Ab Initio Characterizations of Molecular Structures, Conformation Energies, and Hydrogen-Bonding Properties for Polyurethane Hard Segments

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ABSTRACT: *Ab initio* Hartree–Fock and MP2 calculations with 3-21G and 6-31G* basis sets were conducted for a group of urethane model molecules and hydrogen-bonded dimers to study the intra- and intermolecular interactions for polyurethanes. Conformational structures and energies of internal bond rotations were calculated and compared with available experimental results. Three types of hydrogen bonds that formed between the urethane N–H group and (1) the urethane carbonyl oxygen, (2) the ester oxygen, and (3) the ether oxygen were studied. The vibrational frequency shifts of the N–H, C═O, and C–O–C stretching modes computed for the dimers at the HF/6-31G* level qualitatively agree with the experimental observations of polyurethanes and support the assignment of the 3295-cm^{-1} band to the N–H stretching mode in the N–H···O(ether) hydrogen-bonding structure.

I. Introduction

Polyurethane copolymers, as a group of important materials,[1] have been extensively studied by using different experimental methods. It is well accepted that polyurethane copolymers undergo microscopic phase separation at normal use temperature, leading to hard-segment (polyurethane) rich domains, soft-segment (polyester or polyether) rich matrix, and an interphase between the two phases.[2] The hard segments, which are extensively hydrogen bonded, serve as both cross-links and filler particles in the soft-segment matrix. The elasticity, toughness, and other physical properties of polyurethane copolymers are directly related to the stability of the hard-segment domains. To understand the physical and chemical properties of polyurethanes from a microscopic point of view, it is of interest to quantitatively study the molecular structures, conformation states, and hydrogen-bonding properties for the urethane functional group.

With regard to the molecular structures and conformation energies of polyurethanes, both experimental and theoretical approaches have been reported in the literature. The X-ray structures have been solved for a number of carbamate crystals including methyl carbamate,[3] ethyl carbamates,[4] and a group of diphenylmethane urethane model compounds.[5-9] Conformation energies are difficult to measure experimentally, and the results are highly sensitive to the experimental conditions, the method used, and the procedures for data interpretation. Published values[10-15] of the activation energies for rotations about the C–N bond in *N,N*-disubstituted carbamates fall in the large range of 10.8–22.7 kcal/mol. Theoretical calculations have been conducted by several research groups to elucidate the structural and conformational properties of urethane molecules. Among them, Alsenoy et al.[16] calculated *trans* and *cis* conformations of carbamic acid at the Hartree–Fock (HF) level with a 4-21G basis set.[17] Calculations of the same level were extended to methyl and ethyl carbamates by Manning et al.[18] Remko and Scheiner[19] optimized the geometries of conformations for carbamic acid and its alkyl and phenyl derivatives by using several basis sets including MINI-I,[20] 3-21G,[21] and 6-31G*.[22] They also calculated the Møller–Plesset second-order perturbation (MP2)[23] energies for some of the species using the HF/6-31G* optimized structures. However, their HF/6-31G* results[19] are found to be in serious disagreement with the results calculated at the same level of theory in this study (details to be discussed). In addition, all calculations reported in the literature[17-19] were subjected to certain geometrical assumptions which may have a strong impact on the conformation energies obtained.

Hydrogen bonding has long been considered to be one of the most important intermolecular interactions in polyurethanes. Since vibrational spectra are highly sensitive to changes of molecular structures and local environment, the hydrogen bonding of polyurethanes has been extensively studied by using various spectroscopic methods.[24-43] Three types of hydrogen bonds may be expected in most polyurethanes; they may be formed between the proton donor, the urethane N–H group, and one of the proton acceptors: the urethane carbonyl oxygen O═C, the ether oxygen O(ether), and the ester oxygen O(ester). The frequency shifts of the hydrogen-bonded groups, such as N–H, C═O, and C–O–C, have been interpreted as measurements of the hydrogen bond strengths and related to the phase separation and morphology of polyurethanes. Traditionally, the N–H···O═C bond between urethane–urethane groups in the hard segment has been considered to be the strongest force. It is well accepted that the bonded and free N–H modes appear at 3320 and 3420 cm^{-1}, respectively,[27,28] while the corresponding C═O stretching modes are mostly found at 1703 and 1733 cm^{-1}, respectively.[27,28] However, recent studies[26,37-38] show that the N–H···O(ether) interaction is perhaps as strong as the N–H···O═C interaction, and a 3295-cm^{-1} band has been proposed[37] for the N–H bonded with O(ether). If the frequency shift is an accurate measurement of the hydrogen bond strength, this assignment also suggests that the N–H···O(ether) bond is slightly stronger than the N–H···O═C bond. However, the accuracy of the correlation between frequency shifts and bonding strengths deserves a thorough investigation. Furthermore, the same vibrational band 3295 cm^{-1} has been proposed for N–H bonded with O(ester) by Bandekar and Klima,[43] who used the urethane C–O–C stretching modes to study the hydrogen-bonding properties. This brings up another question: is there any difference between the two acceptors, O(ether) and O(ester)? Or, one can ask in a general way: what are the relative strengths of the

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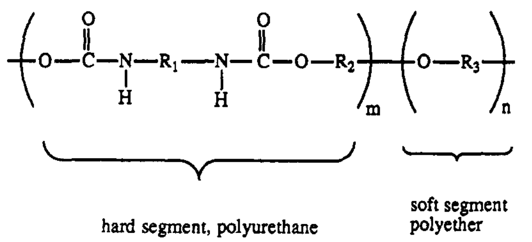
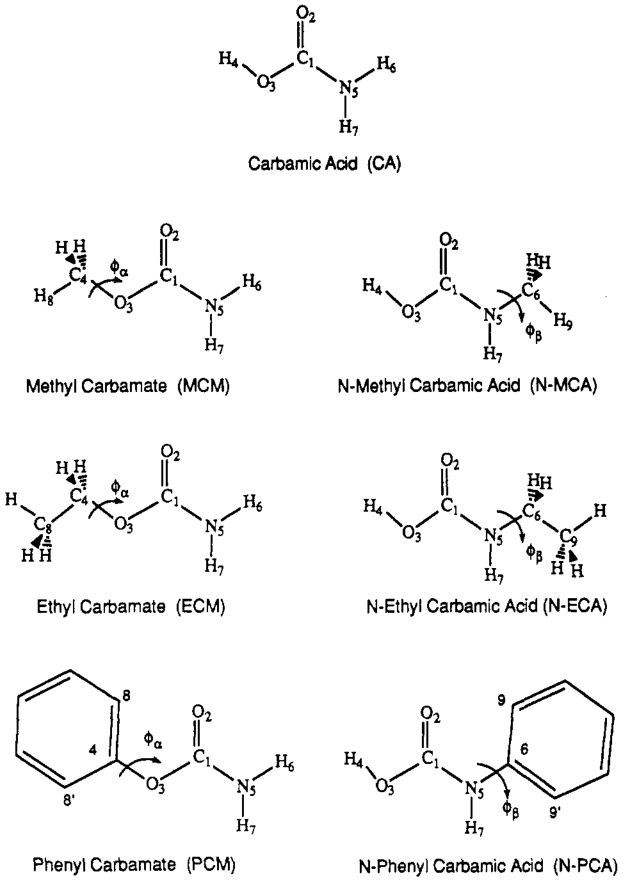

$$\left[\left(-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R_1-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R_2-\right)_m\left(-O-R_3-\right)_n\right]$$

Figure 1. Schematic illustration of poly(ether urethane) copolymer.


Carbamic Acid (CA)

Methyl Carbamate (MCM)

N-Methyl Carbamic Acid (N-MCA)

Ethyl Carbamate (ECM)

N-Ethyl Carbamic Acid (N-ECA)

Phenyl Carbamate (PCM)

N-Phenyl Carbamic Acid (N-PCA)

Figure 2. Urethane model compounds.

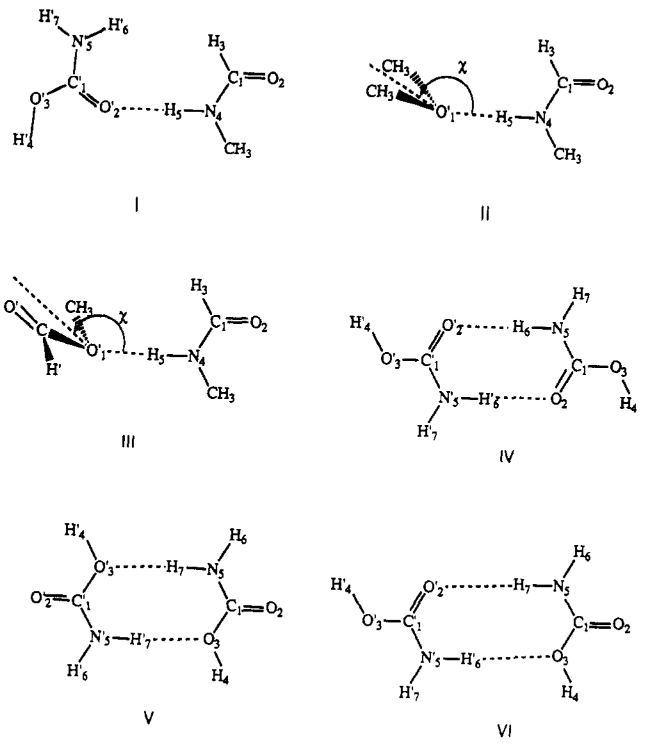


Figure 3. Hydrogen-bonded dimers.

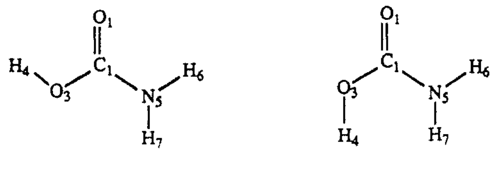
three types of hydrogen bonds found in polyurethanes? In principle, quantum mechanics *ab initio* calculations can be used to tackle these problems. However, to the author's best knowledge, these questions have not been solved theoretically, although a few attempts have been reported.[44,45]

In the course of developing an *ab initio* force field for molecular dynamics simulations on polyurethanes, quantum mechanical calculations were conducted on urethane model compounds and hydrogen-bonded dimers to systematically investigate the intra- and intermolecular interactions for polyurethanes. Full geometry optimizations were performed at several levels of theory to calculate the conformational energies and structures. Energy profiles of internal rotations about the bonds along the backbone of the polyurethane hard segment were calculated. The intermolecular hydrogen-bonding properties were studied for the three types of hydrogen bonds. The present paper reports the results of these calculations.

II. Calculations

The chemical structure of a typical polyurethane copolymer, poly(ether urethane), is schematically illustrated in Figure 1. Seven urethane model compounds—carbamic acid (CA), *N*-methylcarbamic acid (*N*-MCA), methyl carbamate (MCM), *N*-ethylcarbamic acid (*N*-ECA), ethyl carbamate (ECM), *N*-phenylcarbamic acid (*N*-PCA), and phenyl carbamate (PCM)—were calculated in this study. These molecules are illustrated in Figure 2. The hydrogen-bonded dimers studied here are shown in Figure 3. Dimers I, II, and III represent three types of hydrogen bonds: NH···O=C, NH···O(ether), and NH···O(ester), respectively. In these dimers, the proton donor N–H is represented by *N*-methylformamide, and the three acceptors are represented by carbamic acid (C=O), dimethyl ether (O(ether)), and methyl formate (O(ester)). In addition, three cyclic dimers of carbamic acid, labeled as IV, V, and VI, were included in the calculations. Each of these cyclic dimers contains two hydrogen bonds: two NH···O=C in dimer IV, two NH···O(ester) in dimer V, and NH···O=C and NH···O(ester) in dimer VI. The atom numbers which are used in this paper are also given in both Figures 2 and 3.

All calculations reported in this study were conducted on an IBM RISC/6000 550 workstation by using *ab initio* software packages Turbomole[46,47] and Gaussian90.[48] Full geometry optimizations were carried out by using the gradient minimization method provided by the software packages to obtain the minimum energy and transition states for the molecular systems studied. These calculations were conducted at HF and MP2 levels of theory, using different basis sets. Most monomers and dimers calculated in this study belong to C_1 symmetry because of the puckered nitrogen center of the urethane groups. Symmetry constraints were used only when it was necessary and reasonable. Internal rotation energies were calculated by performing torsion constrained optimizations in which a torsion angle was fixed to a given value whle all other internal coordinates were allowed to relax. The association energies of the dimers were estimated with and without corrections of the basis set superposition errors (BSSE). The BSSE corrections were estimated by using the regular counterpoise method.[49] The normal mode vibrational frequencies were calculated by diagonalizing the analytic Hessian matrix on minimized dimers and corresponding monomers.



trans cis

Figure 4. *Trans* and *cis* conformers of carbamic acid.

III. Results and Discussion

Optimized Geometries and Energies of Carbamic Acid, Consideration of Basis Sets, and Electron Correlation. Remko and Scheiner[19] compared several basis sets up to 6-31G* with HF calculations on planar carbamic acid. In the present study, the influences of the basis set and electron correlation for calculations on urethane molecules were studied up to the 6-311G** basis set and MP2 level, with optimized structures of *trans* and *cis* carbamic acid (Figure 4). The *trans* conformers were fully optimized, and the cis conformers were optimized with the dihedral angle H4–O3–C1–N5 fixed at 0°. To compare the calculated results of the present study with those previously published,[18,19] constrained optimizations were also conducted for planar *trans* and *cis* conformers. The 6-311G** basis set was chosen as the largest basis set for this study because the exponents and expansion coefficients of this basis set have been determined so as to minimize the energy of the atomic ground state at the MP2 level rather than at the corresponding HF level.[23] Table I summarizes the calculated structural parameters and total energies. The structural parameters of planar structures show little change from those of fully optimized structures. Consequently, the geometric parameters of planar structures are not listed in Table I, only energies are given.

The 6-31G* basis set in this study is slightly different from the conventional one. Instead of six d orbitals, five d polarization functions ($d_{3z^2-r^2}$, $d_{x^2-y^2}$, d_{xy}, d_{yz}, d_{zx}) are employed. The results calculated from both conventional and the (5-d) 6-31G* basis sets are given in Table I. Comparison of these two sets of data shows that the structural parameters agree well with each other; the total energies are slightly different but the relative energies (energy differences between the *trans* and *cis* conformers) are the same for these two basis sets.

Examination of the results in Table I shows significant changes in the bond lengths of the C1=O2, C1–O3, and O3–H4 bonds, which decrease as the size of the basis set is expanded. However, the improvement of the basis set has less influence on other bonds listed in this table. Inclusion of the electron correlation at the MP2 level has the opposite effect: it increases all bond lengths by 0.01–0.03 Å. Since the errors caused by truncating the basis set can be partly canceled by the errors caused by neglecting the electron correlation in predicting bond lengths,[50,53] most HF/3-21G and HF/4-21G values agree well with that of the MP2/6-311G**. The impact of the basis set and electron correlation seems less pronounced on bond angles except for the C1–O3–H4 angle, which is reduced about 3° as the basis set is improved from 3-21G to 6-311G** at the HF level of theory, and is further reduced another 3° or so when the MP2 correction is included. It seems that the oxygen atom is more sensitive to the improvement of the basis set and the inclusion of electron correlation than the nitrogen atoms in carbamates, presumably because there are two pairs of unshared lone pair electrons on the oxygen atom so that more extensive basis functions are needed to describe the electrons and the correlations between those electrons are more important.

Although most bond lengths and angles calculated at a low level of theory agree reasonably well with the high-level MP2/6-311G** values, the conformational energies calculated at the low levels of theory do not agree with the results obtained at higher levels. As one can see from Table I, the *trans–cis* energy difference decreases as the basis set is improved or the electron correlation is included. The value obtained at the MP2/6-311G** level is 2.5 kcal/mol lower than that calculated at the HF3-21G level for the fully optimized structures. This difference is smaller, 2.0 kcal/mol, for the planar structures, presumably due to the planar NH_2 group causing more steric repulsion with the OH groups in the *cis* conformation.

The calculated pucker angles of the nitrogen center of carbamic acid, which is measured by the angle between the C1–N5 bond and the H6–N5–H7 plane, are listed in Table I. At the HF/3-21G and HF/4-21G levels of theory, this angle is predicted to be zero (planar structure). As the basis set is improved, this angle becomes larger. Inclusion of the electron correlation at the MP2 level further increases the pucker angle. This conclusion is true for all alkyl and some phenyl derivatives of carbamic acid; we will come back to this issue later in this paper.

At the HF/3-21G and HF/4-21G levels, the results of planar structures agree well with those reported.[18,19] Although the total energies calculated in the present study are slightly lower, the energy difference between the *trans* and *cis* (10.7 kcal/mol) and all structural parameters are the same as those reported in the literature.[18,19] However, considerable discrepancies were found for the structural and energetic parameters between our results and those reported in the literature[19] at the HF/6-31G* level (the conventional (6-d) 6-31G* basis set was used for direct comparison). For example, the *trans–cis* energy difference of the planar structures was found to be 9.4 cal/mol in this study but 11.4 kcal/mol in previous work;[19] the C=O bond length was found to be 1.194 Å (for both planar and nonplanar structures) in this study but 1.220 Å in the literature.[19] Careful examination of the calculation details did not indicate any errors in this study. In fact, the total energies calculated in this study are significantly lower than those reported,[19] which indicates that the structures obtained in this study are more stable. As far as the software is concerned, both Turbomole and Gaussian90 produced the same results when the (6-d) 6-31G* basis set was used. Finally, the results obtained in this study demonstrate a progressive change in geometries and energies as the basis set is improved at the HF level of theory (as given in Table I), but the values found in the literature[19] are not consistent with this pattern.

The observed pattern of systematic change in structures and energies can be used as a reference for the calculations of larger molecules. Comparison of the results given in Table I shows that the basis sets and the electron correlation are sensitive to the molecular properties calculated in the range of HF/3-21G to MP2/6-311G**. Larger basis sets and higher levels of correction of electron correlation (MP3, MP4, or CI) may still have significant impact on the calculated properties, particularly on the conformational energies. However, calculations with larger basis sets and higher order of electron correlation were prevented because extremely large computations would be involved for most molecules studied in this paper. Choosing a "best" combination of basis set and method from the affordable range of theoretical levels is risky because it may give misleading results in certain aspects. To overcome these difficulties and to obtain a better sense of accuracy for the properties calculated, calculations at

Table I. Structural and Energetic Parameters of *Trans* and *Cis* Conformers of Carbamic Acid

	HF					MP2	
	3-21G	4-21G	6-31G*[a]	6-31G*[b]	6-311G**	6-31G*[b]	6-311G**
			Trans Geometry				
			Bond Lengths (Å)				
C1=O2	1.209	1.211	1.194	1.194	1.187	1.221	1.209
C1-N5	1.342	1.344	1.346	1.346	1.346	1.363	1.366
C1-O3	1.362	1.365	1.333	1.333	1.332	1.367	1.360
N5-H7	0.995	0.994	0.993	0.993	0.991	1.009	1.005
N5-H6	0.995	0.994	0.993	0.993	0.991	1.009	1.005
O3-H4	0.966	0.966	0.950	0.951	0.944	0.977	0.963
			Bond Angles (Deg)				
O2-C1-N5	127.1	127.1	125.6	125.6	125.7	126.1	126.1
O3-C1-N5	110.1	110.6	111.2	111.3	111.1	110.1	110.0
C1-N5-H7	120.4	120.4	120.7	120.5	120.4	119.1	117.6
C1-N5-H6	119.3	119.3	118.0	117.8	117.9	116.5	115.1
C1-O3-H4	110.8	110.6	107.4	107.3	107.6	104.7	104.5
			Pucker Angles (Deg)				
O2-N5/H6-N5-H7	0.0	0.0	13.0	14.7	13.0	24.2	31.1
			Cis Geometry				
			Bond Lengths (Å)				
C1=O2	1.201	1.203	1.184	1.185	1.178	1.213	1.201
C1-N5	1.362	1.363	1.370	1.370	1.370	1.388	1.390
C1-O3	1.364	1.367	1.334	1.334	1.333	1.366	1.359
N5-H7	0.994	0.994	0.995	0.995	0.994	1.012	1.008
N5-H6	0.996	0.996	0.996	0.996	0.994	1.012	1.008
O3-H4	0.963	0.964	0.947	0.948	0.941	0.973	0.960
			Bond Angles (Deg)				
O2-C1-N5	124.5	124.6	123.8	123.8	123.9	124.4	124.5
O3-C1-N5	114.6	115.7	114.9	114.8	114.7	114.4	114.0
C1-N5-H7	124.3	124.6	120.2	120.0	119.9	118.7	117.5
C1-N5-H6	117.5	117.5	114.0	113.9	114.1	112.3	112.0
C1-O3-H4	116.2	115.9	113.1	113.1	112.8	110.8	109.5
			Pucker Angles (Deg)				
O2-N5/H6-N5-H7	0.0	0.0	32.1	32.5	31.9	38.0	40.3
			Energies				
E_{trans}[c]	-242.45993	-243.24271	-243.82033	-243.81860	-243.89761	-244.45656	-244.67662
E_{cis}[c]	-242.44280	-243.22565	-243.80586	-243.80417	-243.88354	-244.44252	-244.66363
$E_{trans} - E_{trans}$[d]	10.7	10.7	9.1	9.1	8.8	8.8	8.2
			Planar Structures				
E_{trans}[c]	-242.45993	-243.24271	-243.82032	-243.81858	-243.89760	-244.45642	-244.67616
E_{cis}[c]	-242.44280	-243-22565	-243.80537	-243.80363	-243.88309	-244.44156	-244.66231
$E_{trans} - E_{trans}$[d]	10.7	10.7	9.4	9.4	9.1	9.3	8.7
$E_{inversion}$[e]	0.0	0.0	0.01	0.01	0.01	0.09	0.29

[a] Calculated using the 6-d 6-31G* basis set. [b] Calculated using the 5-d 6-31G* basis set. [c] Hartrees. [d] In kcal/mol. [e] Differences of E_{trans} between planar and fully-optimized structures, in kcal/mol.

three levels, HF/3-21G, HF/6-31G*, and MP2/6-31G*, were carried out for most molecular systems in this study.

Optimized Geometries of Alkyl and Phenyl Derivatives of Carbamic Acid. The optimized bond lengths and angles of the urethane group of the alkyl and phenyl derivatives of carbamic acid are given in Table II. For comparison, X-ray structural parameters of methyl carbamate,[3] ethyl carbamate,[4] and diphenylmethane urethane model compounds[5-9] are also given in the same table. However, it is important to comment that the comparison of properties calculated for isolated molecules with those measured for crystals is not strictly valid because the structural parameters are sensitive to local molecular environments. That the published X-ray data of a group of diphenylmethane urethane crystals demonstrate large deviations[9] reflects this fact in part. Consequently, one seeks a qualitative, general agreement rather than a quantitative, rigorous comparison between the calculations of isolated molecules and the experiments of large molecules in the condensed phases.

Data in Table II show that the calculated bond lengths and angles agree reasonably well with experimental data. Detailed comparison shows that the HF/3-21G bond lengths are overall in the best agreement with the X-ray values, the HF/6-31G* bond lengths are generally too short, and the MP2/6-31G* values are between the other two. This trend is consistent with the earlier discussion. The bond angles are less sensitive to the calculation methods and the calculated values are in good agreement with experimental data at all three levels.

The calculated values of C3-O4 bond lengths of ethyl carbamate are systematically smaller than that reported from X-ray measurement.[4] As given in Table II, the crystal value reported is 1.472 Å,[4] but the calculated values are 1.457, 1.424, and 1.445 Å at the HF/3-21G, HF/6-31G, and MP2/6-31G* levels, respectively. Comparison of the calculated and experimental values of the same bond for methyl carbamate[3] and diphenylmethane urethane compounds[9] reveals good agreement between the theory and the experiments. For methyl carbamate, the X-ray value[3] is 1.440 Å and the calculated values are 1.450, 1.429, and 1.437 Å at the HF/3-21G, HF/6-31G*, and MP2/6-31G* levels, respectively. For diphenylmethane carbamates, the X-ray values[9] are in the range of 1.443–1.450 Å, in agreement with that reported for methyl carbamate[3] and the calculated values. These trends indicate that the value of 1.472 Å reported for the ethyl carbamate[4] may be overestimated.

Table II. Bond Lengths, Bond Angles, Pucker Angles, and Total Energies of the Derivatives of Carbamic Acid

	N-MCA	MCM	*N*-ECA	ECM	*N*-PCA	PCM
			Bond Lengths (Å)			
C1=O2						
HF/3-21G	1.213	1.211	1.213	1.211	1.193	1.210
HF/6-31G*	1.196	1.194	1.196	1.194	1.193	1.189
MP2/6-31G*	1.224	1.221	1.225	1.221	1.223	1.216
expt[a]		1.227		1.219 (1.223)	1.205–1.215	
C1–O3						
HF/3-21G	1.362	1.356	1.361	1.355	1.335	1.361
HF/6-31G*	1.335	1.333	1.336	1.327	1.335	1.341
MP2/6-31G*	1.370	1.362	1.370	1.362	1.370	1.381
expt		1.338		1.342 (1.333)	1.345–1.361	
C1–N5						
HF/3-21G	1.340	1.347	1.339	1.345	1.351	1.343
HF/6-31G*	1.343	1.347	1.344	1.353	1.351	1.349
MP2/6-31G*	1.356	1.370	1.360	1.371	1.365	1.365
expt		1.334		1.341 (1.349)	1.333–1.358	
O3–C4						
HF/3-21G		1.450		1.457		1.396
HF/6-31G*		1.429		1.424		1.381
MP2/6-31G*		1.437		1.445		1.399
expt		1.440		1.472 (1.473)	1.443–1.450	
N5–C6						
HF/3-21G	1.460		1.466		1.408	
HF/6-31G*	1.445		1.450		1.408	
MP2/6-31G*	1.448		1.454		1.409	
expt					1.419–1.430	
			Bond Angles (Deg)			
O2–C–1O3						
HF/3-21G	122.6	123.1	122.8	123.8	122.6	124.9
HF/6-31G*	122.8	123.2	122.6	124.8	122.6	125.0
MP2/6-31G*	123.4	124.7	123.5	124.9	123.3	125.6
expt		123.0		123.4 (123.4)	123.0–124.3	
O2–C1–N5						
HF/3-21G	127.0	126.7	126.3	126.5	127.7	126.3
HF/6-31G*	126.0	125.5	126.1	124.7	127.7	125.4
MP2/6-31G*	126.7	125.7	126.8	125.5	128.0	126.3
expt		124.2		124.9 (122.4)	126.2–127.6	
C1–O3–C4						
HF/3-21G		117.0		117.5		127.8
HF/6-31G*		117.4		116.9		120.0
MP2/6-31G*		113.5		114.0		116.9
expt		115.2		115.6 (116.8)	114.4–117.3	
C1–N5–C6						
HF/3-21G	121.7		120.5		128.5	
HF/6-31G*	121.9		122.2		128.5	
MP2/6-31G*	121.6		120.2		128.0	
expt					124.5–127.0	
			Pucker Angles (Deg)			
HF/3-21G	0.1	0.1	0.2	0.0	0.0	0.0
HF/6-31G*	11.2	21.9	9.5	22.5	0.0	16.6
MP2/6-31G*	10.7	30.0	17.7	30.5	0.0	26.2
			Total Energies (hartrees)			
HF/3-21G	–281.274299	–281.272825	–320.097021	–320.097093	–470.728496	–470.725342
HF/6-31G*	–282.848611	–282.844476	–321.886464	–321.884147	–473.362252	–473.354449
MP2/6-31G*	–283.617498	–283.611266	–322.788160	–322.783068	–474.762343	–474.751898

[a] X-ray data of methyl carbamate, ref 3; ethyl carbamate, ref 4; and alkyl *N*-phenylcarbamates, ref 9. Two sets of data, measured at –105 and 25 °C, were reported for ethyl carbamate. Values in parentheses are measured at 25 °C.

The calculated pucker angles of the nitrogen center of carbamate molecules, which is measured by the angle between the C1–N5 bond and the C(or H)6–N5–H7 plane, are also listed in Table II. Similar to what was observed for carbamic acid, at the HF/3-21G level of theory, all compounds are predicted to be planar with zero or very small values of the pucker angle. At the HF/6-31G* level, most of them became puckered. The pucker angles are further increased by inclusion of the electron correlation at the MP2 level. The chemical structures influence the pucker angle as well. The nitrogen center becomes more planar when one of the amide hydrogens is replaced by a methyl or ethyl group, and it becomes more puckered if the alkyl group is attached to the ester oxygen atom. All three level calculations predict a planar structure for *N*-phenylcarbamic acid. Apparently, the lone pair electrons of nitrogen are involved in a conjugated electron structure which spans both urethane and phenyl groups, and the planar structure is energetically favorable in this case.

Despite the large pucker angles, the inversion energies were found to be small for the carbamates. The values for carbamic acid are reported in Table I. The energy differences between the planar and the puckered structures are the inversion energies. It is apparent that the inversion energies are closely related to the pucker angles: the height increases as the pucker angle increases. Nevertheless, the inversion energies are only 0.01 kcal/mol at the HF/6-31G* and HF/6-311G** levels, 0.09 kcal/mol at the MP2/6-31G* level, and 0.29 kcal/mol at the MP2/6-311G** level.

Table III. Calculated Torsion Angles (Deg) of the Derivatives of Carbamic Acid

molecules	*N*-MCA	MCM	*N*-ECA	ECM	*N*-PCA	PCM
		ϕ_α (C1–O3–C4–C8)				
HF/3-21G		179.7		179.7		0.0
HF/6-31G*		178.7		179.7		65.6
MP2/6-31G*		177.2		179.9		59.1
		ϕ_β (C1–N5–C6–C9)				
HF/3-21G	0.0		76.4		0.0	
HF/6-31G*	83.9		85.3		0.0	
MP2/6-31G*	99.7		78.5		0.0	

These values are significantly lower than the corresponding values calculated for the ammonia molecule: 1.6 kcal/mol at the HF/3-21G level and 6.5 kcal/mol at the HF/6-31G* level.[50] It is interesting to note that the HF/6-31G* value agrees well with the experimental value of 5.8 kcal/mol for ammonia.[51]

Torsion angles, ϕ_α and ϕ_β, were defined to measure the chain conformation of rotations about the O3–C4 and N5–C6 bonds, respectively, in this study. A 180° dihedral angle corresponds to a *trans* conformation for alkyl substitutions, and a 0° (or 180° by symmetry) dihedral angle corresponds to a planar structure for the phenyl compounds. The calculated values of these two angles are given in Table III. A *trans* conformation about the O3–C4 bond was found for methyl and ethyl carbamates. For phenyl carbamate, the torsion angle ϕ_α was found to be 0° at the HF/3-21G level, but 65.6° at the HF/6-31G* level and 59.1° at the MP2/6-31G* level. These results are similar to those found in phenyl carbonate and phenylformamide.[52,53] The experimental results[54] support the skewed structures calculated at higher levels of theory. The conformations of rotation about the N5–C6 bond are more complicated. The torsion angle ϕ_β was found to be 0° in *N*-methylcarbamic acid at the HF/3-21G level but 83.9° and 99.7° at the HF/6-31G* and the MP2/6-31G* levels, respectively. For *N*-ethylcarbamic acid, 76.4°, 85.3°, and 78.5° were obtained at the three levels of theory, respectively. A Newman projection along the N5–C6 bond is given in Figure 5, where the torsional angle ϕ_β is set at 90°. This diagram shows that a staggered conformation is more stable due to less steric repulsion. When a phenyl ring is bonded to the nitrogen, the torsion angle becomes 180.0° and the ring is in the plane of the urethane group.

Internal Rotation Energy Functions. The energy profiles of rotations about the bonds along the backbone of urethane were calculated. Six bonds—C1–O3, C1–N5, O3–C4, O3–C4(p), N5–C6, and N5–C4(p)—where C(p) denotes a phenyl carbon, were studied. The values of the largest energy barrier height of complete (360°) rotation about each of these bonds are listed in Table IV. These values were calculated by taking energy differences between the optimized transition states and the minimum energy states of rotations about the corresponding bonds. Large differences exist between the results of HF/3-21G and HF/6-31G* calculations, but the differences between the HF/6-31G* and MP2/6-31G* values are small, mostly about the fraction of a kcal/mol. The largest difference between the HF/6-31G* and MP2/6-31G* results is for the N–C(p) bond rotation: the barrier height is 2.4 kcal/mol at the HF/6-31G* level, but 3.4 kcal/mol at the MP2/6-31G* level. Based on this analysis, the energy curves were calculated at the HF/6-31G* level only. The results are reported in Figures 6–11.

(1) Rotation about the Partial Double Bonds: C1–O3 and C1–N5. The planar geometry of the carbamate group allows certain overlap between the carbonyl π orbital and the lone pair electron orbitals of the amide nitrogen (N5) and the ester oxygen (O3) to form partial double bonds C1–O3 and C1–N5. This explains important features of the rotational energy functions of these two bonds.

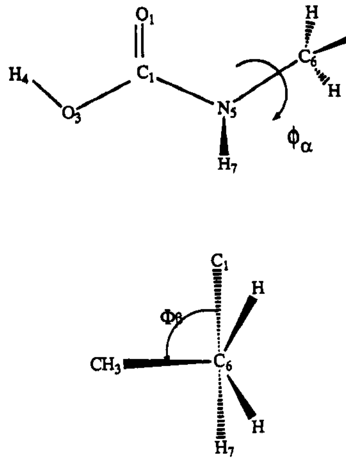


Figure 5. Conformations of rotation about the N5–C6 bond of *N*-ethylcarbamic acid and the Newman projection along the N5–C6 bond.

Table IV. Calculated Rotational Barriers (kcal/mol)

bond	molecule	HF/3-21G	HF/6-31G*	MP2/6-31G*
C1–O3	carbamic acid	12.4	12.1	12.1
C1–N5	carbamic acid	20.0	16.3	15.3
	N-methylcarbamic acid	20.5	15.6	14.7
O3–C4	ethyl carbamate	5.6	7.5	7.6
O3–C4(p)	phenyl carbamate	2.9	1.0	1.4
N5–C6	*N*-ethylcarbamic acid	4.6	4.8	4.9
N5–C6(p)	*N*-phenylcarbamic acid	5.2	2.4	3.5

In Figure 6, two energy curves of rotations about the C1–O3 bond are plotted. The curves were calculated from carbamic acid and methyl carbamate. The purpose was to investigate the influence of replacing a hydrogen atom by a methyl group. Apparently, the two curves are similar. A transition state can be found around ±(60–70°) on each of these curves with barrier heights of ca. 12 kcal/mol. These energy barrier heights, which are substantially higher than that of a single bond (1–3 kcal/mol), demonstrate the characteristics of a partial double bond. The *cis* (0°) conformers are ca. 10 kcal/mol less stable than the *trans* (180°) conformers for both molecules. The geometrical parameters calculated at the MP2/6-31G* level for the minimum energy (*trans*) state, the transition state, and the local minimum energy (*cis*) state of the rotation about the C1–O3 bond in carbamic acid are given in Table V. Comparison of the data reveals that the most significant change is in the C1–O3 bond. It is 1.368 Å for the minimum energy state, 1.390 Å for the transition state, and 1.372 Å for the *cis* conformer.

The energy profiles of rotation about the C1–N5 bond were calculated on carbamic acid and *N*-methylcarbamic acid. Since the nitrogen center of the urethane group was found to be puckered in most calculations, a dummy atom X was defined to facilitate the measurement of the torsion and the pucker angles simultaneously. The dummy atom X was placed in the R6–N5–H7 plane and the vector N5–X bisected the angle of R6–N5–H7. Hence, the torsion was measured by the dihedral angle O3–C1–N5–X and the pucker angle was measured by the angle between vectors N5–X and C1–N5. The energy profiles of rotations about the C1–N5 bond are plotted in Figure 7. Similar to the case of C1–O3 rotation, substitution of a methyl group for

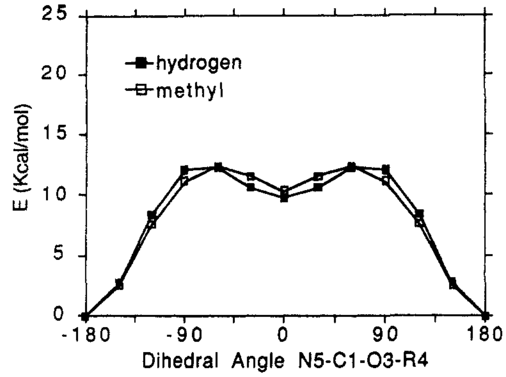


Figure 6. Energy profiles of rotation about the C1–O3 bond.

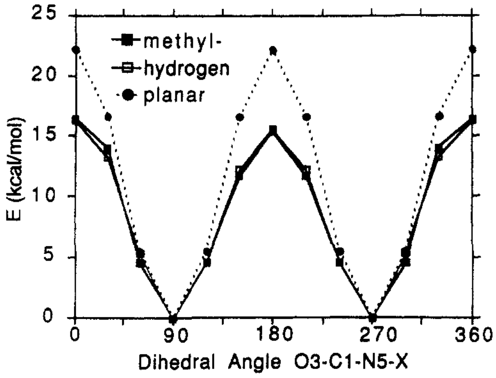


Figure 7. Energy profiles of rotation about the C1–N5 bond.

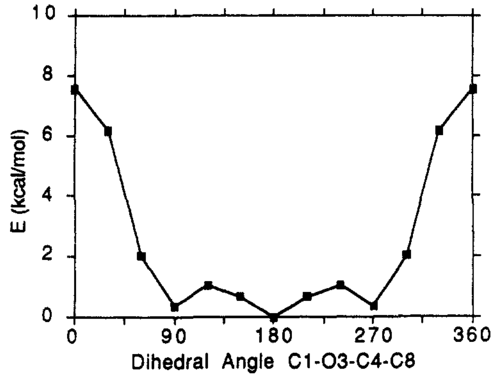


Figure 8. Energy profile of rotation about the O3–C4 bond.

hydrogen on the N atom does not change the rotation energy profile very much. The minimum energy state is located around 90° of the torsion angle. Two slightly different transition states are located at 0° and 180°, respectively. The 180° transition state corresponds to a structure in which the N5–R6 and N5–H7 bonds point toward the same side of the carbonyl group. The energy barrier heights calculated for both transition states are ca. 16 kcal/mol, while the 180° barrier is slightly lower in energy than the 0° barrier. This value falls in the range of experimental data: 10.8–22.7 kcal/mol.[10-15]

The results calculated for C1–N5 rotation in the present study disagree with that reported by Remko et al.,[19] who calculated the energy barrier height by assuming a planar geometry for the nitrogen center in both the minimum energy and transition states. Examination of the structural parameters in Table VI reveals that the pucker angle is increased from 24.4° to 59.6° and 62.1° from the minimum energy state to the transition states. A "planar" rotation was calculated by fixing the pucker angle of the nitrogen center to zero, and the resulting energy curve is given in Figure 7. The energy barrier height is increased to ca. 22 kcal/mol in the "planar" rotation, which is close to the result reported by Remko et al.[19]

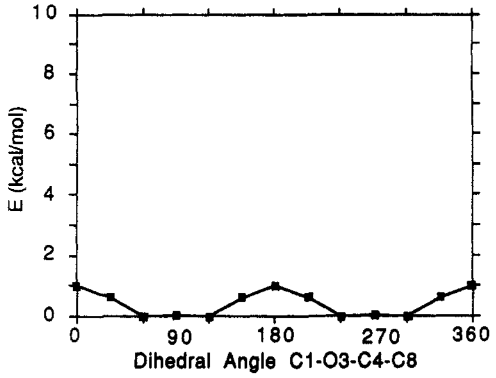


Figure 9. Energy profile of rotation about the O3–C4(p) bond.

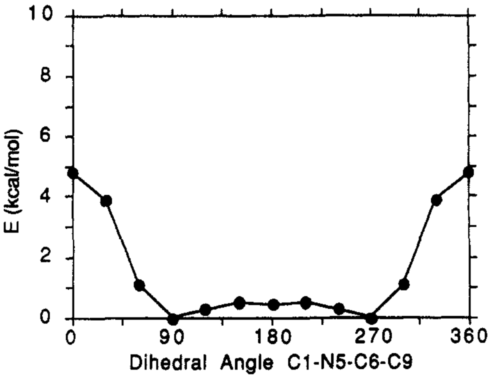


Figure 10. Energy profile of rotation about the N5–C6 bond.

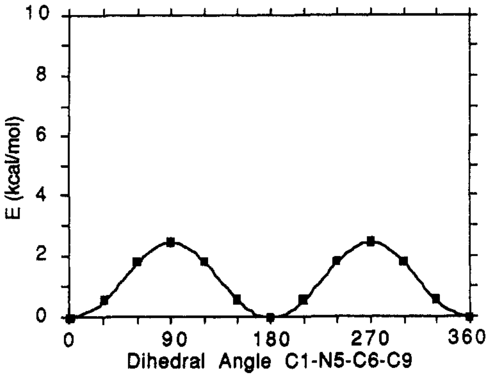


Figure 11. Energy profile of rotation about the N5–C6(p) bond.

Table V. MP2/6-31G* Structural Parameters Optimized for Conformational States of Rotation about the C–O Bond in Carbamic Acid

	dihedral angle (deg) N5–C1–O3–H4		
	180.0	67.5	0.0
	Bond Lengths (Å)		
C1=O2	1.221	1.214	1.215
C1–O3	1.368	1.390	1.372
O3–H4	0.976	0.973	0.972
C1–N5	1.344	1.344	1.344
N5–H6	0.993	0.993	0.993
N5–H7	0.992	0.992	0.992
	Bond Angles (Deg)		
O2–C1–O3	123.6	122.3	120.2
O2–C1–N5	126.3	125.1	124.6
C1–O3–H4	104.6	109.0	111.9
C1–N5–H7	121.3	121.3	121.3
C1–N5–H6	118.5	118.5	118.5

Along with the increase of the pucker angle from 24.4° and 59.6° and 62.1° from the minimum energy state to the transition states, the bond angle C1–N5–H6(7) is decreased from 117.8° to 107.9° and 106.6°. Note that the pucker

Table VI. MP2/6-31G* Structural Parameters Optimized for Conformational States of Rotation about the C–N Bond in Carbamic Acid

	dihedral angle (deg) O3–C1–N5–X		
	90	0	180
	Bond Lengths (Å)		
C1=O2	1.220	1.211	1.218
C1–O3	1.366	1.366	1.348
O3–H4	0.976	0.979	0.979
C1–N5	1.362	1.426	1.431
N5–H6	1.009	1.021	1.021
N5–H7	1.009	1.021	1.021
	Bond Angles (Deg)		
O2–C1–O3	123.8	122.8	123.3
O2–C1–N5	126.4	125.2	126.8
C1–O3–H4	104.7	105.8	105.4
C1–N5–H7	117.8	107.9	106.6
C1–N5–H6	117.8	107.9	106.6
	Pucker Angle (Deg)		
	24.4	59.6	62.1

angle of 60° and the bond angle of 109.5° are typical values for a symmetric tetrahedral center (e.g., CH_4), which indicates the lone pair electrons are localized to the nitrogen atom when the bond is twisted. Another significant change was found for the bond length of C1–N5, which is increased by 0.07 Å from the minimum energy state to the transition states. The extent of this change is larger than that found for the C1–O3 bond, consistent with the observation that the energy barrier height of the C1–N5 rotation is 3 kcal/mol higher than that of the C1–O3 rotation.

(2) Rotation about the O3–C4 and O3–C4(p) Bonds. The energy profiles of rotation about the O3–C4 and O3–C4(p) bonds were calculated on ethyl and phenyl carbamates. The resulting energy curves for these two bonds are given in Figures 8 and 9, respectively. For the ethyl carbamate, the equilibrium energy state corresponds to a *trans* conformer with 180° for the C1–O3–C4–C9 dihedral angle; a secondary minimum energy structure is a staggered conformer with the dihedral angle around 90° (and 270° by symmetry). The secondary minimum is only 0.3 kcal/mol higher in energy than the global minimum. The transition state of a complete rotation is a *cis* conformer, which is 7.5 kcal/mol higher in energy than the minimum. However, the energy curve is very flat in a wide range between 60° and 300°. These results indicate that the molecule is easy to deform about this bond rather than to be completely rotated about this bond. The geometrical parameters for both the minimum energy and transition states of ethyl carbamate are given in Table VII. Unlike the cases of rotation about the partial double bonds C1–O3 and C1–N5, the bond length of O3–C4 is not changed very much from the minimum energy state to the transition state. Rather, the most significant change can be found for the C1–O3–C4 angle, which increases from 114.0° to 123.6° from the minimum energy state to the transition state (*cis* conformer), thus reducing the steric repulsion between the methyl group and the carbonyl group.

Substitution of a phenyl group for the ethyl group changes the energy profile significantly. As given in Figure 9, the energy curve is very flat and a complete rotation (ring flipping) costs only 1.0 kcal/mol (1.4 kcal/mol based on MP2/6-31G* calculation). The maximum energy barrier is located at dihedral angle of 0°, which corresponds to a structure in which the phenyl ring is in the plane of the urethane NCOO group. The phenyl ring is twisted by ca. 60° in the minimum energy state, as we discussed earlier. Another transition state, which is only ca. 0.1–0.2 kcal/mol higher in energy than the minimum energy state, is located at 90° (and 270° by symmetry). These results are similar to that found for phenyl carbonate[52,53,55] and indicate that the ring flipping about the C_{phenyl}–$C_{carbonate}$ bond is easy in an isolated molecule. It has been shown that the intrinsic barrier for phenyl rotation in phenyl carbonates arises mostly from the rotation barrier for 2,2-diphenylpropane and the need to simultaneously rotate both phenyl groups,[53] and the ridigity of bulk poly(phenyl carbonates) is mostly due to a packing effect, contributed from nonbond interactions.[52,55]

Table VII. MP2/6-31G* Structural Parameters Optimized for the Conformational States of Rotations about the O–C and O–C(p) Bonds

	ethyl carbamate		phenyl carbamate	
	Dihedral Angle (Deg)			
C1–O3–C4–C8	180.0	0.0	59.1	0.0
	Bond Lengths (Å)			
C1–O2	1.221	1.222	1.216	1.219
C1–O3	1.362	1.361	1.381	1.375
C1–N5	1.371	1.364	1.365	1.360
O3–C4	1.445	1.451	1.399	1.397
N5–H6	1.010	1.007	1.009	1.007
N5–H7	1.010	1.007	1.009	1.007
	Bond Angles (Deg)			
O2–C1–O3	124.9	127.8	125.6	127.2
O2–C1–N5	125.5	124.3	126.2	125.2
C1–O3–C4	114.0	123.6	116.9	123.6
C1–N5–H6	115.4	118.1	116.2	118.2

It is of interest to compare the minimized structural parameters between ethyl and phenyl carbamates. As given in Table VII, the most significant differences can be found in the bond lengths of C1–O3 and O3–C4. The C1–O3 bond length is 1.362 Å for ethyl carbamate and 1.381 Å for phenyl carbamate, and the O3–C4 bond length is 1.445 Å for ethyl carbamate and 1.399 Å for phenyl carbamate. The relatively longer C1–O3 bond and shorter O3–C4 bond in phenyl carbamate reflect that the electron density is delocalized from the C1–O3 region to the O3–C(p) region, forming a partial π bonding between the O3 and the phenyl ring. In principle, such a delocalization reinforces the O3–C4(p) bond strength and leads to higher rotation energy barrier. However, as discussed in the polycarbonates,[52] the total energy function of ring flipping is a result of two counteracting factors: the conjugation effect tends to maintain a planar structure and steric repulsion between the phenyl ring and the carbonyl group tends to push the ring out of the plane. The steric repulsion is evident by the bond angle C1–O3–C4, which is 123.6° in the planar structure and is reduced to 116.9° in the minimum energy state.

(3) Rotation about the N–C and N–C(p) Bonds. The energy curves of rotations about the N5–C6 bond of *N*-ethylcarbamic acid and the N5–C6(p) bond of *N*-phenylcarbamic acid are given in Figures 10 and 11, respectively. The geometrical parameters for the minimum energy and transition states of these two molecules are given in Table VIII.

There are some similarities between the N5–C6 and O3–C4 rotations. The energy for rotation about the N5–C6 bond is also flat in a wide range between 60° and 300° of the dihedral angle C1–N5–C6–C9. However, the minimum energy state for rotation about the N5–C6 bond was found to be staggered rather than *trans*. The transition state of a complete rotation about this bond is 4.5 kcal/mol higher in energy than the minimum, which is 3 kcal/mol lower than that for the C3–O4 rotation.

Table VIII. MP2/6-31G* Structural Parameters Optimized for the Conformational States of Rotations about the N–C and N–C(p) Bonds

	N-ethylcarbamic acid		*N*-phenylcarbamic acid	
	Dihedral Angle (Deg)			
O3–C1–N5–C6	78.5	0.0	0.0	90.0
	Bond Lengths (Å)			
C1=O1	1.225	1.224	1.223	1.221
C1–O3	1.370	1.376	1.370	1.371
C1–N5	1.358	1.356	1.365	1.363
O3–H4	0.977	0.977	0.977	0.977
N5–H6	1.012	1.012	1.013	1.012
N5–C7	1.454	1.461	1.409	1.426
	Bond Angles (Deg)			
O1–C1–O3	123.5	122.4	123.3	123.8
O1–C1–N5	126.1	129.0	128.0	126.6
C1–O3–H4	104.5	104.2	104.7	104.5
C1–N5–H6	116.9	114.6	127.9	121.8

The rotation energy function given in Figure 11 shows that the minimum energy structure of phenylcarbamic acid is planar (0° or 180°), despite the large repulsion between the phenyl ring and the carbonyl group, which is also indicated by a large C1–N5–C6 bond angle of 128.0° in the transition state. Comparison of Figure 11 with Figure 9 shows that the rotation about the N5–C6(p) bond is more restricted than rotation about the O3–C4(p) bond. The energy barrier for ring flipping is 2.4 kcal/mol (and 3.4 kcal/mol at the MP2/6-31G* level), which is higher than the value for rotation about the O3–C4(p) bond but is still quite low in general. Based on the discussion for carbonates, one can except that the energy barrier for ring flipping in a condensed phase is much higher than that calculated for an isolated molecule.

Comparison of the structural parameters given in Table VIII shows evidence of a partial double bond between the N5 and C6(p) atoms. The N5–C6(p) bond length of *N*-phenyl substitution is 1.409 Å but the N5–C6 bond length of *N*-ethyl substitution is 1.454 Å. The difference of 0.045 Å is comparable with the value of 0.046 Å found for the C–O bond. However, it is interesting to note that the C1–N5 bond length is changed by only 0.007 Å from *N*-ethylcarbamic acid to *N*-phenylcarbamic acid, while the corresponding change in the C1–O3 bond is 0.019 Å. This indicates that the formation of a partial double bond between N5–C6 involves less delocalization of the electron density from the C1–N5 region.

Intermolecular Hydrogen-Bonding Properties. In this section, three types of hydrogen bonds are studied based on *ab initio* calculations performed on six hydrogen-bonded dimers (Figure 3). These calculations were intended to interpret or predict hydrogen-bonding properties—bonding energies, structures, and vibrational frequency shifts—for bulk polyurethanes. As we discussed earlier in this paper, the comparison of the calculated results for isolated molecules at zero temperature with the properties measured for bulk materials at finite temperature needs to be approached with considerable caution. Quantitative comparison of the absolute values between calculations and experiments is not valid for many properties simply because the local moleclar environment can significantly influence those properties. However, relative comparison of the theoretical results in the same level of theory (provided the underlying approximation of the theory is reasonable) for similar molecular systems is usually beneficial and significant. Furthermore, to link the theoretical comparisons to experimental observations, the following hypothesis is used in this paper: At the same level of theory, the *ab initio* predicted hydrogen-bonding properties of different types of hydrogen bonds of small, isolated dimers are equally good or bad for interpretating the properties measured for bulk polymers. In other words, we assume that the systematic errors are same for different types of hydrogen bonds at the same level of theory.

Table IX. Association Energies of Hydrogen-Bonded Dimers[a]

	method		
	HF/3-21G	HF/6-31G*	MP2/6-31G*
	Dimer I (One N–H···O=C Bond)		
δE_1 (kcal/mol)	6.1	5.0	5.5
δE_2 (kcal/mol)	9.0	5.5	7.1
	Dimer II (One N–H···O(ether) Bond)		
δE_1 (kcal/mol)	6.4	4.3	5.5
δE_2 (kcal/mol)	10.0	5.0	7.5
	Dimer III (One N–H···O(ester) Bond)		
ηE_1 (kcal/mol)	3.3	1.7	2.9
δE_2 (kcal/mol)	6.4	2.3	4.5
	Dimer IV (two N–H···O=C Bonds)		
δE_1 (kcal/mol)	14.0	11.7	13.1
δE_2 (kcal/mol)	21.8	12.8	16.1
	Dimer V (Two N–H···O(ester) Bonds)		
δE_1 (kcal/mol)	6.2	4.2	6.7
δE_2 (kcal/mol)	10.3	5.0	8.7
	Dimer VI (N–H···O=C and N–H···O(ester) Bonds)		
δE_1 (kcal/mol)	10.2	7.8	9.7
δE_2 (kcal/mol)	17.4	8.7	12.2

[a] δE_1 and δE_2 are values calculated with and without the BSSE corrections, respectively.

(1) **Association Energies and Structural Parameters.** Table IX presents the total association energies of the dimers, based on fully minimized structures at the HF/3-21G, HF/6-31G*, and MP2/6-31G* levels of theory. Table X summarizes the structural parameters of internal coordinates involved in hydrogen bonding.

Two association energies are reported for each of the dimers at each level of theory. One was calculated by simply subtracting the total energy of the dimer from the total energies of related monomers at their optimized structures. Another was calculated by using the standard counterpoise method[49] to correct the basis set superposition error (BSSE). The counterpoise results are often considered to be an upper bound of the BSSE,[56,57] and the range of the corrected and uncorrected values reflects the extent of BSSE for a given basis set. Table IX shows that at the HF level the counterpoise corrections are large for the inadequate basis set 3-21G but are significantly reduced for the 6-31G* basis set. When electron correlation is included at the MP2/6-21G* level, the counterpoise corrections are slightly increased, indicating a larger basis set is needed for the electron correlations. This trend is consistent with that found for hydrogen-bonded dimers of water, hydrogen fluoride, ammonia, and other small molecular complexes reported in the literature.[56-59]

Examination of the data given in Table IX shows that the association energies are decreased by expansion of the basis set and increased by inclusion of the electron correlations. This cancellation, like that found in the prediction of intramolecular bond lengths, may lead to a good prediction of structures and energies for hydrogen-bonded dimers at the HF level with a modest basis set. Frisch, Del Bene, Binkely, and Schaefer[58] systematically investigated the basis set and electron correlation effects for a group of hydrogen-bonded complexes and showed that at the HF level, with a modest basis set such as 6-31+G(d), the calculated structural parameters and association energies agree well with those calculated at a

Table X. Calculated Structural Parameters of Hydrogen Bonds

	method		
	HF/3-21G	HF/6-31G*	MP2/6-31G*
Dimer I (One N–H···O=C Bond)			
N4–H5	1.003(0.007)	0.997(0.003)	1.015(0.004)
C′1=O′2	1.216(0.007)	1.199(0.005)	1.227(0.006)
N4···O′2	2.926	3.083	3.037
χ(N4···O′2=C′1)	154.9	147.5	148.2
Dimer II (One N–H···O(ether) Bond)			
N4–H5	1.006(0.010)	0.998(0.004)	1.018(0.007)
O′1–C′	1.438(0.005)	1.397(0.006)	1.420(0.005)
N4···O′	2.883	3.086	2.962
χ	169.3	171.2	170.3
Dimer III (One N–H···O(ester) Bond)			
N4–H5	1.001(0.005)	0.995(0.001)	1.013(0.002)
O′1–C′	1.462(0.006)	1.424(0.005)	1.448(0.005)
O′1–C(carbonyl)	1.354(0.010)	1.323(0.006)	1.355(0.008)
N4···O′1	2.994	3.243	3.096
χ	174.7	175.4	179.2
Dimer IV (Two N–H···O=C Bonds)			
N5–N7 (free)	0.996(0.001)	0.993(0.001)	1.008(0.001)
N5–H6 (bond)	1.012(0.017)	1.002(0.010)	1.021(0.014)
C1=O2	1.227(0.018)	1.206(0.012)	1.235(0.014)
C1–O3	1.359(0.003)	1.331(–0.002)	1.364(0.003)
N5···O′2	2.832	2.988	2.929
χ(N5···O′2=C′1)	122.0	120.7	118.1
Dimer V (Two N–H···O(ester) Bonds)			
N5–H6 (free)	0.996(0.001)	0.993(0.001)	1.008(0.001)
N5–H7 (bond)	1.000(0.005)	0.996(0.004)	1.014(0.007)
C1=O2	1.209(0.000)	1.193(–0.001)	1.221(0.000)
C1–O3	1.379(0.017)	1.344(0.011)	1.383(0.016)
N5···O′3	3.182	3.195	3.059
χ(N5···O′3–C′1)	132.0	129.8	130.1
Dimer VI (N–H···O=C and N–H···O(ester) Bonds)			
N5–H6 (free)	0.996(0.001)	0.993(0.001)	1.008(0.001)
N′5–H′7 (Free)	0.996(0.001)	0.993(0.001)	1.008(0.001)
N5–H7 (bond to O=C)	1.009(0.014)	1.000(0.008)	1.019(0.012)
N′5–H′6 (bond to O)	1.005(0.010)	0.996(0.004)	1.014(0.007)
C′1=O′2 (bond)	1.224(0.015)	1.209(0.015)	1.232(0.011)
C1=O2 (free)	1.211(0.002)	1.193(–0.001)	1.222(0.001)
C1–O3 (bond)	1.385(0.023)	1.348(0.015)	1.387(0.020)
C′1–O′3(free)	1.355(0.007)	1.329(–0.004)	1.362(0.005)
N′5···O3	2.909	3.164	3.024
N5···O′2	2.862	3.024	2.962
χ(N′5···O3–C1)	127.9	126.8	127.1
χ(N5···O′2=C′1)	122.7	124.9	121.8

very high level of theory, such as MP4/6311++G(3df,3dp). Assuming that this argument is correct for the molecules calculated in this study, we expect HF/6-31G* results to be reasonably good.

Comparison of the association energies among the different dimers listed in Table IX reveals differences in the bond strengths for the three types of hydrogen bonds studied. At the HF/3-21G level, it was found that the N–H···O(ether) is the strongest bonding, N–H···O=C is slightly less stable, and N–H···O(ester) is the weakest. At the HF/6-31G* level, while the N–H···O(ester) remains the weakest, the order of the other two is reversed: N–H···O=C is more stable than N–H···O(ether) by 0.7 kcal/mol with the BSSE correction and 0.5 kcal/mol without the correction. At the MP2/6-31G* level, the order of these two bonds is reversed again, but the differences are even smaller: 0.0 kcal/mol with the BSSE correction and 0.4 kcal/mol without the BSSE correction. Based on these results, one can conclude that the N–H···O=C and N–H···O(ether) bonds are comparably strong and the N–H···O(ester) bond is only ca. 50–60% as strong as the other two.

The hydrogen bonds in the cyclic dimers are systematically stronger than those found in the linear dimers. Note that two types of hydrogen bonds are modeled by the cyclic dimers IV–VI: N–H···O=C and N–H···O(ester). However, the methyl group attached to N(amide) or O(ester) is replaced by a H atom to reduce the computational expense. It has been tested that this simplification has very little impact on the hydrogen bond strengths calculated.[60] Dividing the total association energies of dimers IV and V by 2 gives the bond strengths of NH···O=C and NH···O(ester), respectively. The values obtained are generally 10–20% larger than the values of corresponding single-bonded dimers, presumably due to polarization effects. Additivity is not obeyed for the bonding energies from linear dimers to cyclic dimers but is nearly so for bonds in similar molecular environments. For example, dimer VI, which contains NH···O=C and NH···O(ester) bonds, has a total association energy of 7.8 kcal/mol at the HF/6-31G* level. This value is significantly larger than the sum of 5.0 and 1.7 kcal/mol, taken from the linear dimers I and III, but is quite close to the sum of 5.85 and 2.1 kcal/mol, taken from the cyclic dimers IV and V.

Examination of the minimized structures reveals that two monomers in dimers I, IV, V, and VI are in a plane or roughly in a plane, while two monomers in dimers II and III are perpendicular to each other: the (H acceptor) C–O–C planes of ether and ester groups are twisted by ca. 90° from the (H donor) urethane plane. Table X lists the hydrogen-bonding-related bond distances and angles, taken from the optimized structures of the dimers. The results are dependent on the level of theory employed. Comparison of the data with X-ray results[9] shows that the HF/6-31G* and MP2/6-31G* results are roughly in the range of experimental data. The hydrogen bond lengths N···O are directly related to the bond strength: a stronger hydrogen bond corresponds to a shorter N···O length. At the HF/6-31G* level, the H···O bond lengths calculated are 3.083 Å in the chain dimer I, 3.024 Å in cyclic dimer VI, and 2.988 Å in cyclic dimer IV (the X-ray bond lengths are in the range 2.89–3.07 Å[9]), while the least stable N–H···O(ester) bond lengths are 3.343 Å in the chain dimer III, 3.164 Å in dimer VI, and 3.195 Å in dimer VI. The hydrogen bond angles, which measures the orientations of the hydrogen bonds relative to the acceptor oxygens are also given in Table X. In dimer I, the hydrogen bond is at an angle of ca. 150° with the C=O bond, which falls in the range 147–172°, reported from the X-ray studies.[9] This angle is reduced to ca. 120° in the cyclic dimers where the two hydrogen bonds are parallel to each other (see Figure 3). The hydrogen bond angles for dimers II and III are measured between the C–O–C plane and the N···O bond, and the values are in the range 170–180°. The predicted intramolecular bond lengths of C=O, N–H, and C–O are also listed in Table X, together with the increments of these bond lengths from monomers to dimers. Although the sizes of the shifts are generally proportional to the strengths of the hydrogen bonds, careful examination shows that exceptions exist. For example, at the HF/6-31G* level, the shift of the N–H bond length in dimer I, is smaller than that in dimer II, although the hydrogen bond of dimer I is predicted to be stronger than that of dimer II at the same level of theory.

(2) Vibrational Frequency Shifts. To study the hydrogen-bonding-induced frequency shifts of the N–H, C–O–C, and C=O stretching modes, normal mode vibrational analyses were conducted at the HF/6-31G* level of theory for the dimers and related monomers. HF/3-21G and MP2/6-31G* calculations were not performed due to large BSSE corrections or computational expense. Al-

Table XI. HF/6-31G* Frequencies (cm^{-1}) and Assignments of the N–H Stretching Mode

	freq	shift	int (au)	assignment
N-Methylformamide N–H				
monomer	3887		0.041	0.91(N–H)
dimer I[a]	3849	−37	0.252	0.63(N–H) + 0.13(N–H′) + 0.16(N–H′)
dimer II	3838	−49	0.309	0.91(N–H)
dimer III	3873	−14	0.184	0.91(N–H)
Carbamic Acid N–H				
monomer	3982		0.085	0.51(N–H6) − 0.48(N–H7)
	3851		0.071	0.47(N–H6) + 0.51(N–H7)
dimer IV	3945	−37	0.367	0.10(N–H6) − 0.40(N–H7) + 0.10(N–H′6) − 0.40(N–H′7)
	3945	−37	0.000	−0.09(N–H6) + 0.40(N–H7) − 0.09(N–H′6) + 0.40(N–H′7)
	3759	−92	0.762	0.43(N–H6) + 0.06(N–H7) − 0.43(N–H′6) − 0.06(N–H′7)
	3736	−115	0.000	−0.44(N–H6) − 0.05(N–H7) − 0.44(N–H′6) − 0.05(N–H′7)
dimer V	3974	−8	0.372	−0.30(N–H6) + 0.19(N–H7) + 0.30(N–H′6) − 0.19(N–H′7)
	3974	−8	0.000	−0.31(N–H6) + 0.10(N–H7) − 0.31(N–H′6) + 0.18(N–H′7)
	3838	−12	0.342	0.17(N–H6) + 0.32(N–H7) − 0.17(N–H′6) − 0.32(N–H′7)
	3831	−20	0.000	0.16(N–H6) + 0.33(N–H7) + 0.16(N–H′6) + 0.33(N–H′7)
dimer VI	3968	−14	0.200	0.34(N–H6) − 0.59(N–H′7)
	3951	−31	0.177	0.73(N–H′6) − 0.20(N–H7)
	3827	−24	0.217	0.64(N–H6) + 0.29(N–H′7)
	3772	−79	0.319	0.12(N–H′6) + 0.80(N–H7)

[a] The assignment of the symmetric NH_2 stretching mode of the carbamic acid in dimer I is given as follows: frequency, 3854; shift, 3; intensity, 0.140; assignment, 0.37(N–H) − 0.25(N–H′6) − 0.31(N–H′7).

Table XII. HF/6-31G* Frequencies (cm^{-1}) and Assignments of the C=O Stretching Mode

	freq	shift	int (au)	assignment
C=O in Carbamic Acid				
monomer	2023		0.694	0.47(C=O)
dimer I	1999	−24	0.682	0.42(C=O)
dimer IV	1996	−27	1.472	0.22(C=O) − 0.22(C′=O′)
	1959	−64	0.000	0.19(C=O) + 0.19(C′=O′)
dimer VI	2020	−3	0.656	0.44(C=O)
	1984	−39	0.929	0.42(C=O)

Table XIII. HF/6-31G* Frequencies (cm^{-1}) and Assignments of the Ether C–O–C Stretching Mode

	freq	shift	int (au)	assignment
C–O–C in Dimethyl Ether				
monomer	1350		0.166	0.30(O1–C2) − 0.30(O1–C3)
	1046		0.042	0.28()1–C2) + 0.28(O1–C3)
dimer II	1341	−9	0.160	0.28(O1–C2) − 0.28(O1–C3)
	1033	−13	0.088	0.26(O1–C2) + 0.26(O1–C3)

Table XIV. HF/6-31G* Frequencies (cm^{-1}) and Assignments of the Ester C–O–C and Acid C–O Stretching Modes

	freq	shift	int (au)	assignment
C–O–C in Methyl Formate				
monomer	1393		0.407	0.21(O1–C2) − 0.39(O1–C3)
	1039		0.035	0.49(O1–C2) + 0.08(O1–C3)
dimer III	1375	−18	0.359	0.19(C1–O2) − 0.36(O1–C3)
	1023	−16	0.070	0.46(C1–O2) + 0.09(O1–C3)
C–O of Carbamic Acid				
monomer	1067		0.020	0.42(C–O)
dimer IV	1056	−11	0.000	0.25(C–O) + 0.25(C′–O′)
	1055	−12	0.071	0.22(C–O) − 0.22(C′–O′)
dimer IV	1089	22	0.019	0.42(C–O)
	1051	−16	0.071	0.49(C–O)

though the HF calculations using a modest basis set such as 6-31G* systematically overestimate frequencies, it has been shown that this basis set can predict the frequency shifts reasonably well for hydrogen-bonded complexes.[58,59]

Tables XI–XIV present the results calculated for the N–H, C=O, C–O–C(ether) and C–O–C(ester) stretching modes, respectively. Since only stretching modes were of interest in this study, a simple scheme based on the *B*-matrix method[61] was used to assign the normal mode to internal coordinates. The coefficients reported in Tables XI–XIV reflect the percentage of the contributions. It is apparent that the N–H modes are largely stretching modes since the total weights (sum of the coefficients on N–H modes) are generally larger than 90%. The C=O and C–O–C modes are weighted around 50% only, and both are heavily coupled with bending modes which are not given in the tables. The frequency shifts were calculated by subtracting the dimer frequencies from the corresponding frequencies of the monomers.

The N–H frequency was found to be 3887 cm^{-1} for *N*-methylformamide monomer. When the N–H group is hydrogen bonded to C=O, O(ether), and O(ester) in dimers I, II, and III, the frequencies are shifted to 3849, 3838, and 3873 cm^{-1}, respectively. It is important to note that the shift of N–H bonded with O(ether) is larger than the shift of N–H bonded with O=C. This order supports the assigment of the 3295-cm^{-1} band to the mode of N–H bonded to O(ether), proposed by Lee, Wang, and Hsu.[37] However, these results also suggest that the sizes of frequency shifts do not precisely reflect the hydrogen bond strengths, because the N–H···O–C bonding is predicted to be stronger than the N-H···O(ether) bonding at the same level of theory.

Since the 3849-cm^{-1} N–H mode of *N*-methylformamide consists of a 29% contribution from the symmetric NH_2 stretching mode of carbamic acid (Table XI) in dimer I, it was questioned whether the smaller shift found in the NH mode bonded to O=C is related to this coupling. Careful examination of the results excluded this suspicion. The frequency of the symmetric NH_2 stretching mode of carbamic acid is 3851 cm^{-1} in the monomer, which is very close to the frequency of 3849 cm^{-1} calculated for the N–H mode of *N*-methylformamide in dimer I. Clearly, the large coupling between the N–H of *N*-methylformamide and the NH_2 of carbamic acid in dimer I is due to the small energy difference between these two modes. However, this coupling induces only a 3-cm^{-1} shift (to 3854 cm^{-1}) for the symmetric NH_2 stretching mode in dimer I (data for this mode are given in footnote *a* of Table XI). Since these two modes are mutually coupled, it is reasonable to estimate that a shift of similar size is added to the N–H mode due to the coupling.

Usually, a Morse function is a good approximation of the intramolecular potential of the X–H (X = C, O, N, F) bonds.[62] Consequently, the bond lengths are closely related to the stretching frequencies for these bonds,[58–59,62] and the order of bond length increments provides a good estimation of the order of frequency shifts. Comparison of the N4–H5 bond lengths calculated at the HF/6-31G* level (Table X) shows an agreement between the order of bond length increments and the order of frequency shifts: the increments of the N4–H5 bond lengths are 0.003, 0.004, and 0.001 Å for dimers I, II, and III, respectively. In addition, it is of interest to note that the bond length shifts calculated at all three levels of theory demonstrate the same pattern among the three types of hydrogen bonds.

The calculated frequency shifts in dimers I, II, and III only qualitatively agree with the experimental results of polyurethanes: the sizes of the shifts predicted are significantly smaller than those measured experimentally. There are several possible reasons to explain this discrepancy. However, the polarization effect,[63] which is extremely important for condensed hydrogen-bonded systems, is perhaps the major factor that needs to be considered.[62] A good example supporting this argument can be found in the hydrogen fluoride systems. It is understood that the monomer hydrogen fluoride vibrates at a frequency of 3962 cm^{-1},[64] and the frequencies of the dimer are shifted to 3929 and 3868 cm^{-1}, by 33 and 94 cm^{-1}, respectively,[65] which were predicted very well by *ab initio* calculations[59] and by semiclassical[62] and quantum Monte Carlo[66] simulations. However, the peak of the H–F stretching band in the liquid was found to be around 3450 cm^{-1},[67] shifted by some 500 cm^{-1} from the monomer and 400 cm^{-1} from the dimer. It has been shown[62] that the large frequency shifts found in the liquid of hydrogen fluoride cannot be predicted correctly by the same model used successfully for small clusters, unless the effective multipole moments are increased by 10%.[62] The increment essentially measures the size of the induced multipole moments from the polarization.

The polarization effect in urethane systems can be partly seen by comparing the calculated dipole moments of carbamic acid in its monomer and dimer structures. The dipole moments calculated at the HF/6-31G* level are 2.552 D for the monomer, 2.716 D for single H-bonded dimer I, and 2.805 D for double H-bonded dimer IV. The induced dipole moment of carbamic acid in the cyclic dimer is larger than that in the chain dimer, presumably because stronger bonding causes more intramolecular charge transfer in the former case. Meanwhile, the sizes of the frequency shifts calculated for dimer IV are significantly larger than that calculated for dimer I. The shifts related to the hydrogen-bonded N-H6 and N-H6′ modes, as indicated by the larger coefficients of these two bonds, are 92 and 115 cm^{-1}, respectively, which are in fact close to what is reported for bulk polyurethanes.[27,28]

The C=O stretching mode was calculated for carbamic acid monomer and dimers I, IV, and VI, and the results are presented in Table XII. In the dimer I, the C=O group is bonded to the N–H group and the shift calculated is 24 cm^{-1}. In dimer IV, symmetric and asymmetric combinations of the two C=O stretching modes are shifted by 64 and 27 cm^{-1}, respectively. In dimer VI, one C=O bond is free to hydrogen bonding and the frequency is shifted slightly by 3 cm^{-1}; another C=O bond is hydrogen bonded to the N–H group and the frequency is shifted by 39 cm^{-1}.

The ether C–O–C stretching modes are presented in Table XIII. Two frequencies, 1350 and 1046 cm^{-1}, were assigned to the symmetric and asymmetric C–O–C stretching modes of the monomer. These two modes are shifted to 1341 and 1033 cm^{-1} by 9 and 13 cm^{-1}, respectively, upon forming a N–H···O(ether) hydrogen bond in dimer II. The shifts are modest, considering the strong hydrogen bonding found in the dimer II. However, the frequency shifts of the ester C–O–C modes are surprisingly large. As given in Table XIV, the frequencies of the C–O–C stretching modes of methylformamide are 1039 and 1393 cm^{-1} for the monomer and 1023 and 1375 cm^{-1} for dimer III. The shifts of 18 and 16 cm^{-1} are larger than those found for the (ether) C–O–C stretching modes in dimer II, despite the N–H···O(ester) bond being much weaker than the NH···O(ether) bond. These results once again show that the sizes of shifts are not sufficient enough to determine the strengths of corresponding hydrogen bonds. Table XIV also lists the frequency shifts calculated for the C–O stretching modes of carbamic acid. For dimer V, which contains two N–H···O(ester) bonds, the shifts are 11 and 12 cm^{-1}; for dimer VI, which contains one N–H···O(ester) bond, the shift is 16 cm^{-1}.

Bandekar and Klima[43] studied the frequency shift of the ester C–O–C stretching mode and suggested that NH···O(ester) is a strong hydrogen bond based on the large shifts found for the ester C–O–C mode. They also suggested the 3295-cm^{-1} mode be assigned to the N–H mode bonded to the ester oxygen. Although these authors stated that the N–H···O(ether) and N–H···O(ester) are different hydrogen bonds expected in polyurethanes, they did not explicitly distinguish the differences between the two proton acceptors,[44] nor did they report the frequency shifts for the ether C–O–C stretching modes. The calculations reported in this paper suggest the N–H···O(ether) bond is about twice as strong as the N–H···O(ester) bond and that the 3295-cm^{-1} mode should be assigned to the N–H mode in the structure with N–H bonded to the ether oxygen and not the ester oxygen. The large shifts found for the ester C–O–C modes are due to a weak hydrogen bond N–H···O(ester). Our results also suggest that comparable shifts should be found for the ether C–O–C mode in polyurethane/ether copolymers.

IV. Summary

Quantum mechanics *ab initio* calculations at the HF and MP2 levels of theory were conducted for carbamate molecules and several hydrogen-bonded dimers to characterize intra- and intermolecular interactions for polyurethanes.

The methods and basis sets employed were examined up to the MP2/6-311G** level. It was found that the HF method with the small basis set 3-21G can predict most geometrical parameters reasonably well for the molecules calculated in the present study. However, for overall description of the geometrical and energetic properties, larger basis sets with polarization functions and electron correlation effects are required. Three levels of calculations—HF/3-21G, HF/6-31G*, and MP2/6-31G*—were conducted for most molecular systems in this study.

Based on the calculations, the carbamate group was found to be a rigid planar group due to delocalization of lone pair electrons and formation of the two partial double bonds C1–O3 and C1–N5. The rotation barrier heights were found to be more than 12 kcal/mol for the C1–O3 bond and 16 kcal/mol for the C1–N5 bond. Single bonds O3–C4 and N5–C6 in the backbone of polyurethanes were found to be easily deformed in a large range of dihedral angles. Substitution of a phenyl ring for the alkyl group bonded to the ester oxygen or amide nitrogen changes the rotational energy profiles but does not increase the rotational barrier heights substantially for the isolated molecules. It is suggested that the rigidity introduced by a phenyl ring is largely due to the intermolecular interactions.

The intermolecular hydrogen bonding was studied by conducting calculations on several hydrogen-bonded dimers. The BSSE correction was investigated at the three levels of theory, and the HF/6-31G* calculation was found to be less sensitive to the BSSE correction. The HF/6-31G* and MP2/6-31G* results agree reasonably well with available experimental data. Three types of hydrogen bonds—NH···O=C, NH···O(ether), and NH···O(ester)—were studied and compared based on the calculations. Among them, the N–H···O=C and N–H···O(ether) bonds are found to be comparably strong, and the N–H···O(ester) bond is only ca. 50–60% as strong as the former two bonds.

The calculated vibration frequency shifts for the dimers qualitatively agree with the experimental results reported for polyurethanes and support the assignment of the 3295-cm^{-1} mode to the N–H bond stretch in the N–H···O-(ether) structure. Although it is generally true that the frequency shifts induced by the hydrogen bonding are related to the strength of the bonding, it does not warrant that hydrogen bond strengths can be precisely estimated from the frequency shifts. In fact, the calculated frequency shifts demonstrate that larger shifts in the N–H and C–O–C modes were found for weaker hydrogen bonds. It is predicted that the frequency shifts for the ether C–O–C stretch modes are similar to that of ester C–O–C in polyurethane/ether copolymers.

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