Microwave Spectrum and Dipole Moment of Methylenecyclobutenone

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The microwave spectrum of Methylenecyclobutenone has been investigated in the vibrational ground state in the range of 8 to 26.5 GHz. From a least square fit of 12 lines with $J \leqq 4$ the rotational constants have been calculated as $A = 5.775664 \pm 0.000009$ GHz, $B = 4.312314 \pm 0.000007$ GHz, $C = 2.467814 \pm 0.000008$ GHz. The inertia defect $\Delta = -0.09$ amuÅ^2 indicates that the molecule is planar.

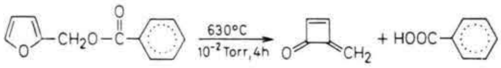
From Stark-effect measurements the components of the molecular electric dipole moment were obtaied as $|\mu_a| = 2.04 \pm 0.02$ D, $|\mu_b| = 2.70 \pm 0.03$ D, $|\mu_{total}| = 3.39 \pm 0.05$ D.

Introduction

The preparation of 3-Methylencyclobuten(1)one-4 (Methylencyclobutenone) has been reported recently [1]. Since the microwave spectra and rotational Zeeman effect of Cyclobutene [2, 3] and 3,4-Dimethylencyclobutene [4, 5] have been investigated, it is of interest to study the effects when one methylengroup in Dimethylencyclobutene is substituted by the carbonylgroup. In this communication we report the rotational spectrum in the ground vibrational state and the dipole moment of Methylencyclobutenone.

Preparation

Methylencyclobutenone has been prepared by gas phase pyrolysis of furfuryl benzoate [1].



The ester was synthesized from furfuryl alcohol and benzoyl chloride by a conventional Schotten-Baumann-reaction with pyridine as solvent. The pyrolysis of 1.07 g of furfuryl benzoate was carried out in a quartz tube filled with pieces of quartz at an oven temperature of about 630 °C, an evaporation temperature for the ester of about 80 °C and a pressure of ca. 10^{-2} Torr. Under these conditions the reaction took 4 hours.

The resulting benzoic acid cristallized immediately after the oven at the walls (room temperature) of the vacuum system. All other reaction products were collected in a sequence of three traps, kept at temperatures of −10 °C, −70 °C and −190 °C respectively. Methylencyclobutenone has been found in the second trap cooled down to −70 °C and was identified by its 60 MHz proton-NMR spectrum and its liquid phase IR-Spectrum.

The compound was found to be stable for weeks when cooled by liquid air and for several days at a temperature of −70 °C.

Microwave Spectrum of Methylenecyclobutenone

The microwave spectrum of methylencyclobutenone has been investigated in the frequency region from 8 to 26.5 GHz with a conventional Stark-effect modulated spectrometer described previously [6, 7]. The absorption cell, an oversized cell, with an inner cross section of 1 cm × 4.7 cm had a length of 8 m. A modulation frequency of 33 KHz was used. All measurements were made at a pressure of about 10^{-2} Torr and at temperatures between −50 °C and −60 °C.

In order to assign the lines preliminary rotational constants had been calculated for an estimated structure. The geometry of the ring (including the ring protons) has been taken from cyclobuten [2]; those for the carbonylgroup from cyclobutanone [8] and for the methylengroup from fulven [9]. Assuming the rigid rotor approximation a spectrum has been calculated from these preliminary rotational constants. With the help of the predicted spectrum μ_a- and μ_b-lines have been found and their assignment was confirmed by their Stark-patterns. Since the pyrolysis of furfuryl benzoate yields many other products besides methylencyclobutenon which could not be seperated completely from the main product the assignment of the spectrum was complicated by additional lines.

The lines which have been measured up till now are listed in Table 1. From these the rotational constants given in Table 2 were calculated using the rigid rotor approximation. The small value of the inertia defect $\Delta = I_{aa} + I_{bb} - I_{cc} = -0.99$ amuÅ^2 indicates, that the nuclear frame is planar. Although the structure of the molecule cannot be determined from the rotational constants of one isotopic species a tentative structure which is in close agreement with the observed rotational constants is given in Figure 1.

Table 1. Rotational transitions of methylencyclobutenone used for the calculation of the rotational constants.

Transition JK_-K_+ $J'K'_-K'_+$	Observed frequency ν_0 [MHz]	Calculated frequency ν_c [MHz]	$\Delta\nu = \nu_0 - \nu_c$ [MHz]
a-type transitions			
$1_{01} - 2_{02}$	12 589.482	12 589.429	0.053
$1_{10} - 2_{11}$	15 404.758	15 404.757	0.001
$1_{11} - 2_{12}$	11 715.752	11 715.758	−0.006
$2_{20} - 3_{21}$	23 188.793	23 188.879	−0.086
$2_{11} - 3_{12}$	22 223.189	22 223.308	−0.119
b-type transitions			
$1_{01} - 2_{12}$	13 179.135	13 179.108	0.027
$1_{11} - 2_{02}$	11 126.049	11 126.079	−0.030
$1_{11} - 2_{20}$	22 610.230	22 610.136	0.094
$1_{10} - 2_{21}$	19 794.879	19 794.807	0.071
$3_{03} - 3_{12}$	10 854.597	10 854.592	0.005
$2_{11} - 3_{22}$	24 730.502	24 730.437	+0.065
$4_{31} - 4_{40}$	13 732.954	13 733.041	−0.087

Table 2. Rotational constants and moments of inertia of methylencyclobutenone. The values were calculated from the transitions given in Table 1; conversion factor $5.05376 \cdot 10^5$ [amu Å$^2 \cdot$ MHz] [11].

A	5 775.664 ± 0.009 MHz
B	4 312.314 ± 0.007 MHz
C	2 467.814 ± 0.008 MHz
$\varkappa = \dfrac{2B - A - C}{A - C}$	0.115 226 ± 0.086
I_a	87.501 ± 0.001 amu Å^2
I_b	117.194 ± 0.004 amu Å^2
I_c	204.787 ± 0.006 amu Å^2
$\Delta I = I_a + I_b - I_c$	−2.092 ± 0.011 amu Å^2

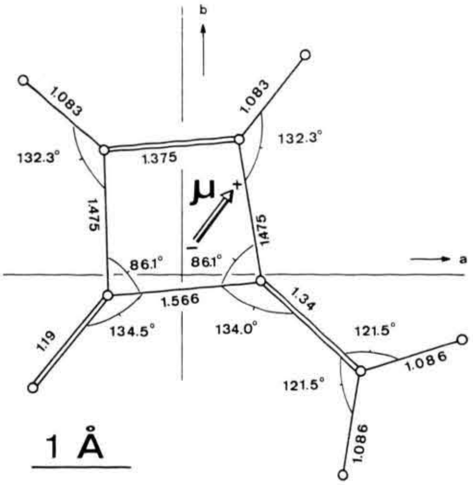


Fig. 1. Tentative structure of methylencyclobutenon which would be in close agreement with the observed rotational constants. Calculated rotational constantants: $A = 5.777063$ GHz; $B = 4.312504$ GHz; $C = 2.469245$ GHz.

Dipole Moment

The dipole moment of methylencyclobutenone for the ground vibrational state has been calculated from the second order Stark-effect of the $1_{10} - 2_{21}$, $2_{11} - 3_{12}$ and $2_{11} - 3_{22}$ transitions (see Table 3). The absorption cell was calibrated by using the $J = 1 - 2$ transition of $^{16}O^{12}C^{32}S$ taking the dipole moment of OCS as 0.71521 D [10].

Using the structure shown in Fig. 1 an INDO-calculation was made to calculate the electric dipole moment of the molecule. The values obtained are $\mu_a^{\mathrm{INDO}} = 1.66$ D and $\mu_b^{\mathrm{INDO}} = 2.41$ D. They indicate that the orientation of the dipole moment within the molecule should be as shown in Figure 1.

Table 3. Electric dipole moment of methylencyclobutenone from Stark-effect measurements. Complete diagonalisation of the Hamilton-matrix combined with a least squares fitting procedure was used to calculate the absolute values of the components of the dipole moment $|\mu_a|$ and $|\mu_b|$. The direction of the dipole moment within the molecule is shown in Fig. 1. (The sign of μ_a and μ_b follows from a comparison with an INDO-calculation.) The experimental uncertainties are standard deviations The experimental uncertainty of the Stark-field calibration was ±0.5%.

Transition JK_-K_+ $J'K'_-K'_+$	M	E [V/cm]	$\Delta\nu_{\mathrm{obs}}$ [MHz]	$\Delta\nu_{\mathrm{cal}}$ [MHz]	$\Delta\nu_{\mathrm{ob}} - \Delta\nu_{\mathrm{cal}}$ [MHz]
$1_{10} - 2_{21}$	0	316.12	2.842	2.841	0.001
$2_{11} - 3_{12}$	0	637.16	2.372	2.378	−0.006
	1	1474.63	−1.838	−1.900	−0.062
$2_{11} - 3_{22}$	0	423.79	1.211	1.200	0.011
	1	424.57	−3.120	−3.089	−0.031

$|\mu_a| = 2.04 \pm 0.02$ D; $|\mu_b| = 2.70 \pm 0.03$ D; $|\mu_{\mathrm{total}}| = 3.39 \pm 0.05$ D.

Acknowledgement

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