A Contribution to the Microwave Spectra of cis- and trans-2,3-Dimethyloxirane by Fourier Transform Spectroscopy

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Microwave Fourier transform spectroscopy was used to reinvestigate the rotational spectra of cis- and trans-2,3-dimethyloxirane. The potential barriers hindering the internal rotation, internal rotation parameters, and partial r_s-structures were determined.

Introduction

In course of our efforts to investigate with the presently possible accuracy the microwave rotational spectra of molecules containing two hindered methyl internal rotors [1–5] we reinvestigated the rotational spectra in the torsional ground-state of cis-2,3-dimethyloxirane (cis-2,3-epoxybutane, CEB, cis-$CH_3CH\underset{O}{\overline{\quad\;}}CH-CH_3$) and trans-2,3-dimethyloxirane (trans-2,3-epoxybutane, TEB, trans-CH_3–$CH\underset{O}{\overline{\quad\;}}CH$ $-CH_3$) first investigated by Sage [6] and Emptage [7] at Harvard University.

In addition we were able to measure and assign the ^{13}C-isotopomers in natural abundance. So a partial r_s-structure could be derived.

In a following publication we will present our results for 2,2-dimethyloxirane.

The barrier V_3 hindering internal rotation, other internal rotation parameters, rotational and centrifugal distortion constants could be determined with high precision.

For comparison quantum chemical calculations were performed with Gaussian 88 [8].

Experimental

Both substances were purchased from Fa. Aldrich, Steinheim, FRG, and used without further purification.

We used our microwave Fourier transform (MWFT) spectrometers in the waveguide (WG) [9, 10] and molecular beam (MB) [11, 12] versions.

The measurements with WG-MWFT spectrometers were made at pressures of 1.5 to 0.5 mTorr (0.2–0.07 Pa) and at a temperature of -58 °C. The frequencies of multiplet components were refined by evaluation of the time domain signal [13].

For the measurements with the MB-MWFT spectrometer a mixture of 2% substance in argon with a backing pressure of approximately 1 bar was used. No additional refinement for the frequencies was applied in this case.

The results for CEB and two ^{13}C-isotopomers are given in Tables 1 and 2, for TEB and two ^{13}C-isotopomers in Tables 3 and 4. For the isotopomers only the hypothetical rigid rotor frequencies of the torsion multiplets are given. In the Tables 1 and 3 only selections of the measured transitions are given. A complete list is deposited under TNA 28 at the library of the University of Kiel, Westring 400, W-2300 Kiel, or in [14].

The deviations $\delta_{\Delta\nu}$ given in Tables 1 and 3 were calculated with the complete line sets.

In Figs. 1–3 we present three representative measurements.

Analysis

The assignment of the measured μ_b and μ_c-type lines of CEB and μ_b-type lines of TEB was performed without difficulties on the basis of the reported data [6, 7].

The internal rotation analysis was based on two methods: a modified principal axis method (PAM) [3] and the internal axis method (IAM) in the formulation given by Woods [15, 16].

The invariance group of the Hamiltonian for CEB is $C_3^- \otimes C_{3v}^+$, for TEB $C_{3v}^- \otimes C_3^+$ [17]. The point groups are C_s and C_2 respectively.

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Table 1. Selection of rotational transitions of cis-2,3-dimethyloxirane (CEB) in the ground state. $\delta_{\Delta\nu}$: difference between observed ($\Delta\nu$) and calculated frequency splitting (in MHz) $\delta^{(a)}_{\Delta\nu}$: calculated with program KC3IAM; $\delta^{(b)}_{\Delta\nu}$: with TTWF 2. Exact designation of the AA, EE, AE and EA symmetry species Γ are AA_1, $[E_aE+E_bE]$, AE, and $[E_aA_1+E_bA_1]$. (1): MB-MWFT-, (2): WG-MWFT-spectrometer.

$J'K'_-K'_+ - J K_- K_+$	Γ	ν(obs.)	$\Delta\nu$	$\delta^{(a)}_{\Delta\nu}$	$\delta^{(b)}_{\Delta\nu}$	
1 1 1−0 0 0	AA	11 526.395				(1)
	EE	11 526.303	0.092	0.000	−0.003	
	AE	11 526.215	0.179	−0.005	−0.004	
	EA	11 526.203	0.191	−0.004	−0.004	
2 1 2−1 0 1	AA	18 463.445				(2)
	EE	18 463.333	0.112	0.005	0.004	
	AE	18 463.222	0.223	0.009	0.011	
	EA	18 463.222	0.223	0.009	0.005	
2 2 1−2 1 2	AA	13 767.933				(1)
	EE	13 767.643	0.290	−0.000	0.000	
	AE	13 767.471	0.462	0.004	0.003	
	EA	13 767.231	0.701	−0.002	0.001	
3 1 2−2 2 1	AA	14 365.767				(1)
	EE	14 365.739	0.028	−0.011	−0.010	
	AE	14 365.576	0.191	−0.009	−0.008	
	EA	14 365.824	−0.057	−0.011	−0.009	
3 3 0−3 2 1	AA	19 729.589				(2)
	EE	19 730.476	−0.887	0.003	0.002	
	AE	19 729.109	0.480	0.002	0.000	
	EA	19 733.081	−3.492	0.007	0.007	
3 3 0−3 2 2	AA	20 587.727				(2)
	EE	20 588.591	−0.864	−0.004	−0.004	
	AE	20 587.146	0.580	−0.004	−0.005	
	EA	20 591.219	−3.492	−0.002	−0.002	
4 1 3−3 2 2	AA	23 856.516				(2)
	EE	23 856.323	0.193	0.002	0.002	
	AE	23 856.109	0.408	0.002	−0.001	
	EA	23 856.157	0.359	0.002	0.003	
4 1 3−4 0 4	AA	10 887.539				(1)
	EE	10 887.189	0.350	−0.003	0.001	
	AE	10 886.843	0.696	−0.010	0.004	
	EA	10 886.831	0.708	0.015	0.003	
4 2 2−4 1 3	AA	10 099.282				(1)
	EE	10 099.145	0.137	−0.005	0.000	
	AE	10 099.003	0.279	−0.006	−0.001	
	EA	10 099.013	0.269	0.000	−0.001	
4 3 2−4 2 2	AA	18 635.151				(2)
	EE	18 634.801	0.350	0.003	−0.002	
	AE	18 634.801	0.350	−0.003	−0.006	
	EA	18 634.112	1.039	−0.011	−0.012	
5 3 2−4 4 1	AA	12 238.925				(1)
	EE	12 244.719	−5.794	−0.007	−0.007	
	AE	12 239.024	−0.099	−0.009	−0.007	
	EA	12 251.454	−12.529	−0.005	−0.004	
5 2 3−5 1 4	AA	10 771.642				(1)
	EE	10 771.423	0.220	−0.000	0.003	
	AE	10 771.203	0.440	−0.001	−0.009	
	EA	10 771.203	0.440	0.007	0.006	
7 3 5−7 2 5	AA	11 973.035				(1)
	EE	11 973.130	−0.096	−0.002	−0.002	
	AE	11 973.239	−0.205	−0.007	−0.004	
	EA	11 973.211	−0.176	−0.001	−0.004	
8 3 6−8 2 6	AA	9 168.741				(2)
	EE	9 168.916	−0.175	−0.001	−0.002	
	AE	9 169.090	−0.349	−0.000	0.007	
	EA	9 169.090	−0.349	−0.011	−0.013	
12 4 9−12 3 9	AA	9 275.664				(2)
	EE	9 276.067	−0.403	−0.001	−0.001	
	AE	9 276.470	−0.807	−0.003	0.009	
	AE	9 276.470	−0.807	−0.011	−0.014	
15 5 11−15 4 11	AA	12 374.713				(2)
	EE	12 375.360	−0.647	0.004	0.002	
	AE	12 376.006	−1.293	0.009	0.018	
	EA	12 376.006	−1.293	−0.001	−0.007	

Table 2. Rigid rotor transitions of cis-2,3-dimethyloxirane (CEB) ^{13}C-isotopomers. Measured with MB-MWFT cavity spectrometer. Frequencies in MHz, calculated from measured multiplets with program KC3 IAM.

$J'K'_-K'_+ - J K_- K_+$	Methyl ^{13}C		Ring ^{13}C	
	ν	δ_ν	ν	δ_ν
1 1 1−0 0 0	11 371.300	0.001	11 477.866	0.000
1 1 0−0 0 0	12 340.008	−0.001	12 257.107	0.000
2 2 0−2 1 1	11 005.067	0.005	10 945.964	−0.001
3 1 2−3 0 3	7 702.972	0.002	7 735.510	0.002
3 2 1−3 1 2	10 317.697	−0.004	10 261.643	0.002
3 2 2−3 1 2	9 499.508	−0.006	−	−
4 1 3−4 0 4	10 694.588	−0.003	10 768.453	−0.001
4 2 2−4 1 3	10 104.188	0.006	10 066.352	−0.001

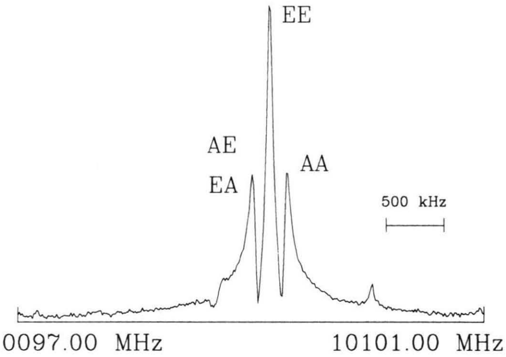

Fig. 1. WG-MWFT measurements of cis-2,3-dimethyloxirane (CEB). $J'K'K'-JKK = 4\,2\,2-4\,1\,3$. The EA and AE component is not resolved. Temperature: 215 K, pressure 0.16 Pa, sampling interval 10 ns, 4 k data points, 1600 k averaging cycles, polarizing frequency 10099 MHz.

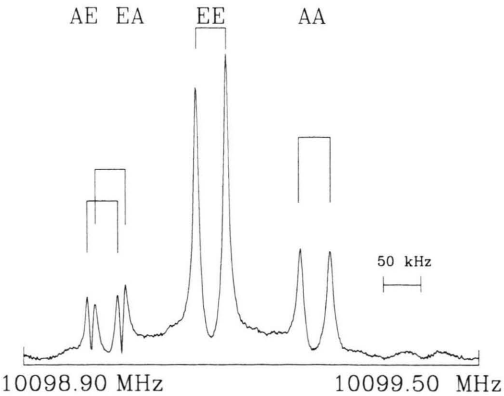

Fig. 2. MB-MWFT measurement of cis-2,3-dimethyloxirane (CEB), transition see Figure 1. The splitting between EA and AE is 10 kHz, sampling interval 100 ns, 8 k data points, 500 averaging cycles, 2% in Ar, backing pressure 1 bar.

Table 3. Selection of rotational transitions of trans-2,3-dimethyloxirane (TEB) in the ground state. $\delta_{\Delta\nu}$: difference between observed ($\Delta\nu$) and calculated frequency splitting. $\delta^{(a)}_{\Delta\nu}$: calculated with program KC3IAM; $\delta^{(b)}_{\Delta\nu}$: with TTWF2, transitions marked with −/− are not included in the TTWF2 fit. Exact designation of the AA, EE, AE and EA symmetry species are A_1A, $[EE_a+EE_b]$, $[A_1E_a+A_1E_b]$, and EA. (1): MB-MWFT-, (2): WG-MWFT-spectrometer.

$J'K'_-K'_+ - JK_-K_+$	Γ	ν(obs.)	$\Delta\nu$	$\delta^{(a)}_{\Delta\nu}$	$\delta^{(b)}_{\Delta\nu}$	
1 1 1–0 0 0	AA	15 309.892				(1)
	EE	15 309.841	0.051	0.001	−0.005	
	AE	15 309.793	0.099	−0.002	−0.013	
	EA	15 309.793	0.099	−0.002	−0.015	
1 1 0–1 0 1	AA	9 165.064				(1)
	EE	9 165.009	0.055	0.005	0.001	
	AE	9 164.961	0.103	0.003	−0.006	
	EA	9 164.961	0.103	0.003	−0.004	
2 1 2–1 0 1	AA	21 454.727				(2)
	EE	21 454.676	0.051	−0.001	−0.007	
	AE	21 454.625	0.102	−0.001	−0.013	
	EA	21 454.625	0.102	−0.001	−0.014	
2 2 0–2 1 1	AA	26 453.578				(2)
	EE	26 453.488	0.090	−0.001	−0.009	
	AE	26 453.282	0.296	−0.002	−0.024	
	EA	26 453.510	0.068	0.000	−0.009	
3 0 3–2 1 2	AA	10 970.628				(1)
	EE	10 970.683	−0.055	−0.007	−0.008	
	AE	10 970.736	−0.108	−0.012	−0.014	
	EA	10 970.736	−0.108	−0.012	−0.013	
3 1 2–3 0 3	AA	10 085.941				(1)
	EE	10 085.891	0.050	0.001	−0.005	
	AE	10 085.842	0.099	0.001	−0.011	
	EA	10 085.842	0.099	0.001	−0.011	
3 3 0–4 2 3	AA	18 980.394				(2)
	EE	18 981.221	−0.827	−0.015	0.007	
	AE	18 979.911	0.483	−0.001	−0.029	
4 1 3–4 0 4	AA	10 867.761				(1)
	EE	10 867.712	0.048	0.001	−0.007	
	AE	10 867.664	0.097	0.001	−0.014	
	EA	10 867.664	0.097	0.001	−0.014	
4 3 2–5 2 3	AA	12 172.421				(1)
	EE	12 171.514	0.908	0.002	−0.037	
	EE*	12 526.439	−354.438	0.001	−/−	
	AE	12 171.929	0.493	0.006	−0.017	
	EA	12 170.205	2.217	0.000	−/−	
	EA*	12 525.571	−353.150	−0.006	−0.080	
4 3 1–5 2 4	AA	12 529.082				(1)
	EE	12 529.496	−0.414	0.007	0.023	
	EE*	12 174.141	354.942	0.018	−/−	
	AE	12 528.599	0.484	0.002	−0.023	
	EA	12 530.331	−1.249	−0.002	0.032	
	EA*	12 174.962	354.120	0.007	−/−	
5 2 3–5 1 4	AA	24 739.611				(2)
	EE	24 739.464	0.147	−0.001	−0.007	
	AE	24 739.319	0.292	−0.003	−0.019	
	EA	24 739.319	0.292	0.003	−0.012	
6 2 4–6 1 5	AA	24 078.643				(2)
	EE	24 078.502	0.141	−0.005	−0.010	
	AE	24 078.360	0.283	−0.008	−0.022	
	EA	24 078.360	0.283	−0.008	−0.018	
7 1 6–6 2 5	AA	23 172.420				(2)
	EE	23 172.564	−0.144	0.002	−0.005	
	AE	23 172.712	−0.292	0.001	−0.015	
	EA	23 172.712	−0.292	0.001	−0.011	
7 2 5–7 1 6	AA	23 465.688				(2)
	EE	23 465.546	0.142	−0.001	−0.006	
	AE	23 465.404	0.285	−0.000	−0.012	
	EA	23 465.404	0.285	−0.000	−0.011	
7 4 4–8 3 5	AA	10 707.821				(2)
	EE	10 706.207	1.614	0.002	−0.037	
	EE*	10 791.931	−84.109	−0.009	−/−	
	AE	10 707.159	0.663	−0.001	−0.025	
	EA	10 704.356	3.466	0.004	−0.075	
	EA*	10 790.164	−82.343	−0.000	−/−	
9 2 8–8 3 5	AA	12 673.534				(2)
	EE	12 673.752	−0.218	−0.001	0.005	
	AE	12 674.001	−0.467	−0.003	0.011	
	EA	12 673.941	−0.407	−0.003	0.009	
10 5 6–11 4 7	AA	9 130.296				(2)
	EE	9 128.036	2.260	0.001	−0.022	
	EE*	9 146.329	−16.034	0.010	−/−	
	AE	9 129.470	0.825	0.000	−0.022	
	EA	9 125.486	4.810	0.007	−0.039	
	EA*	9 144.493	−14.198	−0.002	−/−	
14 4 11–13 5 8	AA	10 678.711				(2)
	EE	10 677.986	0.725	−0.002	−/−	
	EE*	10 798.716	−120.004	−0.007	−/−	
	AE	10 679.534	−0.823	−0.001	−/−	
	EA	10 676.659	2.052	0.002	−/−	
	EA*	10 797.507	−118.796	−0.015	−/−	
15 7 9–16 6 10	AA	12 482.501				(2)
	EE*	12 481.889	0.612	0.000	−/−	
	AE	12 481.408	1.092	0.000	−/−	
	EA*	12 481.107	1.393	0.000	−/−	
16 4 12–15 5 11	AA	24 334.933				(2)
	EE	24 335.767	−0.834	0.004	−/−	
	AE	24 335.767	−0.834	−0.002	−/−	
	EA	24 337.248	−2.315	−0.001	−/−	
15 7 8–16 6 11	AA	12 482.822				(2)
	EE*	12 482.342	0.481	0.000	−/−	
	AE	12 481.730	1.092	0.000	−/−	
	EA*	12 482.031	0.791	0.000	−/−	
17 5 12–16 6 11	AA	12 365.856				(2)
	EE	12 368.342	−2.486	−0.002	−/−	
	EE*	12 343.634	22.222	−0.001	−/−	
	AE	12 366.828	−0.971	−0.004	−/−	
	EA*	12 345.781	20.075	−0.004	−/−	
17 5 13–16 6 10	AA	12 341.078				(2)
	EE	12 339.559	1.518	0.000	−/−	
	EE*	12 364.268	−23.189	−0.001	−/−	
	AE	12 342.047	−0.969	−0.003	−/−	
	EA*	12 363.087	−22.010	0.002	−/−	
19 5 14–18 6 13	AA	25 768.124				(2)
	EE	25 770.109	−1.985	−0.000	−/−	
	EE*	25 696.990	71.132	0.002	−/−	
	AE	25 769.103	−0.979	−0.011	−/−	
19 5 15–18 6 12	AA	25 693.758				(2)
	EE	25 692.740	1.018	−0.000	−/−	
	EE*	25 765.861	−72.103	−0.005	−/−	
	AE	25 694.727	−0.969	−0.004	−/−	
25 8 18–24 9 15	AA	10 602.780				(2)
	EE*	10 603.318	−0.539	−0.004	−/−	
	AE	10 604.028	−1.248	0.005	−/−	
	EA*	10 603.816	−1.036	−0.010	−/−	
26 11 16–27 10 17	AA	12 529.970				(2)
	EE*	12 529.281	0.689	0.005	−/−	
	AE	12 528.656	1.315	−0.007	−/−	
	EA*	12 528.594	1.376	0.007	−/−	
28 9 19–27 10 18	AA	12 242.677				(2)
	EE*	12 243.404	−0.727	−0.005	−/−	
	AE	12 243.973	−1.296	−0.001	−/−	
	EA*	12 244.132	−1.456	−0.005	−/−	

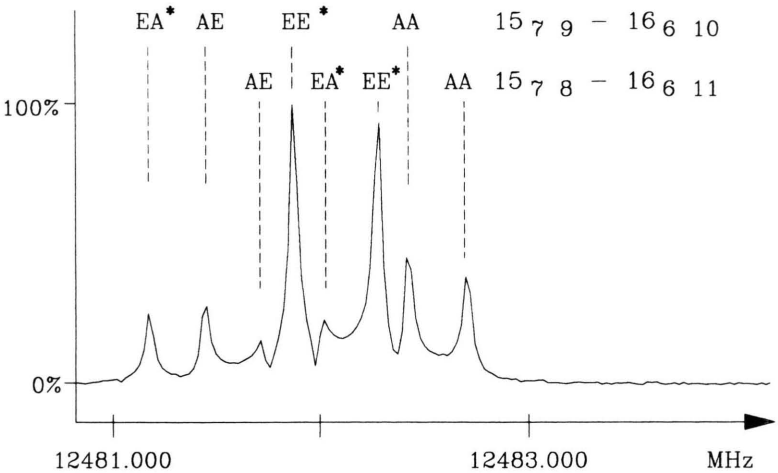

Fig. 3. trans-2,3-Dimethyloxirane (TEB), WG-MWFT measurement. $J'K'K'-JKK$ = 15 7 9–16 6 10 and 15 7 8–16 6 11. The EA* and EE* components belong to the transitions 15 7 9–16 6 11 and 15 7 8–16 6 10. The occurrence of these c-type spectra is caused by the near degenerate K-doublet. Temperature 215 K, pressure 0.07 Pa, sampling interval 10 ns, 4 k data points, 1600 k averaging cycles, polarizing frequency 12 482 MHz.

Table 4. Rigid rotor transitions of trans-2,3-dimethyloxirane (TEB) ^{13}C-isotopomers. Measured with MB-MWFT cavity spectrometer. Frequencies in MHz, calculated from measured multiplets with program KC3 IAM.

$J'K'_-K'_+-JK_-K_+$	Methyl ^{13}C ν	Methyl ^{13}C δ_ν	Ring ^{13}C ν	Ring ^{13}C δ_ν
1 1 1–0 0 0	15 181.085	0.002	15 244.189	0.003
1 1 0–1 0 1	9 183.005	−0.001	9 112.826	−0.003
2 1 1–2 0 2	9 529.163	−0.001	9 468.000	−0.002
3 0 3–2 1 2	10 447.686	0.003	10 957.176	0.001
3 1 2–3 0 3	10 065.940	0.000	10 019.343	0.000
4 0 4–3 1 3	17 199.433	−0.003	17 858.117	−0.001
4 1 3–4 0 4	10 813.870	0.001	10 788.572	0.001

Table 5. Rotational and centrifugal distortion constants of cis-2,3-dimethyloxirane (CEB). Watson's A reduction in I^r representation, σ: single standard deviation.

	KC3IAM +ZFAP4	TTWF2	Sage [6]	Gaussian 88 [8]
A (MHz)	8057.7691(6)	8057.9225(12)	8057.71	8349.992
B (MHz)	4461.3325(4)	4461.3746(9)	4461.36	4422.084
C (MHz)	3468.5166(4)	3468.3162(5)	3468.60	3474.358
Δ_J (kHz)	2.102(7)	2.101(10)	–	–
Δ_{JK} (kHz)	−6.153(23)	−6.453(30)	–	–
Δ_K (kHz)	13.570(24)	13.903(34)	–	–
δ_J (kHz)	0.688(2)	0.689(4)	–	–
δ_K (kHz)	1.591(46)	1.843(90)	–	–
σ (kHz)	2.0	3.7	–	–

We used the program TTWF2 [3] for the PAM, the program KC3IAM [18] for the IAM-analysis.

The centrifugal distortion analysis followed Watson's A reduction [19] representation I^r [20]. The program ZFAP4 [21] was used. For TEB the program TTWF2 used the representation II^r.

Table 6. Freedom cofreedom matrix of Table 5 (program TTWF 2).

A	0.161							
B	0.651	0.113						
C	0.867	0.583	0.135					
Δ_J	0.895	0.763	0.801	0.191				
Δ_{JK}	0.845	0.677	0.749	0.957	0.026			
Δ_K	0.677	0.647	0.919	0.887	0.703	0.154		
δ_J	0.876	0.702	0.716	0.944	0.102	0.738	0.024	
δ_K	0.958	0.753	0.610	0.786	0.515	0.709	0.459	0.083

Table 7. Internal rotation parameters of cis-2,3-dimethyloxirane (CEB).

		KC3IAM	TTWF2	Sage [6]
V_3	(kJ/mol)	6.912(22) [a]	6.892(18)	6.728(630)
V_3	(kcal/mol)	1.6509(6) [a]	1.6461(5)	1.607(150)
$\omega_1(s)$	(10^{-6})	−89.105(86)	–	–
I_α	(amuÅ^2)	3.165(10)	3.169(9)	[3.194] [b]
$\sphericalangle(i,a)$	(deg.)	56.61(6)	56.67(5)	–
$\sphericalangle(i,b)$	(deg.)	42.29(6)	42.34(4)	–
$\sphericalangle(i,c)$	(deg.)	67.22(11)	67.07(7)	–
σ	(kHz)	5.9	5.6	–

[a] Calculated from $\omega_1(s)$. – [b] [...]: assumed.

The internal rotation and centrifugal distortion analyses of the spectra were made in an alternating sequence until the fits converged with errors of the order of the experimental errors.

The rotational constants apply to frequencies of a hypothetical rigid rotor calculated in course of the IAM-analysis.

The internal rotation analysis resulted in a determination of the barrier height V_3 (PAM) or the reduced barrier height s, via the Fourier coefficient $w_1(s)$

Table 8. Rotational and centrifugal distortion constants of trans-2,3-dimethyloxirane (TEB). Watson's A reduction, σ: single standard deviation.

Repres.	KC3IAM +ZFAP4 I^r	TTWF2 II^r	Emptage [7]	Gaussian 88 [8]
A (MHz)	12 237.4418(7)	12 237.4616(160)	12 237.38	12 718.318
B (MHz)	3 422.9051(2)	3 422.9519(21)	3 423.02	3 429.668
C (MHz)	3 072.4168(3)	3 072.3538(190)	3 072.52	3 097.750
Δ_J (kHz)	0.601(2)	16.831(5)	–	–
Δ_{JK} (kHz)	−1.532(15)	−50.284(15)	–	–
Δ_K (kHz)	34.102(5)	34.230(9)	–	–
δ_J (kHz)	0.0825(4)	−8.196(3)	–	–
δ_K (kHz)	0.982(3)	16.408(4)	–	–
σ (kHz)	4.0	3.8	–	–

Table 9. Freedom cofreedom matrix of Table 8 (program ZFAP4).

A	0.072							
B	0.415	0.116						
C	0.462	0.762	0.116					
Δ_J	0.583	0.702	0.618	0.009				
Δ_{JK}	0.583	0.706	0.673	0.108	0.007			
Δ_K	0.639	0.747	0.730	0.407	0.309	0.055		
δ_J	0.777	0.664	0.842	0.604	0.663	0.768	0.112	
δ_K	0.670	0.771	0.737	0.328	0.317	0.467	0.715	0.042

Table 10. Internal rotation parameters of trans-2,3-dimethyloxirane (TEB).

		KC3IAM	TTWF2	Emptage [7]
V_3	(kJ/mol)	10.318(22) [a]	10.323(35)	10.232(630)
V_3	(kcal/mol)	2.4644(6) [a]	2.4658(9)	2.607(150)
$\omega_1(s)$	(10^{-6})	−7.967(16)	–	–
I_α	(amuÅ^2)	3.165(7)	[3.165] [b]	[3.194] [b]
$\sphericalangle(i, a)$	(deg.)	23.20(29)	23.64(8)	–
$\sphericalangle(i, b)$	(deg.)	78.88(55)	78.54(8)	–
$\sphericalangle(i, c)$	(deg.)	69.91(31)	[69.62] [b]	–
σ	(kHz)	5.9	22.9	–

[a] Calculated from $\omega_1(s)$. – [b] [...]: assumed.

Table 11. Rotational constants of ^{13}C-isotopomers.

	CEB		TEB	
	ring ^{13}C	methyl ^{13}C	ring ^{13}C	methyl ^{13}C
A (MHz)	8023.833(1)	7975.859(1)	12 178.540(1)	12 182.078(1)
B (MHz)	4433.290(1)	4364.165(1)	3 410.862(1)	3 335.768(1)
C (MHz)	3454.037(1)	3395.445(1)	3 065.680(1)	2 999.040(1)

(IAM), the moment of inertia I_α of the methyl group and the angles between the internal rotation axis i and the principal inertia axes $g = a, b, c$: $\sphericalangle(i, g)$. Hereby the sum of the squares of the direction cosines of the three angles was fixed to 1.

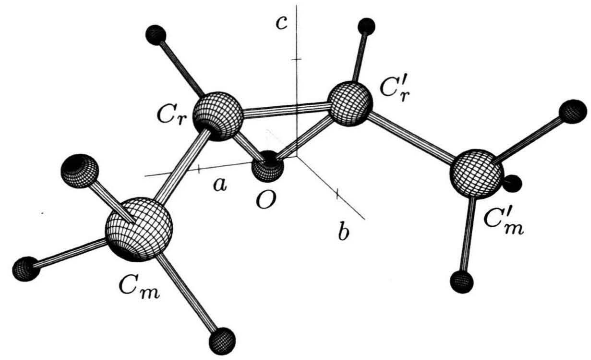

Fig. 4. Perspective drawing of (CEB) cis-2,3-dimethyloxirane in its principal axes system with the symmetry plane b, c. In Figs. 4 and 5 the position of the methyl hydrogens results from Gaussian calculations.

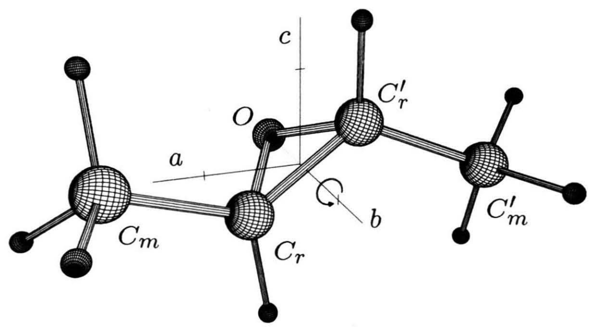

Fig. 5. Perspective drawing of trans-2,3-dimethyloxirane in its principal axes system with b the C_2 axis.

For TEB the measured lines up to the rotation quantum number $J = 12$ contain not enough information to determine I_α and all $\sphericalangle(i, g)$. They were taken in this case from an IAM-analysis of lines up to $J = 30$. The PAM-analysis of the same set of lines was prevented by computer restrictions although all calculations were made with a Cray X-MP/216 computer. The larger off-diagonal elements in the PAM-matrices require larger matrices to get a sufficient accuracy.

The results are compiled for CEB in the Tables 5–7, for TEB in Tables 8–10. The Tables 6 and 9 give the freedom cofreedom matrix proposed in [22]. Small diagonal elements indicate a high interdependence of parameters in the multi-variate fit. Small off-diagonal elements show the connections to the interdependent parameters.

The central frequencies of the multiplets of the ^{13}C-isotopomers given in Tables 2 and 4 were calculated with an IAM-analysis. In some cases the EE component in the designation of the normal isotopomer was

Table 12. Cartesian coordinates of the C-atoms in the principal axis system (r_s-structure).

	CEB		TEB	
	ring ^{13}C	methyl ^{13}C	ring ^{13}C	methyl ^{13}C
a (Å)	±0.73114(3)	±1.58154(5)	±0.58699(4)	±1.96991(2)
b (Å)	0.28457(7)	0.81646(9)	0.14181(17)	0.43134(6)
c (Å)	0.43492(5)	−0.12765(60)	∓0.42697(6)	∓0.10207(25)

Table 13. Comparison of angles between the ring C (C_r)–methyl C (C_m) bonds and the axes of inertia with internal rotation axes. ∢ (i, g): angle between bond respective internal rotation axis and principal axis g. ∢ (i, i'): angle between both bonds or internal rotation axes.

	CEB			TEB		
	r_s	ab initio	int. rot.	r_s	ab initio	int. rot.
∢ (i, a) (deg.)	55.48	54.48	56.67(5)	23.56	23.51	23.20(29)
∢ (i, b) (deg.)	42.80	43.14	42.34(4)	78.94	78.98	78.88(55)
∢ (i, c) (deg.)	67.98	68.86	67.07(7)	69.47	69.50	69.91(31)
∢ (i, i') (deg.)	69.05	70.84	66.65	157.87	157.96	157.77

Table 14. Comparison of structure.

		CEB		TEB		Propenoxid
		r_s	ab initio	r_s	ab initio	r_s
$r(C_r-C_m)$	(Å)	1.501	1.506	1.509	1.505	1.518
$r(C_r-C_r')$	(Å)	1.462	1.458	1.452	1.454	1.451
$r(C_r-O)$	(Å)	–	1.407	–	1.408	1.436/ 1.416
∢ $(C_r-C_r'-C_m)$	(Å)	124.5	125.4	122.3	123.0	121.6
∢ $(O-C_r-C_m)$	(Å)	–	117.4	–	117.9	116.2

observed to be slightly split according to the invariance group $C_3^{(1)} \otimes C_3^{(2)}$ [17]. Here the mean value was taken. The rotational constants of the CEB- and TEB ^{13}C-isotopomers are given in Table 11. They were calculated using the centrifugal distortion constants of the normal isotopomer.

Structure

For both molecules three sets of rotational constants were available. In Figs. 4 and 5 we give drawings of both molecules in their principal axes systems. So r_s coordinates and a partial r_s-structure could be calculated [23]. The results are given in Tables 12 and 13 together with calculations with Gaussian 88 using a 6-31G* basis set. From the experimental data a tilt angle of 1.3° for CEB and 0.4° for TEB resulted. Here the tilt angle is half of the difference of the angle between the internal rotation axes i, i': ∢ (i, i') and the angle of the axes between the bonds $C_r C_m$ and $C_r' C_m'$: ∢ $(C_r C_m, C_r' C_m')$. The planes defined by the sides of these angles do not coincide.

In Table 14 we compare structures obtained by different methods and the structure of the related propenoxide $H_2C\underbrace{\quad}_{O}CH-CH_3$ [24].

The determination of a more complete r_s-structure of the ring requires the measurement of the spectra of the ^{18}O-isotopomers.

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