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Microwave Spectrum, Conformational Equilibrium and Quantum Chemical Calculations of Urethane (Ethyl Carbamate)

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The microwave spectrum of urethane ($H_2NCO_2CH_2CH_3$) has been investigated in the 16.5–56.0 GHz spectral region at room temperature. Two rotamers denoted conformer **I** and conformer **II** were assigned. The C=O and –O–CH_2 bonds are oriented in the *syn* conformation in both these rotamers. The H_2NCO_2CC atoms are co-planar in conformer **I** with the methyl group *anti* to the $C_{carbonyl}$–O bond. The ethyl group is rotated 98° in conformer **II** from the position it has in **I**.

Conformer **I** is found to be 0.5(5) kJ mol^{-1} more stable than **II** by relative intensity measurements. The ground vibrational state was assigned for **I**, whereas the ground and one vibrationally excited state were assigned for **II**.

The microwave work has been assisted by *ab initio* computations at the MP2/cc-pVTZ level of theory, as well as density theory calculations at the B3LYP/6-31G* level. Both these methods predict similar geometrical structures for the two conformers and rotational constants that are close to the experimental ones. Both theoretical procedures predict a shallow pyramid around the nitrogen nucleus.

The carbamate group, –$HNCO_2$–, appears in many drugs[1–3] as well as in industrially important polyurethane polymers.[4] The prototype molecule of this class, methyl carbamate ($H_2NCO_2CH_3$), has very recently been studied in this laboratory.[5] The important next homologue, urethane, ethyl carbamate, ($H_2NCO_2CH_2CH_3$), is the subject of the present work.

Rotational isomerism is possible for this compound by rotating around the C1–O2 and the O2–C2 bonds (Fig. 1). It is known from other ethyl esters[6] that two low-energy conformers exist. The first of these would in the present case have C_s symmetry with the non-hydrogen atoms in one plane. The ethyl group is rotated roughly 90° around the O2–C2 bond from this plane in the second form. The carbonyl group (C1=O1) and the O2–C2 bonds are *syn* in both these rotamers.[6] These two forms are drawn in Fig. 1, and denoted conformers **I** and **II**, respectively.

The structural and conformational properties of urethane have been studied by several physical and theoretical methods such as infrared spectroscopy in solution,[7] X-ray crystallography[8] and *ab initio* quantum chemical methods.[9,10]

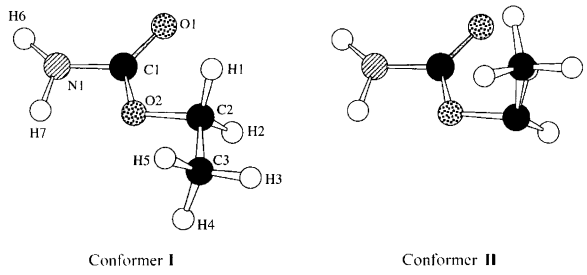

Fig. 1. Conformers **I** and **II** of urethane which were assigned in this work. Atom numbering is indicated on conformer **I**. Conformer **II** is obtained from **I** by rotating 82° around the C2–O2 bond. Conformer **I** was found to be 0.5(5) kJ mol^{-1} more stable than **II**.

Urethane prefers conformer **I** in the crystalline state, where the molecules are hydrogen-bonded into planar layers.[8] In the IR study[7] of dilute solutions, doubling of the stretching vibration of the carbonyl group was taken as evidence that more than one rotameric form exists in this phase.

No experimental information about the conformational composition of urethane in the free state is available, but *ab initio* computations at the 4-21G level[9] indicate that the conformational make-up in the gas is similar to that of other ethyl esters in that two rotamers

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similar to conformers **I** and **II** were predicted to have nearly the same energy.

No microwave (MW) studies have previously been reported for the title compound. Since MW spectroscopy can provide accurate information about geometrical structures and energy differences between conformers, it was decided to carry out an investigation for urethane. The experimental work has been assisted by quantum chemical calculations made at different and/or much higher levels than previously reported.[9,10]

Experimental

Our sample was purchased from Aldrich and used as received. The crystalline compound has a low vapour pressure at room temperature, at which the measurements were made. A study at lower temperatures, where intensities are significantly enhanced, was therefore not possible. The sample was specified to be at least 99% pure. No impurities were seen in the MW spectrum. The Oslo spectrometer, which is described in Ref. 11, was employed. The 16.5–56 GHz spectral region was investigated using a microwave absorption X-band brass cell. Both ordinary Stark spectroscopy measurements as well as microwave radiofrequency double resonance (MWRFDR) experiments as described in Ref. 12 employing the equipment mentioned in Ref. 13, were carried out. The pressure of the gas was about 5 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.[14] The nitrogen nucleus has spin = 1. The resulting quadrupole coupling with the molecular rotation often leads to broadening or distortion of the spectral lines. The accuracy of the frequency measurements is therefore assumed to be no better than ± 0.12 MHz.

Results and discussion

Quantum chemical calculations. The Gaussian 94 program package[15] running on the IBM RS6000 cluster in Oslo was employed in all the quantum chemical calculations.

Density functional theory (DFT) computations (6-31G* basis set) employing the B3LYP method[16] were first made in order to locate low-energy conformers, because these calculations are inexpensive and rather accurate. Various starting geometries were chosen and full geometry optimisation was carried out in each case. The two rotamers (conformers **I** and **II**) shown in Fig. 1 were found to be much more stable than any other forms of the molecule, and our work was therefore concentrated on these forms that can be observed experimentally.

Vibrational frequencies were computed for **I** and **II** by the B3LYP procedure. No imaginary frequencies were seen. **I** and **II** are thus true minima on the potential energy hypersurface.[17] The B3LYP geometries are listed in Table 1 (atom numbering in Fig. 1).

It has recently been reported[18] that equilibrium bond lengths of diatomic molecules are very well predicted at the MP2/cc-pVTZ level. Such computations are very expensive for a molecule as large as urethane, but were nevertheless carried out using the B3LYP geometries as the starting point. Full geometry optimisations were made in these calculations as well, with the results shown in Table 1. Computation of vibrational frequencies at this high level could not be made because of lack of resources. Table 1 also includes selected bond lengths and bond angles taken from the X-ray structure[8] (conformer **I**) for comparison.

Comments are warranted for some of the results in this table. Conformers **I** and **II** are calculated to be close (within 1 kJ mol^{-1}) in energy by both the B3LYP and the MP2 methods. The total dipole moments and their components along the principal inertial axes are found to be similar in both procedures.

There are no large structural differences between the MP2 and the B3LYP structures. The bond lengths agree within better than 1 pm, bond angles within better than 2°, and dihedral angles within better than 3°. The bond lengths in the crystalline phase are similar to the theoretical predictions for **I**. The largest difference is seen for the C1N1 bond length, which is about 3 pm shorter in the crystal. This difference is presumably caused by intermolecular hydrogen bonding that is present here.

Conformer **II** is obtained from **I** essentially by rotating 81.9 (MP2), 84.6° (B3LYP), around the O2–C2 bond from the *syn* position [respectively, 98.1 (MP2) and 95.4° (B3LYP) from *anti*]. The corresponding dihedral angles measured from *anti* are about 95° in ethyl formate,[6b] ethyl chloroformate,[6c] ethyl cyanoformate,[6c] and in ethyl glycolate,[6d] respectively. This unusual dihedral angle has been attributed to steric interaction between the carbonyl and ethyl groups preventing it from taking the normal 120° (from *anti*) dihedral angle.[6]

The non-hydrogen atoms are computed to be nearly co-planar in **I**, as can be seen from the O1C1O2C2 and C2O2C1N1 dihedral angles. The amide group is calculated to be non-planar in **I** as well as in **II** at both levels of theory, as seen from the O1C1N1H6 and O1C1N1H6 dihedral angles which deviate roughly 16–18° from the values they would have had in the case of a completely planar amide group (0 and 180°, respectively). The pyramid around the nitrogen atom is found to be slightly more shallow in the B3LYP than in the MP2 calculations.

MW spectrum and assignment of conformer **I**. The MW spectrum of urethane is dense and comparatively weak at room temperature in spite of the fact that the molecule has a fairly large dipole moment [$(8–9) \times 10^{-30}$ C m; Table 1]. The reason for this weakness is attributed to be the presence of two rotameric forms each with comparatively small rotational constants and several low-frequency vibrational modes, as indicated in the B3LYP calculations above (but not included in Table 1). All this results in a low Boltzmann population of each quantum state at room temperature, and hence a weak spectrum.

The quantum chemical computations above indicate

Table 1. Structure[a] of urethane at various levels of theory and X-ray structure.[b]

Rotamer:	Conformer I			Conformer II	
Method:	MP2/cc-pVTZ	B3LYP/6-31G*	X-ray	MP2/cc-pVTZ	B3LYP/6-31G*
Bond lengths/pm					
C1O1	121.1	121.5	121.9(4)	121.2	121.5
C1O2	135.4	135.9	134.2(4)	135.5	136.0
C2O2	143.8	144.3	147.2(4)	143.9	144.4
C2C3	150.8	151.8	152.4(6)	151.2	152.1
C1N1	136.7	137.1	134.1(4)	136.7	137.0
C2H1	108.8	109.5		108.7	109.3
C2H2	108.8	109.5		108.6	109.3
C3H3	108.8	109.5		108.9	109.6
C3H4	108.7	109.5		108.7	109.4
C3H5	108.8	109.5		108.8	109.5
N1H6	100.3	100.9		100.3	100.9
N1H7	100.3	101.0		100.3	101.0
Bond angles/°					
O1C1O2	124.8	124.9	123.4(3)	125.1	125.2
C1O2C2	113.8	115.1	115.6(3)	114.3	115.7
O2C2C3	106.9	107.4	105.0(3)	111.2	111.5
O2C1N1	109.8	110.0	111.7(3)	109.6	109.8
O2C2H1	109.0	109.0		108.9	108.8
O2C2H2	109.0	109.0		104.3	104.2
C2C3H3	109.8	109.8		109.8	109.9
C2C3H4	110.7	110.9		110.3	110.4
C2C3H5	110.7	111.0		110.5	110.8
C1N1H6	115.2	115.8		115.2	115.9
C1N1H7	117.5	118.6		117.5	118.6
Dihedral angles/°					
O1C1O2C2	0.8	1.0		2.7	2.3
C1O2C2C3	179.8	179.9		81.9	84.6
C2O2C1N1	−177.2	−177.3		−175.5	−176.2
C1O2C2H1	59.0	58.5		−41.0	−38.3
C1O2C2H2	−58.5	−58.6		157.9	−154.9
O2C2C3H3	−179.9	180.0		176.2	175.7
O2C2C3H4	−60.1	−60.2		−64.3	−64.8
O2C2C3H5	60.3	60.3		56.6	56.0
O1C1N1H6	17.8	16.3		17.6	15.9
O1C1N1H7	162.8	164.2		163.0	164.4
Total energy/kJ mol^{-1}					
	−848533.01	−850022.27		−848533.84	−850022.95
Energy relative to conformer I/kJ mol^{-1}					
	0.0	0.0		−0.83	−0.68
Rotational constants/MHz					
A	8991.1	8928.8		7519.4	7514.2
B	2152.7	2117.1		2451.3	2379.5
C	1776.5	1750.0		2143.6	2088.2
$I_a+I_b-I_c$ [c]/10^{-20} u m^2					
	6.50	6.52		37.62	37.63
Dipole moment[d]/10^{-30} C m					
μ_a	1.95	1.53		1.42	1.63
μ_b	8.07	7.71		7.87	7.31
μ_c	2.51	2.43		0.76	0.83
μ_{tot}	8.73	8.23		8.03	7.54

[a]See Fig. 1 for atom numbering. Dihedral angles measured from *syn*=0°. [b]Taken from Ref. 8. Structure determined at −105 °C. [c]I_a, I_b and I_c are the principal moments of inertia. Conversion factor: 505379.05 u m^2 MHz. [d]1 Debye = 3.33564×10^{-30} C m.

that conformer **I** is a low-energy form of the molecule. The largest dipole moment component of this rotamer is μ_b (Table 1). Searches were first made for the strong ^bQ-branch transitions using the rotational constants obtained in the MP2 computations as the starting point. These transitions were soon identified close to their predicted frequencies. The assignments were confirmed by their fit to Watson's Hamiltonian[19] using the quartic centrifugal distortion constants, Stark modulation patterns and intensities.

The *b*-type *R*-branch transitions were considerably weaker than the *b*-type *Q*-branch lines. Initial attempts to find them using a trial-and-error procedure were unsuccessful. This rotamer has a small μ_a dipole moment component. MWRFDR searches were next made for the $J = 13 \leftarrow 12$ and the $J = 14 \leftarrow 13$ ^aR-transitions, which are the strongest *a*-type transitions present within the range of our spectrometer. These searches turned out to be successful. The assignments were confirmed by Stark effect studies. Accurate predictions of the frequencies of several ^bR-branch lines could now be made. These transitions were soon identified and included in the least-squares fit. Attempts to find μ_c-lines were futile, presumably because this dipole moment component is small (Table 1), or perhaps zero (see below), resulting in insufficient intensities for such transitions.

A total of about 80 lines with a maximum value of $J = 35$ were ultimately identified. A portion of the spectrum is shown in Table 2;* the spectroscopic constants (*A*-reduction, I^r-representation)[19] found using 65 transitions are listed in Table 3.

Several of the *b*-type transitions were seen to be broad, or to have non-symmetrical appearances. It is assumed that this is a result of the nuclear quadrupole interaction of the nitrogen nucleus with the molecular rotation. Attempts to determine the quadrupole coupling constants of conformer **I** were futile, because of the weakness of the key lines (the low-K_{-1} lines), which have the largest splittings and therefore are used for this purpose.

Determination of the dipole moment would have been a sensitive test whether **I** has a symmetry plane, or not. μ_c would have been zero if conformer **I** had C_s symmetry. Unfortunately, the dipole moment could not be determined because the low-*J* lines are so weak. The closely related compound, methyl carbamate, was shown to have such a symmetry plane from dipole moment measurements.[5] It is therefore believed that this is case for urethane as well.

The value of $I_a + I_b - I_c$ represents a fairly sensitive test for C_s symmetry. A value of about 6.40×10^{-20} u m^2 would have been expected for a completely rigid compound possessing four out-of-plane sp^3 hybridised hydrogen atoms. Out-of-plane vibrations increase this value somewhat. It is e.g. 6.683 7(13) in methoxyacetamide,[20] and 6.813 73(27) (same units) in propionamide,[21] both of which are assumed to have C_s symmetry. Urethane is a more flexible molecule than methoxyacetamide and propionamide. A somewhat larger value than 6.8×10^{-20} u m^2 is therefore expected for $I_a + I_b - I_c$. The experimental value of $7.092\,37(38) \times 10^{-20}$ u m^2 (Table 3) is consistent with this expectation.

Table 2. Selected transitions of the MW spectrum of the ground vibrational state of conformer **I** of urethane.

Transition $J'_{K'_{-1},K'_{+1}} \leftarrow J''_{K''_{-1},K''_{+1}}$	Observed frequency[a]/MHz	Obs.−calc. freq./MHz
$3_{3,1} \leftarrow 3_{2,2}$	35 198.37	0.02
$5_{1,5} \leftarrow 4_{0,4}$	23 994.17	0.06
$5_{2,3} \leftarrow 5_{1,4}$	18 903.60	−0.18
$6_{2,4} \leftarrow 6_{1,5}$	18 342.17	0.23
$6_{4,3} \leftarrow 6_{3,4}$	49 203.92	−0.03
$7_{0,7} \leftarrow 6_{1,6}$	22 767.25	0.10
$7_{2,5} \leftarrow 7_{1,6}$	17 898.82	−0.12
$8_{4,5} \leftarrow 8_{3,6}$	49 145.25	0.03
$9_{1,9} \leftarrow 8_{0,8}$	35 855.90	−0.20
$9_{3,7} \leftarrow 9_{2,8}$	36 402.47	0.09
$11_{2,10} \leftarrow 11_{1,11}$	33 819.15	0.17
$11_{2,9} \leftarrow 11_{1,10}$	18 666.83	0.03
$12_{3,9} \leftarrow 12_{2,10}$	29 374.13	0.08
$13_{0,13} \leftarrow 12_{1,12}$	47 122.23	−0.06
$13_{2,11} \leftarrow 13_{1,12}$	21 273.57	−0.26
$13_{7,7} \leftarrow 12_{7,6}$	51 128.57	0.09
$13_{7,6} \leftarrow 12_{7,5}$	51 128.57	0.09
$14_{7,7} \leftarrow 13_{7,6}$	55 079.95	0.01
$14_{7,8} \leftarrow 13_{7,7}$	55 079.95	0.01
$15_{2,13} \leftarrow 15_{1,14}$	25 665.91	0.25
$16_{3,14} \leftarrow 16_{2,15}$	44 038.99	0.16
$17_{4,13} \leftarrow 17_{3,14}$	42 056.14	0.13
$18_{3,15} \leftarrow 18_{2,16}$	27 543.01	−0.06
$20_{3,17} \leftarrow 20_{2,18}$	30 254.56	−0.17
$21_{4,17} \leftarrow 21_{3,18}$	36 597.51	0.04
$23_{4,19} \leftarrow 23_{3,20}$	35 375.29	−0.08
$24_{3,21} \leftarrow 24_{2,22}$	41 700.98	−0.14
$26_{4,22} \leftarrow 26_{3,23}$	37 163.53	0.05
$29_{5,24} \leftarrow 29_{4,25}$	44 198.89	−0.04
$35_{5,30} \leftarrow 35_{4,31}$	49 777.36	0.01

[a] ±0.12 MHz.

Table 3. Spectroscopic constants[a,b] of the ground vibrational state of conformer **I** of urethane.

No. of transitions:	65
R.m.s. dev.[c]/MHz:	0.142
A_0/MHz	8999.137(14)
B_0/MHz	2146.270 0(78)
C_0/MHz	1776.159 1(78)
Δ_J/kHz	0.483(23)
Δ_{JK}/kHz	1.510(31)
Δ_K/kHz	1.70(72)
δ_J/kHz	0.046 37(86)
δ_K/kHz	0.190(55)
$I_a + I_b - I_c$[d]/10^{-20} u m^2	7.092 37(38)

[a] *A*-reduction. I^r-representation.[19] Nuclear quadrupole interaction has been neglected. [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation. [d] Same conversion factor as in Table 1.

* The complete spectra are available from the authors upon request, or from The National Institute of Science and Technology, Microwave Data Center, Optical Technology Division, Bldg. 221, Rm. B208, Gaithersburg, MD 20899, USA, where they have been deposited.

Attempts to find vibrationally excited states of conformer **I** were unsuccessful presumably because of the weak spectrum.

Assignment of conformer **II**. This rotamer has a μ_b which is much larger than the other two principal axis dipole moment components (Table 1), just as in the case of conformer **I**. The ^bQ-lines were assigned in a manner very similar to that described above for **I**. These transitions are, however, somewhat stronger than the corresponding ones found for **I**, because of a small energy difference between these two rotamers, and the fact that **II** has twice the statistical weight of **I** (see below).

A successful trial-and-error search for ^bR-lines was carried out next. The hypothetical frequencies of *a*- and *c*-type lines could now be predicted accurately. However, no assignments of such transitions could be made, presumably because they are too weak owing to small μ_a and μ_c components (Table 1). A total of about 160 transitions with a maximum value of $J=50$ were ultimately assigned for this rotamer. Some selected lines are listed in Table 4. The spectroscopic constants are found in Table 5.

Attempts to determine the quadrupole coupling constants of the ^{14}N nucleus as well as the dipole moment met with the same lack of success for the same reason as described above for conformer **I**.

However, in this case we were able to assign one vibrationally excited state of conformer **II**. Its spectroscopic constants are listed in Table 5. Relative intensity measurements, which were carried out as described in Ref. 22, yielded 61(15) cm^{-1} for this fundamental vibration.

The rotational constants of this excited state change significantly from the rotational constants of the ground vibrational state, as can be seen in Table 5. This is typical for vibrations involving heavy atoms. The lowest vibrational fundamental predicted in the B3LYP calculations (not given in Table 1) is the C2–O2 torsional frequency at 79 cm^{-1}. The excited state shown in Table 5 is thus assigned as the first excited state of this mode.

Energy difference between conformers **I** *and* **II**. Relative intensity measurements were carried out as described in Ref. 22 in order to determine the energy difference between **I** and **II**. The dipole moment components along the *b*-axis found in the B3LYP calculations (Table 1) were used. The statistical weights of **I** and **II** represent a difficult problem. If **I** had a completely planar amide moiety, its weight should be half that of **II**. If the amide group were non-planar the statistical weights of **I** and **II** would be equal. However, slightly non-planar geometries are calculated for this group (Table 1). It is difficult to say whether this non-planar amide group is an artefact of the theoretical calculations, or not. Arguments were given above that **I** indeed has a symmetry plane. Assuming that the statistical weight of **II** is twice that of **I**, the energy difference was found to be $E_{II}-E_I=$ 0.5 kJ mol^{-1}, with **I** as the most stable rotamer. One standard deviation was estimated to be $\pm$0.5 kJ mol^{-1}. (Identical statistical weights of **I** and **II** would have yielded $E_{II}-E_I=-1.1(5)$ kJ mol^{-1}.)

The experimental value of $E_{II}-E_I=0.5(5)$ kJ mol^{-1} should be compared to $E_{II}-E_I=-0.83$ kJ mol^{-1} found in the B3LYP computations, and to $E_{II}-E_I=-0.68$ kJ mol^{-1} found in the MP2 calculations

Table 4. Selected transitions of the MW spectrum of the ground vibrational state of conformer **II** of urethane.

Transition $J'_{K'_{-1},K'_{+1}}$	←	$J''_{K''_{-1},K''_{+1}}$	Observed frequency[a]/MHz	Obs.−calc. freq./MHz
$3_{1,3}$	←	$2_{0,2}$	18002.74	0.04
$4_{2,2}$	←	$3_{1,3}$	35104.21	0.04
$5_{2,3}$	←	$4_{1,4}$	40473.28	−0.17
$7_{0,7}$	←	$6_{1,6}$	40845.65	−0.02
$7_{3,5}$	←	$7_{2,6}$	26907.11	−0.21
$8_{4,5}$	←	$8_{3,6}$	36998.13	0.08
$9_{1,9}$	←	$8_{0,8}$	40938.69	0.05
$9_{3,7}$	←	$9_{2,8}$	27536.95	0.00
$11_{1,11}$	←	$10_{0,10}$	48727.19	−0.10
$11_{4,7}$	←	$11_{3,8}$	36092.32	−0.04
$12_{3,9}$	←	$12_{2,10}$	21784.37	0.06
$14_{4,11}$	←	$14_{3,12}$	37277.13	−0.20
$15_{4,12}$	←	$15_{3,13}$	37522.66	−0.05
$16_{3,13}$	←	$16_{2,14}$	20181.97	−0.07
$16_{5,12}$	←	$16_{4,13}$	47041.04	0.03
$17_{4,14}$	←	$17_{3,15}$	38334.51	−0.21
$18_{3,15}$	←	$18_{2,16}$	21221.27	0.05
$21_{3,19}$	←	$21_{2,20}$	43038.71	0.10
$22_{5,17}$	←	$22_{4,18}$	40840.78	0.03
$23_{3,20}$	←	$23_{2,21}$	30869.79	0.01
$25_{4,21}$	←	$25_{3,22}$	27853.63	0.05
$26_{4,22}$	←	$26_{3,23}$	29149.21	−0.09
$27_{3,24}$	←	$27_{2,25}$	43882.21	−0.07
$28_{6,22}$	←	$28_{5,23}$	49573.09	0.10
$30_{4,26}$	←	$30_{3,27}$	38770.45	−0.09
$32_{5,27}$	←	$32_{4,28}$	34353.64	0.14
$34_{6,28}$	←	$34_{5,29}$	40109.99	0.00
$39_{6,33}$	←	$39_{5,34}$	40786.79	0.09
$44_{7,37}$	←	$44_{6,38}$	44966.71	−0.18
$50_{8,42}$	←	$50_{7,43}$	50534.58	−0.01

[a] $\pm$0.12 MHz.

Table 5. Spectroscopic constants[a–d] of conformer **II** of urethane.

Vibrational state:	Ground	1st excited C2–O2 tors.
No. of transitions:	142	109
R.m.s. dev.[c]/MHz:	0.119	0.155
A_v/MHz	7565.399 5(56)	7551.699 6(93)
B_v/MHz	2414.760 3(43)	2397.828 9(69)
C_v/MHz	2116.351 7(43)	2105.343 6(69)
Δ_J/kHz	0.797(26)	1.123(40)
Δ_{JK}/kHz	0.400 0(94)	1.708(17)
Δ_K/kHz	12.73(20)	9.00(39)
δ_J/kHz	0.083 83(22)	0.123 79(36)
δ_K/kHz	−3.549(14)	−8.346(23)
$I_a+I_b-I_c$[d]/10^{-20} u m^2	37.291 54(10)	37.641 95(16)

[a–d] Comments as for Table 3.

(Table 1). There is thus good agreement between theory and experiment for a small energy difference between the two conformers.

Two previous experimental studies of energy differences in ethyl esters are available: In ethyl formate[6b] the *gauche* form corresponding to **II** was found to be 0.78(25) kJ mol^{-1} less stable than *anti* (corresponding to **I**). The corresponding value for the energy difference in ethyl glycolate[6d] was 1.9(5) kJ mol^{-1}. The heavy-atom planar rotamers are thus found to be the slightly more stable forms in all these three ethyl esters.

Structure. Comparison of the rotational constants in Table 1 with those in Tables 3 and 5 shows good agreement (within better than 2%) in all cases, with the MP2 rotational constants somewhat closer to the experimental ones than the B3LYP rotational constants. It is assumed that this good agreement is not fortuitous, but reflects that the MP2/cc-pVTZ structures are indeed accurate, as pointed out before,[18] perhaps with the exception of the hydrogen atoms of the amide group. It is felt that the pyramid around the nitrogen atom is computed to be too acute.

It is expected that any experimental structure that might be determined in the future for **I** and **II** will be very close to the MP2/cc-pVTZ structures given in Table 1, which are taken to be the plausible structures of the two conformers, with the exception of the amide group hydrogen atoms that are assumed to be co-planar with the other atoms of this group.

Conclusions

The gas phase of urethane, $H_2NCO_2CH_2CH_3$, is made up of two conformers with nearly the same energy. All the non-hydrogen atoms form a plane in one of these rotamers (conformer **I**). In the other rotamer (conformer **II**) the methyl group has an unusual conformation and is nearly perpendicular to this plane. The amide moiety is likely to be planar in both rotamers. Elaborate MP2/cc-pVTZ calculations predict structures and energy differences that are close to the experimental ones. The much less demanding B3LYP/6-31G* computations produce results that are remarkably close to the MP2/cc-pVTZ predictions.

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