

Microwave Spectrum of 2-Nitrothiophene

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The microwave spectrum of 2-nitrothiophene has been studied in the frequency region 18 000–26 500 MHz. The rotational transitions of the ground state and the first four torsionally excited states have been assigned. The molecule has been shown to be planar in the equilibrium conformation. The first torsional frequency and the barrier to internal rotation of the nitro group have also been estimated.

The present work reports a microwave spectroscopic investigation of 2-nitrothiophene and is an extension of the recently published article on 3-nitrothiophene.¹ As in our previous work the aim of the present study was to determine the equilibrium conformation of the molecule and to estimate the torsional frequency and the barrier to internal rotation of the nitro group.

EXPERIMENTAL

The sample of 2-nitrothiophene was purchased from Ega-Chemie KG and used without further purification. Microwave spectra were recorded at room temperature in the frequency region 18–26.5 GHz using a Hewlett-Packard 8460A spectrometer. Sample pressures ranged between 15 and 70 mTorr.

MICROWAVE SPECTRUM AND ROTATIONAL CONSTANTS

The rotational transitions of the ground state of 2-nitrothiophene (*cf.* Fig. 1) were assigned together with four vibrational satellites with regularly decreasing intensities. Since the torsional vibration of the nitro group is expected to be the lowest frequency vibration, the observed satellites were assigned to this mode.

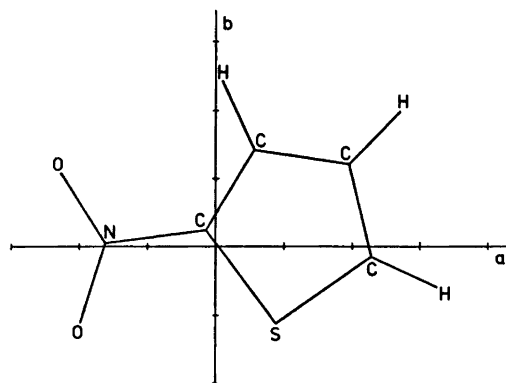


Fig. 1. 2-Nitrothiophene.

The measured and calculated transition frequencies of the ground state are listed in Table 1. The measured transition frequencies of the four assigned torsionally excited states are obtainable upon request from the authors. Only *R*-branch *a*-type transitions of the common ³²S species were identified in the spectrum. The rotational constants, calculated by a least squares method, are presented in Table 2. Since the agreement between the measured and calculated frequencies was good, the centrifugal distortion coefficients were not included in the fit. Table 2 contains also moments of inertia and inertial defects for all vibrational species.

RESULTS AND DISCUSSION

The expected planarity of the molecule of 2-nitrothiophene is clearly demonstrated by the small negative value ($\Delta = -0.164 \text{ amu \AA}^2$) of the inertial defect in the ground state (*cf.* Table 2) and an equally small but positive

Table 1. Rotational transitions (MHz) of 2-nitrothiophene in the ground state.

Transition	ν_{obs}^a	$\nu_{\text{obs}} - \nu_{\text{calc}}$	Transition	ν_{obs}^a	$\nu_{\text{obs}} - \nu_{\text{calc}}$
$8_{1,8} \leftarrow 7_{1,7}$	18 437.50	-0.01	$10_{1,10} \leftarrow 9_{1,9}$	22 815.05	0.00
$7_{3,5} \leftarrow 6_{3,4}$	18 467.80	0.20	$10_{0,10} \leftarrow 9_{0,9}$	22 843.14	0.03
$7_{4,4} \leftarrow 6_{4,3}$	18 500.85	0.19	$9_{9,2} \leftarrow 8_{9,1}$	23 640.13	-0.15
$8_{0,8} \leftarrow 7_{0,7}$	18 533.01	0.07			
$7_{1,6} \leftarrow 6_{1,5}$	18 770.68	-0.06	$9_{7,3} \leftarrow 8_{7,2}$	23 673.87	-0.05
$7_{3,4} \leftarrow 6_{3,3}$	18 948.44	0.01			
$7_{2,5} \leftarrow 6_{2,4}$	19 629.87	0.09	$9_{7,2} \leftarrow 8_{7,1}$	23 823.73	0.05
$8_{2,7} \leftarrow 7_{2,6}$	20 202.28	0.11	$9_{5,4} \leftarrow 8_{5,3}$	23 896.39	0.15
$9_{1,9} \leftarrow 8_{1,8}$	20 630.59	-0.03	$9_{4,6} \leftarrow 8_{4,5}$	24 104.46	-0.02
$9_{0,9} \leftarrow 8_{0,8}$	20 683.34	0.02	$9_{5,4} \leftarrow 9_{4,4}$	24 965.22	0.00
$8_{7,2} \leftarrow 7_{7,1}$	21 017.16	0.04	$9_{3,6} \leftarrow 8_{3,5}$	24 994.37	-0.01
$8_{7,1} \leftarrow 7_{7,0}$	21 035.86	0.04	$11_{1,11} \leftarrow 10_{1,10}$	25 092.03	-0.01
$8_{1,7} \leftarrow 7_{1,6}$	21 054.08	0.09	$9_{2,7} \leftarrow 8_{2,6}$	25 285.35	-0.04
$8_{6,3} \leftarrow 7_{6,2}$	21 079.13	0.11	$10_{1,9} \leftarrow 9_{1,8}$	26 171.52	-0.06
$8_{6,2} \leftarrow 7_{6,1}$	21 287.40	0.01	$10_{3,8} \leftarrow 9_{3,7}$	26 263.48	-0.17
$8_{3,6} \leftarrow 7_{3,5}$	21 930.62	0.05	$10_{2,9} \leftarrow 9_{2,8}$	26 294.92	-0.10
$8_{4,4} \leftarrow 7_{4,3}$	22 421.78	0.05	$10_{3,2} \leftarrow 9_{3,1}$	26 341.24	-0.06
$8_{3,5} \leftarrow 7_{3,4}$	22 534.68	0.11	$10_{7,4} \leftarrow 9_{7,3}$		-0.09
$9_{2,8} \leftarrow 8_{2,7}$			$10_{7,3} \leftarrow 9_{7,2}$		

^a ± 0.05 MHz.

 Table 2. Rotational constants (MHz), moments of inertia ($\text{amu } \text{Å}^2$) and inertial defects ($\text{amu } \text{Å}^2$) of 2-nitrothiophene in the ground and torsionally excited states.^a

	$v=0^b$	$v=1$	$v=2$	$v=3$	$v=4$
<i>A</i>	3818.49(8)	3817.72(9)	3816.81(13)	3816.21(14)	3815.49(11)
<i>B</i>	1518.602(3)	1515.521(3)	1512.447(5)	1509.399(5)	1506.351(4)
<i>C</i>	1086.887(3)	1087.777(3)	1088.672(4)	1089.566(4)	1090.473(3)
<i>I_a</i>	132.350	132.376	132.408	132.429	132.454
<i>I_b</i>	332.790	333.467	334.145	334.819	335.497
<i>I_c</i>	464.976	464.595	464.213	463.832	463.447
<i>Δ</i>	-0.164	-1.248	-2.340	-3.416	-4.504

^a The uncertainties represent one standard deviation. ^b $\kappa = -0.6839$.

value ($\Delta = +0.38 \text{ amu } \text{Å}^2$) of the extrapolated inertial defect for the hypothetical torsionless state. The planarity is also demonstrated by the linear variation of the rotational constants *B* and *C* with the torsional quantum number (the variation of the constant *A* has not been considered because of its large standard deviation).

This linear variation as well as the linear variation of the inertial defect with the torsional quantum number, indicate that the torsional mode of vibration of the nitro group is

harmonic (or nearly harmonic). We could thus estimate the first torsional frequency using the well-known formula:²

$$\nu_t = \frac{\hbar}{2\pi^2 c} \frac{1}{\Delta_0 - \Delta_1}$$

where the torsional frequency (ν_t) was calculated from the change of the inertial defect between the ground and the first torsionally excited states. Inserting the values of Δ_0 and Δ_1 from Table 2 we obtained $\nu_t = 62 \text{ cm}^{-1}$.

Unfortunately this value is in less than perfect agreement with the value of the torsional frequency, obtained from relative intensity measurements. These measurements, performed on 10 line pairs at room temperature, gave an intensity ratio of 0.65 ± 0.08 between the first vibrational satellite and the ground state lines. This ratio corresponds to a vibrational frequency $\nu_t = 90 \pm 20 \text{ cm}^{-1}$.

Of the two estimates, higher credibility should be given to the value obtained from the inertial defect variation in view of the fairly harmonic character of the torsional vibration, and the very approximate intensity measurements.

No comparable data are available since no far infra-red investigation on 2-nitrothiophene has yet been reported. The estimated value of the torsional frequency of the nitro group in 2-nitrothiophene, reported in this paper, lies between the corresponding torsional frequencies of nitrobenzene³ and nitroethylene.⁴

Since the torsional frequency is known, the height of the barrier hindering the rotation of the nitro group could be estimated, using the theory of Fateley *et al.*⁵ The results presented in this article yielded only an order of magnitude estimate of the height of the barrier. Approximate calculation gave a value of 20 kJ/mol.

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