Analysis of Internal Rotation and Determination of the Heavy Atom Structure of anti-2,3-Dimethylthiirane by Fourier Transform Microwave Spectroscopy

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We used the advanced technique of Fourier transform microwave spectroscopy to measure and assign the ground state rotational spectrum of anti-2,3-dimethylthiirane, and to analyse the internal rotation of the two methyl groups. The potential parameters obtained are $V_3 = 13.1678(21)$ and $V'_{12} = -1.6678(25)$ kJ/mol. The measurement and assignment of the ^{13}C and ^{34}S isotopomers in the ground state allowed to determine the molecular structure of the heavy atom frame using the r_s and r_0 methods.

Introduction

With this communication we continue to report on our investigations on methyl substituted oxiranes and thiiranes by Fourier transform microwave (FTMW) spectroscopy. This technique allows by its high resolution, accuracy, and sensitivity a very detailed study of the rotational spectrum. Our series of molecules started with 2,2-dimethyl-, syn- and anti-2,3-dimethyloxirane [1, 2, 3], and 2,2-dimethylthiirane [4]. The subject of this publication is anti-2,3-dimethylthiirane, ($CH_3CHSCHCH_3$, trans butylene sulfide, TBS). In contrast to [2,3] we will use the IUPAC nomenclature instead of the older cis/trans notation to label the steric arrangement of the methyl groups.

In the case of the substituted thiiranes, studies of the nuclear quadrupole hyperfine structure (hfs) of ^{33}S in natural abundance are performed and will contribute to the knowledge of the bond situation of sulfur in a three membered ring. First results of the measurements of the ^{33}S TBS isotopomere will be available soon [5].

A similar study of internal rotation and structure was undertaken at the University of Valladolid in cooperation with Kiel concerning methylthiirane, $CH_3C_2H_3S$ [6], additionally the hfs analysis of the ^{33}S methylthiirane is currently performed [7].

The series of molecules will allow to compare the barriers to hindered internal rotation in one and two methyl top molecules in different configurations. As the heavy atom structure could be determined by analyzing the spectra of isotopomers in natural abundance, slight changes of the structure may be correlated to methyl group substitution of the ring.

Experimental

The substance was prepared according to a method of Snyder, Stewart, and Ziegler [8]. A mixture of 50 mmol (3.8 ml) anti-2,3-dimethyloxriane obtained from Bayer, Leverkusen, 50 mmol KSCN and 5 ml water was stirred for 30 h in a 50 ml bulb at a temperature of 50°C. After separating and drying the organic phase with $CaCl_2$, anti-2,3-dimethylthiirane was purified by destillation. A colorless liquid of a strong smell and a boiling point of 91 °C was obtained with approx. 50% yield.

The rotational spectrum in the ground state was recorded with a molecular beam (MB) Fourier transform microwave spectrometer [9] first in a scanning mode from 7.5 to 10 GHz and 11 to 12 GHz. A mixture of 1% TBS in argon with a backing pressure of approximately 1 bar was used. After remeasuring the signals in the high resolution mode [10], the spectrum could be assigned as no lines with higher angular momentum quantum number J overlayed the low J spectrum. With the measurement of additional transitions the assignment could be continued. The lines

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Table 1. Rotational transitions of anti-2,3-dimethylthiirane in the ground state (in MHz). $\delta = \nu(\text{obs.}) - \nu(\text{calc.})$.

J'	K'_-	K'_+	–	J	K_-	K_+	ν(obs.)	δ
1	1	1	–	0	0	0	7788.869	–0.001
2	2	1	–	2	1	2	9126.710	–0.001
2	1	2	–	1	0	1	12535.468	–0.001
2	2	1	–	1	1	0	18619.920	–0.001
2	2	0	–	1	1	1	20127.770	–0.003
2	0	2	–	1	1	1	9475.452	0.001
3	3	0	–	3	2	1	11001.845	0.004
3	1	2	–	3	0	3	7251.387	–0.001
3	3	1	–	3	2	2	12583.932	0.005
3	2	2	–	3	1	3	11031.974	–0.001
3	1	3	–	2	0	2	16884.614	0.000
3	0	3	–	2	1	2	15198.135	0.000
3	1	2	–	2	2	1	13322.808	0.004
4	3	1	–	4	2	2	9834.634	–0.003
4	1	3	–	4	0	4	10999.216	0.000
4	4	1	–	4	3	2	16858.132	0.004
4	3	2	–	4	2	3	13448.310	0.001
4	2	3	–	4	1	4	13563.516	0.000
4	1	4	–	3	2	1	7990.828	0.000
4	1	4	–	3	0	3	21223.254	–0.002
4	2	3	–	3	3	0	10552.495	0.000
4	2	2	–	3	3	1	14787.203	0.003
4	0	4	–	3	1	3	20480.839	0.001
4	1	3	–	3	2	2	20448.084	–0.001
5	5	0	–	5	4	1	21397.666	–0.006
5	3	2	–	5	2	3	9029.257	–0.001
5	2	3	–	5	1	4	9238.855	0.000
5	1	4	–	5	0	5	15204.801	0.000
5	4	2	–	5	3	3	17018.579	0.003
5	3	3	–	5	2	4	14937.340	–0.001
5	2	4	–	5	1	5	16604.212	0.000
5	2	3	–	4	3	2	22893.270	0.001
5	3	2	–	4	4	1	15064.394	–0.003
6	5	1	–	6	4	2	20798.837	0.002
6	3	3	–	6	2	4	9306.975	–0.001
6	2	4	–	6	1	5	12872.598	0.000

had a line width (HWHH) of 4 to 5 kHz and could not be resolved revealing an internal rotation splitting. The frequencies are given in Table 1.

In the same way transitions of $^{34}\mathrm{S}$, $^{13}\mathrm{C}_\mathrm{m}$ (m = methyl) and $^{13}\mathrm{C}_\mathrm{r}$ (r = ring) isotopomers could be identified and assigned. They are given in Table 2.

The rotational lines of excited internal rotation (torsion) states could not be measured with a MB spectrometer, as the excited states are not sufficiently populated. They were measured with different versions of waveguide (WG) FTMW spectrometers [11, 12]. An estimate of vibrational and torsional energy levels with Gaussian 92 [13] allowed to attribute the stronger spectrum to the symmetric $v_{17} = 1$, the weaker to the antisymmetric $v_{33} = 1$ torsional state. This assignment corresponds to the observed spin statistical weights of the of the torsional multiplets as already described in [3]. The measurements are given in Table 3. The rotational assignment was guided by the neighbourhood to the ground state lines of Table 1. Not all lines could be resolved to show an internal rotation splitting.

Table 2. Rotational transitions of anti-2,3-dimethylthiirane isotopomers in the ground state (in MHz); $\mathrm{C_m}$: methyl-C, $\mathrm{C_r}$: ring-C, $\delta = \nu(\text{obs.}) - \nu(\text{calc.})$.

	$^{13}\mathrm{C}_\mathrm{m}$		$^{13}\mathrm{C}_\mathrm{r}$		$^{34}\mathrm{S}$	
	ν(obs.)	δ	ν(obs.)	δ	ν(obs.)	δ
1 1 1 – 0 0 0:	7698.350	–0.002	7760.828	0.000	7592.495	0.000
2 2 1 – 2 1 2:	9149.845	0.002	9078.900	0.000	8730.367	0.000
2 1 2 – 1 0 1:	12346.718	–0.001	12495.324	0.001	12274.837	–0.001
2 2 1 – 1 1 0:	18446.595	0.000	18547.905	0.000	18095.060	0.001
3 1 3 – 2 0 2:	16604.016	0.002	16834.608	–0.001	16565.358	0.000
2 0 2 – 1 1 1:	9177.794	0.001	9449.107	0.000	9531.534	0.000
2 2 0 – 1 1 1:	19884.071	–0.001	20046.191	0.000	19678.955	0.000

Table 3. Rotational transitions of anti-2,3-dimethylthiirane in the torsional excited states in MHz. Γ designates the torsional symmetry of the transition. The label "all" indicates that no torsional splitting was observable. The symmetry label $\Gamma = E_\pm$ indicates that no splitting between the E_- annd E_+ component was observed, $\nu(E_\pm)$ is the mean value $\nu(E_+)$ and $\nu(E_-)$. For the $\Gamma = A$ and the unsplit transitions the absolut frequency ν is given, for the $\Gamma = G$ and E states the splitting $\Delta\nu = \nu(\Gamma) - \nu(A)$ is given. δ shows the observed – calculated value of the frequency or splitting.

$J'K'_-K'_+–JK_-K_+$	$v_{17} = 1$		$v_{33} = 1$	
Γ	ν(obs.) $\Delta\nu$(obs.)	δ $\delta\Delta$	ν(obs.) $\Delta\nu$(obs.)	δ $\delta\Delta$
2 0 2 – 1 1 1				
all	9482.901	–0.007	9463.744	0.001
2 1 2 – 1 0 1				
all	12515.912	0.003	–	–
A	–	–	12520.438	–0.003
G	–	–	0.039	0.004
$E_\pm$	–	–	0.076	0.007
2 2 1 – 1 1 0				
A	18572.055	–0.006	18597.353	–0.003
G	0.072	0.013	0.097	0.004
$E_\pm$	0.117	–0.003	0.191	0.005
2 2 0 – 1 1 1				
A	20082.497	0.013	20102.989	–0.009
G	0.047	–0.014	0.104	0.007
$E_\pm$	0.117	–0.005	0.192	–0.002
2 2 1 – 2 1 2				
A	9084.287	–0.003	9115.404	0.003
G	0.060	0.002	0.088	–0.001
$E_\pm$	0.118	0.003	0.178	–0.001
3 2 2 – 2 1 1				
A	23315.901	–0.003	23338.306	0.007
G	0.068	0.006	0.094	–0.004
$E_\pm$	0.134	0.009	0.189	–0.006

Table 3 (cont).

	$v_{17} = 1$		$v_{33} = 1$	
$J'K'_-K'_+-JK_-K_+$ Γ	ν(obs.) $\Delta\nu$(obs.)	δ $\delta\Delta$	ν(obs.) $\Delta\nu$(obs.)	δ $\delta\Delta$
3 2 2 – 3 1 3				
A	10991.165	–0.001	11017.943	0.002
G	0.057	–0.001	0.089	–0.002
$E_\pm$	0.114	–0.002	0.179	–0.002
3 3 1 – 3 2 2				
A	12513.522	–0.004	12568.768	–0.001
G	0.082	0.000	0.113	–0.003
E_+	0.193	0.001	0.299	–0.002
E_-	0.133	–0.003	0.163	0.001
3 3 0 – 3 2 1				
A	10924.380	0.009	10989.153	0.005
G	0.108	–0.010	0.193	–0.005
E_+	0.197	–0.011	0.322	–0.003
E_-	0.256	–0.008	0.462	–0.003
4 0 4 – 3 1 3				
all	20472.315	–0.001	20456.146	0.001
4 1 4 – 3 0 3				
all	21202.168	0.002	21197.989	–0.003
4 1 3 – 3 2 2				
A	–	–	20422.242	0.008
G	–	–	–0.068	–0.007
$E_\pm$	–	–	–0.129	–0.008
4 1 3 – 4 0 4				
all	10992.168	–0.002	10984.059	–0.001
4 2 3 – 4 1 4				
A	13524.061	0.010	13545.886	–0.003
G	0.050	–0.008	0.090	–0.001
$E_\pm$	0.110	–0.006	0.175	–0.006
4 3 2 – 4 2 3				
A	13382.333	–0.005	13431.789	0.001
G	0.092	0.003	0.138	0.000
E_+	–	–	0.288	0.002
E_-	–	–	0.265	–0.001
$E_\pm$	0.179	0.001	–	–
4 3 1 – 4 2 2				
A	9759.687	0.001	9823.497	0.002
G	0.102	0.000	0.160	–0.001
$E_\pm$	0.203	0.000	0.323	0.000
4 4 1 – 4 3 2				
A	16756.231	0.001	16838.075	–0.004
G	0.000	–0.002	–0.116	0.003
E_+	0.280	0.005	0.427	–0.005
E_-	–0.254	–0.002	–0.825	0.004
4 4 0 – 4 3 1				
A	16227.040	–0.004	16315.721	–0.004
G	0.285	0.005	0.564	0.003
E_+	0.285	0.000	0.456	0.003
E_-	0.817	0.000	1.721	0.007
5 2 4 – 5 1 5				
A	16564.534	0.010	16582.330	0.001
G	0.053	–0.006	0.092	0.000
$E_\pm$	0.106	–0.012	0.183	0.000
5 2 3 – 4 3 2				
A	22962.628	0.000	22863.359	–0.004
G	–0.105	–0.010	–0.146	0.002
$E_\pm$	–0.185	0.006	–0.290	0.005
5 3 3 – 5 2 4				
A	14877.577	–0.003	14918.524	–0.001
G	0.084	0.000	0.131	0.000
$E_\pm$	0.167	0.000	0.261	–0.001
5 3 2 – 5 2 3				
A	8967.384	0.000	9018.808	0.000
G	0.084	0.001	0.132	0.000
$E_\pm$	0.167	0.000	0.263	0.000

Table 3 (cont).

	$v_{17} = 1$		$v_{33} = 1$	
$J'K'_-K'_+-JK_-K_+$ Γ	ν(obs.) $\Delta\nu$(obs.)	δ $\delta\Delta$	ν(obs.) $\Delta\nu$(obs.)	δ $\delta\Delta$
5 4 2 – 5 3 3				
A	16920.114	0.000	16998.206	–0.001
G	0.118	0.000	0.171	0.000
E_+	0.266	–0.001	0.417	–0.001
E_-	0.209	0.003	0.266	–0.001
5 4 1 – 5 3 2				
A	15173.211	0.000	15269.970	0.000
G	0.167	0.000	0.274	–0.001
E_+	0.302	–0.002	0.474	0.001
E_-	0.366	0.002	0.625	–0.001
5 5 1 – 5 4 2				
A	21391.051	–0.001	21498.528	0.001
G	–0.747	0.007	–1.551	–0.002
E_+	0.359	0.002	–	–
5 5 0 – 5 4 1				
A	21262.381	0.000	21372.403	0.003
G	1.110	–0.003	2.112	0.000
E_+	0.358	–0.005	0.555	–0.013
6 1 5 – 6 0 6				
A	19331.203	–0.004	19332.697	0.003
G	0.055	0.001	0.092	0.003
E_+	–	–	0.161	0.012
E_-	–	–	0.200	–0.009
$E_\pm$	0.105	–0.003	–	–
6 2 5 – 6 1 6				
A	19949.100	–0.008	19964.912	0.000
G	0.064	0.004	0.088	–0.001
E_+	–	–	0.208	0.001
E_-	–	–	0.147	0.000
$E_\pm$	0.136	0.016	–	–
6 3 3 – 6 2 4				
A	9267.954	–0.001	9295.346	0.000
G	0.056	0.001	0.089	0.002
$E_\pm$	0.114	0.005	0.184	0.010
6 4 2 – 6 3 3				
A	13616.450	–0.003	13716.087	0.001
G	0.156	0.002	0.244	–0.001
E_+	–	–	0.472	–0.002
E_-	–	–	0.503	–0.002
$E_\pm$	0.310	0.002	–	–
6 5 2 – 6 4 3				
A	21230.581	–0.002	21337.444	–0.005
G	0.067	0.006	–0.007	0.007
E_+	0.355	0.001	0.561	0.006
E_-	–0.098	0.007	–0.561	0.013
6 5 1 – 6 4 2				
A	20657.317	–0.001	20774.680	0.002
G	0.308	0.003	0.586	–0.001
E_+	0.379	0.002	0.586	–0.004
E_-	0.834	–0.003	1.715	–0.005
7 3 4 – 7 2 5				
A	11087.371	0.003	11082.954	0.002
G	0.016	–0.005	0.032	–0.002
$E_\pm$	0.038	–0.003	0.064	–0.003
7 4 3 – 7 3 4				
A	12200.725	0.004	12286.563	0.001
G	0.131	–0.001	0.208	0.000
$E_\pm$	0.264	0.001	0.415	–0.002
7 6 2 – 7 5 3				
A	25902.772	0.002	26035.935	0.005
G	–0.564	0.002	–1.353	–0.007
E_+	0.427	–0.009	0.685	0.001
E_-	–1.970	–0.003	–	–

Table 3 (cont).

$J'K'_-K'_+-JK_-K_+$	$v_{17} = 1$		$v_{33} = 1$	
	ν(obs.)	δ	ν(obs.)	δ
Γ	$\Delta\nu$(obs.)	$\delta\Delta$	$\Delta\nu$(obs.)	$\delta\Delta$
7 6 1 – 7 5 2				
A	25757.112	0.002	25893.967	0.001
G	1.000	–0.006	2.038	0.002
E_+	0.441	–0.004	0.700	0.004
E_-	2.848	0.000	–	–
8 3 5 – 8 2 6				
all	14471.941	–0.001	14437.416	0.000
8 4 4 – 8 3 5				
A	11781.650	0.002	11834.442	–0.001
G	0.090	0.000	0.145	0.001
$E_\pm$	0.180	–0.001	0.288	0.001
8 5 4 – 8 4 5				
A	21490.517	–0.006	21583.755	0.000
G	0.161	0.005	0.242	0.001
E_+	–	–	0.509	0.004
E_-	–	–	0.451	–0.008
$E_\pm$	0.319	0.006	–	–
8 6 2 – 8 5 3				
A	25058.392	–0.001	25204.724	–0.005
G	0.393	0.030	0.699	0.006
E_+	0.465	0.002	0.699	–0.010
E_-	0.996	0.014	2.016	0.009
9 4 6 – 9 3 7				
A	22919.436	0.001	22948.107	–0.005
G	0.086	–0.001	0.140	0.003
$E_\pm$	0.173	–0.001	0.275	0.001
9 4 5 – 9 3 6				
A	12957.517	0.003	12964.163	0.002
G	0.037	–0.001	0.060	–0.002
$E_\pm$	0.072	–0.003	0.120	–0.003
9 5 5 – 9 4 6				
A	22310.148	–0.002	22388.056	0.003
G	0.147	0.004	0.217	–0.006
$E_\pm$	0.293	0.007	0.440	–0.007
9 5 4 – 9 4 5				
A	15691.490	0.002	15820.194	0.000
G	0.190	0.000	0.301	0.000
$E_\pm$	0.381	0.000	0.600	–0.002
9 6 4 – 9 5 5				
A	25409.438	0.000	25538.581	–0.001
G	0.186	0.001	0.264	0.000
E_+	0.421	–0.002	0.666	0.003
E_-	0.316	0.000	0.390	–0.003
9 6 3 – 9 5 4				
A	23789.693	0.002	23952.777	0.000
G	0.272	–0.003	0.455	–0.001
E_+	0.492	–0.005	0.776	0.000
E_-	0.601	–0.002	1.048	0.001
10 4 7 – 0 3 8				
A	25940.024	0.003	25957.324	0.001
G	0.077	–0.003	0.124	–0.001
$E_\pm$	0.156	–0.004	0.247	–0.003
10 5 6 – 10 4 7				
A	23796.062	0.000	23854.502	–0.002
G	0.125	0.001	0.197	0.003
$E_\pm$	0.247	0.000	0.390	0.001
10 5 5 – 10 4 6				
A	14534.972	0.001	14625.038	0.002
G	0.141	0.001	0.218	–0.005
$E_\pm$	0.281	0.001	0.442	–0.004
10 6 5 – 10 5 6				
A	25460.901	0.003	25579.789	0.000
G	0.192	0.000	0.295	0.000
E_+	–	–	0.623	–0.002
E_-	–	–	0.548	–0.008
$E_\pm$	0.367	–0.017	–	–
10 6 4 – 10 5 5				
A	21806.372	–0.002	21986.583	–0.002
G	0.272	0.002	0.430	0.001
E_+	0.529	0.002	0.825	0.001
E_-	0.549	–0.005	0.898	0.005
11 5 6 – 11 4 7				
A	14959.457	–0.005	14989.318	0.001
G	0.079	0.010	0.112	–0.001
$E_\pm$	0.149	0.011	0.223	–0.002
11 6 5 – 11 5 6				
A	19443.118	0.000	19620.769	0.002
G	0.256	0.000	0.400	–0.004
$E_\pm$	0.511	0.000	0.807	–0.001

Table 4. Rotational constants of several isotopomers of anti-2,3-dimethylthiirane (ground state). The centrifugal distortion parameters were taken from the main isotopomer. σ: standard deviation of the fit. n: number of transitions.

		^{34}S	^{13}C$_r$	^{13}C$_m$	^{33}S [5]
A	MHz	5251.3247(3)	5393.5803(4)	5374.1649(8)	5331.1401
B	MHz	3506.4000(3)	3493.4355(3)	3416.3173(7)	3506.3962
C	MHz	2341.1748(1)	2367.2526(1)	2324.1884(3)	2356.9273
σ	kHz	0.7	0.8	1.8	
n		7	7	7	8

Analysis

The rotational spectra in the torsional ground state could be interpreted by the fourth order centrifugal distortion Hamiltonian with Watson A reduction in the representation I^r [14, 15]. No splittings due to internal rotation could be observed for all ground state transitions. Their rotational and centrifugal distortion constants are compiled in Table 4 and 5, additionally the values of the ^{33}S isotopomer have been taken from an investigation concerning the ^{33}S hfs [5]. For the isotopomers the centrifugal distortion constants have been fixed to the values of the most abundant isotopomer. The data of Table 4 and 5 have been used to compare with $\delta = \nu_{obs} - \nu_{calc}$ the experimental and the calculated spectra in Table 1 and 2. The rotational constants of Table 4 and 5 will be the basis for a structure determination in a later chapter.

The rotational assignment of the spectra in excited torsional states was checked by the consistency of

Table 5. Rotational and centrifugal distortion constants of anti-2,3-dimethylthiirane (Watson A reduction, I^r). $B_J = (B + C)/2$, $B_K = A - (B + C)/2$, $B_- = (B - C)/2$. n: number of observations. σ standard deviation of the fit. F: Freedom parameters (see [27]) The revised ground state constants are obtained from the measurements of [1].

		Ground state	F	$v_{17} = 1$	F	$v_{33} = 1$	F
B_J	MHz	2939.85028(26)	.35	2938.65942(57)	.41	2936.23688(42)	.38
B_K	MHz	2475.71757(27)	.37	2461.43563(26)	.32	2472.78976(19)	.33
B_-	MHz	566.54623(15)	.30	566.88483(14)	.37	565.80501(10)	.37
Δ_J	kHz	0.6036(82)	.32	0.5771(166)	.41	0.6078(124)	.38
Δ_{JK}	kHz	0.1609(183)	.21	0.5251(75)	.14	0.0555(57)	.14
Δ_K	kHz	4.5351(161)	.25	3.9986(92)	.22	4.7188(68)	.22
δ_J	kHz	0.1896(28)	.28	0.1921(12)	.26	0.1871(9)	.26
δ_K	kHz	0.8190(170)	.53	0.5768(81)	.28	0.6310(62)	.28
σ	kHz	2.5		4.5		3.3	
n		36		52		53	
Derived parameters							
A	MHz	5415.5679(4)		5400.0951(7)		5409.0266(5)	
B	MHz	3506.3965(3)		3505.5442(6)		3502.0419(5)	
C	MHz	2373.3040(3)		2371.7746(6)		2370.4319(4)	
κ		−0.25510		−0.25122		−0.25518	

Correlation matrix of the parameters from the $v_{17} = 1$ fit. The corresponding matrix of the $v_{33} = 1$ state is almost identical.

B_J	1.000							
B_K	−0.280	1.000						
B_-	0.188	0.023	1.000					
Δ_J	0.910	−0.316	0.178	1.000				
Δ_{JK}	0.045	0.170	0.469	−0.002	1.000			
Δ_K	−0.206	0.455	−0.402	−0.191	−0.742	1.000		
δ_J	0.129	0.105	0.845	0.097	−0.551	0.778	1.000	
δ_K	−0.055	−0.097	0.406	−0.009	0.627	−0.916	−0.760	1.000

Table 6. Internal rotation parameters obtained from the analysis of the torsional excited states of anti-2,3-dimethylthiirane. [...] indicates assumed parameter. The value of I_τ was choosen from anti-2,3-dimethyloxirane [3] $n\Delta$ gives the number of all observed splittings, $\overline{\Delta\nu}$ is the RMS value of all splittings.

V_3	kJ/mol	13.1678(21)		
V_3	cm^{-1}	1100.742(172)		
V'_{12}	kJ/mol	−1.6678(25)		
V'_{12}	cm^{-1}	−139.404(205)		
I_τ	$\mathrm{uÅ}^2$	[3.1975]		
ϵ	rad	0.86722(635)		
δ	rad	0.48153(135)		
Derived parameters			r_s	r_0
$\angle a, i$	deg.	27.59(08)	26.98(63)	27.43(57)
$\angle b, i$	deg.	72.57(18)	73.41(98)	73.41(16)
$\angle c, i$	deg.	69.32(17)	69.35(36)	68.80(09)
F_{ii}	GHz	163.186		
F_{12}	GHz	−4.498		
s		89.920		
σ	kHz	5.3		
$n\Delta$		217		
$\overline{\Delta\nu}$	kHz	532		

the A species components of the multiplets with a centrifugal distorted rigid rotor Hamiltonian (Watson A reduction). The internal rotation analysis followed a procedure, which we call combined axis method (CAM). Details are described in [3], they will not be repeated here. It is an extension of the Woods IAM [3, 16 - 19] including top-top coupling terms in the potential and kinetic energy. It is based on a model consisting of a rigid frame and two rigid tops leading to two internal and three overall degrees of freedom in order to describe the internal and the overall rotation. For a better fit of the high J lines fourth order centrifugal distortion in Watson A reduction [14] has been added.

The determinable potential parameters of TBS were the coupling term V'_{12} of $V'_{12}\sin(3\tau_1)\sin(3\tau_2)$ with the torsional angles τ_1 and τ_2 (usually designated α_i) in addition to V_3, the height of the threefold barrier. Furthermore the polar coordinates δ_i and ϵ_i of the internal rotation axis of the top i, ($i = 1, 2$) with respect to the principal axes were determined [3]. The moment of inertia of the tops $I_{\tau,i}$ ($=I_\alpha$) has been fixed to the value of anti-2,3-dimethyloxirane (Table 1 fit 1 of [3]). The internal rotation parameters are given in Table 6, together with some derived parameters: the angles $\angle(g, i)$, $g = a, b, c$, the internal rotation constant F, the kinetic coupling parameter F_{12}, and the reduced barrier s. The $\delta\Delta = \Delta\nu_{obs} - \Delta\delta_{calc}$ values of Table 3 were calculated with the parameters of Table 5 and 6.

The dipole moment of TBS was determined with the $J_{K_-K_+} = 2\ 1\ 2 - 1\ 0\ 1$ transition using a conventional Stark spectrometer with Stark voltages of 125, 150, and 175V. Second order pertubation theory was used to analyze the splittings. Due to the C_2 symmetry, TBS possesses only one dipole moment component in b direction with a magnitude of 2.13(2) Debye.

Structure

The ground state rotational constants of the five isotopomers given in Table 4 and 5 are an information to determine the structure of the molecule. A picture of the molecule is given in Figure 1. Following [20], the r_s structure of the heavy atom frame was calculated. The cartesian coordinates in the principal axis system are given in Table 7. For sulfur two values result for ^{33}S and ^{34}S. The mean value was used to derive the bond lengths and angles of Table 8. The given errors were estimated according to van Eijck [21].

In a second procedure the r_0 structure [20] was determined using the program ru111j written by

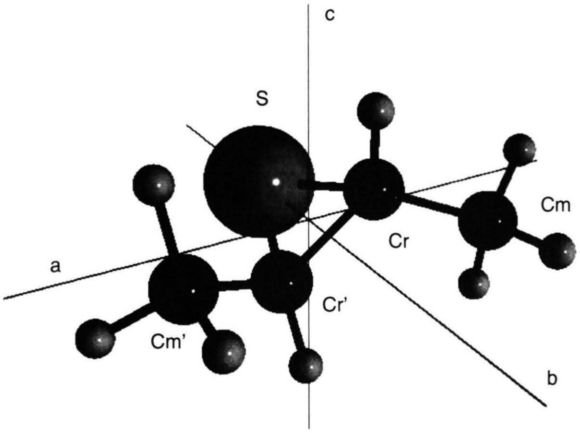

Fig. 1. Anti-2,3-dimethylthiirane and the principal inertia axes *a*, *b*, and *c*. The *b*-axis is the C_2-axis.

Table 7. Cartesian coordinates (in Å) of anti-2,3-dimethylthiirane in the principal axis system of the ^{32}S isotopomer. The errors of the r_s coordinates are estimated according to [21].

	a		*b*		*c*	
	r_s	r_0	r_s	r_0	r_s	r_0
C_r:	-0.5918(14)	-0.6062(49)	-0.4443(18)	-0.4469(25)	-0.4336(18)	-0.4308(4)
C_r':	0.5918(14)	0.6062(49)	-0.4443(18)	-0.4469(25)	0.4336(18)	0.4308(4)
C_m:	-1.9410(4)	-1.9454(13)	-0.8765(9)	-0.8777(16)	0.1007(79)	0.1149(14)
C_m':	1.9410(4)	1.9454(13)	-0.8765(9)	-0.8777(16)	-0.1007(79)	-0.1149(14)
^{34}S:	0.0	0.0	1.22334(25)	1.2251(4)	0.0	0.0
^{33}S:	0.0	0.0	1.22329(25)	1.2254(4)	0.0	0.0

Rudolph [22]. As the rotational constants of the heavy atom substituted isotopomers were not sufficient to determine the position of the hydrogen atoms, structural parameters for bond lengths and angles were assumed. For the methyl group a distance C_m-H_m = 1.09 Å and an angle $\angle C_r$-C_m-H_m = 109.4° were taken. The parameters for the hydrogens attached to the ring were derived from the reported structure of thiirane [23]. We fitted the heavy atom structure directly to the rotational constants, furthermore we assumed all rotational constants to have the same statistical weight and to be uncorrelated. The results were included in Table 7 and 8. Also the values of the angles between the internal rotation axes, assumed collinear to the C_r-C_m bond, and the axes of inertia are included for comparison with results of the internal rotation analysis given in Table 6.

Table 8. Structural parameters (in Å and degree) of anti-2,3-dimethylthiirane (compare Fig. 1). The r_s parameters were obtained from the cartesian coordinates of Table 7. [. . .]: assumed parameters, ^{a}: derived parameters. ^{b}: assumption of the angular position of the methyl group. ^{c}: assumption of the C_{3v} symmetry of the methyl group. X_r is the midpoint of the C_r - C_r' bond.

		r_s	r_0
dist.	X_r-C_r	0.734(2)	0.744(4)
in Å	X_r-S	1.668(2)	1.672(3)
	C_r-C_m	1.514(3)	1.509(6)
	C_r-C_r'	1.467(2)	1.487(9)^a
	C_r-S	1.822(2)	1.830(3)^a
	C_r-H_r		[1.078]
	C_m-H_m		[1.09]
angles	C_m-C_r-C_r'	120.70(30)	120.93(13)
in deg.	C_m-C_r-S	117.83(17)	118.02(32)^a
	S-C_r-C_r'	66.26(10)	66.02(13)^a
	C_r-S-C_r'	47.49(7)	47.96(25)^a
	C_r'-C_r-H_r		[117.80]
	S-C_r-H_r		[114.72]
	C_r-C_m-H_m		[109.4]
dihedral	C_m-C_r-C_r'-S	109.39(17)	109.44(20)
angles	C_m-C_r-C_r'-C_m'	141.23(19)	141.12(40)^a
	S-C_r'-C_r-H_r		[106.50]
	C_r'-C_r-C_m-H_m		[0.0]^b
	H_m'-C_m'-C_r-C_m-H_m		[120.0]^c

In a following publication on 2,2-dimethyloxirane we will give a comparison of the structures obtained for the methyl substituted oxiranes and thiiranes.

Discussion

The internal rotation analysis of the two torsional excited states together yielded values for the potential barrier V_3 and the potential top-top coupling term V_{12}' (other names are V_{33}' or V_{ss}). The value of V_6 could not be determined because, in contrast to anti-2,3-dimethyloxirane [3], the ground state transitions showed no internal rotation splittings.

The parameter V_3 describes mainly the height of the potential barrier for a 120 degree rotation of one methyl group. Comparing the value of 13.168(2) kJ/mol with the value of anti-2,3-dimethyloxirane (10.52 kJ/mol), it turns out that the barrier of TBS is about 27% larger. This relative difference is in agreement with the values of metyhlthiirane [6,24] and -oxirane [25] (26 % larger) and with 2,2-dimethylthiirane [4] and -oxirane [1] (33% larger). A compilation of the potential parameters is given in Table 9.

The effect in the spectra of the potential top-top coupling parameter V_{12}', together with the kinetic interaction term F_{12}, is to split the symmetric (v_{17} = 1) and the antisymmetric (v_{33} = 1) torsional modes

Table 9. Internal rotation constants of several oxiranes and thiiranes obtained by microwave spectroscopy.

V_3 in kJ/mol	oxirane	thiirane
monomethyl-	10.72(29) [25]	13.49(11) [6]
anti-2,3-dimethyl-	10.396(4) [3]	13.168(2)
syn-2,3-dimethyl-	6.912(22) [2]	-
2,2-dimethyl-	11.280(7) [19]	15.172(36) [4]
V'_{12} in kJ/mol	oxirane	thiirane
anti-2,3-dimethyl-	-0.4240(6) [3]	-1.668(3)
syn-2,3-dimethyl-	-	-
2,2-dimethyl-	-1.055(26) [19]	-1.258(12) [4]

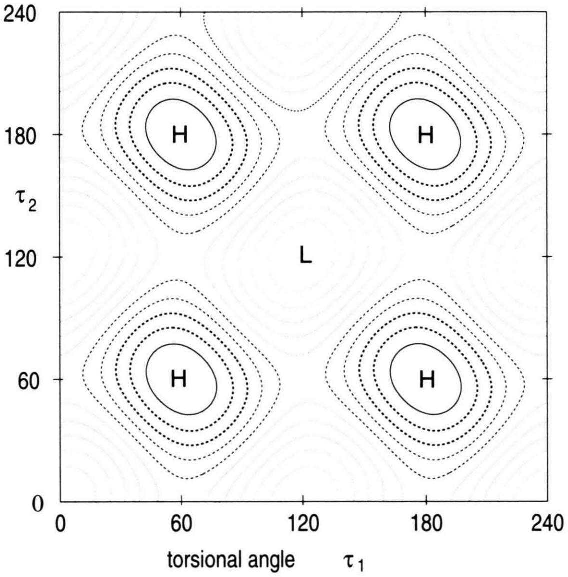

Fig. 2. Potential surface of internal rotation as a function of the torsional angles τ_1 and τ_2. The values of Table 6 were used. The deformation of the surface is produced by the potential coupling term V'_{12}. The minima are designated by L, the maximas by H.

specified under the group C_2. The estimated magnitude of this splitting is about 56 cm^{-1}, but this value has to be experimentally verified by vibrational spectroscopy. Figure 2 shows the potential energy surface of TBS. It can be seen that the valleys are stretched in the diagonal direction ($\tau_1 - \tau_2$ = const) and are narrowed in the antidiagonal direction ($\tau_1 + \tau_2$ = const).

In the hypothetical case without any potential $V'_{12} = 0$ and kinetic coupling $F_{12} = 0$, the symmetric and antisymmetric torsional motions are degenerate. In this case the potential surface becomes isotropic, with circular potential walls around the minimas. This corresponds to an isotropic two dimensional oscillator in the high barrier limit.

In our case the degeneracy is lifted; near the minimas the potential surface can be approximated by a two axis elliptical paraboloid with two eigenvectors pointing in the diagonal and antidiagonal direction. The curvature at the minimum is smaller in the diagonal direction, the antidiagonal direction has a larger curvature. Two normal modes with different force constants result, where the diagonal mode has a smaller force constant than the antidiagonal mode.

The diagonal or symmetric mode, lower in energy, is connected in the mode picture to an antigearing [26] of the methyl groups. As it is lower in energy, the tunnelling is less probable. For the antisymmetic mode the energy level is higher. Here the mode picture reminds to a gearing of the methyl groups, which favours tunnelling. This semi-classical picture should be used with caution.

Comparing the magitude of the V'_{12} parameters for several molecules, the large absolute value of V'_{12} of TBS is remarkable. The value of $V'_{12} = -1.668$ kJ/mol is four times larger than the value of the analogous oxirane [3] (V'_{12}=-0.424 kJ/mol); furthermore the absolut value of V'_{12} of TBS is higher than that of 2,2-dimethylthiirane (−1.26 kJ/mol) and its analogon 2,2-dimethyltoxirane (−1.08 kJ/mol). One expects that TBS should have a value similar to the analogous oxirane because the positions of the methyl groups is not changed considerably. Furthermore it was expected that the top-top coupling of molecules were the methyl groups are attached to the same atom (e. g. 2,2-dimethyloxirane/thiirane), contributes more to the potential function. This is true for the oxiranes, but the value of TBS here appears much to large.

A possible explanation of the magnitude of V'_{12} can be found in the interaction of a torsional mode with another vibrational motion of the molecule. In our case a frequency calculation with Gaussian 92 showed that the lowest vibration is the symmetric bending of the molecule, which may interfer with the symmetric torsion. An interaction shifts the symmetric torsional motion to lower energy, therefore a larger distance between both torsional modes is achived. In our simplified model without considering other vibrations, the enlarged distance between these modes leads to an increased magnitude of the V'_{12} parameter. To obtain an accurate potential surface of TBS, it would be necessary to include this bending motion, but neither the experimental data nor the theoretical background is presently available.

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