

Microwave spectrum and barrier to internal rotation in 5 methyl isoxazole

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The microwave spectrum of 5 methyl isoxazole was measured in the range 12-39 GHz. Transitions of the A- and E- species in the ground torsional state have been assigned, and confirmed by observing many double resonances. The following molecular constants have been derived :

$$A = 9241.360 \pm 0.031 \text{ MHz}, B = 3559.377 \pm 0.011 \text{ MHz}$$

$$C = 2610.221 \pm 0.011 \text{ MHz}, V_3 = 782.6 \pm 1.8 \text{ cal mole}^{-1},$$

$$I_\alpha = 3.185 \pm 0.019 \text{ amu } \text{Å}^2.$$

Barrier height V_3 has been obtained by the IAM procedure applicable to low barriers

1. INTRODUCTION

Barriers to internal rotation for methyl groups in planar five membered heterocyclic rings have been studied by microwave spectrum analysis only in some cases (1-3), and from the symmetry considerations alone it is not possible to explain the barrier heights in different molecules. If a large number of such system be studied, it is then expected to arrive at some interesting conclusions. We have accordingly begun a programme of work on such systems. In an earlier communication (2) we have reported the microwave spectrum and barrier heights in 3 methyl and 5 methyl pyrazoles. The geometry and electron distribution of isoxazole have been studied by Nösberger et al. (4) by studying the isotopic substitution in its natural abundance by microwave-microwave double resonance technique. We, therefore, selected to work on 5 methyl isoxazole taking into consideration that the isoxazole and pyrazole frames differ only in the respect that the -O- in isoxazole is replaced by -NH- in pyrazole.

2. EXPERIMENTAL

The sample of 5 methyl isoxazole was commercially procured and was distilled twice under vacuum before use. Spectra were recorded with a conventional 100 kHz Stark modulated spectrometer in the range 12-39 GHz with the cell at the room temperature. Nuclear quadrupole splittings could not be resolved, but their contributions in terms of broadening in some of the lines were often observed. Frequency measurements are generally accurate to within 0.1 MHz.

Double resonance measurements were made in the same spectrometer by essentially conventional methods (5) with the pump frequencies always lower than the signal frequencies

3. RESULTS AND DISCUSSIONS

Assuming the structure of isoxazole ring (4) unchanged by the methyl substitution in position 5 of the ring, the following rigid rotor constants are predicted :

$$A \quad 9210 \text{ MHz} \quad B \quad 3541 \text{ MHz} \quad C \quad 2599 \text{ MHz}$$

The dipole moment and its direction is assumed to be the same as that in isoxazole (6), i.e. $\mu = 2.95 \text{ D}$ and hence the dipole moments along the inertial axes are predicted to be the following :

$$\mu_a \quad 1.0 \text{ D} \quad \mu_b \quad 2.6 \text{ D} \quad \mu_c \quad 0.$$

Thus 5 methyl isoxazole should give both a- and b- dipole spectra. The calculated spectrum on the rigid rotor model exhibits strong b-dipole Q-branch lines in the region 12–39 GHz for J-values between 3 and 17, whereas both a- and b-dipole R-branch lines are comparatively quite weak.

Barrier to internal rotation V_3 of the methyl top in position 5 of the isoxazole ring was guessed to be few hundred cal mole⁻¹, and hence Internal Axis Method (IAM) computer programme written by Tipton, Coffey and Boggs (7) was thought to be good for calculating the internal rotor splittings. In this analysis we have assumed $V_6 = 0$.

Some of the high J ($J \geq 10$) Q-branch lines are supposedly observed as strong doublets. They were tentatively assigned following Tabor's method (8) of comparing the measured frequencies on the plot of $\log \Delta E(k)$ vs k , and finally by the usual graphical method of $\nu_{\text{obs}} / \Delta E(k) [= \frac{1}{2} (A-C)]$ vs k . The high J Q-branch lines do not give a good intersection point owing to the fact that centrifugal distortion corrections become important. The following double resonances finally confirmed these assignments : (the first-named transition in each case is the pump transition and is of lower frequency than the coupled transition) :

$$\begin{array}{ll} 7_{16} \rightarrow 7_{25} \rightarrow 7_{31} ; & 7_{25} \rightarrow 7_{16} \rightarrow 7_{07} \\ 8_{17} \rightarrow 8_{26} \rightarrow 8_{35} ; & 9_{27} \rightarrow 9_{18} \rightarrow 9_{08} \\ 10_{28} \rightarrow 10_{37} \rightarrow 10_{46} ; & 11_{29} \rightarrow 11_{38} \rightarrow 11_{47} \end{array}$$

The frequencies of these transitions are given in Table 1. These assignments were fitted to a preliminary set of rigid rotor constants, which was used to identify other Q-branch lines, especially the low J lines. Thus from the Q-branch lines we could determine the values of $\frac{1}{2} (A-C)$ and k , and from

these constants the possible values of B were calculated for $I_a + I_b - I_c$ lying in between 3.0 and 3.2 amu A². Accordingly the low J R-branch lines were predicted and measured. The assignment of R-branch lines were confirmed from the following doublet resonances :

$$4_{14} \rightarrow 5_{05} \rightarrow 6_{16}$$

The lines thus assigned are listed in table 1. All these lines were then used in the least square fit to derive the rigid rotor constants and centrifugal

Table 1 Observed and calculated frequencies in MHz for 5 methyl isoxazole in its ground torsional state

Transitions	A		E		A/E splittings	
	Obs	Calc-Obs	Obs	Obs	Calc-Obs	
R-branch						
$3_{03} - 4_{14}$	26364.40	0.32	26347.81	16.59	0.31	
$3_{11} - 4_{04}$	19881.30	0.44	19897.24	-15.17	-0.47	
$4_{14} - 5_{05}$	26295.24	0.23	26306.18	-10.94	-0.21	
$5_{05} - 6_{16}$	35267.56	0.28	35255.35	12.21	-0.09	
$5_{23} - 6_{16}$	26864.57	-0.11	26928.50	-63.93	-0.03	
$6_{10} - 7_{07}$	38210.38	-0.32	38214.33	-3.95	-0.00	
$6_{25} - 7_{10}$	34942.84	-0.35	34991.03	-48.19	-0.10	
Q-branch						
$3_{12} - 3_{21}$	16231.80	-0.18	16310.13	-78.33	0.49	
$3_{17} - 3_{25}$	21381.62	-0.05				
$4_{04} - 4_{11}$	12138.12	-0.07	12127.91	10.21	0.41	
$4_{17} - 4_{22}$	15506.82	-0.07	15513.06	-6.24	-0.04	
$4_{14} - 4_{25}$	23391.12	0.22	23298.07	93.05	0.65	
$4_{22} - 4_{29}$	31128.08	0.07				
$5_{05} - 5_{11}$	15797.45	0.30	15787.86	9.59	0.04	
$5_{14} - 5_{21}$	15303.40	0.06	15287.32	16.05	0.64	
$5_{20} - 5_{22}$	28488.25	-0.46	28720.02	-231.77	0.07	
$5_{10} - 5_{24}$	25924.25	0.10	25858.31	65.94	0.17	
$5_{24} - 5_{25}$	31669.74	0.54				
$6_{05} - 6_{15}$	20390.66	-0.08	20380.67	9.99	-0.62	
$6_{15} - 6_{24}$	15890.41	0.03	15868.88	21.53	-0.19	
$6_{24} - 6_{25}$	26971.69	-0.25	27092.31	-120.62	-0.56	

Table 1. (Contd.)

Transitions	A		E	A/E splittings	
	Obs	Calc-Obs	Obs	Obs	Calc-Obs
6 ₂₅ - 6 ₃₄	32562.46	0.01	32290.42	271.04	2.30
7 ₀₇ - 7 ₁₆	25697.09	-0.20	25686.11	10.98	0.25
7 ₃₁ - 7 ₂₆	17467.94	-0.04	17449.25	18.69	0.04
7 ₂₆ - 7 ₃₁	25343.38	-0.06	25365.90	-22.52	-0.40
7 ₁₇ - 7 ₂₈	32473.20	0.56	32422.80	50.40	0.89
7 ₂₆ - 7 ₁₆	33883.17	-0.21	33713.36	169.81	0.47
8 ₁₆ - 8 ₁₇	31406.88	0.20	31391.67	15.21	0.75
8 ₁₇ - 8 ₂₁	20172.22	-0.05	20159.46	12.76	0.11
8 ₂₆ - 8 ₃₅	23974.73	-0.08	23950.78	23.95	-0.32
8 ₁₆ - 8 ₂₇	36394.57	-0.24	36344.33	50.24	-0.25
8 ₂₇ - 8 ₃₆	35689.62	0.19	35575.44	114.18	0.66
9 ₁₀ - 9 ₁₉	37226.95	-0.29	37203.15	23.80	-0.49
9 ₁₆ - 9 ₂₇	24042.51	0.15	24036.50	6.01	0.14
9 ₂₇ - 9 ₃₆	23250.04	0.09	23212.48	37.56	0.01
9 ₃₆ - 9 ₄₅	38368.57	-0.16	38564.77	-196.20	2.93
9 ₂₆ - 9 ₃₇	38015.49	-0.48	37928.29	87.20	0.85
10 ₁₀ - 10 ₂₉	28969.23	0.37	28967.97	1.26	0.04
10 ₂₉ - 10 ₃₇	23489.23	0.00	23453.85	35.38	0.36
10 ₃₇ - 10 ₄₆	36200.26	-0.09	36268.44	-68.18	-0.56
11 ₁₀ - 11 ₁₉	34688.48	0.18	34688.48	0.00	0.19
11 ₂₀ - 11 ₃₉	24917.01	-0.24	24890.48	26.17	-0.03
11 ₃₉ - 11 ₄₇	33941.78	0.32	33925.65	16.13	0.02
12 ₂₀ - 12 ₂₉	27660.69	-0.20	27647.67	13.02	-0.07
12 ₃₀ - 12 ₃₉	32007.65	0.27	31954.61	53.04	0.09
13 ₂₀ - 13 ₂₉	31729.42	-0.47	31729.42	0.00	-0.60
13 ₃₀ - 13 ₃₉	30826.73	0.05	30766.91	59.82	0.50
14 ₂₀ - 14 ₂₉	36973.83	0.43	36985.61	-11.78	0.78
14 ₃₀ - 14 ₃₉	30756.35	0.19	30706.01	50.34	0.77
15 ₂₀ - 15 ₂₉	32043.44	0.22	32010.82	32.62	0.49
16 ₃₀ - 16 ₃₉	34814.81	-0.25	34803.23	11.58	-0.41
17 ₃₀ - 17 ₃₉	38164.39	-0.15	38081.85	82.54	2.76

distortion constants given in table 2. However the centrifugal distortion constants listed in table 2 may also be interpreted as the fitting parameters to reduce the deviations between observed and calculated frequencies. The difference between the calculated and observed frequencies are listed in column 3 of Table 1. The value of $I_a + I_b - I_c$ comes out to be $3.056 \text{ amu } \text{Å}^2$, which suggests that the barrier height is more than $700 \text{ cal mole}^{-1}$.

Microwave spectrum of 5 methyl isoxazole

Table 2. Molecular rotational constants of 5 methyl isoxazole from the A-state spectrum

A	9241.360 ± 0.031	MHz
B	3559.377 ± 0.011	MHz
C	2610.221 ± 0.011	MHz
k	- 0.71373	
I_a	54 686	amu A ²
I_b	141 984	amu A ²
I_c	193 614	amu A ²
$I_a + I_b - I_c$	3.056	amu A ²
D_J	0.0 assumed	MHz
D_{JK}	0.0 assumed	MHz
D_K	0.0214 ± 0.0016	MHz
DD_J	0.0 assumed	MHz
DD_K	0.0021 ± 0.0002	MHz

using the conversion factor of 505376 MHz per amu A²

If the barrier height is higher than 700 cal mole⁻¹, the internal rotor splittings for the lines 11_{3,11}-11₁₇ and 16_{3,11}-16_{1,11} should be less than 30 MHz. The measured splittings are found to be 16.13 and 11.58 respectively from which V_3 is estimated to be around 780 cal mole⁻¹. For V_3 770, 780 and 790 cal mole⁻¹ and I_α 3.135, 3.185, 3.205 amu A² A/E splittings have been calculated for all the lines for J = 0 to 20 in its ground torsional state using the IAM computer programme. It was then found that the series $J_{n,J} - J_{1,J-1}$ has A/E splittings around 10 to 25 MHz and has the least dependence on the value of I_α . The E-state lines thus predicted were measured and assigned. The double resonances mentioned earlier for the A-state lines were carried out for the E-state lines also, and hence the assignments were confirmed. The E-state spectrum of this molecule does not follow the rigid rotor basis even after correcting for centrifugal distortion.

From the least square fitting of the A/E splittings, the barrier height V_3 and the moment of inertia of the top I_α are determined and given in table 3 along with the standard errors. The direction cosine λ_z is assumed to be 0.9949 as obtained from the geometry. Using the rotational constants of table 2 and the internal rotor constant of table 3, the A/E splittings were calculated. The observe A/E splittings along with the difference between the calculated and observed splittings are listed in table 1.

Table 3. Internal rotor constants of the methyl top in 5 methyl isoxazole

V	782.64 ± 1.79	cal mole ⁻¹
s	21.66 ± 0.05	
I_{α}	3.185 ± 0.019	amu A ²
λ_r	0.9949 assumed	

The difference between the observed and calculated frequencies remain, in many cases, larger than what is expected in the spectrum of more rigid molecules. The following factors may contribute to the difficulty of better fitting. We have not included the effects of nuclear quadrupole hyperfine structure due to the nitrogen nuclei. Centrifugal distortion correction has been included only incompletely. And perhaps the neglect of the six-fold barrier contribution V_6 may also not be justified. Due to these reasons, it would not be justified to claim the accuracy in the value of $V_3 = 782.6$ cal mole⁻¹ to be equal to the standard error of 1.8 cal mole⁻¹. Perhaps an uncertainty in the value of V_3 equal to ± 18 cal mole⁻¹ would predict its range and may take into account the factors listed above. This value of V_3 seems to be reasonably accurate to the internal rotation of methyl top studied by microwave spectroscopy.

From the barrier data of methyl top in different position in 5 membered heterocyclic molecules it has not been possible to arrive at any fruitful conclusions at this stage, since these data are still very few in number to make any systematic substitutional studies. However, if we compare the barrier data of 5 methyl isoxazole with those of 5 methyl pyrazole (2) and 2 methyl furan (9) we find that (a) replacing -O- from isoxazole -NH- in pyrazole at the first neighbour decreases the barrier height by about 450 cal mole⁻¹, and (b) replacing -N- from isoxazole by -CH- in furan at the next neighbour increases the barrier height by about 410 cal mole⁻¹.

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