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Microwave Spectrum, Barrier Height to Internal Rotation of Methyl Group, and Dipole Moment of 3-Methylfuran

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The microwave spectrum of 3-methylfuran was measured in the frequency region from 8.2 to 30 GHz. By observing the *A*-*E* splittings due to the hindering rotation of the methyl group, the barrier height was determined to be 1.09 kcal/mol. The value is nearly the same as that of 2-methylfuran. The dipole moment was determined to be 1.03 D, which is a little larger than that of furan.

A few studies of the potential barrier to the internal rotation of the methyl group which is attached to a heterocyclic five-membered ring have recently been carried out by measuring the microwave spectra.[1–3] The barrier height to the rotation of the methyl group of 2-methylfuran was determined by Norris and Krisher[1] to be 1190 cal/mol.

Since the difference in the position of the methyl group which is attached to the furan ring may be expected to affect the value of the barrier height, it seemed that it would be interesting to determine the value for 3-methylfuran.

Experimental

The sample of 3-methylfuran was prepared and purified according to the method of Cornforth.[4] The infrared spectrum of 3-methylfuran thus obtained agreed with that previously reported.[5] The purity was checked with a vapor-phase chromatograph obtained by means of a 4-m column of dioctyl phthalate coated on celite. Runs at 120°C indicated only one component in the sample.

The microwave spectrum was investigated in the frequency region from 8.2 to 30 GHz by using a conventional 100-kHz Stark modulation spectrometer.[6] The measurements were made at about −20°C by using a 6-m absorption cell.

Results and Discussion

Microwave spectrum. In order to assign the absorption lines, the preliminary rotational constants were calculated by using the r_s-structure of furan obtained by Bak *et al.*[7] and the usual values of the bond lengths and the bond angles for the methyl group. By assuming a pseudo-rigid rotor approximation, the transition frequencies were calculated from the preliminary rotational constants. The lines of the *a*- and *b*-type transitions could be found quite close to their predicted frequencies and were assigned by their Stark patterns. The intensities of the *b*-type lines are weaker than those of the *a*-type lines. By considering the Stark patterns and the intensities, several pairs of the lines, which are separated by about few MHz, could be identified as doublets due to the transitions of the *A*- and the *E*-levels caused by the hindering rotation of the methyl group. The observed frequencies of the *a*- and *b*-type transitions of the *A*-levels for the vibrationally-ground state are shown in Table 1. The pseudo-rigid rotational constants for the *A*-levels were determined so as to get the best fit between the observed and the calculated frequencies by the use of the least-squares method. The constants thus obtained are shown in Table 2. By

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES OF *A*-LEVELS (MHz)[a]

Transition	ν_{obs}	$\nu_{obs}-\nu_{calc}$
a-type		
$1_{01}\rightarrow2_{02}$	11593.80	−0.10
$1_{11}\rightarrow2_{12}$	10804.93	0.06
$1_{10}\rightarrow2_{11}$	12580.18	0.13
$2_{02}\rightarrow3_{03}$	17152.28	0.03
$2_{12}\rightarrow3_{13}$	16149.15	0.36
$2_{11}\rightarrow3_{12}$	18804.80	0.13
$2_{21}\rightarrow3_{22}$	17538.95	0.26
$2_{20}\rightarrow3_{21}$	17925.17	0.03
$3_{03}\rightarrow4_{04}$	22464.63	−0.08
$3_{22}\rightarrow4_{23}$	23307.69	−0.34
$3_{31}\rightarrow4_{32}$	23563.03	−0.01
$3_{30}\rightarrow4_{31}$	23603.85	−0.21
b-type		
$0_{00}\rightarrow1_{11}$	11372.40	−0.08
$1_{01}\rightarrow2_{12}$	16331.29	0.17
$2_{12}\rightarrow3_{03}$	12415.00	−0.03
$3_{12}\rightarrow3_{21}$	15797.84	0.06
$3_{03}\rightarrow3_{12}$	9052.39	−0.01
$4_{04}\rightarrow4_{13}$	11528.80	0.13
$4_{13}\rightarrow4_{22}$	15084.60	−0.06
$4_{14}\rightarrow4_{23}$	22507.75	−0.07

a) Experimental uncertainty in the frequency measurements is ±0.1 MHz.

TABLE 2. ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA[a] OF *A*-LEVELS

$A_A=8893.16\pm0.15$ MHz
$B_A=3366.91\pm0.05$
$C=2479.32\pm0.05$
$I_a^A=56.8276$ amu·Å^2
$I_b^A=150.101$
$I_c=203.837$

a) Conversion factor 5.05377×10^5 amu·Å^2·MHz.

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using these constants, the transition frequencies were calculated. The differences between the observed and calculated frequencies are listed in Table 1. The agreement is such that centrifugal distortion can be said not to be an important effect in the range studied.

TABLE 3. MOLECULAR STRUCTURE OF 3-METHYLFURAN

Assumed structural parameters	
$r(\text{O–C}_2)=1.362$ Å	$\angle\text{C}_5\text{–O–C}_2=106°33'$
$r(\text{C}_2\text{–C}_3)=1.361$ Å	$\angle\text{O–C}_2\text{=C}_3=110°41'$
$r(\text{C}_3\text{–C}_4)=1.431$ Å	$\angle\text{C}_2\text{=C}_3\text{–C}_4=106°03'$
$r(\text{C–H})_{\text{ring}}=1.075$ Å	$\angle\text{O–C}_2\text{–H}=115°55'$
$r(\text{C–H})_{\text{methyl}}=1.090$ Å	$\angle\text{H–C–H}=109°28'$
Fitted structural parameters	
$r(\text{C}_3\text{–CH}_3)=1.520$ Å	
$\angle\text{C}_4\text{–C}_3\text{–(CH}_3)=128°57'$	
Calculated rotational constants	
$A=8890.92$ MHz	
$B=3366.03$ MHz	
$C=2479.90$ MHz	

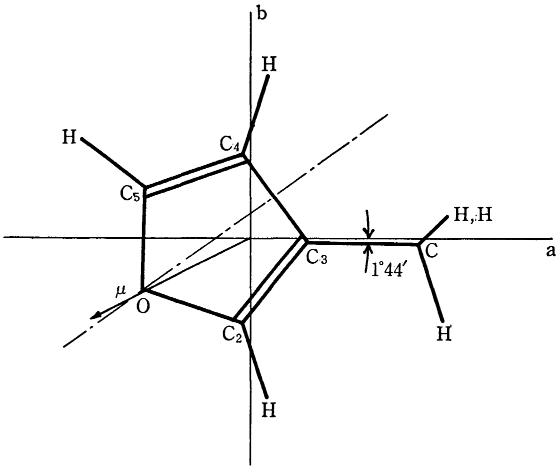

Fig. 1. Molecular structure and dipole moment of 3-methylfuran.

Molecular Structure and Internal Rotation. In order to determine the molecular structure, some of the molecular parameters were assumed by using the r_s-structure described above with the additional assumptions that all the C-H bond lengths and all the valency angles of the methyl group were 1.090 Å and 109°28′ respectively. These assumed values are listed in Table 3, in which the number attached to the symbol of each atom is shown in Fig. 1. By using these parameters, the angle of $\angle\text{C}_4\text{C}_3(\text{CH}_3)$ and the bond length of $\text{C}_3\text{–CH}_3$ were determined so as to get a good fit between the calculated rotational constants and the observed constants of A_A, B_A, and C. The results are shown in Table 3. Although it should be taken into account that the observed values of A_A and B_A are affected by the contribution of the hindering rotation of the methyl group, it is certain that the differences between these rotational constants and the unperturbed values of A and B are small enough to affect the molecular parameters determined above. From Table 3 it can be seen that the change in the structure of the furan ring caused by the substitution of the methyl group in the 3-position is negligible.

The potential energy function of the hindering rotation of the methyl group for this molecule may be expressed as usual by the following equation:

$$V(\alpha) = \frac{V_3}{2}(1-\cos 3\alpha) + \frac{V_6}{2}(1-\cos 6\alpha) + \cdots$$

where α is the relative angle of the internal rotation and where V_3 and V_6 are the potential constants. In this paper only the V_3 term is considered, for the V_6 term would introduce only a minor correction in the value of V_3.

The Hamiltonian can be written in the following manner:

$$H_A = A_A P_z^2 + B_A P_y^2 + C P_x^2$$

and

$$H_E = A_E P_z^2 + B_E P_y^2 + C P_x^2 + F W_{0E}^{(1)} \mathscr{P} + F W_{0E}^{(3)} \mathscr{P}^3$$

where

$$F = \hbar^2/2rI_\alpha, \qquad r = 1 - \sum_{g=a,b} \lambda_g^2 I_\alpha / I_g$$
$$\alpha = \lambda_a I_\alpha / I_a, \qquad \beta = \lambda_b I_\alpha / I_b$$
$$\mathscr{P} = \alpha P_z + \beta P_y$$
$$A_\sigma = A + F\alpha^2 W_{0\sigma}^{(2)}, \quad B_\sigma = B + F\beta^2 W_{0\sigma}^{(2)}$$
$$(\sigma = A \text{ or } E)$$

The notations have the same meanings as in Hershbach's paper.[8] The table of Hayashi and Pierce[9] was the source for the values of the perturbation coefficients, $W_{v\sigma}^{(n)}$. From the assigned transitions of the A- and E-levels, a rough estimate of the value of s, a parameter of the Mathieu equation, could be made. By using this value of s and the internal-rotation parameters shown in Table 4, the transition frequencies of the E-levels were calculated for the transitions which have large A-E splittings; the lines of the E-levels were found near the calculated frequencies and consequently assigned. Then, the accurate value of s was determined so as to give the best fit to the observed A-E splittings by means of the least-squares method, using a HITAC-5020 computer of the Computer Center of Tokyo University. The transition frequencies, ν_E, of the E-levels thus assigned and the A-E splittings, $(\nu_A-\nu_E)_{\text{obs}}$, are listed in Table 5, together with the calculated values of $(\nu_A-\nu_E)_{\text{calc}}$ which were obtained by using the cor-

TABLE 4. BARRIER HEIGHT TO INTERNAL ROTATION OF METHYL GROUP

Internal-rotation parameters	
$\alpha=0.056118$	$\beta=0.000134$
$F=1.678\times10^5$ MHz	$I_\alpha=3.19$ amu·Å^2 [a]
Results	
$s=30.22\pm0.08$	
$A_A-A=2.33$ MHz	$B_A-B=0.00$ MHz
$V_3=1088\pm3$ cal/mol	

a) By using this assumed value the uncertainty of V_3 was estimated.

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[9] See, J. E. Wollrab, "Rotational Spectra and Molecular Structure," Appendix 12, Academic Press, New York and London (1967). The authors are grateful to Dr. M. Hayashi for making a copy of the table.

TABLE 5. OBSERVED FREQUENCIES[a] OF E-LEVELS AND A-E SPLITTINGS (MHz)

Transition	ν_{obs}	$(\nu_A-\nu_E)_{obs}$	$(\nu_A-\nu_E)_{calc}$	Deviation
a-type				
$1_{01}\rightarrow2_{02}$	11593.80	···	0.06	
$1_{11}\rightarrow2_{12}$	10805.94	−1.01	−0.88	−0.13 (−0.14)
$1_{10}\rightarrow2_{11}$	12579.35	0.83	0.88	−0.05 (−0.04)
$2_{02}\rightarrow3_{03}$	17152.28	···	0.22	
$2_{12}\rightarrow3_{13}$	16149.15	···	−0.18	
$2_{11}\rightarrow3_{12}$	18804.80	···	0.27	
$2_{21}\rightarrow3_{22}$	17564.48	−25.53	−25.48	−0.05 (−0.03)
$2_{20}\rightarrow3_{21}$	17900.20	24.97	25.26	−0.29 (−0.31)
$3_{03}\rightarrow4_{04}$	22464.07	0.56	0.47	0.09 (0.09)
$3_{22}\rightarrow4_{23}$	23314.12	−6.43	−6.04	−0.39 (−0.39)
$3_{31}\rightarrow4_{32}$	23581.14	−18.11	−18.15	0.04 (0.08)
$3_{30}\rightarrow4_{31}$	23586.15	17.70	17.91	−0.21 (−0.25)
b-type				
$0_{00}\rightarrow1_{11}$	11367.74	4.66	4.82	−0.16 (−0.14)
$1_{01}\rightarrow2_{12}$	16327.27	4.02	3.94	0.08 (0.12)
$2_{12}\rightarrow3_{03}$	12418.80	−3.80	−3.66	−0.14 (−0.17)
$3_{12}\rightarrow3_{21}$	15796.63	1.21	1.17	0.04 (0.21)
$3_{03}\rightarrow3_{12}$	9049.31	3.08	3.04	0.04 (0.07)
$4_{04}\rightarrow4_{13}$	11525.90	2.90	2.79	0.11 (0.13)
$4_{13}\rightarrow4_{22}$	15077.87	6.73	6.60	0.13 (0.20)
$4_{14}\rightarrow4_{23}$	22494.02	13.73	13.37	0.36 (0.43)

[a] Experimental uncertainty in the frequency measurements is ±0.1 MHz.

rected value of s. For the transitions in which the A-E splitting is less than 0.3 MHz, the splittings could not be measured; such transitions are shown by the dotted lines in the third column of Table 5. By using the Hamiltonian H_E mentioned above, the calculations were made by taking into account the terms of $FW_{0E}^{(1)}\mathscr{P}$ and $FW_{0E}^{(3)}\mathscr{P}^3$. The values shown in parentheses in the last column of Table 5 were tentatively calculated by neglecting the $FW_{0E}^{(3)}\mathscr{P}^3$ term. It can be seen that this neglect does not affect the result beyond the limits of experimental error. The determined value of s and the differences in A_A-A and B_A-B are shown in Table 4.

The value of V_3 calculated from the value of s is 1088±3 cal/mol. The uncertainty in the barrier arises primarily from the uncertainty in the assumed value of I_a. This assumed value, however, may be fairly reasonable, because the pseudo-inertial defect, $\Delta'=I_a-(I_a+I_b-I_c)$, is calculated to be 0.084 amu·Å^2, not very different from the value of 0.0458 amu·Å^2 [7] of the inertial defect of furan, where the unperturbed moments of inertia of 3-methylfuran, I_a, I_b, and I_c, are 56.8423 amu·Å^2, 150.101 amu·Å^2, and 203.837 amu·Å^2 respectively.

The barrier height of 3-methylfuran is not very different from that of 2-methylfuran, which is 1190 cal/mol.[1]

Dipole Moment. The dipole moment of 3-methylfuran for the ground vibrational state was determined from the second-order Stark effects of the $1_{01}\rightarrow2_{02}$, $2_{02}\rightarrow3_{03}$, $3_{03}\rightarrow3_{12}$, and $4_{04}\rightarrow4_{13}$ transitions of the A-level. The dipole moment and the observed and calculated Stark coefficients are given in Table 6.

TABLE 6. STARK EFFECT AND DIPOLE MOMENT OF 3-METHYLFURAN[a]

Transition		Stark coefficient (MHz(kV/cm)$^{-2}$) Observed	Calculated
$1_{01}\rightarrow2_{02}$	$M=0$	−4.50±0.15	−4.47
	$M=1$	6.64±0.15	6.74
$2_{02}\rightarrow3_{03}$	$M=0$	−1.12±0.12	−1.07
	$M=2$	3.47±0.13	3.50
$3_{03}\rightarrow3_{12}$	$M=3$	5.94±0.13	5.85
$4_{04}\rightarrow4_{13}$	$M=4$	2.92±0.10	2.87

$\mu_a=0.91\pm0.01$ D

$\mu_b=0.48\pm0.03$ D

$\mu=1.03\pm0.02$ D

[a] The absorption cell was calibrated by using the $J=1\rightarrow2$ transition of OCS, taking the dipole moment of OCS as 0.7152 D.[10]

The difference of 0.97 D between the dipole moment of tetrahydrofuran (1.63 D)[11] and that of furan (0.661 D)[12] is mainly due to the π-moment, μ_{mig}, caused by the migration of the π-electron of the oxygen atom in the furan ring. The μ_{mig} was calculated by Nagakura and Hosoya[13] to be 0.61 D and by Pujol and Julg[14] to be 0.89 D, pointing from a positive oxygen atom "up" the C(3)–C(4) bond. Therefore, it is certain that the direction of the total moment of furan is opposite to that of the μ_{mig}. Furthermore, it is known[15] that the moment, μ_b, along the b principal axis of the *trans* isomer of furfural is markedly smaller than that of the *cis* isomer. This fact is evidence in favor of this view. Based on the rule of vector addition for dipole moments, a relation among the dipole moment, μ, of 3-methylfuran, the μ_f value of the parent molecule, and the difference, μ_d, between the group moment of CH$_3$–C(sp^2) and the bond moment of H–C(sp^2) can be easily written as follow:

$$\frac{\sin(\theta+\varphi)}{\mu}=\frac{\sin\theta}{\mu_f}=\frac{\sin\varphi}{\mu_d}$$

where θ is the angle between μ and the C–CH$_3$ axis and φ, the angle between μ and the C_2 symmetry axis of the ring.

There are four possibilities for the direction of the experimentally-determined value of μ. However, by taking into account the fact that the value of μ_d is usually near 0.3 D,[16] only the direction shown in Fig. 1 is found to be possible. For this case, the θ and φ angles are 29±2° and 9±2° respectively. From the above relation we can calculate $\mu_f=0.80\pm0.06$ D and $\mu_d=0.27\pm0.04$ D, which points the negative end towards the C-atom of the ring. The values of μ_f and μ_d are resonable.

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