267		-4		
U-A	-165		8		-91

*denotes the functional group involved in hydrogen bond.

Conclusions

The presence of the hydrogen bonding between model urethane, ethere and alcohol compounds are studied by quantum mechanical methods. Various conformations of hydrogen bonded pairs are obtained. The relative stability of model compounds with respect to their monomers is used as the basis of detecting hydrogen bonds. In all cases presented here, O·····H distances correspond to hydrogen bonds. The relative shifts of the IR absorptions of functional groups upon the formation of hydrogen bonds can be observed in all structures.

In conclusion, we have shown that the quantum mechanical calculations can be powerful tools for detecting hydrogen bonds in polymers. A careful analysis of the conformational structures as well as the vibrational spectra can be utilized to understand the strength of such interactions. In addition to a better understanding of the interaction between monomers, the existence of various conformations may be utilized to explain the extent of the hydrogen bonding in longer chains which may be the final step of correlating fundemental interactions to the material properties.

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