Microwave Spectrum and Barrier to Internal Rotation of 5-Methylisoxazole

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The ground state rotational spectrum of 5-methylisoxazole has been studied in the region 18 000 – 36 000 MHz. The A and E state transitions have been assigned.

The rotational constants are $A = 9230.831$ MHz, $B = 3559.334$ MHz and $C = 2610.255$ MHz and the three-fold barrier to internal rotation of the methyl group was calculated to be 777.2 ± 5.5 cal mol^{-1}.

Introduction

Previous microwave studies of rotational barriers for methyl groups attached to heterocyclic five-membered ring molecules show that the barrier height varies strongly between different types of rings and different positions in the rings. This is shown in Table 1.

5-Methylisoxazole (Fig. 1) appears particularly interesting from this point of view since the deviation of the barrier height from that of 2-methylfuran is related to the presence of the N heteroatom in the ring.

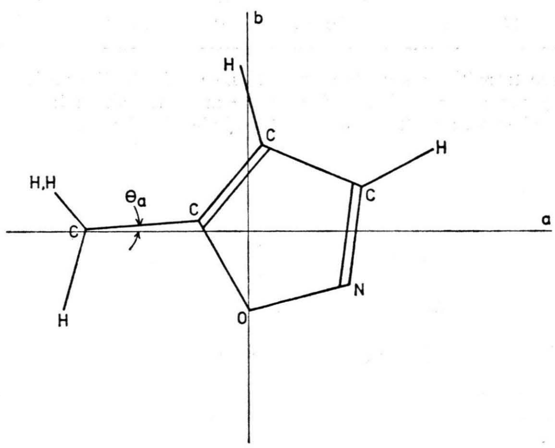

Fig. 1. Molecular structure of 5-methylisoxazole. The orientation of the a and b principal axes is indicated.

Experimental

The sample of 5-methylisoxazole was purchased from Aldrich and was used without further purification.

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Microwave spectra in the region 18 000 – 36 000 MHz were recorded, using a Hewlett-Packard 8460 A spectrometer equipped with a phase-stabilized source oscillator. The Stark modulation frequency was 33.33 kHz. All measurements were made at room temperature.

Microwave Spectrum and Internal Rotation

The microwave spectrum of 5-methylisoxazole in the K- and R-band region is dominated by a number of intense, high J, b-type, Q-branch transitions, in particular the branch $J_{4,J-4} \leftarrow J_{3,J-3}$. These lines show moderate A-E splittings up to a few tens of MHz. In contrast, splittings of several hundred MHz were encountered in some of the low J, R- and Q-branch transitions. The assigned A and E state transitions are listed in Table 2.

The expected internal rotation splittings of the excited torsional states are so large – many thousands of MHz – that a perturbational treatment of these splittings would scarcely be feasible. For this reason, no attempt was made to assign these transitions although many torsional satellites could be observed in the spectrum.

The A state spectrum follows a pseudo-rigid rotor pattern to within about 1 MHz, while some of the E state transitions show much larger deviations. The main part of the deviations of the A state transitions can be accounted for by using a pseudo-centrifugal distortion correction. The values of these centrifugal distortion coefficients were found to be in reasonable agreement with those calculated from internal rotation theory.

Our theoretical treatment followed the principal axis method (PAM) as formulated by Herschbach [6]. The potential barrier hindering the internal rotation

Table 1. Internal rotation barriers (cal/mol) for some methyl derivatives of heterocyclic five-membered ring compounds.

Molecule	Barrier (cal/mol)	Ref.
3-methyl-1,2,5-oxadiazole (3-methylfurazan)	722	1
2-methylfuran	1190	2
3-methylfuran	1088	3
2-methylthiophene	555	4
3-methylthiophene	740	5

Table 2. Observed ground-state rotational transitions in 5-methylisoxazole.

Transition	A state ν_{obs}	A state $\nu_{obs}-\nu_{calc}$	E state ν_{obs}	E state $\nu_{obs}-\nu_{calc}$	A−E (obs)	A−E (calc)
a-Type						
$4_{1,3} \leftarrow 3_{1,2}$	26333.04	0.21	26330.85	0.42	2.19	2.39
$5_{1,5} \leftarrow 4_{1,4}$ [a]	28072.64	—	28072.44	—	—	0.19
$6_{1,6} \leftarrow 5_{1,5}$	33490.41	−0.19	33489.60	−0.04	0.81	0.97
b-Type						
$4_{1,4} \leftarrow 3_{0,3}$	26364.72	0.00	26348.01	0.18	16.71	16.90
$5_{0,5} \leftarrow 4_{1,4}$	26295.19	−0.09	26306.30	0.02	−11.11	−11.00
$6_{1,6} \leftarrow 5_{0,5}$	35267.85	−0.15	35255.77	−0.66	12.08	12.16
$6_{3,4} \leftarrow 6_{2,5}$	32562.70	0.99	32290.04	0.15	272.66	271.82
$8_{2,6} \leftarrow 8_{1,7}$	20172.20	0.60	20159.40	0.75	12.80	12.95
$8_{3,5} \leftarrow 8_{2,6}$	23974.60	0.34	23950.81	0.34	23.79	23.79
$8_{3,6} \leftarrow 8_{2,7}$	35689.88	0.88	35575.36	0.65	114.52	114.29
$9_{2,7} \leftarrow 9_{1,8}$	24042.65	0.66	24036.42	0.88	6.23	6.45
$9_{3,6} \leftarrow 9_{2,7}$	23250.11	0.29	23212.57	0.23	37.54	37.48
$10_{3,7} \leftarrow 10_{2,8}$	23489.25	0.25	23453.68	0.23	35.57	35.54
$11_{3,8} \leftarrow 11_{2,9}$	24916.85	0.24	24890.91	0.25	25.94	25.95
$11_{4,7} \leftarrow 11_{3,8}$	33941.98	−0.27	33925.41	−0.05	16.57	16.80
$12_{3,9} \leftarrow 12_{2,10}$	27660.60	0.20	27647.89	0.34	12.71	12.85
$12_{4,8} \leftarrow 12_{3,9}$	32007.82	−0.39	31954.75	−0.32	53.07	53.14
$13_{3,10} \leftarrow 13_{2,11}$ [a]	31729.13	—	31729.63	—	—	−0.49
$13_{4,9} \leftarrow 13_{3,10}$	30826.74	−0.49	30766.53	−0.71	60.21	59.99
$14_{4,10} \leftarrow 14_{3,11}$	30756.51	−0.67	30705.69	−0.80	50.82	50.69
$15_{4,11} \leftarrow 15_{3,12}$	32043.61	−0.91	32010.87	−0.85	32.74	32.80
$16_{4,12} \leftarrow 16_{3,13}$	34814.46	−1.24	34803.53	−1.01	10.93	11.16

[a] The splittings of these transitions were too small to be resolved. The positions of the A and E components were calculated from the mean transition frequencies and the calculated splittings. They were not included in the fit.

Table 3. Rotational constants (MHz) and moments of inertia (amu Å²) [a].

A	$= 9230.831 \pm 0.033$
B	$= 3559.334 \pm 0.020$
C	$= 2610.255 \pm 0.020$
I_a	$= 54.74870 \pm 0.00020$
I_b	$= 141.9861 \pm 0.0008$
I_c	$= 193.6117 \pm 0.0015$
$\varkappa$	$= -0.713$
$I_a+I_b-I_c$	$= 3.1231$
Δ'	$= I_a-(I_a+I_b-I_c) = 0.0806$
A_A	$= 9241.308$ [b]
B_A	$= 3559.404$ [b]
C_A	$= 2610.218$ [b]

[a] Conversion factor equal to 505 376 MHz amu Å².
[b] Calculated with allowance for pseudo-centrifugal distortion.

of the methyl group is thus assumed to have the following form

$$V(\alpha) = \tfrac{1}{2} V_3 (1 - \cos 3\,\alpha)\,.$$

In Herschbach's notation, the Hamiltonian for the single top problem is then written as

$$H = H_r + F(p - \mathcal{P})^2 + V(\alpha)$$

where H_r is the rigid-rotor Hamiltonian, p is the total angular momentum of the internal rotor along its symmetry axis, I_α is the moment of inertia of the internal rotor about its symmetry axis, λ_a, λ_b and λ_c are the direction cosines between the internal rotor axis and the principal axes of the molecule, $\alpha = \lambda_a I_\alpha / I_a$, $\beta = \lambda_b I_\alpha / I_b$, $\gamma = \lambda_c I_\alpha / I_c$, $\mathcal{P} = \alpha P_a + \beta P_b + \gamma P_c$, $r = 1 - \alpha \lambda_a - \beta \lambda_b - \gamma \lambda_c$ and $F = \hbar^2 / 2\, r\, I_\alpha$.

The Hamiltonian can be divided into three parts as follows

$$H = H_{\mathrm{R}} + H_{\mathrm{T}} + H_{\mathrm{TR}}$$

where

$$H_{\mathrm{R}} = H_r + F\,\mathcal{P}^2\,,$$
$$H_{\mathrm{T}} = F\,p^2 + \tfrac{1}{2} V_3 (1 - \cos 3\,\alpha)\,,$$
$$H_{\mathrm{TR}} = -2\,F\,\mathcal{P}\,p\,.$$

The terms H_{R} and H_{T} represent the rotational and torsional parts, while H_{TR} represents the coupling between internal and overall rotation.

In Herschbach's procedure [6], successive Van Vleck transformations are applied to reduce those matrix elements from the coupling term which are non-diagonal in the torsional quantum number. This results in an effective Hamiltonian for each torsional state:

$$H_{v\sigma} = H_r + F \sum_n W_{v\sigma}^{(n)} \mathcal{P}^n\,.$$

The perturbation coefficients $W_{v\sigma}^{(n)}$ have been extensively tabulated as functions of the reduced barrier height:

$$s = (4/9)\,(V_3/F)\,.$$

In the present work, the coefficients $W_{v\sigma}^{(n)}$ were obtained from tables using an interpolation formula:

$$\ln W_{v\sigma}^{(n)} = A + B \ln s + C\, s^{1/2} + D\, s\,.$$

The matrix elements of $\mathcal{P}^n$ in the symmetric rotor basis up to $n=4$ have been given by Herschbach [6] and corrected by Hirota [7].

In the present work, terms through $n=4$ in the perturbation series were used. The Stelman denominator correction [8] was not applied. For diagonalizing the complex Hamiltonian matrix, the EISPACK EIGENSYSTEM PACKAGE was used with an IBM 360/75 computer.

In the least squares analysis of the experimental results the coefficients A, B, C, s, α and I_α were simultaneously fitted. For inverting the normal matrix during the fitting, we used the diagnostic method of Lees [9]. This method has the advantage of improving the conditioning of a near-singular matrix. The results of the least-squares fit are listed in Tables 3 and 4.

Table 4. Internal rotation parameters.

s	$= 21.638 \pm 0.023$	α	$= 0.05798 \pm 0.00020$
θ_a	$= 7.730° = 7°\,44'$ [a]	β	$= 0.00304$
I_α	$= 3.204 \pm 0.016$ amu Å^2	γ	$= 0$
λ_a	$= 0.990914$	F	$= 167\,438.5$ MHz
λ_b	$= 0.134499$	V_3	$= 777.2 \pm 5.5$ cal/mol
λ_c	$= 0$	r	$= 0.942135$

[a] θ_a is the angle between the internal rotor axis and the a principal axis.

The main contributions to the A-E splittings come from the $\mathcal{P}$ and $\mathcal{P}^2$ terms in the expansion of the effective Hamiltonian. The deviations of the A state transitions from the rigid-rotor pattern are mainly caused by the $\mathcal{P}^4$ term which contributes $1-2$ MHz to the transition frequencies.

The pseudo-inertial defect, $\Delta' = I_a - (I_a + I_b - I_c)$, was calculated to be 0.0806 amu Å^2. This is of the same order of magnitude as for 3-methylfuran (0.084 amu Å^2) or 3-methylthiophene (0.081 amu Å^2). If I_α obtained from the internal rotation data were exactly equal to the average structure value of I_α, then Δ' would represent the harmonic contribution to the intertial defect [10]. The available data do not permit any conclusion as to the validity of this assumption.

We were unable to determine the dipole moment. The weak intensity of the low J lines and the abundance of vibrational and torsional satellites made the resolution of the Stark components impossible. A CNDO/2 calculation [11] based on an assumed structure gave the following approximate values: $\mu_a = 1.85$ D, $\mu_b = 2.43$ D and $\mu_c = 0$ D.

No quadrupole hyperfine structure was observed in the spectrum, although we used pressures as low as 5 mTorr in an attempt to resolve the lines with the highest estimated quadrupole splittings.

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[1] E. Saegebarth, J. Chem. Phys. **52**, 1476 [1970].
[2] W. G. Norris and L. C. Krisher, J. Chem. Phys. **51**, 403 [1969].
[3] T. Ogata and K. Kozima, Bull. Chem. Soc. Japan **44**, 2344 [1971].
[4] N. M. Pozdeev, L. N. Gunderova, and A. A. Shapkin, Opt. Spektrosk. **28**, 254 [1970].
[5] T. Ogata and K. Kozima, J. Mol. Spectrosc. **42**, 38 [1972].
[6] D. R. Herschbach, J. Chem. Phys. **31**, 91 [1959].
[7] E. Hirota, J. Chem. Phys. **45**, 1984 [1966].
[8] D. Stelman, J. Chem. Phys. **41**, 2111 [1964].
[9] R. M. Lees, J. Mol. Spectroscop. **33**, 124 [1970].
[10] D. R. Herschbach and V. W. Laurie, J. Chem. Phys. **40**, 3142 [1964].
[11] D. P. Santry, J. Amer. Chem. Soc. **90**, 3309 [1968].