The Microwave Spectrum of 4-Methylthiazole: Methyl Internal Rotation, ^{14}N Nuclear Quadrupole Coupling and Electric Dipole Moment

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The microwave spectrum of 4-methylthiazole has been investigated in the frequency region from 8 to 36 GHz, employing both Fourier transform and Stark spectroscopy. The results of ^{14}N quadrupole hyperfine structure, methyl internal rotation and fourth order centrifugal distortion analyses are given. The dipole moment components could be determined from the Stark splittings of some rotational lines.

Introduction

The microwave spectra of the monomethyl derivatives of the aromatic heterocycles furan [1, 2, 3] and thiophen [4, 5] have been investigated some years ago. Comparison of the potential barrier hindering methyl internal rotation shows a reduction up to 50% with substituting oxygen by sulphur in the ring. Recently the studies on the heterocyclic compounds 2-, 4- and 5-methyloxazole [6] and 3-, 4- and 5-methylisoxazole [7, 8] with two heteroatoms were completed. These studies shall be extended to the sulphur homologue compounds to find out a characteristic trend of the potential barrier with substituting oxygen as a heteroatom out of the first row of the periodic system by the next element in the column.

Experimental

The sample was obtained from Aldrich-Chemie, Steinheim/Albuch, Germany and used without further purification.

The narrow splitting of the rotational lines due to ^{14}N quadrupole coupling made it necassary to use the high resolution capability of microwave Fourier transform (MWFT) spectroscopy. MWFT spectrometers were used in Ku- [9] and K-band [10] (8–26 GHz) at sample pressures below 2 mTorr and at temperatures of about $-60\,^\circ$C.

To check the assignment of lines we used both a MWFT double resonance bridge spectrometer [11] as well as a conventional double resonance spectrometer with pump modulation and phase sensitive detection [12].

The Stark effect measurements for determination of the dipole moment components were performed with a conventional 100 kHz modulated Stark spectrometer in the frequency region from about 18 to 36 GHz.

Analysis

To facilitate the assignment of the microwave spectrum estimations of the rotational constants were made. One set was obtained by taking the r_s-structure of thiazole [13] as basis and substituting the hydrogen atom in the 4-position by a methyl-group with an assumed structure (C – C distance 1.52 Å, C – H distance 1.1 Å, C – C – H angle 110.0°, C – C – CH_3 – angle = C – C – H – angle in thiazole). The other set was derived from the optimized geometry calculated by the semi-empirical MNDO-method [14]. The assignment on the basis of these constants was confirmed by means of double resonance spectroscopy. An example of the verifications of the assignment using a special pulse sequence technique [15] is shown in Figure 1.

The effects of methyl internal rotation, ^{14}N quadrupole coupling and centrifugal distortion were treated as independent contributions to the rigid rotor Hamiltonian. Since the hyperfine structure (hfs) due to ^{14}N quadrupole coupling of the torsional A- and E-species

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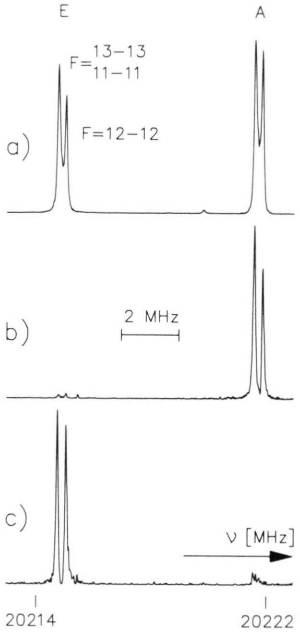

Fig. 1. FT spectra of the rotational transition $J'(K'_-, K'_+) - J''(K''_- K''_+) = 12(3, 9) - 12(2, 10)$ with ^{14}N-NQHFS and internal rotation A-E-splitting. a) no pump radiation, conventional MWFT-spectrum with polarizing signal radiation at 20 217.940 MHz. b) with pump radiation at 10 324.400 MHz, near resonant with A-species of transition $J'(K'_-, K'_+) - J''(K''_-, K''_+) = 12(3, 9) - 12(3, 10)$. c) with pump radiation at 10 332.650 MHz, near resonant with E-species of the above transition. The resonance frequencies for the μ_a-type pump transition were approximated from the molecular constants and not measured directly.

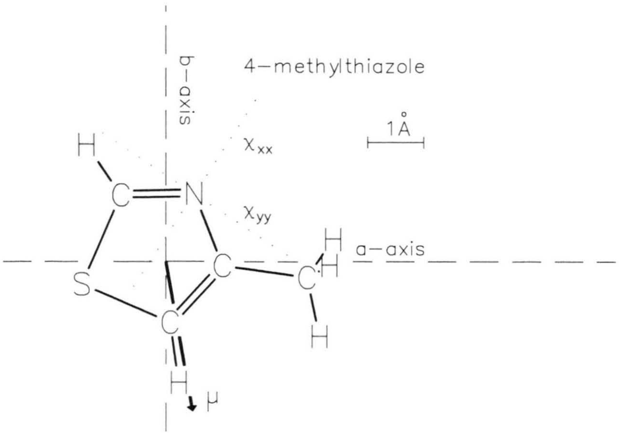

Fig. 2. Alignment of the principal inertia axes a and b, the dipole moment vector and the ^{14}N nuclear quadrupole coupling tensor in 4-methylthiazole. – – – principal inertia axes; · · · · · nuclear quadrupole coupling tensor axes; —— most probable alignment of the dipole moment vector.

do not differ significantly the ^{14}N-hfs analysis was done only for the A-species. With the determined constants χ_+ and χ_- derived from a first order perturbation treatment hypothetical line frequencies, not affected by nuclear quadrupole coupling, were calculated. These frequencies were used to analyze the torsional fine structure of the rotational lines employing the internal axis method (IAM) [16, 17]. The results of the IAM analysis, i.e. the Fourier coefficient $w_1(s)$, the angle between the principal inertia axis a and the internal rotation axis i $\sphericalangle$ a, i and the moment of inertia of the methyl group I_α, were used to calculate hypothetical unsplit line frequencies which only contain deviations from the rigid rotor behaviour due to centrifugal distortion. The rotational constants A, B, and C and five fourth-order centrifugal distortion constants Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K followed from an analysis according to Watson's A reduction of these frequencies [18].

Because of the limited sensitivity of the used Stark-spectrometer the following comparatively strong transitions with relatively high J-quantum numbers were measured to determine the electric dipole moment components μ_a and μ_b namely $J(K_-, K_+) = 6(0, 6) - 5(1, 5)$, $6(3, 4) - 6(2, 5)$, $7(1, 7) - 6(0, 6)$ and $8(4, 4) - 8(3, 5)$. Field strengths up to 1800 V/cm were applied.

Results and Discussion

Frequencies of some measured lines with low J-quantum numbers, including ^{14}N-hfs and A-E internal rotation splittings, are given in Table 1. A complete list is available under No. TNA11 (W. Jäger, H. Mäder) from the Universitätsbibliothek, University of Kiel, Westring 400, D-2300 Kiel.

The results of the hfs-analysis given in Table 2 are in good agreement with the predicted constants $\chi_{aa} = -0.05$ MHz, $\chi_{bb} = -2.53$ MHz and $\chi_{cc} = 2.58$ MHz. These constants were obtained by projecting the principal axes of the quadrupole coupling tensor as known in the thiazole ring [13] on the principal inertia axes of an assumed structure of 4-methylthiazole (see Figure 2). This agreement leads to the conclusion that the electronical surrounding of the nitrogen atom in thiazole is not much changed upon methyl substitution in 4-position.

In Table 3 the internal rotation parameters derived by an IAM-analysis are given. The value of the poten-

Table 1. Measured transitions of 4-methylthiazole. Γ: torsional symmetry species; ν_{obs}; observed frequency, Ku-band data evaluated from line shape simulations [23], K-band data obtained from transient emission signal analyses [24]; ν_A^0, ν_E^0: hypothetical centre line frequencies of A-respectively E-species calculated from measured hfs-component frequencies with calculated hfs-splittings; ν_A^0 (calc), ν_E^0 (calc): hypothetical centre line frequencies obtained by centrifugal distortion calculations respectively methyl internal rotation calculations. Frequencies in MHz.

$J'(K'_-, K'_+) - J''(K''_-, K''_+)$	$F' - F''$	Γ	ν_{obs}	ν_A^0	ν_A^0(calc)	ν_E^0	ν_E^0(calc)
2 (2, 0) − 2 (1, 1)				14 415.707	14 415.705		
	3 − 3	A	14 415.824				
	2 − 2	A	14 415.301				
	1 − 1	A	14 416.112				
2 (2, 1) − 2 (1, 2)				16 241.261	16 241.259		
	3 − 3	A	16 241.055				
	2 − 2	A	16 241.967				
	1 − 1	A	16 240.557				
2 (1, 2) − 1 (0, 1)				13 016.303	13 016.300	13 012.639	13 012.644
	3 − 2	A	13 016.466				
	3 − 2	E	13 012.812				
	2 − 1	A	13 015.739				
	2 − 1	E	13 012.084				
	1 − 0	A	13 016.793				
	1 − 0	E	13 013.110				
2 (2, 1) − 1 (1, 0)				23 843.789	23 843.788	23 784.749	23 784.750
	3 − 2	A	23 843.887				
	3 − 2	E	23 784.842				
	2 − 1	A	23 843.238				
	2 − 1	E	23 784.203				
2 (2, 0) − 1 (1, 1)				24 529.377	24 529.367	24 570.643	24 570.654
	3 − 2	A	24 529.217				
	3 − 2	E	24 570.506				
	2 − 1	A	24 530.089				
	2 − 1	E	24 571.332				
3 (2, 1) − 3 (1, 2)				13 739.960	13 739.960		
	4 − 4	A	13 740.068				
	3 − 3	A	13 739.625				
	2 − 2	A	13 740.232				
3 (2, 2) − 3 (1, 3)				17 217.521	17 217.520		
	4 − 4	A	17 217.299				
	3 − 3	A	17 218.198				
	2 − 2	A	17 216.977				
3 (1, 3) − 2 (0, 2)				16 526.863	16 526.863	16 523.566	16 523.564
	4 − 3	A	16 527.039				
	4 − 3	E	16 523.752				
	3 − 2	A	16 526.338				
	3 − 2	E	16 523.038				
	2 − 1	A	16 527.259				
	2 − 1	E	16 523.954				
4 (2, 2) − 4 (1, 3)				13 116.013	13 116.015	13 113.300	13 113.304
	5 − 5	A	13 116.090				
	5 − 5	E	13 113.375				
	4 − 4	A	13 115.798				
	4 − 4	E	13 113.089				
	3 − 3	A	13 116.166				
	3 − 3	E	13 113.452				
4 (2, 3) − 4 (1, 4)				18 534.249	18 534.246	18 519.750	18 519.754
	5 − 5	A	18 534.008				
	5 − 5	E	18 519.508				
	4 − 4	A	18 534.912				
	4 − 4	E	18 520.421				
	3 − 3	A	18 533.774				
	3 − 3	E	18 519.269				

Table 1 (continued)

$J'(K'_-, K'_+) - J''(K''_-, K''_+)$	$F' - F''$	Γ	ν_{obs}	ν_A^0	ν_A^0(calc)	ν_E^0	ν_E^0(calc)
4 (1, 4) − 3 (0, 3)				19 822.100	19 822.102	19 819.020	19 819.013
	5 − 4	A	19 822.276				
	5 − 4	E	19 819.190				
	4 − 3	A	19 821.642				
	4 − 3	E	19 818.563				
	3 − 2	A	19 822.404				
	3 − 2	E	19 819.328				
4 (0, 4) − 3 (1, 3)				13 697.781	13 697.782	13 700.634	13 700.640
	5 − 4	A	13 697.698				
	5 − 4	E	13 700.553				
	4 − 3	A	13 698.077				
	4 − 3	E	13 700.934				
	3 − 2	A	13 697.509				
	3 − 2	E	13 700.355				

Table 2. ^{14}N Quadrupole Coupling Constants of 4-Methylthiazole. χ_+, χ_-: quadrupole coupling constants ($\chi_+ = \chi_{bb} + \chi_{cc}$ and $\chi_- = \chi_{bb} - \chi_{cc}$) resulting from a least squares analysis involving all lines up to rotational quantum number $J = 11$; σ: standard deviation of the fit; $\overline{\Delta\nu_{\text{exp}}}$: mean experimental hfs-splitting; standard errors in brackets.

		Correlation matrix	
χ_+	0.3097 (60) MHz	1.000	
χ_-	− 4.7672 (71) MHz	− 0.041	1.000
σ	0.006 MHz		
$\overline{\Delta\nu_{\text{exp}}}$	0.375 MHz		
χ_{aa}	− 0.3097 (60) MHz		
χ_{bb}	− 2.2288 (66) MHz		
χ_{cc}	2.5385 (66) MHz		

Table 3. Internal Rotation Parameters of 4-Methylthiazole. $w_1(s)$: first Fourier coefficient; I_α: moment of inertia of the methyl group; $\sphericalangle(i, a)$: angle between the internal rotation axis i and the principal inertia axis a; s: reduced barrier height; V_3 potential coefficient; F: reduced rotational constant; σ: standard deviation of the fit; $\overline{\Delta\nu_{AE}}$: mean experimental splitting; standard errors in brackets. All measured splittings were taken for the internal rotation analysis.

			Correlation matrix		
$w_1(s)$	$-0.11585(3) \cdot 10^{-2}$		1.000		
I_α	3.1743 (10)	amuÅ^2	− 0.625	1.000	
$\sphericalangle(i, a)$	$6.85(9)^0$		− 0.967	0.725	1.000
s	28.5741 (14)				
V_3	1 022.3 (4)	cal/mol			
F	166.79 (6)	Ghz			
σ	0.012	MHz			
$\overline{\Delta\nu_{AE}}$	14.054	MHz			

Table 4. Rotational and Centrifugal Distortion Constants of 4-Methylthiazole A, B, C: rotational constants; Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K: fourth order centrifugal distortion constants according to Watson's A reduction; σ: standard deviation of the fit; standard errors in brackets.

			Correlation matrix							
A	7 312.4263 (6)	MHz	1.000							
B	2 528.4147 (2)	MHz	0.663	1.000						
C	1 900.6345 (2)	MHz	0.599	0.743	1.000					
Δ_J	0.1544 (16)	kHz	0.686	0.581	0.753	1.000				
Δ_{JK}	0.406 (13)	kHz	0.011	0.042	−0.291	−0.492	1.000			
Δ_K	2.394 (64)	kHz	0.657	0.353	0.518	0.877	−0.633	1.000		
δ_J	0.03611 (63)	kHz	0.138	0.168	−0.338	−0.373	0.866	−0.368	1.000	
δ_K	0.362 (20)	kHz	−0.190	−0.156	0.191	0.293	−0.918	0.357	−0.943	1.000
σ	0.004	MHz								

Table 5. Dipole Moment Components of 4-Methylthiazole. μ_a, μ_b: dipole moment components in direction of the principal inertia axes a and b; μ_{total}: total dipole moment; σ: standard deviation of the fit; $\overline{\Delta\nu_{\text{exp}}}$: mean experimental splitting; standard errors in brackets.

		Correlation matrix	
μ_a	0.240(1) D	1.000	
μ_b	1.327(2) D	0.040	1.000
μ_{total}	1.349(2) D		
σ	0.080 MHz		
$\overline{\Delta\nu_{\text{exp}}}$	5.115 MHz		

tial barrier V_3 is decreased by 16.5% compared with 4-methyloxazole [6]. This agrees with the trend observed in the comparison of 3-methylfuran ($V_3 = 1088$ cal/mol) [3] with 3-methylthiophen ($V_3 = 740$ cal/mol) [5].

It seems that the height of the potential barrier is correlated with the degree of the ring aromaticity in the sense that increasing aromaticity results in decreasing barrier height. The non-local part of the 'out-of-plane' -suszeptibility of ring compounds accessible by rotational Zeeman-spectroscopy can be seen as a measure of the ring aromaticity [19]. A survey of the corresponding datas of several 5-membered heterocyclic compounds is given in [20]. Unfortunately only a few methyl-substituted aromatic compounds have been analyzed so far [21, 22].

The measured transitions are sufficient to determine the three rotational constants A, B and C and the five fourth-order centrifugal distortion constants with satisfactory accuracy. The parameters obtained from a least squares fit with use of all measured lines are summarized in Table 4.

The analysis of the Stark-effect measurements lead to the results given in Table 5. The determined dipole moment components agree with those derived from the semiempirical CNDO-method as $\mu_a = 0.3$ D, $\mu_b = 1.3$ D. In Fig. 2 the most probable alignment of the dipole moment vector is shown.

Further studies on the other methyl derivatives of thiazole and isothiazole are presently undertaken to find out the systematics of the molecular constants, in particular the hindering potential, on methyl substitution in the different positions in the rings. The results will be given in forthcoming papers.

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