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The structural and conformational properties of 1-amino-1-ethynylcyclopropane as studied by microwave spectroscopy and quantum chemical calculations[☆]

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Abstract

The microwave spectrum of 1-amino-1-ethynylcyclopropane has been investigated in the 19.0–62.0 GHz spectral region at about -30°C . One rotamer denoted Conformer **I** was assigned in this work. Conformer **I** has a symmetry plane (C_s symmetry). Both the hydrogen atoms of the amino group are involved in intramolecular hydrogen bonds with the π -electrons of the triple bond. The dipole moment components and the total dipole moment are (in units of 10^{-30} C m): $\mu_a = 1.353(22)$, $\mu_b = 1.502(9)$, $\mu_c = 0.0$ (for symmetry reasons), and $\mu_{\text{tot}} = 2.022(79)$. Three vibrationally excited states belonging to three different normal modes were assigned and their frequencies determined by relative intensity measurements.

The microwave work has been assisted by quantum chemical computations at the MP2/6-311++G** (frozen core) and B3LYP/6-31G* levels of theory. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Microwave spectroscopy; Structure; Conformation; Dipole moment; Intramolecular hydrogen bonding

1. Introduction

The Oslo laboratory has for a long time been interested in intramolecular hydrogen (H) bonding. Recent examples include 3,3,3-trifluoropropanol [1], dicyclopropyl carbinol [2], 1,2-diphosphinoethane [3], 1,2-ethanedithiol [4], 2-nitroethanol [5] and 1-cyclopropylcyclopropanol [6]. For reviews see Refs. [7,8]. The amino group is the one that often takes part in such bonding. In the majority of cases it acts as a proton

acceptor ('base'). Much fewer examples of the amino group acting as proton donor ('acid') have been reported. However, in recent years the amino group has been found to be proton donor towards a number of acceptors. This has been seen in ethylamines, $\text{H}_2\text{NCH}_2\text{CH}_2\text{X}$, where $\text{X} = \text{F}$ [9], NH_2 [10], $\text{C}\equiv\text{N}$ [11], $\text{C}\equiv\text{CH}$ [12], OCH_3 [13,14] $\text{C}=\text{CH}_2$ [15] as well as in $\text{H}_2\text{NCH}_2\text{CHF}_2$ [16]. Further examples include $\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$ [17], $\text{H}_2\text{NCH}_2\text{C}\equiv\text{N}$ [18–20], $\text{H}_2\text{NCH}_2\text{C}=\text{CH}_2$ [21–24] and aminomethylcyclopropane [25].

1-Amino-1-ethynylcyclopropane (AEC) was chosen for study as an extension of these studies. In this compound there are two possible conformations that may be stabilised by internal H-bonds. These two forms are drawn in Fig. 1. In Conformer **I** both

[☆] Dedicated to Professor Peter Klæboe on the occasion of his 70th birthday.

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Table 1

Structure, rotational constants, dipole moment and energy differences of Conformers **I** and **II** of 1-amino-1-ethynylcyclopropane as calculated at the MP2/6-311++G** (frozen-core) and B3LYP/6-31G* levels of theory. Atom numbering is given in Fig. 1

Conformer ^a	I		II	
	MP2	B3LYP	MP2	B3LYP
<i>Bond distance (pm)</i>				
N1–H1	101.7	102.0	101.7	102.0
C1–N1	144.7	145.2	144.9	145.4
C1–C2	144.8	145.0	144.6	144.7
C2–C3	122.3	121.0	122.1	120.8
C3–H2	106.5	106.7	106.5	106.6
N1–H3	101.7	102.0	101.6	101.8
C1–C4	151.6	152.1	150.9	151.4
C1–C5	151.6	152.1	152.5	153.1
C4–C5	150.9	150.1	151.5	150.8
C4–H4	108.4	108.6	108.4	108.5
C4–H5	108.4	108.5	108.6	108.8
C5–H6	108.4	108.6	108.5	108.8
C5–H7	108.4	108.5	108.4	108.6
<i>Angle (°)</i>				
H1–N1–C1	109.6	109.5	109.9	109.4
N1–C1–C2	118.2	117.9	113.6	113.2
N1–C1–C3	118.2	117.9	114.2	113.2
N1–C1–H2	118.2	117.9	114.1	113.1
H3–N1–C1	109.6	109.5	110.2	109.6
N1–C1–C4	115.1	115.1	117.3	117.5
N1–C1–C5	115.1	115.1	121.3	121.6
C1–C4–H4	115.3	115.4	117.6	117.8
C1–C4–H5	117.2	117.5	116.3	116.5
C1–C5–H6	115.3	115.4	116.0	116.4
C1–C5–H7	117.2	117.5	118.1	118.5
<i>Dihedral angle^b (°)</i>				
H1–N1–C1–C2	58.6	58.0	–69.7	–68.3
H1–N1–C1–C3	58.5	57.4	–69.1	–67.5
H1–N1–C1–H2	58.5	57.3	–69.1	–67.5
H3–N1–C1–C2	–58.7	–58.0	172.1	175.0
H1–N1–C1–C4	–88.1	–89.0	147.4	148.5
H1–N1–C1–C5	–154.8	–155.0	77.6	79.2
N1–C1–C4–H4	2.7	3.6	139.5	138.7
N1–C1–C4–H5	146.3	145.8	–3.6	–2.9
N1–C1–C5–H6	–2.7	–3.6	–2.4	–3.1
N1–C1–C5–H7	–146.3	–145.8	–146.8	–146.4
<i>Rotational constants (MHz)</i>				
<i>A</i>	5908.1	5893.2	5883.8	5862.2
<i>B</i>	3048.5	3047.9	3070.8	3071.9
<i>C</i>	2423.4	2418.6	2423.3	2418.0
$(I_a + I_b - I_c)^c (10^{-20} \text{ m}^2 \text{ u})$	42.78	42.62	42.35	41.72
<i>Dipole moment components and total dipole moment (10^{–30} C m)</i>				
μ_a	1.73	1.80	4.80	4.35
μ_b	0.30	0.75	2.07	1.43
μ_c	0.00	0.0	3.60	3.68
μ_{tot}	1.77	1.95	6.33	5.87

Table 1 (continued)

Conformer ^a	I		II	
	MP2	B3LYP	MP2	B3LYP
Energy difference ^d (kJ mol ⁻¹)	0.0	0.0	16.0	17.9

^a Conformer **I** has C_s symmetry (see text).

^b Measured from syn = 0°. Clockwise rotation corresponds to positive dihedral angle.

^c Principal moments of inertia. Conversion factor 505379.05 × 10⁻²⁰ m² u MHz.

^d Relative to Conformer **I**. Total energy of **I** obtained in the MP2 computations: -652991.34 kJ mol⁻¹. Total energy of **I** obtained in the B3LYP computations: -654753.69 kJ mol⁻¹.

hydrogen atoms are involved in H-bonding with the π -electrons of the triple bond of the ethynyl group. This conformer has a symmetry plane (C_s symmetry) formed by the ethynyl group and the C1N1 bond.

The amino group has been rotated 120° in Conformer **II** from the position it had in **I**. Only one of the H atoms of the amino group can participate in intramolecular H-bonding with the π -electrons in this case.

Two compounds related to AEC have recently been studied by microwave (MW) spectroscopy. A rotamer whose conformation of the amino group corresponds to that of **I**, is the only conformation assigned for both for H₂NCH₂C≡CH [17] and for H₂NCH₂C≡N [18–20]. Moreover, the conformation of the amino group in aminocyclopropane [26] and in

tricyclopropylamine [27] is similar to that shown for Conformer **I**. It was therefore conjectured that **I** would be the preferred form.

H-bonding is of course not the only effect that may be of importance for the conformational preferences of AEC. Other effects such as repulsion between the dipoles of the amino group and the C≡CH group, as well as interactions between the electrons of the cyclopropyl ring and the amino group [26] are likely to play a role.

No experimental studies of the conformational properties of the title compound have been reported. MW spectroscopy is ideal for investigating conformational equilibria in which polar conformers are present because of its high selectivity and specificity. Rotamers **I** and **II** would each possess a dipole moment

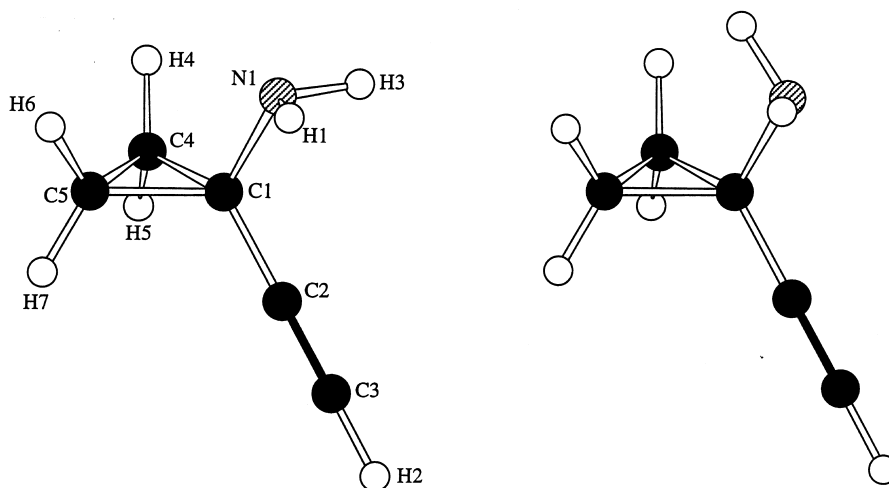


Fig. 1. Conformers **I** and **II** of 1-amino-1-ethynylcyclopropane. Atom numbering is shown on Conformer **I**, which was assigned in this work. This rotamer was calculated by the MP2/6-311++G** procedure to be 16.0 kJ mol⁻¹ more stable than **II**.

Table 2

Selected transitions of the MW spectrum of the ground vibrational state of Conformer **I** of 1-amino-1-ethynylcyclopropane

Transition $J'_{K'-1,K'+1} \leftarrow J''_{K''-1,K''+1}$	Observed frequency ^a (MHz)	Obs. – calc. frequency (MHz)
4 _{0,4} \leftarrow 3 _{0,3}	21164.16	0.00
4 _{2,2} \leftarrow 3 _{2,1}	22781.21	0.16
5 _{1,5} \leftarrow 4 _{1,4}	25591.12	–0.08
5 _{3,2} \leftarrow 4 _{3,1}	27936.89	0.14
6 _{0,6} \leftarrow 5 _{0,5}	30843.10	–0.11
6 _{2,5} \leftarrow 5 _{2,4}	32593.15	–0.08
7 _{1,6} \leftarrow 6 _{1,5}	39016.63	–0.07
7 _{5,2} \leftarrow 7 _{4,3}	27903.61	0.13
8 _{2,6} \leftarrow 7 _{2,5}	46264.43	0.03
8 _{3,6} \leftarrow 8 _{2,7}	19720.17	0.07
8 _{4,5} \leftarrow 8 _{3,6}	22265.63	0.06
9 _{1,9} \leftarrow 8 _{1,8}	45276.31	0.04
9 _{5,5} \leftarrow 9 _{4,6}	27787.49	0.14
10 _{1,9} \leftarrow 9 _{1,8}	53423.28	–0.06
10 _{5,5} \leftarrow 10 _{4,6}	26185.71	–0.04
10 _{6,5} \leftarrow 9 _{6,4}	55640.38	–0.08
11 _{6,6} \leftarrow 10 _{6,5}	61309.91	0.05
12 _{5,8} \leftarrow 12 _{4,9}	28120.13	–0.02
14 _{5,10} \leftarrow 14 _{4,11}	29571.70	0.10
16 _{4,13} \leftarrow 16 _{3,14}	35372.91	–0.10
17 _{6,11} \leftarrow 17 _{5,12}	24946.89	0.05
19 _{6,13} \leftarrow 19 _{5,14}	22778.29	–0.04
20 _{7,14} \leftarrow 20 _{6,15}	39191.11	–0.01
22 _{8,14} \leftarrow 22 _{7,15}	37744.32	–0.13
25 _{8,17} \leftarrow 25 _{7,18}	30756.80	0.00
28 _{8,20} \leftarrow 28 _{7,21}	31278.78	–0.08
31 _{9,22} \leftarrow 31 _{9,22}	33587.68	0.15
34 _{10,34} \leftarrow 34 _{9,25}	36269.95	–0.08

^a ± 0.10 MHz.

which is a prerequisite for a MW spectrum. All this makes AEC well suited for a MW conformational investigation.

Advanced quantum chemical computations are often found to be useful in predicting rotational constants, dipole moments and energy differences for the various conformers that are sufficiently close to the experimental ones to be really helpful starting points in the spectral analysis. In addition, they may give important information about rotamers that for whatever reason have not been assigned by MW spectroscopy. Such calculations are therefore of interest in their own right as well.

2. Experimental

The sample used in this work was synthesised and

purified as described in Ref. [28]¹. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. [29]. Most measurements were made in the 20–40 GHz spectral region. Selected parts of the 40–62 GHz region were also investigated. The X-band brass Stark absorption cell was cooled to about –45°C during the experiments. Radiofrequency microwave double resonance experiments

¹ 1-Amino-1-ethynylcyclopropane (AEC) was prepared in five steps starting from [(trimethylsilyl)ethynyl]cyclopropane by a sequence of deprotonation at the propargylic position, carboxylation, protidesilylation, Curtius degradation to the *Boc*-protected amine, and finally deprotection of the amino group. The overall yield was 71%. Spectral data: ¹H NMR (250 MHz, CDCl₃): δ = 0.83–0.90[m, 2 H, 2(3)-H], 0.91–0.98[m, 2 H, 2(3)-H], 1.85–2.01(bs, 2 H, NH₂), 2.17(s, 1 H, 2'-H). ¹³C NMR (62.9 MHz, CDCl₃): δ = 17.88(C-1), 24.08[C-2(3)], 66.49(C-2'), 89.37(C-1'). The detailed procedure will be published separately.

Table 3

Spectroscopic constants (A -reduction, I' -representation [37]; uncertainties represent one standard deviation) of the ground and vibrationally excited states of Conformer **I** of 1-amino-1-ethynylcyclopropane

Vibrational state	Ground vibrational state	First ex. lowest bending vibration	First ex. second lowest bending vibration	1st ex. C–N torsional vib.
No. of transitions	148	93	42	27
RMS dev. ^a (MHz)	0.086	0.081	0.073	0.073
A_v (MHz)	5905.554 5(40)	5858.726 9(52)	5965.21(14)	5904.401(11)
B_v (MHz)	3068.881 9(19)	3077.389 1(21)	3071.042 9(51)	3069.934 8(56)
C_v (MHz)	2433.709 4(19)	2435.156 1(22)	2436.163 1(51)	2433.072 7(62)
Δ_J (kHz)	0.434(12)	0.462(13)	0.464(18)	0.478(23)
Δ_{JK} (kHz)	4.657(20)	4.392(31)	4.576(38)	4.498(41)
Δ_K (kHz)	–2.021(82)	–5.816(93)	–2.021 ^b	–2.021 ^b
δ_J (kHz)	0.090 9(14)	0.094 2(26)	0.090 9 ^b	0.090 9 ^b
δ_K (kHz)	2.244(26)	2.237(43)	2.244 ^b	2.244 ^b
$(I_a + I_b - I_c)^c$ (10^{-20} m ² u)	42.597 53(11)	42.949 66(18)	41.835 1(25)	42.503 4(21)

^a Root-mean-square deviation.

^b Kept constant at this value in the least-squares fit.

^c Principal axis moments of inertia. Conversion factor: 505379.05 m² u MHz.

(RFMWDR) were carried out as described in Ref. [30] using the equipment mentioned in Ref. [15]. The spectra were recorded at a pressure of a few Pascal and stored electronically using the computer programs written by Waal [31]. The accuracy of the frequency measurements is presumed to be better than ± 0.10 MHz, and the resolution was approximately 0.5 MHz.

3. Results and discussion

3.1. Quantum chemical calculations

The GAUSSIAN 94 program package [32] running on the IBM RS6000 cluster in Oslo was employed in all the quantum chemical calculations. The 6-31G* and 6-311++G** basis sets provided with the program [32] were employed. Two different computational schemes, the MP2/6-311++G** and B3LYP/6-31G*, were utilised, because we wanted to compare the results obtained in these two different ways.

In the first of these computational schemes, electron correlation was included using the second order Møller–Plesset (MP2) perturbation theory [33] with frozen-core electrons [32]. In the second procedure, density functional theory (DFT) calculations were carried out employing the B3LYP procedure [34].

Full geometry optimisation was made in the MP2 as well as in the B3LYP computations. A number of different starting conformations of the amino group was chosen. However, these geometries always refined to either Conformer **I** or to Conformer **II** (Fig. 1) depending on the starting geometry. These two rotamers are assumed to be minima ('stable') on the potential energy hypersurface, as no imaginary vibrational frequencies [35] were computed for any of them in both the MP2 and in the B3LYP calculations. The existence of further stable rotamers is therefore considered to be unlikely.

The geometries calculated for **I** and **II** are given in Table 1 together with some other parameters of interest. Atom numbering is given in Fig. 1.

Some of these computational results deserve comments. Both the MP2 and B3LYP methods yield very similar geometries which appear to have 'normal' bond lengths, bond angles and dihedral angles. Both methods predict relatively large energy differences (16.0 and 17.9 kJ mol^{–1}, respectively) between the two conformers, with Conformer **I** as the clearly preferred form. The dipole moments computed for each conformer are also calculated in the two procedures to be rather similar, as seen in Table 1.

The distances between the H1 (and H3) atoms and the C2 atom in **I** is calculated to be 272 pm in the MP2

Table 4

Stark coefficients (uncertainties represent one standard deviation) and dipole moment (1 Debye = 3.33564×10^{-30} C m) of Conformer **I** of 1-amino-1-ethynylcyclopropane

Transition	$ M $	$\Delta\nu E^{-2}$ (10^{-6} MHz V $^{-2}$ cm 2)	
		Obs.	Calc.
$5_{2,3} \leftarrow 4_{2,2}$	1	−0.249(4)	−0.252
	2	−0.91(2)	−1.04
	3	−2.19(3)	−2.35
$5_{2,4} \leftarrow 4_{2,3}$	1	0.256(4)	0.234
	2	0.98(2)	0.936
	3	2.15(3)	2.11
$6_{2,4} \leftarrow 5_{2,3}$	2	−0.287(4)	−0.276
	3	−0.623(8)	−0.616
Dipole moment (10^{-30} C m)			
$\mu_a = 1.353(22)$	$\mu_b = 1.502(90)$	$\mu_c = 0.0^a$	$\mu_{\text{tot}} = 2.022(79)$

^a For symmetry reasons; see text.

procedure. The sum of the van der Waals distances for hydrogen (120 pm [36]) and aromatic carbon (170 pm [36]) is slightly larger (290 pm). This indicates that intramolecular H-bonding is rather marginal in Conformer **I**.

3.2. MW spectrum and assignment of the ground vibrational state of Conformer **I**

The quantum chemical computations (Table 1) indicate that there is a comparatively large energy difference between **I** and **II**. The former is predicted to have a small dipole moment, whereas the latter was predicted to have a considerably larger dipole moment. The relatively weak spectrum which was observed, is compatible with that predicted for Conformer **I**.

This conformer is computed (Table 1) to have its largest dipole moment component along the *a*-inertial axis. Searches were therefore first made for the strong ^aR-branch transitions using the rotational constants obtained in the MP2 computations as the starting point because it is our experience [1] that this computational scheme produces accurate rotational constants (and structures). These R-branch transitions were soon identified close to their predicted frequencies. Stark effect studies as well as RFMWDR experiments [30] were carried out to confirm the assignments.

A preliminary set of rotational constants were

obtained from the ^aR-transitions and used to predict medium- and high-*J* ^bQ-branch lines which are the strongest b-type transitions. These lines were readily found. Attempts to assign high-*J* ^bR-lines were unsuccessful, presumably because they are too weak. A few selected transitions are listed in Table 2².

A total of about 160 transitions were ultimately assigned for the ground vibrational state; 148 of which were used to determine the spectroscopic constants (*A*-reduction, *I*^r representation [37]) shown in Table 3. Maximum value of *J* was 34. Only quartic centrifugal distortion constants were employed in the least-squares fit. Inclusion of sextic constants yielded no significant improvement of the fit and insignificant sextic constants.

The nitrogen nucleus is known to produce a quadrupole fine structure. These splittings are much larger for the perpendicular transitions, (the ^bQ-branch lines) than for the parallel transitions (the ^aR-branch transitions). However, no well-resolved splittings were observed in the present case. It was therefore not possible to determine the nuclear quadrupole coupling constants of AEC.

² The full spectra are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Room B208, Gaithersburg, MD 20899, USA, where they have been deposited.

3.3. Vibrationally excited states

The ground state transitions were accompanied by series of transitions presumably belonging to vibrationally excited states of Conformer **I**. Three excited states belonging to three different normal vibrational modes were assigned in the same manner as described for the ground vibrational state lines. The RFMWDR method [30] proved very useful in this respect. The spectroscopic constants obtained for these three excited states are listed in Table 3.

The most intense excited state (Table 3) has about 37% of the intensity of the ground vibrational state at 228 K. Its frequency was determined to be $157(20) \text{ cm}^{-1}$ by relative intensity measurements made largely as described in Ref. [38]. This should be compared to 176 cm^{-1} found in the B3LYP calculations (not given in Table 1) for the lowest bending mode of the acetylenic group.

The first excited state of another fundamental (Table 3) was found to have about 32% of the intensity of the ground vibrational state. A frequency of $178(25) \text{ cm}^{-1}$ was determined by relative intensity measurements [38]. This mode is assumed to be the second lowest bending vibration for the acetylenic group. The B3LYP value for this fundamental was 204 cm^{-1} .

The first excited state of the torsional vibration of the amino group was also assigned and a frequency of $290(30) \text{ cm}^{-1}$ determined by relative intensity measurements compared to 291 cm^{-1} found in the B3LYP calculations.

The fourth lowest fundamental vibration was calculated to have a B3LYP frequency of 373 cm^{-1} . This corresponds to a Boltzmann factor of 0.09 at 228 K. This small value can presumably explain why this weak excited state was not found.

3.4. Dipole moment

The dipole moment was determined in the standard way [16] employing Stark voltages in the 1000–2000 V cm^{-1} range. The results are shown in Table 4.

The MP2 value (Table 1) for μ_a and μ_b were (in units of 10^{-30} C m) 1.73 and 0.30, respectively. The corresponding B3LYP values were (same units) 1.80 and 0.75, respectively. Comparison with the results in Table 4 reveals that the B3LYP predictions are closer

to the experimental values than the MP2 calculations are.

AEC differs from $\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$ in that the two hydrogen atoms in the methylene group in the latter compound are replaced with two methylene groups bonded to each other. The total dipole moment of $\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$ is $2.454(8) \times 10^{-30} \text{ C m}$ [17], somewhat larger than 2.022 (79) (same units) seen for the title compound (Table 4).

All the calculated rotational constants (Table 1) of **I** and **II** are rather similar and close to the experimental rotational constants (Table 3). A discrimination between **I** and **II** cannot therefore be made solely on the basis of the rotational constants. Additional evidence is needed. The dipole moment is predicted (Table 1) to be very different in the two cases. The experimental dipole moment is close to that predicted for **I**, and make us conclude beyond doubt that Conformer **I** has indeed been assigned and not confused with **II**.

3.5. Searches for Conformer **II**

This rotamer is predicted to be less stable, by as much as 16.0 kJ mol^{-1} , than **I** in the MP2 computations above (Table 1). The rotational constants of **I** and **II** are very similar. However, **II** should have a considerably larger dipole moment than **I**, resulting in a much stronger spectrum provided it was present in large amounts. All the strongest lines of the spectrum could be assigned to Conformer **I**. Attempts to find **II** were unsuccessful. The starting points in these searches were the MP2 rotational constants and the B3LYP dipole moment components given in Table 1.

Model calculations of the intensities of the transitions of the hypothetical Conformer **II** makes it possible to estimate a minimum energy difference between Conformers **I** and **II**. These calculations indicate that the transitions of **II** should have been readily observable provided the energy difference were less than 4 kJ mol^{-1} . This value is consistent with the MP2 predictions (16.0 kJ mol^{-1}).

3.6. Structure

The observed (Table 3) and the calculated (Table 1) rotational constants of Conformer **I** agree within 1% in the case of the MP2 as well as in the case of the B3LYP calculations. There is also good agreement for

the values of $I_a + I_b - I_c$. It is believed that this agreement is not fortuitous, but in fact reflects that both the elaborate MP2 and as well as the much less expensive B3LYP structures are rather accurate in this case. The MP2 structure (Table 1) is therefore suggested as a *plausible* structure for Conformer **I**. It is expected that any full experimental structure that is determined in the future will be very close to the MP2 structure.

4. Conclusions

This study has demonstrated that gaseous 1-amino-1-ethynylcyclopropane consists nearly exclusively of Conformer **I**, which is at least 4 kJ mol⁻¹ more stable than **II**. This rotamer is stabilised by a weak internal H-bond formed between the H atoms of the amino group and the π -electrons of the triple bond. Other effects such as dipole–dipole repulsion between the lone pair of the amino group and the dipole of the acetylenic group, as well as interaction between the lone pair of the amino group and the electrons of the cyclopropyl ring may produce additional stability of Conformer **I** as compared to **II**. These effects are likely to be more important than H-bonding.

Accurate predictions of the structure is found in the expensive MP2/6-311++G** calculations as well as in the much less demanding B3LYP/6-31G* computations.

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