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Hydrogen bonding and polyurethane morphology. I. Quantum mechanical calculations of hydrogen bond energies and vibrational spectroscopy of model compounds

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Abstract

Advanced quantum mechanical calculations within ab initio molecular orbital theory and density functional theory were performed using GAUSSIAN98 programs in quantitative determination of hydrogen bond (H-bond) energies between various model compound pairs. Model compounds studied contained functional groups or segments that were similar to those in segmented polyurethanes and polyureas. These model compounds included urea, 1,3-dimethylurea, 1,3-dimethylcarbamate, diethyl ether, methyl acetate and ethyl alcohol. Optimized conformations, H-bond energies and H-bond lengths of the complexes were determined. Quantum mechanical calculations indicated that based on relative magnitudes of H-bond energies, appreciable amount of phase mixing between hard and soft segments in polyether or polyester based polyurethanes and polyureas should be expected. Vibrational spectra of individual compounds and their hydrogen-bonded complexes (with themselves and other compounds) were determined. Correlation between theoretical and experimental spectra was found to be very good. © 2002 Published by Elsevier Science Ltd.

Keywords: Polyurethane; Hydrogen bonding; Quantum calculations

1. Introduction

Thermoplastic, segmented polyurethanes and polyurethaneureas constitute one of the most widely investigated classes of synthetic polymers. Interesting properties and performance of segmented, thermoplastic polyurethane (TPU) and thermoplastic polyurethaneurea (TPUU) copolymers are strongly dependent on their chemical structures and resulting microphase morphologies [1–4]. Microphase separation (or mixing) between hard (urethane or urea) and soft (mainly polyether or polyester) segments in polyurethanes or polyureas is determined by several factors. These include (i) the extent of competitive hydrogen bonding between hard–hard and hard–soft segments [5], (ii) the structure and crystallizability of the hard and soft segments [6–8], (iii) co-crystallizability of mixed hard and soft segments [9,10], (iv) inherent solubility between hard and soft segments [11], and (v) nature of the interdomain interface and related free energy and entropy changes [12,

13]. Lack of any competitive hydrogen bonding between hard and soft segments as in the case of siloxane–urea copolymers [14–16] and crystallizable hard segments [17, 18] favor the formation of well-separated microphase morphologies. Good microphase separation results in the formation of thermoplastic elastomers with excellent mechanical properties. On the other hand, it has been demonstrated that amorphous urethane hard segments show complete miscibility with amorphous polyethers at every composition [19]. Such systems show poor elastomeric properties. In general, highly polar urea hard segments are reported to promote phase separation and also provide more effective hydrogen bonding between the hard segments [2,3, 20]. This results in the formation of very high strength and high performance elastomers.

Traditionally one of the most useful (semi-quantitative) methods of studying the hydrogen bonding in polyurethanes has been the vibrational or infrared (IR) spectroscopy [19–23]. By examining the IR spectra one can estimate the type, extent and strength of competitive hydrogen bonding in TPU or TPUU. This is obtained by determining the magnitude of the frequency shifts in the peak positions of

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Table 1
Chemical structures and codes of model compounds used in quantum mechanical calculations

Chemical name	Chemical structure	Code
Urea	$\begin{array}{c} \text{H O H} \\ \parallel \\ \text{H-N-C-N-H} \end{array}$	U
1,3-Dimethylurea	$\begin{array}{c} \text{H O H} \\ \parallel \\ \text{CH}_3\text{-N-C-N-CH}_3 \end{array}$	DMU
1,3-Dimethylcarbamate	$\begin{array}{c} \text{H O} \\ \parallel \\ \text{CH}_3\text{-N-C-O-CH}_3 \end{array}$	UT
Ethyl alcohol	$\text{CH}_3\text{-CH}_2\text{-OH}$	A
Diethylether	$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	E
Methyl acetate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{-C-O-CH}_3 \end{array}$	ES

the (N–H) and (C=O) stretchings of the urethane or urea groups. It is also possible to estimate the hydrogen bonding capacity of compounds from their solubility parameters, which has a hydrogen bonding component [24].

In addition to these experimental methods, it is also possible to determine the hydrogen bond energies and complete vibrational spectra of molecules or molecular complexes, including the peak shifts due to hydrogen bonding or other interactions, using advanced quantum mechanical calculations. Such calculations have been performed in order to elucidate the structural and conformational properties of urethane molecules [25–28].

In this study in order (i) to better quantify the hydrogen bonding interaction between hard and soft segments in polyether based segmented polyurethanes and polyureas and (ii) to understand the influence of such competitive hydrogen bonding on microphase morphologies of these systems, advanced quantum mechanical calculations, using ab initio and density functional theory (DFT) methods, were performed. Vibrational spectra of model compounds and compound pairs were also determined by quantum mechanical calculations and compared with experimental FTIR spectra. Comparative experimental studies on the phase behavior of model urethane, urea and polyether systems and their blends were investigated by differential scanning calorimetry (DSC) and were compared with the results of quantum mechanical calculations, to understand the influence of competitive hydrogen bonding on the extent of phase mixing. Furthermore, crystalline morphologies of model urethane/polyether and urea/polyether systems were also investigated by hot-stage, polarized optical microscopy (OM).

In this manuscript results of the advanced quantum mechanical calculations on the determination of the hydrogen bonding between model compound pairs will be

reported. Chemical structures of the model compounds used in this study are given in Table 1. These are urea (U), 1,3-dimethylurea (DMU), 1,3-dimethylcarbamate (UT), ethyl alcohol (A), diethyl ether (E) and methyl acetate (ES).

Results of experimental studies (by FTIR, DSC and hot-stage, polarized OM) on the morphological behavior of the blends of 1,3-dimethylurea and PEO and a model urethane and PEO are discussed in the accompanying manuscript [29].

2. Quantum mechanical calculations

Quantitative determination of the existence and strength of the hydrogen bonding between similar or different molecules or chemical groups have been one of the most challenging problems of quantum mechanics. Computation of the interaction energy between various hydrogen (proton) donor–acceptor pairs goes through a super-molecule approach where the ground state energy of the hydrogen-bonded complex (E_{COMPLEX}) is calculated and compared to the sum of the ground state energies ($E_1 + E_2$) of the individual components. Hydrogen bond energy for the complex, which is also referred as the stability of the complex is then defined as $E_{\text{HB}} = (E_1 + E_2) - E_{\text{COMPLEX}}$. Highly accurate determination of the interaction energy is a complicated process where the basis set superposition errors must be accounted for. The results generally depend on the basis set used and the method of calculation.

In this investigation calculations are performed within ab initio molecular orbital theory and DFT using GAUSSIAN98 programs. The geometry of monomers has been optimized within DFT approach utilizing the Becke three-parameter exchange-correlation-functional (B3LYP) with the basis sets of 6-31G(d,p) and 6-311 + G(3df,2p), MP2 with the basis set of 6-31G(d,p). Additionally, MP2 single-point energies with 6-311 + G(3df,2p) basis set have also been calculated. The scaling factors for zero-point energy (ZPE) corrections and frequencies are taken as 0.9804, 0.9613 for (6-31G(d,p)/B3LYP), 0.9676, 0.9434 for (6-31G(d,p)/MP2) and 0.9890, 0.9890 (6-311 + G(3df,2p)/B3LYP), respectively. The geometry of the hydrogen-bonded complexes are optimized with 6-31G(d,p)/B3LYP. The initial structures for complexes are obtained from exhaustive searches with MOPAC7 using AM1 parametrization. Once the geometry of the complex has been obtained, single-point energy calculations are also carried out with 6-311 + G(3df,2p)/B3LYP and 6-31G(d,p)/MP2.

The interaction strengths of various hydrogen-bonded complexes are calculated from super molecule approach as the difference between complexes and isolated monomers with ZPE corrections. Especially in the case of the smaller basis sets, this approach results in an increased stabilization. Basically, one monomer has additional stability due to the extra basis sets localized on the other monomer. This error is

called as basis set superposition error (BSSE) and it diminishes as the basis sets become larger. The sizes of the molecules considered here do not allow us exhaustive searches of the potential-energy surfaces by larger basis sets. However, the magnitude of the BSSE can be roughly obtained by counter-poise correction. Using the basis set of the dimer and replacing the atoms of the second monomer by ghost atoms, a reasonable guess can be calculated even though the method does not provide an upper bound to the error.

Once the geometry of the hydrogen-bonded complex is calculated, the distances of the intermolecular N–H···O=C (urethane, urea or ester) and N–H···O (ether) bonds are utilized to identify the existence of the hydrogen bonds. Vibrational frequencies in the complexes are compared to same vibrations in monomers to calculate the shifts due to hydrogen bond formation. Peak shifts obtained by quantum mechanical calculations compare very well with those observed experimentally in IR spectra of polyurethane copolymers or model urethane polyether blends.

3. Results and discussion

Quantum mechanical calculations have extensively been used to study the energetics of simple chemical reactions and to understand the electrostatic interactions between compounds. Their application to polymeric systems, until very recently was not available. This was mainly due to very large number of atoms in polymeric structures requiring powerful computers and very long computer times. With advances in both computer and software technology, now it is possible to do quantum mechanical calculations or precise simulations on polymeric systems.

It is well documented that hydrogen bonding plays critical roles in determining the morphology and properties of segmented polyurethanes [1–4]. However, the experimental data available in the literature generally provide a qualitative description of this phenomenon. It is especially important to get quantitative information on the competitive hydrogen bonding between hard (urethane) and soft (ether or ester) segments in order to completely understand the microphase morphologies of these systems. Ab initio quantum mechanical calculations on urethane model compounds have been reported by Sun [25]. However, the model compounds chosen in that study all contained OH or NH₂ end groups, which result in stronger than expected hydrogen bonding. Also, there was no attempt to calculate the competitive hydrogen bonding between urethane and ether or ester type groups, which is very critical in determining the extent of phase mixing between hard and soft segments in polyurethanes. In our investigations quantum mechanical calculations were supported with complementary experimental measurements in order to better understand the morphologies of segmented polyurethanes and polyureas. In this manuscript we report the

results of advanced quantum mechanical calculations on model compounds and compound pairs. These included calculations of hydrogen bond energies, bond distances and IR spectra of model compounds or compound pairs. Peak shifts due to hydrogen bonding have also been determined in model compound pairs. Ref. [29] discusses the experimental results on the IR spectroscopy, crystallization behavior and crystal morphologies of blends of model urea and polyether compounds.

3.1. Structures and the stability of hydrogen-bonded complexes

As a first step in the quantum mechanical calculations the geometries (or conformations) of U–U, DMU–DMU, UT–UT, U–ES, DMU–ES, DMU–E, UT–A UT–E and UT–ES complexes (dimers) were fully optimized by carrying out a conformational search along the potential energy surfaces with the relatively fast AM1 method. Local minima found within this approach were further optimized by using 6-31G**/B3LYP. As a result of this second optimization, a number of minima converged to the same geometrical structure and some of them have disappeared altogether. The conformations of the most stable dimer structures obtained through the more rigorous optimization are described below.

As an illustrative example of our calculations, the most stable conformations of urea–urea (U–U) dimers are given in Fig. 1. Optimization studies show basically two different geometries for urea dimers. In one of them, there are two simultaneous bond formation involving both carbonyl groups and amine hydrogens of each urea molecule (Fig. 1a). In the other structure two amine hydrogens form

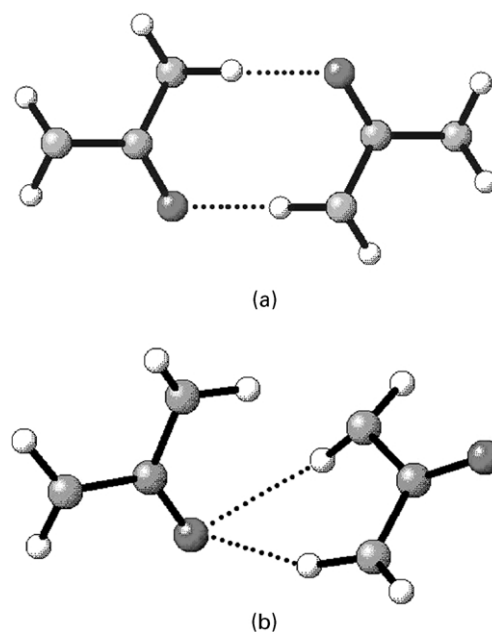


Fig. 1. Most stable conformations of hydrogen bonded urea (U–U) dimers. H-bond lengths: (a) 1.85 Å; (b) 1.99 Å.

Table 2
Hydrogen bond energies of urea–urea (U–U) complex shown in Fig. 1b calculated by different methods

Method	H-bond energy (kJ/mol)
B3LYP/6-31G(d,p)	81.1
ZPE corrected	65.1
BSSE corrected	60.6
MP2/6-31G(d,p)//MP2/6-31G(d,p)	85.1
ZPE corrected	68.3
MP2/6-31G(d,p)//B3LYP/6-31G(d,p)	84.5
B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d,p)	59.3

a dihedral hydrogen bonding with the oxygen of the carbonyl group (Fig. 1b). Complex structure shown in Fig. 1a is more stable than that shown in Fig. 1b by 14 kJ/mol. There are slight deviations from planarity in urea molecules, which are in good agreement with other results reported recently [30,31]. None of these structures have negative frequencies indicating that they are true minima. Structure in Fig. 1a is the global minimum and its H-bond energy (E_{HB}) calculated by using different methods and corrections is given in Table 2. H-bond length in most stable U–U dimer given in Fig. 1a is calculated to be 1.85 Å. Electron

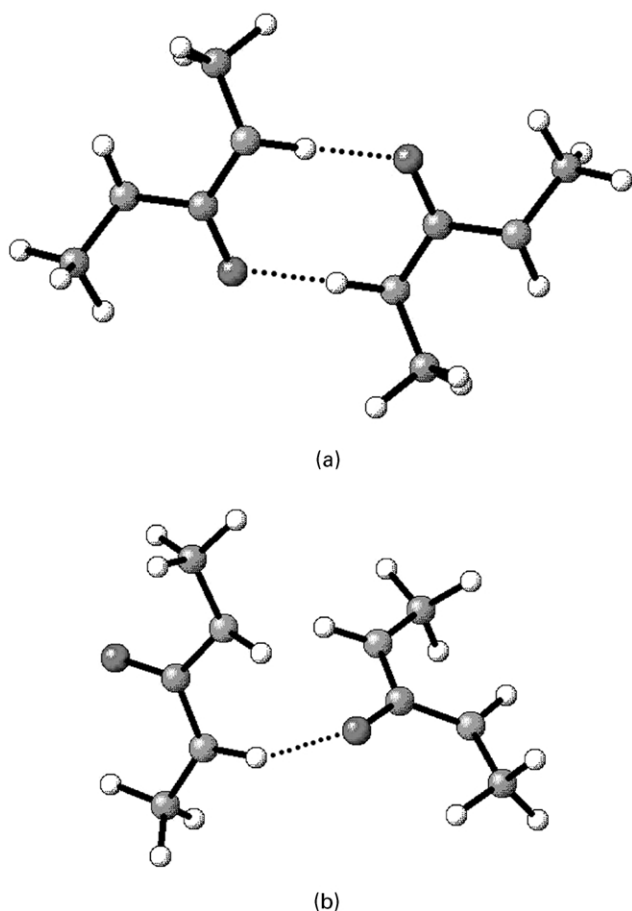


Fig. 2. Most stable conformations of hydrogen bonded dimethylurea (DMU–DMU) dimers. H-bond lengths: (a) 1.83 Å; (b) 2.02 Å.

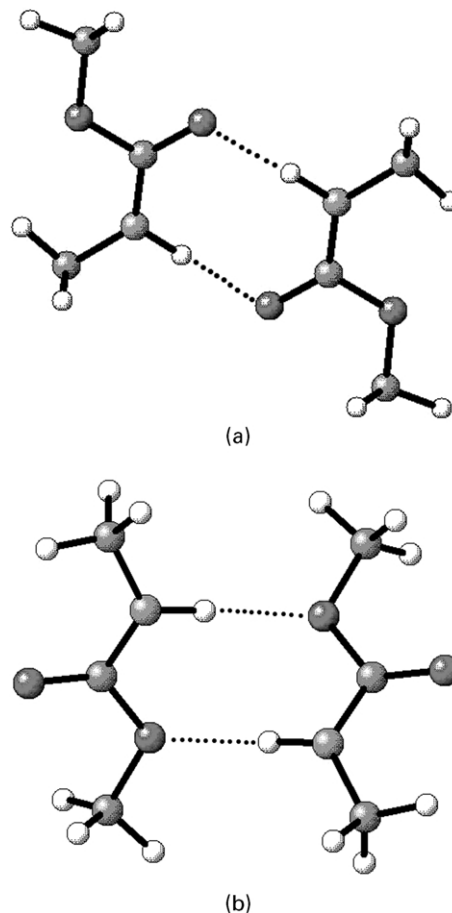


Fig. 3. Most stable conformations of hydrogen bonded urethane (UT–UT) dimers. H-bond lengths: (a) 1.87 Å; (b) 1.96 Å.

correlation effects on the geometry obtained from MP2 calculations are very small and can be neglected.

As it can clearly be seen in Table 2, uncorrected values of stabilization or H-bond energies lie in the range of 81.1–85.1 kJ/mol, depending on the calculation method. These values are fairly close to each other, indicating very good agreement between the methods used. ZPE and BSSE corrected results and those obtained by much more accurate B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d,p) calculations, which do not need correction, lie in the range of 59.3–68.3 kJ/mol. These results also show excellent agreement. ZPE is in the order of 20% and BSSE is in the order of 25%. Large basis set calculations such as B3LYP/6-311 + G(3df,2p)//B3LYP/6-31G(d,p) do not require BSSE correction since diffuse functions used describe weak bonding very accurately. However, these calculations require tremendous amount of CPU times.

Optimum geometries for most stable forms of DMU–DMU, UT–UT and DMU–ES and DMU–E are given in Figs. 2–5. Hydrogen bonding in these complexes is indicated by a dotted line. Complexes shown in part (a) of Figs. 1–4 make the strongest. Dimers of dimethylurea (Fig. 2) and urethane (Fig. 3) show the same characteristics as that of urea, that is there are at least two distinct minima

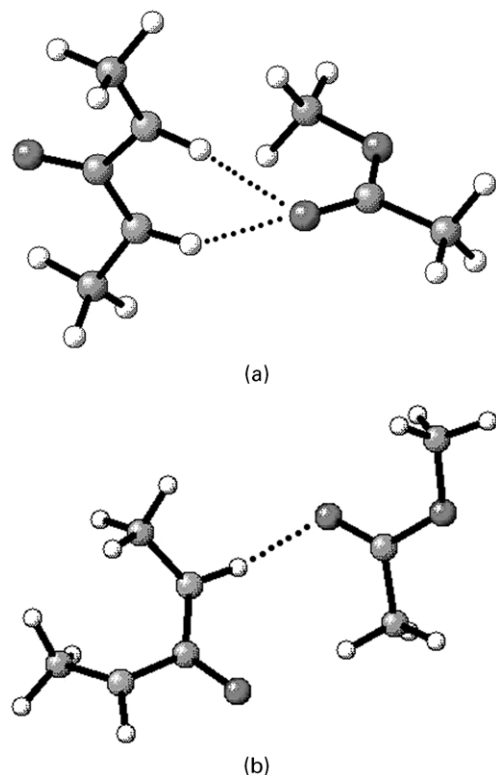


Fig. 4. Most stable conformations of hydrogen bonded dimethylurea-ester (DMU-ES) dimers. H-bond lengths: (a) 2.20 Å; (b) 1.99 Å.

corresponding to one structure with a single hydrogen bond which may or may not involve two hydrogen atoms and oxygen of the carbonyl and a lower energy conformer where two simultaneous bonds are formed between protons and carbonyl groups.

In case of DMU-ES complex (Fig. 4), carbonyl oxygen of the ester interacts with urea protons. There is one additional structure where the urea protons form hydrogen bonding with the singly bonded oxygen of the ester, however, this is much weaker than the others, and therefore, is not reproduced here. In DMU-E (Fig. 5) and UT-E

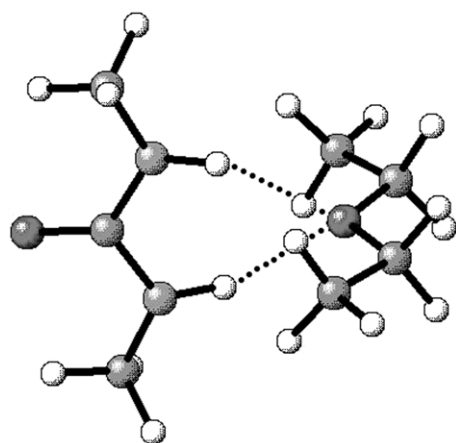


Fig. 5. Most stable conformation of hydrogen bonded dimethylurea-ether (DMU-E) dimer. H-bond length: 2.19 Å.

Table 3

Hydrogen bond energies (E_{HB}) and hydrogen bond lengths of most stable dimers

Complex	Hydrogen bond energies (kJ/mol)		H-bond length (Å)
	B3LYP	B3LYP-ZPE corrected	
U-U	81.1	65.1	1.85
U-ES	44.6	34.4	1.98
DMU-DMU	67.7	58.5	1.83
DMU-E	36.1	29.4	2.19
DMU-ES	35.8	29.7	2.20
UT-UT	52.0	46.5	1.87
UT-E	27.5	23.6	1.96
UT-ES	29.8	25.9	2.00
UT-A	38.9	32.5	2.00

complexes there is only one optimum structure where urea or urethane hydrogen and oxygen of the ether are bonded. These bonds are generally slightly weaker than internal complexes of urea and urethane. Urethane-alcohol dimers show several structures where C=O, N-H and O-H groups are involved in hydrogen bonding. It is interesting to note that H-bond between urethane proton and alcohol oxygen is stronger than that of alcohol proton and oxygen of urethane carbonyl.

Hydrogen bond energies (E_{HB}) of most stable dimers discussed above are given in Table 3. Also included in Table 3 are the H-bond lengths for these structures. As expected, depending on the E_{HB} values of the dimers, hydrogen bond lengths lie between 1.8 and 2.2 Å. The results presented in Table 3 are obtained by using B3LYP calculations with ZPE corrections. As indicated before, only the hydrogen bond energies of the most stable structures are given in Table 3, but it does not represent an exhaustive list of other possible conformations with intermediate stabilization energies. In many systems there are a large number of local minima that differ mainly by the distribution of torsional angles. A database of such locally stable structures can be very useful to correlate the material properties of polymers to the hydrogen bonding with different conformations. However, this is beyond the scope of this study. Correlation between hydrogen bonding and macromolecular properties definitely depends on the relative strength of various hydrogen bonds and the number of such bonds in the bulk system.

A close examination of Table 3 provides valuable information on the quantitative assessment of the competitive hydrogen bonding in polyether or polyester based polyurea or polyurethanes. This information can in turn be used to better understand the extent of phase mixing in these systems. Hydrogen bond energies for DMU-DMU, DMU-E and DMU-ES are 63.1, 29.4 and 29.7 kJ/mol, respectively. These results show that energies of competitive DMU-E or DMU-ES type hydrogen bonding are about half that of DMU-DMU. This indicates that in mixtures of DMU and E or ES, (or in polyether based segmented

polyureas) appreciable amount of phase mixing due to hydrogen bonding is expected. For urethane complexes H-bond energies of UT–UT, UT–E and UT–ES are 46.5, 23.6 and 25.6 kJ/mol, respectively. As expected H-bond energies between UT–UT are much lower than that of DMU–DMU. However, it is interesting to note that, similar to DMU containing complexes, hydrogen bond strength in UT–UT is approximately twice as those of UT–E and UT–ES. This also indicates that in urethane–ether or urethane–ester systems extensive phase mixing due to competitive hydrogen bonding is expected. However, as indicated before, there are other factors, which need to be considered for a complete picture of phase separation (or mixing) in segmented polyurethanes and polyureas. These are (i) the molar ratio of urethane (or urea) to ether (or ester), (ii) the crystallization energies of urethane (or urea) hard segments and polyether (or polyester) soft segments, and (iii) co-crystallizability of hard and soft segments and their energies of crystallization. The influence of these factors on phase morphologies is addressed in Ref. [29].

3.2. Vibrational spectroscopy of hydrogen-bonded complexes

IR spectroscopy is an important experimental technique, which is widely used to determine the extent of hydrogen bonding in polymeric systems [21,32] and especially in polyurethanes [2,20,33]. By determining the shifts in peak positions, a semi-quantitative measure of the hydrogen bond strength can be obtained from IR spectra [17,19,34–38].

Quantum mechanical calculations are also very useful in constructing the IR spectrum of single molecules or complex systems, where peak shifts and related energy changes due to hydrogen bonding can quantitatively be obtained. Upon the formation of hydrogen bonds, it is expected that vibrations involving the proton-donating group (N–H) and the proton-accepting groups (C=O, N–H or C–O–C) should show shifts in their absorption frequencies towards lower energy. The magnitude of these shifts, as well as changes in the absorption characteristics depend on the type and the strength of the hydrogen bonds. Since our ultimate aim is to quantitatively assess the effect of competitive hydrogen bonding on the phase separation in segmented polyurethanes (and polyureas), we proceed to catalogue all possible local minima and their effects on the IR spectra. For the complexes included in this study, there are several basic vibrations to be affected, namely (C=O) stretching of U, DMU, UT and ES, (N–H) vibrations of U, DMU, and UT and C–O–C stretching in E.

As a model system, urea has been one of the most challenging problems in terms of structure determination and its vibrational spectrum using quantum mechanical calculations [30,31,39]. Basically the problems arise in comparison of the computed gas-phase vibrations and experimentally measured solid-state data. Recently a number of results have appeared on detailed calculations

Table 4
IR peak positions for single molecules obtained by using different basis sets

Molecule	Basis set	Method	$\gamma(\text{N-H})$ (cm^{-1})	$\gamma(\text{C=O})$ (cm^{-1})
Urea	6-31G(d,p)	B3LYP	3488	1750
	6-31G(d,p)	MP2	3508	1749
	6-311 + G(3df,2p)	B3LYP	3574	1748
Dimethylurea	6-31G(d,p)	B3LYP	3507	1728
	6-31G(d,p)	MP2	3494	1723
	6-311 + G(3df,2p)	B3LYP	3603	1728
Urethane	6-31G(d,p)	B3LYP	3520	1756
	6-31G(d,p)	MP2	3534	1749
	6-311 + G(3df,2p)	B3LYP	3606	1765
Methyl acetate	6-31G(d,p)	B3LYP	–	1764
	6-31G(d,p)	MP2	–	1730
	6-311 + G(3df,2p)	B3LYP	–	1779
Diethyl ether	6-31G(d,p)	B3LYP	–	1125 ^a
	6-31G(d,p)	MP2	–	1129 ^a
	6-311 + G(3df,2p)	B3LYP	–	1134 ^a

^a Ether (C–O–C) frequency.

of monomers and dimers of urea, its extensions and aggregates [31]. An important point to be considered in comparing the calculated spectrum with the experimental one is the planarity of the monomer in the gas phase. Nowadays, it is accepted that the molecule is not planar in the gas-phase, however, X-ray as well as neutron-diffraction data have established that the solid-state structures are planar [30,31].

For our purposes, an absolute characterization of the vibrational spectrum of urea is not necessary. We are mainly

Table 5
Vibrational frequencies (cm^{-1}) of (C=O) stretchings in hydrogen bonded systems

Dimer	Frequency (cm^{-1})	Comments	Shift (cm^{-1})
U–U	1707	Symmetric (f)	43
	1730	Asymmetric (m)	20
U–ES	1717	Ester C=O (w)	48
	1741	Urea C=O (s)	9
DMU–DMU	1670	Symmetric (f)	55
	1700	Asymmetric (m)	25
DMU–E	1717	DMU C=O (s)	8
DMU–ES	1716	Asymmetric, DMU (s)	9
	1728	Symmetric, ES (w)	37
UT–UT	1706	Symmetric (f)	50
	1737	Asymmetric (s)	19
UT–E	1752	Non-bonding (s)	8
UT–ES	1730	ES bonding (s)	35
	1755	UT non-bonding (m)	5
UT–A	1765	UT non-bonding (s)	0

s: strong; m: medium; w: weak; f: forbidden.

Table 6
Vibrational frequencies (cm^{-1}) of the most intense N–H stretching absorptions in single molecules and hydrogen bonded dimers

Molecule or dimer	Frequency (cm^{-1})	IR intensity (kM/mol)
U	3488	55
U–U	3223	1690
U–ES	3342	479
DMU	3507	34
DMU–DMU	3216	2186
DMU–E	3460	243
DMU–ES	3467	192
UT	3520	34
UT–UT	3267	1640
UT–E	3349	478
UT–ES	3390	513
UT–A	3355	341

interested in the changes (shifts) in the (N–H) and carbonyl (C=O) stretchings due to the hydrogen bonding, going from a single molecule to a hydrogen bonded dimer. Therefore, even though both planar and non-planar structures are optimized, energy of the planar structure (due to its similarity to solid state material) is used to determine the interaction energy and vibrational spectrum of urea complexes. Table 4 gives the IR peak positions for (C=O) and (N–H) stretchings for single molecules calculated by using different basis sets. It is clear that there is very good agreement between different methods. Table 5 gives the calculated (C=O) peak positions for hydrogen bonded, most stable dimers. Also included in Table 5 are the approximate shifts in (C=O) stretching due to hydrogen bonding. Depending on the H-bond strength $5\text{--}55\text{ cm}^{-1}$ shifts in C=O peaks were observed in different systems. Table 6 provides the vibrational frequencies of the most intense (N–H) stretching absorptions in single molecules and hydrogen bonded dimers, together with the peak intensities. It is interesting to note that the intensities of hydrogen bonded (N–H) stretching peaks of dimers are substantially higher than those of model single molecules without hydrogen bonding. In order to make a direct comparison between IR peak positions obtained by quantum mechanical calculations and those by experiments, the literature data on

Table 7
Characteristic IR absorption frequencies for polyurethanes and polyureas [12,16,26]

Group	Mode	Frequency (cm^{-1})
N–H	Free	3445–3450
N–H	N–H \cdots N–H	3315–3340
N–H	N–H \cdots O (ether)	3260–3290
C=O (urethane)	Free	1730–1740
C=O (urethane)	C=O \cdots H–N	1703–1710
C=O (urea)	Free	1690–1700
C=O (urea)	C=O \cdots H–N	1660–1670 (disordered)
C=O (urea)	C=O \cdots H–N	1630–1645 (ordered)

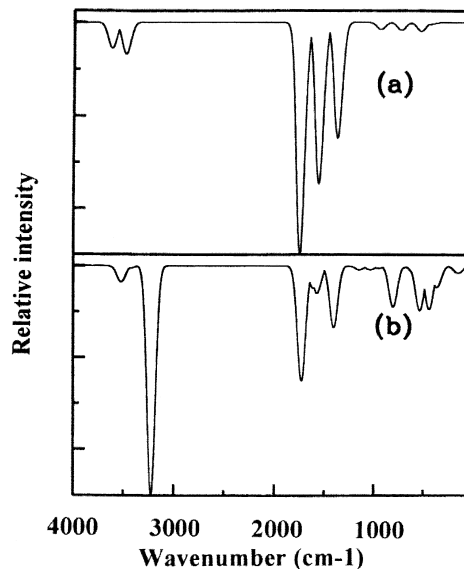


Fig. 6. (a) Calculated IR spectrum of single urea molecule, showing no hydrogen bonding; (b) calculated IR spectrum of hydrogen bonded urea (U–U) dimer.

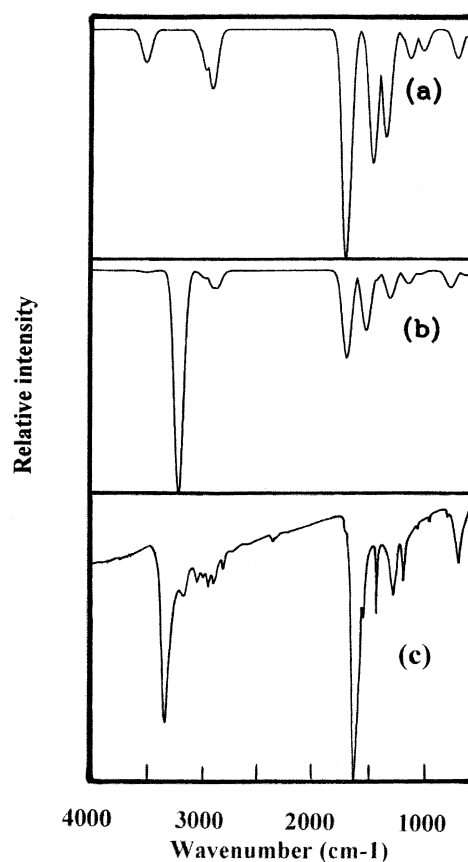


Fig. 7. (a) Calculated IR spectrum of single dimethylurea molecule, showing no hydrogen bonding; (b) calculated IR spectrum of hydrogen bonded dimethylurea (DMU–DMU) dimer; (c) experimentally obtained IR spectrum of dimethylurea.

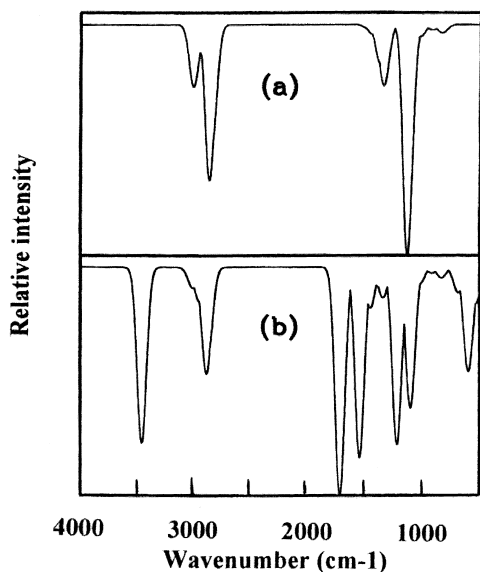


Fig. 8. (a) Calculated IR spectrum of diethylether; (b) calculated IR spectrum of hydrogen bonded dimethylurea–diethylether (DMU–E) dimer.

segmented polyurethane and polyurea systems for (N–H) and (C=O) stretching are given in Table 7.

Complete IR spectra of selected single molecules and hydrogen-bonded dimers are also provided in Figs. 6–8. In one case experimental spectrum is also provided in order to make a better comparison. Fig. 6a gives the calculated IR spectrum of a single urea molecule, whereas Fig. 6b gives the spectrum of the hydrogen bonded urea dimer. When these two spectra are compared, as expected, major shifts are observed in (N–H) and (C=O) stretchings due to hydrogen bonding. Peak intensities also show substantial changes. These results are given in Table 5. For single urea molecule a weak (N–H) stretching peak at 3488 cm^{-1} and a strong (C=O) stretching peak at 1750 cm^{-1} are observed. Upon dimer formation intensity of (N–H) peak increases dramatically. In addition, (N–H) and (C=O) peaks shift to 3223 and 1710 cm^{-1} , respectively.

Calculated vibrational (IR) spectra of DMU and its hydrogen bonded dimer (DMU–DMU) are reproduced in Fig. 7a and b. Similar observations are also made in this system regarding the shifts in (N–H) and (C=O) peaks due to hydrogen bonding, which are tabulated in Table 5. For a direct comparison, the experimental FTIR spectrum of DMU is also given in Fig. 7c. Experimental spectrum was obtained by casting a thin film of DMU on KBr disc from THF solution. It is remarkable to note that calculated DMU–DMU spectrum is identical to the experimental spectrum. This clearly shows the power of advanced quantum mechanical calculations in understanding the behavior of real systems.

As the final example, calculated vibrational spectra of diethyl ether and DMU–E complex are reproduced in Fig. 8a and b. The shift and the intensity change in (N–H) stretching due to hydrogen bonding can clearly be seen. On

the other hand, no change in the frequency of ether oxygen (C–O–C) is observed.

4. Conclusions

Hydrogen bond energies between model compound pairs were determined by ab initio molecular orbital theory and DFT calculations using GAUSSIAN98 programs. Urea, 1,3-dimethylurea, 1,3-dimethylcarbamate, ethyl alcohol, diethyl ether, and methyl acetate were chosen as model compounds because of their similarities to hard and soft segment structures in segmented polyurethanes and polyureas. Optimized geometries, hydrogen bond lengths and hydrogen bond energies of complexes were determined. It has been demonstrated that B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) provides accurate molecular geometry, hydrogen bond energies and vibrational frequencies for model monomers discussed here. The inclusion of the electron correlation does not alter either the geometry of the molecule or the vibrational structure in a drastic manner. The additional stability of the hydrogen-bonded dimers is calculated by super molecule approach with DFT and MP2 methods. MP2 calculations predict 20–45% higher stability. The corrections due to BSSE reduce hydrogen bond energy by 25%. Vibrational spectra of individual compounds and their hydrogen-bonded complexes (with themselves and with other compounds) were also determined using quantum mechanical calculations. Depending on the complex, C=O stretching peaks show shifts in the range of $10\text{--}50\text{ cm}^{-1}$. N–H stretching of individual compounds, which are extremely weak, becomes very intense in dimers and shows peak shifts in the order of 250 cm^{-1} . These results are very similar to experimental observations. Quantum mechanical calculations indicate that based on relative magnitudes of hydrogen bond energies, extensive phase mixing between hard and soft segments in urethanes and ureas should be expected.

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