dependence of γ-proton coupling in the propyl radical led to the opinion that the coupling was very sensitive to the precise orientation of the radical [6]. Our studies of $CH_3\dot{C}(CN)CH_2CH_3$ and $CH_3\dot{C}(CN)CH_2CH_2CH_3$ radicals lead to the same conclusion. Although these radicals are structurally rather similar, their γ-proton coupling constants differ by a factor of about three. The steric requirements for maximum γ-proton coupling are still not clear.

The hyperfine coupling constants of nitrogen atoms in our radicals are of similar magnitude to those found by other workers for similar radicals. The observation that all nitrogen hyperfine coupling constants in the radicals studied by us are the same, within experimental error, is not surprising since for the nitrile group a significant orientation-dependence is not expected. A dependence of the nitrogen hyperfine coupling constant on ϱ (Table 3) might be expected [31], but the effect is too small to be detected in our experiments.

It is noticeable (Table 2) that the linewidths, although small in all cases, increased with increasing radical size. This may be understood in a general way, since correlation times are proportional to the effective volumes of radicals, if variations in viscosity may be neglected [32].

I am indebted to the Leverhulme Trustees for a Research Fellowship.

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Barrier to Internal Rotation, Centrifugal Distortion Analysis and Structural Considerations of Methanesulfenylchloride

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(Z. Naturforsch. **25 a**, 18—25 [1970]; received 18 October 1969)

An investigation of the microwave spectrum of CH_3SCl^{35} in the excited torsional state has been carried out. The barrier to internal rotation and other connected parameters are thus obtained. A centrifugal distortion analysis of the microwave spectrum of CH_3SCl^{35} in the ground state is also performed to predict high J transitions. A r_0-structure and bond axis quadrupole coupling constants are also considered.

In a preceeding paper the microwave spectrum of methanesulfenylchloride has been investigated [1]. The rotational constants and the quadrupole coupling constants have been given for both isotopic species CH_3SCl^{35} and CH_3SCl^{37} in the ground state. The dipole moment of the CH_3SCl^{35} species has also been determined.

Since a splitting due to internal rotation motion of the CH_3-group could not be observed, the present work was undertaken to investigate high J transitions in the ground state and transitions in the first excited torsional state. Considerations concerning structure and quadrupole coupling constants are also given.

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The microwave spectrometer is a conventional 100 kHz Stark effect spectrometer operating in the range 6 – 37 GHz described elsewhere [2, 3].

Frequency measurements are believed to be accurate within ± 0.03 MHz. The sample of methanesulfenylchloride was prepared by J. ROSENBAUM, Freiburg, and used without further purification.

Centrifugal Distortion Analysis

The centrifugal distortion analysis has been made essentially to predict the high J transition frequencies of CH_3SCl^{35} in the ground state. Thereby it was possible to find such lines and check for a possible splitting due to internal rotation.

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$J_{K-1,K_1} \rightarrow J'_{K'_{-1},K'_1}$	$F \rightarrow F'$	observed frequencies	unsplit frequencies	calculated frequencies	$\nu_{unspl} - \nu_{calc}$	centr. dist. contribution
$0_{00} \rightarrow 1_{01}$	3/2 → 3/2	8311.24	8322.89	8322.88	0.01	− 0.01
	3/2 → 5/2	8325.81				
	3/2 → 1/2	8337.42				
$1_{01} \rightarrow 1_{10}$	1/2 → 3/2	13616.23	13622.56	13622.60	− 0.04	− 0.13
	5/2 → 5/2	13617.37				
	3/2 → 1/2	13623.41				
	5/2 → 3/2	13628.40				
	3/2 → 5/2	13632.01				
$14_{3.12} \rightarrow 14_{3.11}$	25/2 → 25/2	13187.50	13188.60	13188.64	− 0.04	− 29.06
	31/2 → 31/2					
	27/2 → 27/2	13189.71				
	29/2 → 29/2					
$2_{02} \rightarrow 2_{11}$	7/2 → 7/2	14548.61	14551.78	14551.75	0.03	− 0.16
	3/2 → 3/2	14551.79				
$1_{11} \rightarrow 2_{12}$	3/2 → 5/2	15750.42	15761.12	15761.10	0.02	0.00
	5/2 → 5/2	15754.13				
	3/2 → 3/2	15758.15				
	5/2 → 7/2	15764.89				
	1/2 → 1/2	15775.77				
$1_{01} \rightarrow 2_{02}$	1/2 → 3/2	16586.72	16601.20	16601.20	0.00	− 0.08
	5/2 → 5/2	16587.71				
	5/2 → 7/2	16602.43				
	3/2 → 3/2	16612.89				
$12_{48} \rightarrow 11_{57}$	21/2 → 19/2	16666.59	16668.23	16668.25	− 0.02	− 17.05
	27/2 → 25/2					
	23/2 → 21/2	16669.86				
	25/2 → 23/2					
$1_{10} \rightarrow 2_{11}$	3/2 → 5/2	17519.04	17530.34	17530.34	0.00	− 0.11
	3/2 → 3/2	17521.62				
	3/2 → 1/2	17525.30				
	5/2 → 5/2	17529.88				
	5/2 → 7/2	17533.58				
	1/2 → 3/2	17541.22				
	1/2 → 1/2	17544.92				
$8_{36} \rightarrow 9_{27}$	15/2 → 17/2	18029.59	18030.18	18030.15	0.03	− 7.91
	17/2 → 19/2					
	19/2 → 21/2	18030.75				
	13/2 → 15/2					
$4_{04} \rightarrow 4_{13}$	5/2 → 5/2	18136.71	18141.43	18141.44	− 0.01	− 0.55
	11/2 → 11/2	18139.05				
	7/2 → 7/2	18143.28				
	9/2 → 9/2	18145.55				
$15_{3.13} \rightarrow 15_{3.12}$	33/2 → 33/2	18248.11	18249.40	18249.37	0.03	− 43.10
	27/2 → 27/2					
	29/2 → 29/2	18250.68				
	31/2 → 31/2					
$5_{2.4} \rightarrow 6_{1.5}$	11/2 → 13/2	19087.43	19088.36	19088.37	− 0.01	− 2.56
	9/2 → 11/2					
	7/2 → 9/2	19089.21				
	13/2 → 15/2					
$5_{05} \rightarrow 5_{14}$	5/2 → 7/2	20996.43	21000.54	21000.55	− 0.01	− 1.15
	7/2 → 9/2	20998.08				
	11/2 → 13/2	21002.60				
	9/2 → 11/2	21004.42				
$0_{00} \rightarrow 1_{11}$	3/2 → 1/2	21057.12	21060.81	21060.84	− 0.03	− 0.1
	3/2 → 5/2	21060.05				
	3/2 → 3/2	21063.74				

Table 1

$J_{K_{-1},K_1} \rightarrow J'_{K'_{-1},K'_1}$	$F \rightarrow F'$	observed frequencies	unsplit frequencies	calculated frequencies	$\nu_{\text{unspl}} - \nu_{\text{calc}}$	centr. dist. contribution
$6_{06} \rightarrow 6_{15}$	9/2 → 9/2	24 700.19	24 704.04	24 704.04	0.00	— 2.26
	15/2 → 15/2	24 701.60				
	11/2 → 11/2	24 706.20				
	13/2 → 13/2	24 707.72				
$12_{4.9} \rightarrow 13_{3.10}$	25/2 → 27/2	25 551.10	25 551.45	25 551.47	— 0.02	— 25.53
	23/2 → 25/2					
	21/2 → 23/2	25 551.79				
	27/2 → 29/2					
$11_{4.7} \rightarrow 10_{5.6}$	25/2 → 23/2	25 562.52	25 564.67	25 564.65	0.02	— 23.81
	19/2 → 17/2					
	21/2 → 19/2	25 566.81				
	23/2 → 21/2					
$7_{0.7} \rightarrow 7_{1.6}$	11/2 → 11/2	29 312.05	29 315.81	29 315.75	0.06	— 4.10
	17/2 → 17/2	29 313.27				
	13/2 → 13/2	29 318.17				
	15/2 → 15/2	29 319.40				
$9_{3.7} \rightarrow 10_{2.8}$	19/2 → 21/2	29 694.59	29 694.59	29 694.57	0.02	— 14.56
	17/2 → 19/2					
	15/2 → 17/2					
	21/2 → 23/2					
$6_{2.5} \rightarrow 7_{1.6}$	11/2 → 13/2	30 030.91	30 030.91	30 030.94	— 0.03	— 5.02
	13/2 → 15/2					
	9/2 → 11/2					
	15/2 → 17/2					
$4_{1.4} \rightarrow 5_{0.5}$	5/2 → 7/2	31 449.37	31 450.16	31 450.19	— 0.03	— 1.44
	7/2 → 9/2					
	11/2 → 13/2	31 450.52				
	9/2 → 11/2					
$3_{03} \rightarrow 4_{04}$	9/2 → 11/2	32 853.25	32 852.62	32 852.63	— 0.01	— 0.58
	7/2 → 9/2	32 852.78				
$7_{1.6} \rightarrow 7_{2.5}$	11/2 → 11/2	33 028.37	33 029.10	33 029.10	0.00	— 0.52
	17/2 → 17/2					
	13/2 → 13/2	33 030.08				
	15/2 → 15/2					
$8_{1.7} \rightarrow 8_{2.6}$	13/2 → 13/2	33 061.21	33 062.22	33 062.20	0.02	— 1.11
	19/2 → 19/2	33 061.42				
	15/2 → 15/2	33 062.97				
	17/2 → 17/2	33 063.24				
$3_{2.2} \rightarrow 4_{2.3}$	7/2 → 9/2	33 252.79	33 256.53	33 256.47	0.06	— 0.43
	5/2 → 7/2	33 254.85				
	9/2 → 11/2	33 258.67				
$9_{1.8} \rightarrow 9_{2.7}$	15/2 → 15/2	33 858.79	33 859.90	33 859.86	0.04	— 2.59
	21/2 → 21/2	33 859.02				
	17/2 → 17/2	33 860.78				
	19/2 → 19/2	33 861.08				
$8_{0.8} \rightarrow 8_{1.7}$	13/2 → 13/2	34 835.17	34 838.82	34 838.80	0.02	— 6.86
	19/2 → 19/2	34 836.25				
	15/2 → 15/2	34 841.26				
	17/2 → 17/2	34 842.38				
$10_{1.9} \rightarrow 10_{2.8}$	23/2 → 23/2	35 544.46	35 545.46	35 545.51	— 0.05	— 5.36
	17/2 → 17/2					
	19/2 → 19/2	35 546.78				
	21/2 → 21/2					
$13_{2.12} \rightarrow 13_{2.11}$	29/2 → 29/2	36 989.76	36 989.83	36 989.83	0.00	— 38.89
	27/2 → 27/2	36 992.28				

Table 1. Microwave spectrum and centrifugal distortion contribution in MHz for CH_3SCl^{35}.

The WATSON formula [4, 5] for asymmetric nonplanar molecules was the basis of this analysis. The method of least squares was used to obtain the corrections to the three rotational constants and the five centrifugal distortion constants. The lines used for this analysis, corrected for the splitting due to quadrupole coupling, the calculated frequencies and the contributions due to centrifugal distortion are listed in Table 1.

The error estimation follows the method proposed by LINNIK [6] and ZURMÜHL [7].

The correlation coefficients for two of the centrifugal constants indicate an ill-conditioned normal equation, but nevertheless the frequencies are accurately predicted and the assignment was easily made. For a more complete analysis, the measurement of other lines of different subbranches [8] in other frequency ranges may be of value to improve the reliability of the centrifugal distortion constants. However, since the rotational constants of the present analysis are not very different from those obtained from the rigid rotor analysis of the low J lines it is believed that a more extended analysis would not change the rotational constants to a large amount. Therefore no effort was made to extend the investigation beyond the transitions discussed here. It may moreover be noticed that the present centrifugal distortion constants are of the same order of magnitude as those obtained for CH_3SCN [9].

Structural Considerations

Although the six moments of inertia determined from the spectra of CH_3SCl^{35} and CH_3SCl^{37} are insufficient to give the complete structure of this molecule, reasonable assumptions can be made which, combined with these data, yield a possible structure sufficiently accurate for most purposes. In calculating the structure a fixed value of 1.085 Å was assumed for the C – H bond length in the CH_3-group. This value was determined in the investigation of the r_s-structure of CH_3SCN at the microwave laboratory in Freiburg [10]. For the C – S bond length and the HCS angle a series of different values was assumed as listed in Table 2.

	This work (a)	Preceeding work (1)
A (MHz)	17 341.83 ± 0.01	17 341.65 ± 0.03
B (MHz)	4 603.78 ± 0.002	4 603.73 ± 0.03
C (MHz)	3 719.10 ± 0.002	3 719.14 ± 0.03
$\varkappa$	− 0.870117	− 0.870128
$d_J \cdot 10^3$ (MHz)	− 11.67 ± 0.07	
$d_{JK} \cdot 10^3$ (MHz)	− 208.67 ± 2.7	
$d_K \cdot 10^3$ (MHz)	− 369.22 ± 9.1	
$d_{WJ} \cdot 10^6$	3.468 ± 0.015	
$d_{WK} \cdot 10^6$	37.23 ± 0.7	
I_a (AMU/A²)	29.1510	29.1513
I_b (AMU/A²)	109.8080	109.8090
I_c (AMU/A²)	135.9285	135.9269
Δ (AMU/A²)	3.0305	3.0334

(a) The errors given are only due to the least squares treatment, errors due to unaccuracy of the measurements are not inculded.

Table 2. Rotational constants, centrifugal distortion constants and moment of inertia of CH_3SCl^{35}.

Using the different sets of assumed structural parameters, the six rotational constants were fitted by the method of least squares. The resulting different values of the two structural parameters thus determined, the Cl – S bond length and the ClSC angle are listed in Table 2. As may be seen, the ClSC angle and the S – Cl bond length are not very sensitive to the changes of the varied parameter, so they are believed to be sufficiently well determined for later use in this work. The S – Cl bond length agrees reasonably well with the sum of the single covalent bond radii of both atoms [11].

Internal Rotation Barrier

An investigation of the ground state transitions up to $J = 15$ in the frequency range available to the spectrometer gave no observable splittings due to internal rotation. Calculations with an assumed barrier of 2500 cal/mole show indeed that resolvable splittings could not be predicted even for higher J lines. As one expects much larger splittings in the first excited torsional state, the corresponding rotational spectrum was investigated and a determination of the torsional barrier was possible.

First the stronger low-J "a"-type transitions were found and assigned on the basis of their Stark-effect, quadrupole hyperfine structure and fit to the spec-

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(*) The agreement between observed and calculated rotational constants using the listed parameters is always within 4 MHz.
(**) Under the given assumptions this resulting structure may be assumed for later use.

Table 3. r_0-structures for Methanesulfenylchloride. The values in parentesis are assumed.

	C−H	C−S	Cl−S	SĈH	ClŜC
		(1.805)	2.024	(109.25°)	100.04°
		(1.815)	2.016	(109.25°)	100.34°
		(1.825)	2.006	(109.25°)	100.64°
		(1.805)	2.022	(109.75°)	100.10°
(*)	(1.087)	(1.815)	2.014	(109.75°)	100.39°
		(1.825)	2.005	(109.75°)	100.69°
		(1.805)	2.021	(110.25°)	100.14°
		(1.815)	2.012	(110.25°)	100.44°
		(1.825)	2.003	(110.25°)	100.74°
(**)	(1.087)	(1.815 ± 0.01)	2.014 ± 0.01	(109.75° ± 0.5°)	100.39° ± 0.4°

trum of a rigid rotor. The splitting of the lines was small and could not easily be resolved. Therefore "b"-type transitions were investigated for which the splitting was expected to be larger. Their assignment was difficult because of the weak absorption and the poor frequency predictions due to the difficulty in predicting the value of the A constant for this state.

Q-type lines were very helpful at this point because of their characteristic pattern composed of two hfs quartetts, one for the A- and one for the E-species. Table 3 shows the observed and calculated values of the transition frequencies and the splittings due to internal rotation. The usual Hamiltonian for this problem [12–15] has been rearranged to obtain the following expression:

$$\begin{aligned}\Delta\nu = F\cdot\{&[\varrho_a^2\,\Delta\langle P_a^2\rangle + \varrho_b^2\,\Delta\langle P_b^2\rangle + \varrho_c^2\,\Delta\langle P_c^2\rangle]\,\Delta W_{AE}^{(2)} + [\varrho_a^4\,\Delta\langle P_a^4\rangle + \varrho_b^4\,\Delta\langle P_b^4\rangle + \varrho_c^4\,\Delta\langle P_c^4\rangle\\ &+3\,\varrho_a^2\,\varrho_b^2\,\Delta\langle P_a^2 P_b^2 + P_b^2 P_a^2\rangle + 3\,\varrho_b^2\,\varrho_c^2\,\Delta\langle P_b^2 P_c^2 + P_c^2 P_b^2\rangle\\ &+3\,\varrho_c^2\,\varrho_a^2\,\Delta\langle P_c^2 P_a^2 + P_a^2 P_c^2\rangle - (2\,\varrho_a^2\,\varrho_b^2 - 3\,\varrho_b^2\,\varrho_c^2 + 2\,\varrho_c^2\,\varrho_a^2)\,\Delta\langle P_a^2\rangle\\ &-(2\,\varrho_b^2\,\varrho_c^2 - 3\,\varrho_c^2\,\varrho_a^2 + 2\,\varrho_a^2\,\varrho_b^2)\,\Delta\langle P_b^2\rangle - (2\,\varrho_c^2\,\varrho_a^2 - 3\,\varrho_a^2\,\varrho_b^2 + 2\,\varrho_b^2\,\varrho_c^2)\,\Delta\langle P_c^2\rangle]\,\Delta W_{AE}^{(4)}\}\end{aligned} \quad (1)$$

in which the various symbols are defined as follows:

$$F = \hbar^2/2\,r\,I_\alpha \qquad \varrho_g = \lambda_g\,I_\alpha/I_g,$$
$$\Delta W_{AE}^{(n)} = W_{VA}^{(n)}(s) - W_{VE}^{(n)}(s),$$
$$\Delta\langle P_g^{(n)}\rangle = \langle P_g^{(n)}\rangle_{J,\tau} - \langle P_g^{(n)}\rangle_{J',\tau'}.$$

The line splittings were fitted to Eq. (1), which contains only second and fourth order contributions [16]. For some low-J transitions it was necessary to use first order perturbation in addition to account for the observed splittings.

The Tables published by HAYASHI [17] and DOBYNS [18] allow a direct determination of this term, which has the form $-2\sum F\,\varrho_g\,P_g\,p$, in which p is the angular momentum about the CH_3 axis. Thus $s = 4\,V_3/9\,F$ and the direction cosines λ_g were obtained and are listed in Table 4. For the barrier calculations a mean value of I_α is assumed with an error which reflects the uncertainty of the structure. The uncertainty of I_α determines the errors in the barrier height and in the direction cosines λ_g.

The resulting λ_a gives an angle between the CH_3-axis and the "a" principal axis which differs by about 3° from that obtained using the CSCl structural angle.

As found in CH_3SCN [10] and in other compounds containing CH_3-groups [19, 20] a value of $\sim 3°$ could be justified to account for a tilt of the CH_3-group towards the sulfur atome.

A spectrum due to an excited vibrational state has also been observed and is the object of a further investigation.

Quadrupole Coupling Constants

As shown in Table 5 no significant changes are found for the quadrupole coupling constants of the

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$J_{K_{-1},K_1} \rightarrow J'_{K'_{-1},K'_1}$	Γ	$F \rightarrow F'$	observed frequencies	unsplit frequencies	calculated frequencies	$\Delta\nu(\nu_A - \nu_E)$ observed	$\Delta\nu(\nu_A - \nu_E)$ calculated
$0_{00} \rightarrow 1_{01}$	A+E	3/2 → 3/2	8289.75	8301.30	8301.301		− 0.180
	A+E	3/2 → 5/2	8304.16				
		1/2 → 3/2	13589.69				
		5/2 → 5/2	13590.33				
	A	3/2 → 1/2	13596.10	13595.43	13595.414		
		5/2 → 3/2	13601.14				
$1_{01} \rightarrow 1_{10}$		3/2 → 5/2	13604.95			− 1.63	− 1.619
		5/2 → 5/2	13591.96				
	E	5/2 → 3/2	13602.92	13597.06	13597.033		
		3/2 → 5/2	13606.45				
	A+E	3/2 → 5/2	15715.08				
$1_{11} \rightarrow 2_{12}$	A+E	3/2 → 3/2	15722.96	15725.80	15725.776		− 0.300
	A+E	5/2 → 7/2	15729.57				
		3/2 → 5/2	17467.80				
	A	3/2 → 3/2	17470.45	17479.10	17479.130		
		5/2 → 7/2	17482.31				
$1_{10} \rightarrow 2_{11}$						− 0.42	− 0.413
	E	3/2 → 5/2	17468.25	17479.52	17479.543		
		5/2 → 7/2	17482.74				
	A	7/2 → 9/2	26191.80	26190.39	26190.389		
$2_{11} \rightarrow 3_{12}$						− 0.73	− 0.734
	E	5/2 → 7/2	26188.81	26191.12	26191.123		
		7/2 → 9/2	26192.55				
		5/2 → 5/2	18065.66				
	A	11/2 → 11/2	18068.02	18070.40	18070.400		
		7/2 → 7/2	18072.27				
		9/2 → 9/2	18074.64				
$4_{04} \rightarrow 4_{13}$						− 2.55	− 2.590
		5/2 → 5/2	18068.25				
	E	11/2 → 11/2	18070.58	18072.95	18073.003		
		7/2 → 7/2	18074.80				
		9/2 → 9/2	18077.13				
		3/2 → 3/2	15971.27				
	A	9/2 → 9/2	15974.78	15977.42	15977.44		
		5/2 → 5/2	15978.99				
		7/2 → 7/2	15982.58			− 2.14	− 2.131
		7/2 → 7/2	15982.58				
$3_{05} \rightarrow 3_{12}$							
		3/2 → 3/2	15973.40				
	E	9/2 → 9/2	15976.96	15979.55	15979.567		
		7/2 → 7/2	15984.70				
		9/2 → 9/2	24561.00				
	A	15/1 → 15/2	24562.44	24564.89	24564.867		
		11/2 → 11/2	24567.10				
		13/2 → 13/2	24568.57				
$6_{06} \rightarrow 6_{15}$						− 4.09	− 4.049
		9/2 → 9/2	24565.13				
	E	15/2 → 15/2	24566.51	24568.98	24568.931		
		11/2 → 11/2	24571.19				
		13/2 → 13/2	24572.64				
		11/2 → 11/2	29125.18				
	A	17/2 → 17/2	29126.44	29128.98	29128.975		
		13/2 → 13/2	29131.47				
		15/2 → 15/2	29132.61				
$7_{07} \rightarrow 7_{16}$						− 5.14	− 5.082
		11/2 → 11/2	29130.30				
	E	17/2 → 17/2	29131.47	29134.07	29134.057		
		13/2 → 13/2	29136.41				
		15/2 → 15/2	29137.77				

Table 4

$J_{K-1,K_1} \rightarrow J'_{K'-1,K'_1}$	Γ	$F \rightarrow F'$	observed frequencies	unsplit frequencies	calculated frequencies	$\Delta\nu(\nu_A - \nu_E)$ observed	$\Delta\nu(\nu_A - \nu_E)$ calculated
	A	$13/2 \rightarrow 13/2$ $19/2 \rightarrow 19/2$	32 992.94	32 993.85	32 993.851		
$8_{17} \rightarrow 8_{26}$						− 3.71	− 3.712
	E	$13/2 \rightarrow 13/2$ $19/2 \rightarrow 19/2$	32 996.72	32 997.56	32 997.563		
		$15/2 \rightarrow 15/2$ $17/2 \rightarrow 17/2$	32 998.36				
	A	$7/2 \rightarrow 7/2$	34 581.90				
		$13/2 \rightarrow 13/2$	34 582.52	34 583.46	34 583.458		
		$9/2 \rightarrow 9/2$	34 585.64				
		$11/2 \rightarrow 11/2$	34 586.33				
$5_{23} \rightarrow 5_{14}$						− 3.77	− 3.769
	E	$7/2 \rightarrow 7/2$	34 584.26				
		$13/2 \rightarrow 13/2$	34 584.94	34 587.23	34 587.227		
		$9/2 \rightarrow 9/2$	34 588.02				
		$11/2 \rightarrow 11/2$	34588.71				
	A	$13/2 \rightarrow 13/2$	34 593.46				
	A	$19/2 \rightarrow 19/2$	34 594.63	34 597.22	34 597.228		
	A	$15/2 \rightarrow 15/2$	34 599.71				
$8_{08} \rightarrow 8_{17}$	E	$13/2 \rightarrow 13/2$				− 6.23	− 6.240
	A	$17/2 \rightarrow 17/2$	34 600.80				
	E	$19/2 \rightarrow 19/2$					
	E	$15/2 \rightarrow 15/2$	34 605.94	34 603.45	34 603.468		
	E	$17/2 \rightarrow 17/2$	34 607.07				

Table 4. Microwave spectrum of the first excited torsional state of CH_3SCl^{35}.

	A species	E species
A_{eff} (MHz)	17 307.81 ± 0.05	17 309.39 ± 0.05
B_{eff} (MHz)	4 589.04 ± 0.05	4 589.23 ± 0.05
C_{eff} (MHz)	3 712.18 ± 0.05	3 712.19 ± 0.05
χ_{aa} (MHz)	− 58.06 ± 0.20	
χ_{bb} (MHz)	14.61 ± 0.30	
χ_{cc} (MHz)	43.45 ± 0.30	
$\varkappa$	− 0.871033	− 0.870998
I_a (AMU/A²)	29.2083	29.2056
I_b (AMU/A²)	110.1606	110.1560
I_c (AMU/A²)	136.1816	136.1813
Δ (AMU/A²)	3.1873	3.1804

Table 5. Rotational constants, quadrupole coupling constants and inertial moments of the first excited torsional state. The rotational constants result from a centrifugal distortion analysis on all lines given in Table 4.

first excited torsional state with respect to those of the ground state. The principal axis coordinates obtained from the r_0-structure of Table 2 indicate that the S – Cl bond forms an angle of 25° 50′ with the "a" principal axis in CH_3SCl^{35} and that the rotation caused by Cl^{37} substitution is approximately 0.5°. Assuming that the principal axis of the quadrupole tensor is colinear with the S – Cl bond axis, it is possible to determine the value of the quadrupole coupling constants along the S – Cl bond by rotating the χ tensor through the corresponding angles. The transformed values are given in Table 7 where χ_{zz}

$I_\alpha =$	3.14 ± 0.04 AMU/A²(a)
$s =$	70.82 ± 0.15
$V_3 =$	2599 ± 27 cal/mole(b)
$\lambda_a^2 =$	0.3832 ± 0.002
$\lambda_b^2 =$	0.6156 ± 0.002
$F =$	170.88 ± 1.29 GHz
$\sphericalangle\, \alpha a =$	51.66° ± 0.15°
$\sphericalangle\, \alpha b =$	38.32° ± 0.15°

(a) The uncertainty of the I_α value is given to account for the different SCH angles assumed in the structural considerations. The errors given for the other parameters reflect the uncertainty of I_α.

(b) V_6 and rotation-vibration interactions are not considered.

Table 6. Internal rotation parameters for the first excited state.

	Principal axis system		
	CH_3SCl^{35} First torsional exc. state	CH_3SCl^{35} Ground state	CH_3SCl^{37}
χ_{aa}	−58.06 ± 0.20	−58.31 ± 0.10	−46.29 ± 0.10
χ_{bb}	14.61 ± 0.30	14.80 ± 0.20	12.15 ± 0.20
χ_{cc}	43.45 ± 0.30	43.51 ± 0.20	34.14 ± 0.20
	S-Cl bond axis system		
Θ_{az}		25°50′ ± 30′	25°25′ ± 30′
χ_{zz}		−80.69 ± 0.8(**)	−63.29 ± 0.8
χ_{xx}		37.18 ± 0.8	29.16 ± 0.8
χ_{yy}		34.51 ± 0.8	34.13 ± 0.8
η(*)		0.0784 ± 0.013	0.0787 ± 0.013

(*) $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

(**) The errors given for the S – Cl bond axis quadrupole constants reflect the indeterminacy of Θ_{az}.

Table 7. Quadrupole coupling constants of CH_3SCl in MHz.

and χ_{xx} represent the coupling constants along the bond axis and normal to the bond axis, respectively. Under this transformation the y axis corresponds to the c axis and $\chi_{yy} = \chi_{cc}$. From the calculated value of the deviation from cylindrical symmetry η in the bond axis system it is apparent that the charge distribution about the S – Cl bond is approximately cylindrically symmetric. As pointed out by GOLDSTEIN [21] the calculated value of η should suggest about 4% double bond character.

Unfortunately no other microwave studies of a similar S – Cl bond are to be found for comparison.

I thank Prof. Dr. H. D. RUDOLPH and Prof. Dr. H. DREIZLER for the invitation to their laboratory and for their interest in this work. I am further grateful to Dipl.-Phys. H. MÄDER for writing a program and to the Deutsche Forschungsgemeinschaft and the Fonds der Chemie which supported this investigation. – Calculations were made with the IBM 7040 Computer of the Rechenzentrum der Universität Freiburg and with the Electrologica X 8 of the Rechenzentrum der Universität Kiel.

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Mikrowellenspektrum, Hinderungspotential der internen Rotation, Quadrupolkopplungskonstanten und Dipolmoment des 2-Methyl-Pyridins **

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(Z. Naturforsch. **25 a**, 25—35 [1970]; eingegangen am 3. November 1969)

The microwave rotational spectrum of 2-methyl-pyridine (α-picoline) has been investigated in the region from 6 to 30 kmc/s. From the three lowest states of internal rotation $m=0$, 1, 2 the three- and sixfold components V_3 and V_6 of the potential barrier hindering the internal rotation have been determined to be $V_3 = (258{,}4 \pm 0{,}1)$ cal/mole and $V_6 = (-11{,}8 \pm 0{,}1)$ cal/mole. From the splitting of low-J lines $m=0$ the nuclear quadrupole coupling constants for the ^{14}N nucleus have been derived as $\chi_{aa} = (-0{,}33 \pm 0{,}02)$ mc/s, $\chi_{bb} = (-2{,}86 \pm 0{,}02)$ mc/s, $\chi_{cc} = (+3{,}19 \pm 0{,}02)$ mc/s. The hyperfine structure of rotational transitions in excited states of internal rotation could also be accounted for with these coupling constants. The dipole moment components derived from Stark-effect measurements in the ground torsional state $m=0$ are $\mu_a = (0{,}72 \pm 0{,}01)$ Debye and $\mu_b = (1{,}71 \pm 0{,}02)$ Debye.

Das Rotationsspektrum des 2-Methyl-Pyridins (Abb. 1) – im folgenden 2MP genannt – wurde untersucht, um das Hinderungspotential der internen Rotation des symmetrischen CH_3-Kreisels bezüglich des asymmetrischen Rumpfes (Pyridinring) zu bestimmen. Den Rechnungen liegt ein Molekülmodell zugrunde, das sich aus einem ebenen, starr angenommenen Pyridinring (frame) und einer dagegen behindert drehbaren starren symmetrischen Methylgruppe (top) zusammensetzt.

Wegen der C_{3v}-Symmetrie des Teilkreisels bezüglich der Achse der internen Rotation besitzt das Hinderungspotential drei äquivalente Minima und kann in eine Cosinusreihe entwickelt werden, die mit einem dreizähligen Term beginnt:

$$V(\alpha) = \tfrac{1}{2} V_3 (1 - \cos 3\alpha) + \tfrac{1}{2} V_6 (1 - \cos 6\alpha) + \ldots \quad (1)$$

Das Hinderungspotential ist auf Grund der Spiegelsymmetrie des Molekülrumpfes eine gerade Funktion in dem Winkel α, der die relative Drehlage des Teilkreisels gegenüber dem Rumpf angibt.

Wegen der Kopplung von Gesamtrotation und interner Rotation fallen die Rotationsspektren verschieden angeregter interner Rotationszustände im allgemeinen nicht zusammen und erlauben somit Rückschlüsse auf die verschiedenzähligen Potentialterme in der Entwicklung (1). In der vorliegenden Arbeit gelang es, die beiden ersten Potentialkoeffizienten V_3 und V_6 zu bestimmen. Über höhere Potentialterme konnte keine Aussage gemacht werden, da die gemessenen Rotationsübergänge von ihnen viel weniger abhängen als von den beiden ersten Potentialkoeffizienten. Zur Bestimmung von V_3 und V_6 mußten allerdings neben dem Rotationsspektrum im

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