

Microwave Spectrum of 2-Aminooxazole, a Compound of Potential Prebiotic and Astrochemical Interest

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The microwave spectrum in the 26.6–80 GHz spectral range of 2-aminooxazole, which may have played a potential role in the prebiotic generation of pyrimidine ribonucleotides, is reported. A large number of transitions have been assigned, and accurate values of the rotational and quartic centrifugal distortion constants have been obtained for the four lowest vibrational states. The frequencies of the vibrationally excited states have been determined by relative intensity measurements. The microwave spectra should be useful for the identification of this compound in planetary atmospheres or in interstellar space. 2-Aminooxazole is nonplanar with the amino group bent $35(5)^\circ$ out of the oxazole plane. Inversion of the amino group manifests itself in a characteristic doubling of the microwave transitions and the absence of c-type transitions. The microwave work has been augmented by quantum chemical calculations at the MP2/aug-cc-pVTZ and B3LYP/6-311++G(3df,3pd) levels of theory. The spectroscopic constants obtained by these two methods are in good agreement with one another, as well as with their experimental counterparts. The B3LYP method predicts a more accurate value for the angle between the oxazole ring and the plane formed by the amino group than the MP2 procedure.

Introduction

RNA is assumed to have played a prominent role in the early development of life.^{1,2} Researchers have for several decades tried unsuccessfully to find plausible synthetic routes starting with known prebiotic molecules to form the ribonucleotides that are the constituents of RNA.^{1–3} However, very recently Sutherland and co-workers³ have found a possible way (Figure 1) for the spontaneous formation of the pyrimidine (cytosine and uracil) ribonucleotides from cyanamide, cyanoacetylene, glycolaldehyde, glyceraldehyde, and inorganic phosphate, all of which are plausible prebiotic feedstock compounds.^{4–6} Inorganic phosphate, which is first incorporated into the nucleotides at a late stage of the reaction, plays a remarkable role in this reaction sequence acting as acid/base catalyst, a nucleophile catalyst, a pH buffer, and a chemical buffer.³ Side reactions to the sequence of Figure 1 occur, producing “incorrect” nucleotides, but amazingly, exposure to ultraviolet light, which was prominent on early Earth, destroys the “incorrect” nucleotides leaving behind the “correct” cytosine and uracil nucleotides.^{1–3}

The title compound, 2-aminooxazole (**4**), is formed in the first step of this reaction sequence (Figure 1) as a condensation product of glycolaldehyde (**6**) and cyanamide (**5**). One goal of the theories of prebiotic chemistry has been to identify geochemically plausible ways of purifying and concentrating key intermediate such as 2-aminooxazole. It has been pointed out^{1–3} that the relatively high volatility of 2-aminooxazole suggests that it could be purified by sublimation, as it undergoes cycles of gentle warming from the sun and cooling at night (or higher altitudes) and subsequent condensation. The compound would thus behave as a kind of organic snow, which could accumulate as a reservoir for the next step in the RNA synthesis.²

The obvious interest of 2-aminooxazole for prebiotic chemistry was one motivation to perform the present microwave (MW) investigation. This powerful method has been used not only to study physical properties of molecules such as geometrical structures, barriers to internal rotation, conformational compositions, dipole moments, etc. but also to successfully identify the majority of the compounds found in interstellar space, as well as constituents of planetary atmospheres.⁷ For example, three of the feedstock compounds, namely, cyanamide,⁸ cyanoacetylene⁹ and glycolaldehyde¹⁰ are interstellar molecules identified by their microwave (MW) spectra,^{11–13} which is a direct proof of their prebiotic and universal existence. The MW spectrum of glyceraldehyde is known,¹⁴ but this compound has so far not been detected in interstellar space. It is hoped that the MW spectrum of 2-aminooxazole would be of use for the identification of this compound wherever it may exist in the Universe.

2-Aminooxazole consists of an amino group attached to the five-membered oxazole ring, which is aromatic. An X-ray investigation has shown that this compound is indeed completely planar in the crystalline state,¹⁵ which allows for maximum overlap of the lone electron pair of the amino group with the π -electron system of the aromatic oxazole ring.

No MW studies of gaseous five-membered aromatic compounds containing amino groups attached to the ring appear to have been reported previously, so it not known which conformation(s) they prefer. However, more information is available for aromatic compounds having six atoms in the ring. Microwave studies of aniline ($C_6H_5NH_2$),^{16–20} *ortho*-²¹ and *meta*-fluoroaniline ($FC_6H_4NH_2$),²² *meta*-²³ and *para*-chloroaniline²⁴ ($ClC_6H_4NH_2$), and 2-amino-,^{25,26} 3-amino-,²⁷ and 4-aminopyridine ($H_2NC_5H_4N$)²⁷ have shown that the amino group is not coplanar with the benzene or aniline rings in any of these cases. Typically, the planes of the aromatic moiety and the amino group form an angle of 35 – 40° from coplanarity allowing for

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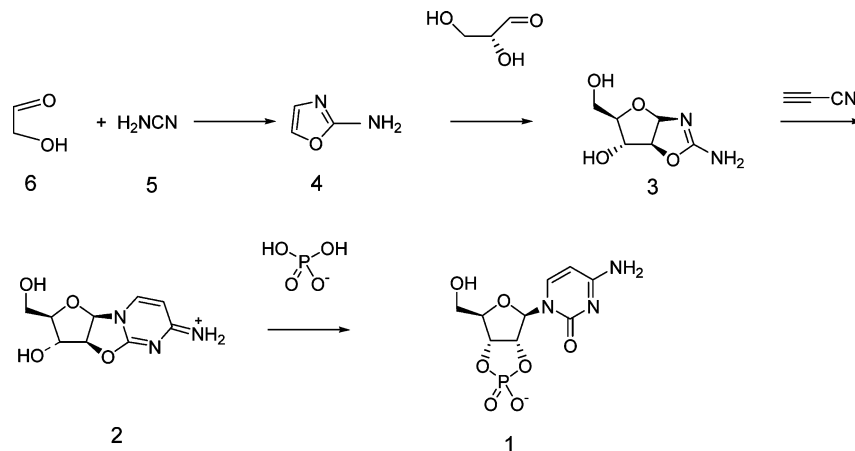


Figure 1. Synthetic route leading to the production of the pyrimidine ribonucleotides (1), which are parts of RNA. The starting materials of this synthesis, cyanamide (5), cyanoacetylene, glycolaldehyde (6), glyceraldehyde, and inorganic phosphate are plausible prebiotic feedstock molecules and the condition of the synthesis is consistent with potential early-Earth geochemical models. The microwave spectrum of 4 is reported in this Article. It is hoped that this spectrum would be useful for the detection of 4 anywhere in the universe.

reduced electron conjugation of the lone electron pair of the nitrogen atom of the amino group with the π -electron system of the aromatic ring. Nonplanarity is found for amides too, with the exception of formamide (HCONH₂), which is planar.²⁸ Another example is vinylamine (H₂C=CHNH₂), which is also not planar.²⁹

An interesting spectroscopic feature observed for the six-membered aromatic amines as well as for vinylamine is a characteristic doubling of the vibrational levels associated with a symmetrical double-minimum potential function for the inversion of the amino group.

The questions we wanted to answer are the following: Does 2-aminooxazole resemble the six-membered aromatic molecules in preferring a nonplanar form in the free state, or does it prefer a planar form, just as it does in the crystalline state? If a nonplanar form is preferred, will a double-minimum potential for the inversion of the amino group manifest itself in the MW spectrum?

MW spectroscopy is very sensitive even to slight deviations from planarity. Moreover, the existence of a double-minimum potential for inversion results in a striking feature in the MW spectrum. MW spectroscopy is therefore the method of choice for the study of nonplanarity and associated inversion phenomena.

The present MW work has been assisted by high-level quantum chemical calculations, which were conducted with the purpose of obtaining information for use in assigning the MW spectrum and investigating properties of the potential-energy hypersurface.

Experimental Section

Compound. 2-Aminooxazole, specified to be at least 97% pure, was purchased from Manchester Organics Ltd. and used as received. No impurities were seen in the MW spectrum. 2-Aminooxazole, which is a solid at room temperature, has a sublimation pressure of roughly 20 Pa at 22 °C.

Microwave Experiment. The spectrum of 2-aminooxazole was studied in the 26.6–80 GHz frequency interval by Stark-modulation spectroscopy using the microwave spectrometer of the University of Oslo. Details of the construction and operation of this device have been given elsewhere.^{30,31} This spectrometer has a resolution of about 0.5 MHz and measures the frequency of isolated transitions with an estimated accuracy of ≈ 0.10 MHz. The experiments were performed at room temperature at a pressure of roughly 10 Pa.

Quantum Chemical Methods. The present ab initio and density functional theory (DFT) calculations were performed employing the Gaussian03 suite of programs,³² running on the Titan cluster in Oslo. Electron correlation was taken into consideration in the ab initio calculations using Møller–Plesset second-order perturbation calculations (MP2).³³ Becke’s three-parameter hybrid functional³⁴ employing the Lee, Yang, and Parr correlation functional (B3LYP)³⁵ was employed in the density functional theory (DFT) calculations. Peterson and Dunning’s³⁶ correlation-consistent triple- ζ wave function augmented with diffuse functions, aug-cc-pVTZ, was used in the MP2, whereas the 6-311++G(3df,3pd) wave function was employed in the B3LYP calculations. The default convergence criteria of Gaussian03 were used in the calculations.

The MP2/aug-cc-pVTZ calculations were performed because it has been pointed out that MP2 calculations with large basis sets predict accurate geometrical structures.³⁷ The B3LYP/6-311++G(3df,3pd) calculations were undertaken because they generally predict molecular parameters of interest accurately and are much less costly than the MP2 calculations. It is also of interest to compare the results of the two methods with one another and with the corresponding experimental results.

Results and Discussion

Quantum Chemical Calculations. A model of 2-aminooxazole with atom numbering is depicted in Figure 2. Rotation about the C1–N8 bond may produce rotational isomerism. A B3LYP/6-311++G(3df,3pd) scan about this bond was performed by stepping the dihedral O6–C1–N8–H9 angle in intervals of several degrees allowing the remaining structural parameters to vary freely. One minimum was located in these calculations. The O6–C1–N8–H9 and O6–C1–N8–H10 dihedral angles being approximately 30 and 165°, respectively, in this form, which is denoted **I** in Figure 2.

MP2/aug-cc-pVTZ and B3LYP/6-311++G(3df,3pd) calculations of the structures, dipole moments, and quartic centrifugal distortion constants of this conformer were then performed for **I**. All the harmonic vibrational frequencies calculated by these two methods were positive, which indicates that this conformer represents a minimum (“stable” conformer) on the energy hypersurface. B3LYP calculations of the electric field gradient were also made for the N7 and N8 atoms and used to calculate the principal axes quadrupole coupling constants employing Bailey’s program.³⁸

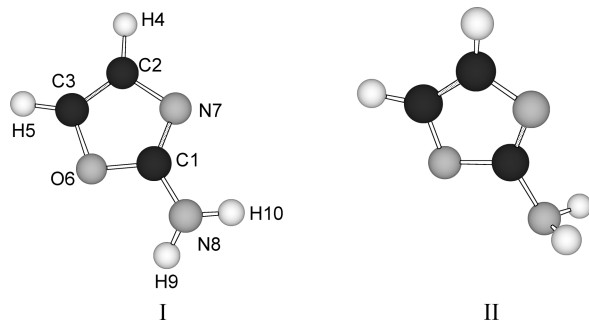


Figure 2. Sketches of the minimum-energy conformer (I) and the nonplanar transition state (II).

TABLE 1: MP2/aug-cc-pVTZ, B3LYP/6-311++G(3df,3pd), X-ray Structure Data for 2-Aminooxazole and Substitution Structure Data for Oxazole

	MP2 ^a	B3LYP ^b	X-ray ¹⁵	oxazole ^{c,39}
Bond Distance (pm)				
C1–O6	135.3	135.1	135.6(3)	135.7(2)
C1–N7	130.0	129.4	129.4(3)	129.2(2)
C1–N8	137.4	136.7	134.3(4)	
C2–C3	135.4	134.5	131.0(4)	135.3(2)
C2–H4	107.5	107.6	107.5(2)	
C2–N7	139.3	139.2	141.0(4)	139.5(2)
C3–H5	107.3	107.3	107.3(2)	
C3–O6	137.9	138.6	139.9(4)	136.9(2)
N8–H9	100.8	100.7		
N8–H10	100.8	100.7		
Angle (deg)				
O6–C1–N7	115.3	114.9	114.6(2)	115.0(1)
O6–C1–N8	116.4	116.9		
N7–C1–N8	128.2	128.1		
C3–C2–H4	128.5	128.6	129.5(1)	
C3–C2–N7	109.6	109.8	110.7(2)	109.1(1)
H4–C2–N7	121.8	121.6		121.8(1)
C2–C3–H5	135.7	135.9		135.0(1)
C2–C3–O6	107.7	107.4	107.5(2)	108.1(1)
H5–C3–O6	116.6	116.7		116.9(1)
C1–O6–C3	103.9	104.1	103.9(2)	103.9(1)
C1–N7–C2	103.5	103.8	103.2(2)	103.9(1)
C1–N8–H9	114.1	115.9	116(2)	
C1–N8–H10	112.1	114.0	122(1)	
H9–N8–H10	113.0	114.7		
Dihedral Angle (deg)				
N7–C1–O6–C3	0.0	–0.1		
N8–C1–O6–C3	176.4	177.0		
O6–C1–N7–C2	0.2	0.3		
N8–C1–N7–C2	–175.6	–176.5		
O6–C1–N8–H9	34.0	28.3		
O6–C1–N8–H10	164.1	164.8		
N7–C1–N8–H9	–150.2	–155.1		
N7–C1–N8–H10	–20.1	–18.6		
H4–C2–C3–H5	0.4	0.2		
H4–C2–C3–O6	180.0	180.0		
N7–C2–C3–H5	–179.2	–179.5		
N7–C2–C3–O6	0.4	0.3		
C3–C2–N7–C1	–0.3	–0.3		
H4–C2–N7–C1	180.0	180.0		
C2–C3–O6–C1	–0.2	–0.1		
H5–C3–O6–C1	179.4	179.7		

^a MP2 electronic energy corrected for zero-point vibrational effects: –789 858.80 kJ/mol. ^b B3LYP electronic energy corrected for zero-point vibrational effects: –791 521.92 kJ/mol. ^c Corresponding substitution bond lengths and angles in oxazole.³⁹

The theoretical structures are listed in Table 1 together with the X-ray structure of Albinati et al.¹⁵ An accurate substitution structure has been derived for oxazole by Kumar et al.³⁹ and structural parameters of oxazole of relevance for the closely related 2-aminooxazole have also been included in the same table.

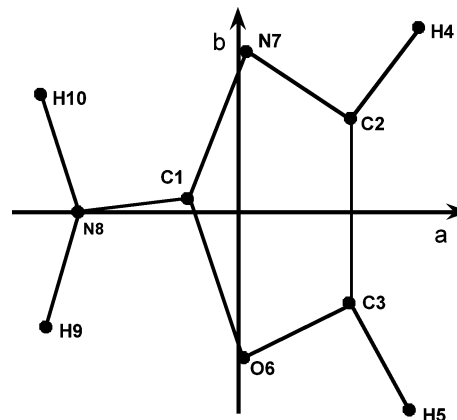


Figure 3. Projection of 2-aminooxazole in the *a*–*b* principal inertial axis plane.

TABLE 2: Theoretical Spectroscopic Constants and Dipole Moments of 2-Aminooxazole

	MP2	B3LYP
Rotational Constants (MHz)		
<i>A</i>	9321.5	9424.1
<i>B</i>	3918.6	3913.9
<i>C</i>	2766.8	2771.2
Moments of Inertia ^a and Inertial Defect ^b (10 ^{–20} u m ²)		
<i>I_a</i>	54.22	53.63
<i>I_b</i>	128.97	129.12
<i>I_c</i>	182.66	182.37
Δ	–0.53	–0.38
Quartic Centrifugal Distortion Constants (kHz)		
Δ_J	0.287	0.285
Δ_{JK}	1.23	1.18
Δ_K	1.69	1.75
δ_J	0.0831	0.0822
δ_K	1.06	1.05
Dipole Moment ^c (10 ^{–30} C m)		
μ_a	2.38	2.96
μ_b	4.22	4.44
μ_c	3.71	3.05

^a Conversion factor: 505 379.05 × 10^{–20} MHz u m². ^b Inertial defect: $\Delta = I_c - I_a - I_b$. ^c 1 D = 3.33564 × 10^{–30} C m.

A projection of the title compound in the *a*–*b* principal inertial axis plane is depicted in Figure 3. Selected parameters of interest for the MW study are displayed in Table 2. The principal-axis dipole moment components in this table have been obtained from the Gaussian03 standard orientation dipole moments, using Bailey's program.³⁸

Calculations of the anharmonic frequencies and the vibrational–rotational interaction constants (the α 's) are costly and this was undertaken only using the B3LYP/6-311++G(3df,3pd) procedure. The harmonic and anharmonic fundamental frequencies are listed in Table 1S (Supporting Information), and the vibration–rotation interaction constants are listed in Table 2S in the Supporting Information.

The lowest normal mode, which is calculated to have an anharmonic frequency of 273 cm^{–1} (Table 1S, Supporting Information), can best be described as an inversion vibration of the amino group. Inversion of the amino group would be expected to have its energy maximum at the planar conformation of the molecule. The transition-state option of Gaussian03 was used to calculate the MP2 and B3LYP structures and vibrational frequencies of this transition state (ts), which turned out to be planar in both procedures, as expected. Only one vibrational

frequency, associated with the inversion motion, was found to be imaginary in each case, which is characteristic for a first-order transition state. The B3LYP and MP2 structures of this ts are listed in Table 3S in the Supporting Information. The energy differences between this ts and conformer **I** were calculated to be 5.13 kJ/mol (MP2) and 2.96 kJ/mol (B3LYP).

The second lowest fundamental frequency of 301 cm^{-1} (Table 1S, Supporting Information) represents the torsion about the C1–N8 bond. The scanning about the C1–N8 bond described above revealed the existence of another maximum of the potential energy hypersurface. The MP2 and B3LYP structures of this transition state (ts) were optimized with the results shown in Table 4S in the Supporting Information. Only one negative vibrational frequency associated with the torsion about the C1–N8 bond was obtained in both the MP2 and B3LYP calculations, which shows that this conformer is also a first-order ts. This form, denoted **II** and depicted in Figure 2, is characterized by O6–C1–N8–H9 and O6–C1–N8–H10 dihedral angles of nearly $\pm 120^\circ$, respectively, which means that the plane of the oxazole ring bisects the plane formed by the amino group. The maximum electron density of the lone pair of the amino group is as close as possible to the oxygen atom of the ring (O6, Figure 2), which indicates that repulsion between the lone electron pairs of the oxygen (O6) and nitrogen atom (N8) is at a maximum in this form. The total MP2 and B3LYP energies of **II** are 19.8 and 10.3 kJ/mol, respectively, higher than the energy of **I**. The variation in the energy difference of 9.5 kJ/mol is remarkably large.

Comparison of the MP2 and B3LYP structures warrant comments: Table 1 reveals that the oxazole ring is predicted to be planar in both methods (within the default convergence criteria). The angle between the amino group and the oxazole plane is calculated to be 42° (MP2) and 36° (B3LYP), respectively (not given in this table). The latter procedure therefore predicts a flatter molecule than the former. All the bond lengths obtained by the two methods are very similar, deviating by less than 1 pm. The bond lengths and bond angles predicted for the oxazole ring are also in good agreement, whereas larger differences are seen for the bond angles and dihedral angles associated with the amino group.

The theoretical structures of **I** should be compared with the X-ray structure.¹⁵ It is seen from Table 1 that the bond lengths agree well with the exception of the C2–C3 and C1–N8 bond lengths, which are much shorter in the crystal. The latter bond length is 134.3(4) pm in the crystal compared to 137.4 (MP2) and 136.7 pm (B3LYP) in the free molecule. The shortening in the crystal is consistent with additional conjugation presumed to be present in this phase where the molecule is planar, compared to the nonplanar free molecule. The short C2–C3 bond in the crystal of only 131.0(4) pm compared to 135.4 (MP2) and 134.5 pm (B3LYP) is harder to explain, but electron conjugation should be more prominent in the solid phase and this is perhaps responsible for a part of this shortening. Crystal effects could be another reason.

Interestingly, the MP2 and B3LYP structures of the oxazole moiety of 2-aminooxazole agree very well with the accurate oxazole substitution structure (Table 1), determined by Kumar et al.,³⁹ which is additional evidence that the theoretical structures are indeed accurate.

Microwave Spectrum and Assignments. The rotational constants of 2-aminooxazole (Table 2) indicate that this compound is a prolate rotor with Ray's asymmetry parameter⁴⁰ $\kappa \approx -0.65$. The dipole moment (same table) has its largest component along the *b*-axis, with minor components along the

a- and *c*-axes. The *c*-type transitions occur between the (+) and (–) states provided the compound has an associated double-minimum potential.

The observed spectrum is dense with absorptions occurring every few megahertz throughout the investigated spectral range (26.6–80 GHz), which is typical for a *b*-type spectrum of a prolate rotor with rotational constants of the order of magnitude shown in Table 2. The MP2 spectroscopic constants were used to predict the frequencies of the ^bQ-branch lines, which should be among the strongest transitions in the spectrum. These lines were found close to their predictions. The assignments of the ^aR- and ^bR-transitions were made next. A useful and characteristic feature for the assignment of the spectrum was that the lines occurred as relatively closely spaced doublets of comparable intensities denoted 0^+ and 0^- , respectively, just as in the cases of the amines of the six-membered aromatic rings mentioned above.

The transitions of each of the 0^+ and 0^- states could be fitted to Watson's A-reduction Hamiltonian employing the I'-representation⁴¹ with a root-mean-square deviation comparable to the experimental uncertainty of $\approx \pm 0.10$ MHz. 2-Aminooxazole contains two nitrogen nuclei with associated quadrupole splitting. The B3LYP nuclear quadrupole coupling constants obtained as described above were $\chi_{aa} = 1.069$ and $\chi_{bb} = 2.381$ MHz for N7, and $\chi_{aa} = 1.891$ and $\chi_{bb} = 2.746$ MHz for N8, which results in a complex quadrupole pattern of each transitions. Predictions using these nuclear quadrupole coupling constants indicate that the quadrupole splittings in general are less than the resolution of about 0.50 MHz. No resolved splittings were observed in accord with these predictions.

The assignments were gradually extended to include higher and higher values of *J*. Ultimately, 527 transitions with *J* up to 67 were included in the least-squares fit for the 0^+ state, whereas 458 transitions were fitted for the 0^- state. Transitions involving even higher values of *J* were searched for but not found presumably because of insufficient intensities caused by a rapid decrease of the Boltzmann factor as *J* becomes this large.

Centrifugal distortion is relatively small in this compound mainly because the five-membered oxazole ring is relatively rigid. Only quartic centrifugal distortion constants were therefore fitted. Inclusion of sextic centrifugal distortion constants were attempted but resulted in insignificant improvement of the least-squares fit.

Attempts to find *c*-type lines failed. However, it was noted that the intensities of the 0^- lines were approximately 71% of the intensities of their 0^+ counterparts, which corresponds to energy difference estimated to be $70(20)\text{ cm}^{-1}$. *c*-Type transitions will therefore occur mainly in the far-infrared region, which is not accessible with our spectrometer.

The spectra of the 0^+ and 0^- states are found in the Supporting Information, Table 5S and 6S, respectively, whereas the experimental spectroscopic constants are listed in Table 3. It is seen from this table that very accurate values have been obtained for the spectroscopic constants. This should make it possible to make accurate predictions of the frequencies of transitions not occurring in the investigated spectral region, which should be useful for analytical identification purposes.

The experimental spectroscopic constants in Table 3 should be compared with the MP2 and B3LYP counterparts (Table 2) to see if it is possible to find out which of the two methods predict the more accurate molecular structure. It is seen from these two tables that the MP2 rotational constants deviate by a few MHz from the 0^+ constants. There is also good agreement (better than about 1%) between the B3LYP and the experimental

TABLE 3: Experimental Spectroscopic Constants^{a,b} of the Ground Vibrational State of 2-Aminooxazole

state	0 ⁺	0 ⁻
Rotational Constants (MHz)		
A	9326.4892(16)	9323.9447(18)
B	3912.38508(65)	3907.47653(72)
C	2760.84451(64)	2760.31584(65)
Moments of Inertia ^c and Inertial Defect ^d (10 ⁻²⁰ u m ²)		
I _a	54.1874939(95)	54.202282(11)
I _b	129.174165(22)	129.336433(24)
I _c	183.052350(43)	183.087410(43)
Δ	-0.30931(3)	-0.45130(3)
Quartic Centrifugal Distortion Constants (kHz)		
Δ _J	0.29626(50)	0.29703(52)
Δ _{JK}	1.1527(55)	1.1568(59)
Δ _K	1.7972(26)	1.7881(27)
δ _J	0.08323(45)	0.08220(41)
δ _K	1.1305(97)	1.141(10)
Root-Mean-Square Deviation (MHz)		
	0.116	0.1201
Number of Transitions		
	527	458

^a A-reduction, I^r-representation.⁴³ ^b Uncertainties represent one standard deviation. Spectra of the 0⁺ and 0⁻ states are listed in Tables 5S and 6S in the Supporting Information. ^c Conversion factor: 505379.05 × 10⁻²⁰ MHz u m². ^d Δ = I_c - I_a - I_b.

rotational constants. Rotational constants alone cannot therefore be used to decide which theoretical method is the superior.

The inertial defect, Δ = I_c - I_a - I_b, is more useful in this respect. Δ is 0.05598(32) × 10⁻²⁰ u m² in the planar oxazole³⁹ molecule, compared to -0.30931(3) (same units and magnitude) in 2-aminooxazole (Table 3). The relatively large deviation of Δ from zero in the title compound shows that 2-aminooxazole is definitely nonplanar. Interestingly, the B3LYP inertial defect Δ = -0.38 × 10⁻²⁰ u m² (Table 2) is closer to the experimental value (-0.30931(3); same units and magnitude) than the MP2 value of Δ = -0.58 × 10⁻²⁰ u m² (Table 2). It is therefore assumed that the angle between the oxazole ring and the amino group is closer to the value obtained in the B3LYP calculations (36°) than to the MP2 result (42°). It therefore appears that the B3LYP calculations are superior in predicting a more correct value for the nonplanarity of 2-aminooxazole. The B3LYP value of Δ (-0.38 × 10⁻²⁰ u m²) is still larger in absolute terms than experimental value (-0.30931(3) × 10⁻²⁰ u m²), which indicates that the molecule is even flatter than the prediction of the B3LYP calculation. We therefore estimate this angle to be 35(5)°.

Both calculation procedures predict quartic centrifugal distortion constants that are in satisfactory agreement with the experimental counterparts (Tables 2 and 3). However, the B3LYP centrifugal distortion constants are a little better than the MP2 constants.

Vibrationally Excited State. According to the B3LYP calculations, the two lowest vibrational states (Table 1S, Supporting Information) occur at 273 (inversion) and 301 cm⁻¹ (torsion). Doublets similar to the 0⁺ and 0⁻ pairs of the ground state were expected to be observed for the first excited states of each of these normal modes. A full assignment was obtained for one of these states, presumably associated with the inversion. The spectra of each member of the pairs could be fitted to the Watson Hamiltonian⁴¹ with satisfactory root-mean-square deviations. 143 transitions with *J*-values up to 38 were assigned for what is assumed to be the first excited state of the inversion vibration (denoted 1⁻), whereas 87 transitions with a maximum

TABLE 4: Experimental Spectroscopic Constants^{a,b} of the First Excited Torsional State of 2-Aminooxazole

state	1 ⁻	1 ⁺
Rotational Constants (MHz)		
A	9255.2708(49)	9275.0154(66)
B	3913.0710(36)	3908.8061(43)
C	2763.6408(36)	2763.2688(42)
Moments of Inertia ^c and Inertial Defect ^d (10 ⁻²⁰ u m ²)		
I _a	54.604461(29)	54.488220(39)
I _b	129.15152(12)	129.29244(14)
I _c	182.86713(24)	182.89175(28)
Δ	-0.88885(12)	-0.88891(3)
Quartic Centrifugal Distortion Constants (kHz)		
Δ _J	0.364(19)	0.240(19)
Δ _{JK}	1.120(20)	1.393(34)
Δ _K	0.413(95)	-0.51(15)
δ _J	0.0847(12)	0.0844(19)
δ _K	0.963(22)	1.070(39)
Root-Mean-Square Deviation (MHz)		
	0.139	0.1459
Number of Transitions		
	143	87

^a A-reduction, I^r-representation.⁴³ ^b Uncertainties represent one standard deviation. Spectra of the 1⁻ and 1⁺ states are listed in Tables 7S and 8S in the Supporting Information. ^c Conversion factor: 505379.05 × 10⁻²⁰ MHz u m². ^d Δ = I_c - I_a - I_b.

J = 38 were assigned for the 1⁺ state. The spectroscopic constants are listed in Table 4 and the corresponding spectra are shown in Table 7S and 8S in the Supporting Information.

The α-constants defined by α_X = X₀ - X₁,⁴² where X₀ and X₁ are rotational constant of the ground and the first excited state, respectively. These parameters are calculated to be α_A = 71.2184(52), α_B = -0.6859(37), and α_C = -2.7963(37) MHz from the entries in Tables 3 and 4 in good agreement with the corresponding B3LYP values (Table 2S, Supporting Information) α_A = 76.38, α_B = -1.04, and α_C = -2.84 MHz for the inversion vibration (Table 2S, Supporting Information).

Relative intensity measurements yielded 205(30) cm⁻¹ for the 1⁻ state, and 297(60) cm⁻¹ for the 1⁺ state above the 0⁺ state. The B3LYP value of the anharmonic inversion vibration is 273 cm⁻¹ (Table 1S, Supporting Information), but these calculations do not take into account the additional complications caused by the double minimum potential of the inversion motion.

Attempts to find the first excited-state pairs of the torsion about the C1-N8 bond were made, but no definite assignments could be made. It is our impression from the intensities of the unassigned lines that this excited state occurs well above 300 cm⁻¹, compared to the B3LYP prediction of 301 cm⁻¹ (Table 1S, Supporting Information).

Conclusions

The microwave spectrum of 2-aminooxazole, which is of potential astrochemical and prebiotic interest, has been investigated in the 26.6–80 GHz spectral interval. The inertial defect deviates considerably from zero, being -0.30931(3) × 10⁻²⁰ u m², which is evidence that this compound is nonplanar. The angle between the amino group and the oxazole group is estimated from this value to be 35(5)° from coplanarity.

A large number of *a*- and *b*-type transitions of the ground state and of the first excited state of the inversion motion of the amino group were assigned and accurate values of the rotational and quartic centrifugal distortion constants have been

obtained. These transitions come in pairs with similar, but not identical, intensities, which is typical for inversion motions. No *c*-type lines were assigned, although μ_c should be roughly 3×10^{-30} C m according to the MP2 and B3LYP predictions. The *c*-type lines presumably occur between states of opposite parity in this case, as a result of an inverting amino group with an associated double-minimum potential. The *c*-type transitions will occur in the far-infrared region not accessible with our spectrometer, because the 0^- state has an energy that is 70(20) cm^{-1} higher than the energy of the 0^+ state. The absence of *c*-type lines in the MW region is therefore additional evidence of the existence of inversion of the amino group of 2-aminooxazole.

The MW work has been augmented with high-level ab initio calculations at the MP2/aug-cc-pVTZ and B3LYP/6-311++G(3df,3pd) levels of theory, which yield rotational constants that are in excellent agreement with their experimental counterparts. There is very good agreement between the MP2 and B3LYP structures of the oxazole ring of 2-aminooxazole. Both methods predict that the amino group and the oxazole ring are nonplanar. However, the B3LYP method predicts a more accurate value for the angle between these two planes. There is also satisfactory agreement between the theoretical and experimental quartic centrifugal distortion constants, with the B3LYP constants a little more accurately predicted than the MP2 constants.

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Supporting Information Available: Results of the MP2/aug-cc-pVTZ and B3LYP/6-311++G(3df,3pd) calculations (vibrational frequencies, vibration–rotation constants, bond distances and angles) and microwave spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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