Microwave Spectrum, Conformation, Barrier to Internal Rotation, ^{14}N Quadrupole Coupling Constants, Dipole Moment and Quantum Chemical Calculations for Methyl Carbamate

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The microwave spectrum of methyl carbamate ($H_2NCO_2CH_3$) has been investigated in the 13.5–40.0 GHz spectral region at room temperature. One conformer was assigned. This rotamer has a symmetry plane (C_s symmetry) and two out-of-plane hydrogen atoms. The methyl and the carbonyl groups are in the *syn* conformation. The barrier to internal rotation of the methyl group is 4235.9(66) J mol^{-1}. The dipole moment is (in units of 10^{-30} C m) $\mu_a = 0.544(7)$, $\mu_b = 7.653(31)$, $\mu_c = 0$ (for symmetry reasons) and $\mu_{tot} = 7.672(31)$. The ^{14}N quadrupole coupling constants were found to be $\chi_{aa} = 1.52(27)$ and $\chi_{bb} = 3.51(15)$ MHz.

The microwave work has been assisted by *ab initio* computations at the HF/6-311++G**, MP2/6-311++G** (frozen core) levels of theory, as well as density theory calculations at the B3LYP/6-31G* level.

The carbamate group, $-HNCO_2-$, appears in many biologically active compounds[1–3] such as local anaesthetics, muscle relaxants, anticonvulsants, anti-cancer agents, antiepileptics, sedatives and hypnotics as well as industrially important polyurethane polymers.[4]

Methyl carbamate is the prototype molecule of this class of compounds. Its structure and conformational properties have been studied by several physical and theoretical methods such as infrared spectroscopy in solution[5] and in the gas phase,[6] X-ray crystallography,[7] as well as semi-empirical and *ab initio* quantum chemical methods.[6,8–10] These studies all agree that the Syn conformation (Fig. 1), which has the methyl and carbonyl groups *syn* to one another, is the preferred form of the molecule in all phases. Quantum chemical calculations[6,8–10] predict that the same conformation of the free molecule is several kJ mol^{-1} more stable than any other rotamer.

The non-hydrogen atoms of methyl carbamate are nearly planar in the crystal, where the molecules are hydrogen-bonded into planar layers.[7] The situation is of course different in the gas phase, where hydrogen bonding is absent. It has been claimed[6] that the nitrogen atom
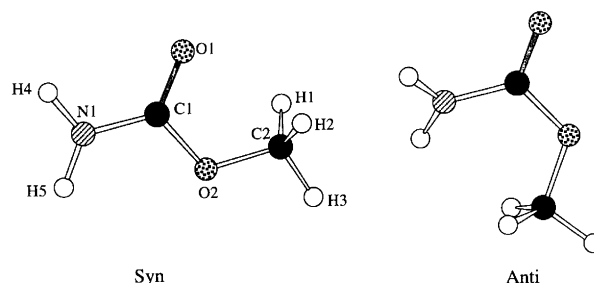

Fig. 1. The Syn and Anti conformations of methyl carbamate. Syn was assigned in this work. MP2/6-311++G** calculations predict Anti to be 35.5 kJ mol^{-1} less stable than Syn.

has a shallow pyramidal equilibrium conformation in the free state. The lowest energy level was found to lie above the barrier opposing planarity.[6]

No microwave (MW) studies have previously been reported for the title compound. Since MW spectroscopy can provide accurate information about geometrical structures, barriers to rotation of methyl groups, dipole moments and nuclear quadrupole coupling constants, it was decided to carry out an investigation for this important prototype compound. The experimental work has been assisted by quantum chemical calculations made

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at different and/or higher levels than previously reported.[6,8-10]

Experimental

The sample (m.p. 56–58 °C specified to be at least 98% pure) utilised in this work was purchased from Aldrich and used as received. No impurities were seen in the MW spectrum. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 11. The 13.5–40 GHz spectral region was investigated with the microwave absorption X-band brass cell held at room temperature. The pressure was about 5 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.[12] The accuracy of the frequency measurements is presumed to be better than ± 0.10 MHz.

Results and discussion

Quantum chemical calculations. The Gaussian 94 program package[13] running on the IBM RS6000 cluster in Oslo was employed in all the quantum chemical calculations. Computations were made for the **Syn** conformer (Fig. 1) at three different levels of theory. Hartree–Fock (HF) and Møller–Plesset (MP2) perturbation calculations with frozen-core electrons[14] were made using the 6-311++G** basis set. In addition, density functional theory computations employing the B3LYP method[15] were carried out using the 6-31G* basis set. Calculations for **Anti** were made only at the highest level (MP2/6-311++G**). Full geometry optimisation was made in each case with the results shown in Table 1 (atom numbering in Fig. 1), which also includes selected bond lengths and bond angles taken from the X-ray structure[7] of the crystalline phase for comparison. Vibrational frequencies (not included in Table 1) were computed in each case. No imaginary frequencies were found for any of the two conformers, which are thus assumed to be true minima on the potential energy hypersurface.[16]

Comments are warranted for some of the results in this table. The MP2 and the B3LYP structures of **Syn** are remarkably similar. The bond lengths are shorter in the case of the HF computations than in the other two cases, presumably because these calculations do not take electron correlation into consideration as the MP2 and B3LYP methods do. The bond lengths of the crystalline phase are similar to the theoretical predictions with the exception of the C1N1 bond length, which is shorter in the crystal. The difference is presumably caused by hydrogen bonding that is present here.

The non-hydrogen atoms are computed to be nearly co-planar in **Syn**, as can be seen from the O1C1O2C2 and C2O2C1N1 dihedral angles. The amide group is calculated to be non-planar at all three levels of theory, as seen from the O1C1N1H4 and O1C1N1H5 dihedral angles, which deviate 10–20° from the values they would have had in the case of a completely planar amide group.

The pyramid around the nitrogen atom is calculated to be more shallow in the HF than in the MP2 or B3LYP calculations.

The non-planarity computed for the amide group manifests itself in the value of $I_a + I_b - I_c$. This value is typically 3.20×10^{-20} u m^2 for a molecule possessing a symmetry plane and two out-of-plane hydrogen atoms attached to a sp^3 hybridised carbon atom. An increase in this value is characteristic for a compound that does not possess such a plane. The MP2 structure of **Syn** has the most non-planar amide group and the largest value of $I_a + I_b - I_c$ (3.467×10^{-20} u m^2; Table 1).

The non-hydrogen atoms of **Anti** are predicted (Table 1) to be slightly non-planar, since the O1C1O2C2 and C2O2C1N1 dihedral angles are calculated to be 171.9 and 168.2°, respectively. A non-planar amide group is computed for this conformation as well. The **Anti** conformer is calculated (see entries in Table 1) to be as much as 35.5 kJ mol^{-1} less stable than **Syn** at the MP2/6-311++G** level.

MW spectrum and assignment of **Syn**. The MW spectrum of methyl carbamate is rather dense and comparatively strong. Theory predicts that all transitions should be split into two components of equal intensity owing to tunnelling of the methyl group. One of these components has the non-degenerate A symmetry whereas the other has the degenerate E symmetry. The quadrupole interaction of the ^{14}N nucleus with the molecular rotation should lead to additional splittings of both the A and the E species lines.

Survey spectra revealed many transitions with characteristic splitting patterns. In addition, several strong lines with resolved Stark effect were noticed.

The quantum chemical computations above and previous work[5-10] indicate that **Syn** is the preferred 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 b-type R-branch transitions were identified next.

Spectroscopic constants and barrier to internal rotation of the methyl group. The assigned lines with $J \leqslant 7$ were selected for fitting to Herschbach's 'principal axes' Hamiltonian[17] using the computer program described in detail in Ref. 18. The rotational constants, the barrier to internal rotation of the methyl group, V_3, the direction cosines of the symmetry axis of the methyl group with respect to the principal inertial axes, λ_a, λ_b, λ_c, and the moment of inertia of the methyl group around its symmetry axis, I_α, are the parameters of this Hamiltonian. Centrifugal distortion and nuclear quadrupole interaction is not taken into account in this Hamiltonian.

The 54 lines with $J \leqslant 7$ used for fitting are shown in Table 2. Centrifugal distortion is assumed to be of little

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

Conformer:	Syn				Anti
Method:	MP2/6-311++G**	HF/6-311++G**	B3LYP/6-31G*	X-ray	MP2/6-311++G**
Bond length/pm					
C1O1	121.3	118.9	121.5	122.7(2)	120.7
C1O2	135.6	132.4	136.0	133.8(2)	135.9
O2C2	143.4	141.6	143.3	144.0(3)	142.7
C2H1	109.1	108.1	109.3		109.3
C2H2	109.1	108.1	109.3		109.6
C2H3	108.8	107.9	109.1		108.9
C1N1	137.4	135.2	137.0	133.4(2)	138.8
N1H4	100.8	99.2	100.9		101.0
N1H5	100.8	99.1	100.9		100.8
Bond angles/°					
O1C1O2	124.6	124.3	124.7	122.9(2)	120.3
C1O2C2	113.7	117.0	114.5	115.2(1)	119.5
O2C2H1	110.6	110.6	110.8		111.3
O2C2H2	110.5	110.5	110.8		111.5
O2C2H3	105.3	107.9	105.5		105.5
O1C1N1	125.6	124.8	125.4	124.2(2)	123.8
C1N1H4	114.8	117.4	115.9		111.8
C1N1H5	117.0	119.7	118.7		118.7
Dihedral angles/°					
O1C1O2C2	1.7	0.9	0.9		171.9
C1O2C2H1	−60.6	−60.8	−60.4		−53.5
C1O2C2H2	60.5	60.5	60.6		70.0
C1O2C2H3	179.9	179.8	−179.9		−172.3
C2O2C1N1	176.3	178.4	177.5		168.2
O1C1N1H4	19.6	10.7	16.0		14.8
O1C1N1H5	162.1	169.4	164.5		150.9
Total energy/kJ mol^{-1}	−745096.4	−742843.6	−746790.3		−745060.9
Rotational constants/MHz					
A	10625	11129	10609		10136
B	4407	4438	4372		4454
C	3183	3238	3161		3171
$I_a + I_b - I_c^{c}/10^{-20}$ u m^2	3.467	3.209	3.353		3.95
Dipole moment[d]/10^{-30} C m					
μ_a	0.16	0.12	1.03		12.16
μ_b	7.88	8.42	7.44		14.01
μ_c	2.81	1.62	2.43		2.73
μ_{tot}	8.37	8.58	7.89		18.75

[a] See Fig. 1 for atom numbering. [b] Taken from Ref. 7. [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.

importance for these transitions. It was also assumed that methyl carbamate has a symmetry plane (see below). λ_a is then the only independent variable direction cosine. The moment of inertia of the methyl group around its symmetry axis, I_α, was kept constant at 3.20×10^{-20} u m^2 in the fit while the other parameters of this Hamiltonian were allowed to vary. The result of the least-squares fit is shown in Table 3.

The A-species transitions depend only on the even-order terms of the angular momentum operator,[17] and may thus be fitted to Watson's Hamiltonian.[19] The result of such a fit of 92 selected transitions with comparatively

small ^{14}N quadrupole splittings is seen in Table 4.* In this fit the maximum value of the J quantum number was 33. It was necessary to vary one of the sextic centrifugal distortion constants (Φ_J) in order to get a fit with a root-mean-square deviation comparable to the experimental uncertainty of ±0.10 MHz.

The A-species spectroscopic constants in Table 4

* The spectrum of the A species is available from the authors upon request, or from the Molecular Spectra Data Center, National Institute for Standards and Technology, Molecular Physics Division, Bldg. 211, Room B265, Gaithersburg, MD 20899, USA, where it has been deposited.

Table 2. MW spectrum of the ground vibrational state of methyl carbamate.

Transition:			Observed[a]/MHz		Calc./MHz
$J'_{K'_{-1},K'_{+1}}$	$\leftarrow$	$J''_{K''_{-1},K''_{+1}}$	ν_A	$\nu_A - \nu_E$	$\nu_A - \nu_E$
$2_{2,0}$	$\leftarrow$	$1_{1,1}$	36 716.56	−35.02	−36.62
$2_{2,0}$	$\leftarrow$	$2_{1,1}$	19 119.71	−33.99	−34.32
$3_{0,3}$	$\leftarrow$	$2_{1,2}$	16 863.13	−5.56	−5.31
$3_{1,3}$	$\leftarrow$	$2_{0,2}$	26 090.91	6.25	6.21
$4_{1,4}$	$\leftarrow$	$3_{0,3}$	31 577.15	5.56	5.67
$3_{2,1}$	$\leftarrow$	$3_{1,2}$	18 021.90	3.43	3.35
$4_{0,4}$	$\leftarrow$	$3_{1,3}$	24 912.22	−4.01	−3.88
$4_{2,2}$	$\leftarrow$	$4_{1,3}$	17 275.83	11.05	11.08
$4_{2,3}$	$\leftarrow$	$4_{1,4}$	27 118.40	22.77	22.96
$5_{0,5}$	$\leftarrow$	$4_{1,4}$	32 614.49	−2.70	−2.48
$5_{1,4}$	$\leftarrow$	$4_{2,3}$	25 063.40	−19.12	−19.09
$5_{1,4}$	$\leftarrow$	$5_{0,5}$	19 567.36	6.23	6.34
$5_{2,3}$	$\leftarrow$	$5_{1,4}$	17 309.55	11.94	12.02
$5_{2,4}$	$\leftarrow$	$5_{1,5}$	30 378.99	20.96	20.89
$6_{0,6}$	$\leftarrow$	$5_{1,5}$	39 909.93	−1.31	−1.27
$5_{3,2}$	$\leftarrow$	$5_{2,3}$	31 458.81	−25.40	−24.77
$6_{1,5}$	$\leftarrow$	$5_{2,4}$	35 010.19	−15.30	−14.71
$5_{3,3}$	$\leftarrow$	$5_{2,4}$	35 917.82	83.99	83.75
$6_{1,5}$	$\leftarrow$	$6_{0,6}$	25 479.41	7.60	7.44
$6_{2,4}$	$\leftarrow$	$6_{1,5}$	18 458.30	10.84	10.97
$6_{2,5}$	$\leftarrow$	$6_{1,6}$	34 277.69	20.56	20.59
$6_{3,3}$	$\leftarrow$	$6_{2,4}$	29 533.40	8.65	8.97
$6_{3,4}$	$\leftarrow$	$6_{2,5}$	37 182.70	48.68	48.95
$7_{2,5}$	$\leftarrow$	$6_{3,4}$	28 507.05	−51.18	−51.13
$7_{1,6}$	$\leftarrow$	$7_{0,7}$	32 144.47	9.33	9.48
$7_{3,4}$	$\leftarrow$	$7_{2,5}$	27 656.66	19.29	19.52
$7_{2,5}$	$\leftarrow$	$7_{1,6}$	20 962.73	9.10	9.23

[a] ±0.10 MHz.

Table 3. Molecular constants[a] of the ground vibrational state of methyl carbamate.

Rotational constants[b]/MHz

$A_0 = 10715.151(25)$ $B_0 = 4398.9521(93)$ $C_0 = 3182.851(10)$

Principal-axes moments of inertia[c]/10^{-20} u m^2

$I_A = 47.16490(11)$ $I_B = 114.88624(24)$ $I_C = 158.78186(46)$
$I_A + I_B - I_C = 3.26928(53)$

Moment of intertia of the methyl group around its symmetry axis/10^{-20} u m^2

$I_\alpha = 3.20^d$

Direction cosine of the methyl group symmetry axis

$\lambda_a = 0.9110(35)$

Barrier to internal rotation of the methyl group/J mol^{-1}

$V_3 = 4235.9(66)$

[a] Uncertainties represent one standard deviation. [b] As defined by Herschbach.[17] [c] Conversion factor 505 379.05 u m^2 MHz. [d] Assumed; see text.

Table 4. Spectroscopic constants[a,b] of the ground vibrational state (A species) of methyl carbamate.

No. of transitions:	92
R.m.s. dev.[c]/MHz:	0.102
A_A/MHz	10719.383 6(92)
B_A/MHz	4399.149 4(32)
C_A/MHz	3182.8696(35)
Δ_J/kHz	0.723(13)
Δ_{JK}/kHz	4.30(11)
Δ_K/kHz	8.806(62)
δ_J/kHz	0.221 9(96)
δ_K/kHz	2.87(18)
$\Phi_J{}^d$/Hz	−0.0845(15)
$I_A + I_B - I_C{}^e$/10^{-20} u m^2	3.246 42(12)

[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] Further sextic centrifugal distortion constants pre-set at zero; see text. [e] Same conversion factor as in Table 1.

intensities are proportional to the square of the dipole moment component.

Interestingly, the rotational constants (Table 3) agree to within better than 1% with those calculated in the MP2 procedure (Table 1). Moreover, λ_a calculated from the MP2 structure in Table 1 is 0.909, close to the experimental value 0.9110(35) given in Table 3. It is assumed that the good agreement seen for the rotational constants as well as for λ_a is not fortuitous, but reflects the fact that MP2/6-311++G** structures in general are quite accurate, as has already been noted.[20]

The barrier of 4235.9(66) J mol^{-1} is compared to the barriers of other substituted methyl formates, e.g. 4769(12) in methyl formate,[21] 5081(371) in methyl acetate,[22] 4447(24) in fluoroformate,[23] 4866(12) in methyl cyanoformate,[24] 5297(126) in methyl propiolate[25] and 5105(126) J mol^{-1} in methyl acrylate.[25] The somewhat smaller barrier seen for the title compound is perhaps a result of π electron delocalisation in the amide moiety.

Dipole moment and planarity of the amide group. A nonplanar conformation of the amide group would produce a component of the dipole moment along the principal inertial c-axis (μ_c) that would be non-zero. The theoretical structures in Table 1 indicate that even a small deviation from planarity produces a significant μ_c for **Syn**. The dipole moment is in fact a rather sensitive test of planarity.

The 15 Stark coefficients shown in Table 5 of A-species transitions with comparatively small quadrupole splittings were used to determine the dipole moment following the standard procedure.[26] Field strengths were typically in the 500–1000 V cm^{-1} range. Quadrupole interaction is small and was not taken into account in the least-squares procedure. Initially, all three principal axes dipole moment components were fitted. However, a small and *imaginary* value was found for μ_c [$(\mu_c)^2 = -0.012$]. This shows that this dipole moment component must be zero

should predict the frequencies of a- and c-type A-species transitions accurately. Such transitions were searched for but not found, presumably because they are very weak. This is evidence that the components of the dipole moment along the a- and c-inertial axes are small, or perhaps zero in the case of μ_c (see below), because the

Table 5. Stark coefficients and dipole moment of methyl carbamate.[a]

Transition[b]	$\lvert M \rvert$	$\Delta v\, E^{-2}/10^{-5}$ MHz V^{-2} cm^2 Obs.	Calc.
$4_{2,2} \leftarrow 4_{1,3}$	4	1.52(2)	1.48
	3	0.488(6)	0.416
$5_{2,3} \leftarrow 5_{1,4}$	5	2.89(3)	2.79
	4	1.84(2)	1.78
	3	1.04(1)	1.00
$8_{3,5} \leftarrow 8_{2,6}$	8	0.990(10)	1.03
	7	0.737(8)	0.772
	6	0.527(5)	0.543
	5	0.340(4)	0.355
$9_{3,6} \leftarrow 9_{2,7}$	9	1.66(1)	1.66
	8	1.30(1)	1.30
	7	0.969(10)	0.987
	6	0.721(8)	0.718
$4_{0,4} \leftarrow 3_{1,3}$	1	0.848(8)	0.841
$4_{3,1} \leftarrow 4_{2,2}$	4	1.21(2)	1.21

Dipole moment[c]/10^{-30} C m

$\mu_a = 0.544(7)$ $\mu_b = 7.653(31)$ $\mu_c = 0.0^d$ $\mu_{tot} = 7.672(31)$

[a]Uncertainties represent one standard deviation. [b]A species. [c]1 debye = $3.335\,64 \times 10^{-30}$ C m. [d]Pre-set at zero; see text.

Table 6. ^{14}N nuclear quadrupole splittings (E_q) of methyl carbamate and diagonal elements of the ^{14}N quadrupole coupling tensor.

Transition[a]	F'	$\leftarrow$	F	E_q/MHz Obs.	Calc.
$5_{1,4} \leftarrow 5_{0,5}$	5	$\leftarrow$	5	-1.67	-1.76
$6_{1,5} \leftarrow 6_{0,6}$	6	$\leftarrow$	6	-1.77	-1.75
$7_{1,6} \leftarrow 7_{0,7}$	7	$\leftarrow$	7	-1.76	-1.65
$2_{2,1} \leftarrow 2_{1,2}$	3	$\leftarrow$	3	0.47	0.47
$3_{2,2} \leftarrow 3_{1,3}$	3	$\leftarrow$	3	-1.42	-1.40
$3_{2,2} \leftarrow 3_{1,3}$	4	$\leftarrow$	4	0.50	0.46
$4_{2,3} \leftarrow 4_{1,4}$	4	$\leftarrow$	4	-1.30	-1.32
$5_{2,4} \leftarrow 5_{1,5}$	5	$\leftarrow$	5	-1.24	-1.27
$6_{2,5} \leftarrow 6_{1,6}$	6	$\leftarrow$	6	-1.29	-1.24
$9_{2,7} \leftarrow 9_{1,8}$	9	$\leftarrow$	9	-1.20	-1.11
$2_{2,0} \leftarrow 1_{1,1}$	3	$\leftarrow$	2	0.29	0.34
$2_{2,0} \leftarrow 1_{1,1}$	2	$\leftarrow$	1	-1.37	-1.44
$3_{1,3} \leftarrow 2_{0,2}$	3	$\leftarrow$	2	0.74	0.84

^{14}N nuclear quadrupole coupling constants[b]/MHz

$\chi_{aa} = 1.52(27)$ $\chi_{bb} = 3.51(20)$

[a]A species. Nuclear quadrupole interaction has been neglected. [b]Uncertainties represent one standard deviation.

or very close to zero. This is a strong indication that the amide group is indeed planar, or very nearly so, and that the molecule has a true symmetry plane (C_s symmetry).

In the final fit μ_c was pre-set at zero yielding the results shown in Table 5. The total dipole moments obtained in the three theoretical computations (Table 1) are all close to the experimental result.

Another evidence that methyl carbamate has a symmetry plane comes from the value of $I_A + I_B - I_C = 3.269\,28(53) \times 10^{-20}$ u m^2 (Table 3). If the contribution from the out-of-plane hydrogen atoms of the methyl group is arbitrarily assumed to be (same units) 3.20, a pseudo-inertial defect of 0.069×10^{-20} u m^2 is obtained. For a completely rigid molecule this value would be exactly zero. The corresponding values are: $-0.006\,510(2)$ for formamide,[27] -0.122 for acetamide,[28] 0.078 for FCH$_2$CONH$_2$,[29] 0.184 for CH$_3$OCH$_2$CONH$_2$,[30] 0.314 for propionamide[31] and 0.156 for acetidinone,[32] all of which are assumed to have planar or very nearly planar, amide groups.

It can be concluded from the preceding that the MP2 structure of Table 1 is likely to be very accurate with the exception of the geometry around the nitrogen atom, which is more shallow than the MP2 computations indicate. This shortcoming of the MP2 procedure in dealing with amide group nitrogen atoms has been discussed before.[33]

^{14}N quadrupole coupling constants. All transitions were split by a small amout by quadrupole interaction. Well resolved quadrupole components were only observed in a few cases. The well-resolved A-species components appearing in Table 6 were used to determine the quadru-

pole coupling constants of the ^{14}N nucleus following the procedure of Ref. 26. The spectroscopic constants in Table 4 were used to predict the 'unperturbed' centre frequencies. The ^{14}N nuclear quadrupole splittings (E_q in Table 6) were found by subtracting the calculated centre frequencies from the frequencies of the resolved quadrupole components. A rigid-rotor Hamiltonian was used in the least squares fitting procedure in order to determine the ^{14}N nuclear quadrupole coupling constants χ_{aa} and χ_{bb}. The results are shown in Table 6.

Conclusions

The **Syn** conformer of methyl carbamate is stabilised by several kJ mol^{-1} relative to any other rotamer. The amide moiety is planar (or very nearly so) and the molecule has C_s symmetry. *Ab initio* calculations at the HF and MP2 levels as well as density theory computations at the B3LYP level fail to predict a planar structure for the amide group. The MP2 and B3LYP methods predict structures that are believed to be accurate with the exception of the hydrogen atoms of the amide group. The calculated total dipole moments at all three levels of theory are close to the experimental one. The barrier to internal rotation methyl group is about 10–20% less than found in other substituted methyl formates.

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