July, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1749—1753 (1977) 1749

The Microwave Spectrum of 1-Propanethiol

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(Received March 1, 1977)

The microwave spectra of 1-propanethiol and its deuterated species ($CH_3CH_2CH_2SD$) were measured in the frequency region from 8.5 to 35 GHz. Several a-type R-branch transitions for the ground and excited vibrational states of the normal species and for the ground state of the deuterated species were identified, and the following rotational constants in MHz were obtained: $A=23429\pm653$, $B=2345.29\pm0.03$, and $C=2250.18\pm0.03$ for the ground state of the normal species; $A=24483\pm945$, $B=2346.30\pm0.04$, and $C=2253.91\pm0.04$ for the excited state of the normal species, and $A=21758\pm461$, $B=2306.71\pm0.03$, and $C=2217.79\pm0.03$ for the ground state of the deuterated species. The spectrum assigned to the ground vibrational states has been attributed to the T–G rotational isomer, and the excited vibrational state has been ascribed to the $-CH_2-CH_2-$ torsional motion.

The chemical thermodynamic properties and rotational isomerism of 1-propanethiol have been reported by Pennington *et al.*[1] In the gas phase, the potential energy of the *trans* form, a conformer with respect to the central C–C bond, is only about 400 cal mol^{-1} lower than that of the *gauche* form.[1] The vibrational assignment and rotational isomerism of 1-propanethiol have been reported by Hayashi *et al.*[2] Taking account of the additional rotational isomerism around the C–S bond, we would expect the five possible rotational isomers, T-T, T-G, G-T, G-G, and G-G′, shown in Fig. 1, where the first symbol refers to the isomerism around the central C–C bond, and the second, to the one around the C–S bond.[2] In the gaseous and liquid states, the T-T isomer, the more stable one, and the G-T isomer have been confirmed to exist.[2]

Microwave spectroscopic studies have shown that the *gauche* form is more stable than the *trans* form for 1-fluoropropane[3] and 1-chloropropane.[4] The 1-propanol molecule has been confirmed by microwave spectroscopy to exist in both *trans* and *gauche* forms.[5] The relative intensity measurement has shown that the *gauche* form is more stable than the *trans* form by 0.29± 0.15 kcal mol^{-1}.[5]

The relative intensity measurement of the microwave spectral lines of ethanethiol showed that the *gauche* isomer is more stable than the *trans* isomer by 142±15 cm^{-1} in their lowest vibrational states.[6]

We are interested in the rotational isomerism of 1-propanethiol, and so we examined the microwave spectra of the normal and deuterated ($CH_3CH_2CH_2SD$) species.

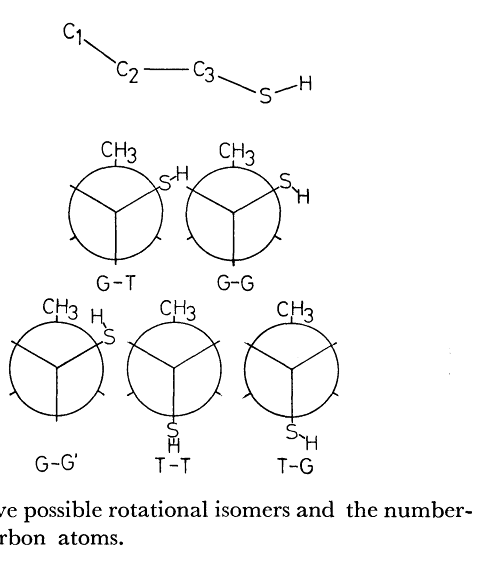

Fig. 1. Five possible rotational isomers and the numbering of carbon atoms.

Experimental

The sample of 1-propanethiol was obtained commercially (Tokyo Kasei Kogyo Co., Ltd.) and was purified by trap-to-trap distillation *in vacuo*. The deuterated species was prepared in the absorption cell by the following procedures. First, the cell was filled with D_2O vapor. It was then evacuated by means of a vacuum pump for about 20 min. At the end of this time, 1-propanethiol, purified beforehand, was admitted into the cell.

The spectrometer used was a conventional 100 kHz sinusoidal and square-wave Stark modulation type, with a phase-sensitive detector. The measurements of the transition frequencies were made with a Hewlett-Packard Model 5245 L frequency counter.

The rotational spectra were observed in the frequency region from 8.5 to 35 GHz at about −40 °C. The measurement of the relative intensity was made at about −40 °C and at room temperature. The sample was renewed about every 30 min.

Results and Discussion

Normal Species. It has been reported that 1-propanethiol exists in the T-T and G-T forms and that the T-T form is more stable than the G-T form in the gaseous and liquid states.[1,2] Consequently, the spectrum of the T-T rotational isomer was searched for at first. The moments of inertia calculated from the assumed structural parameters in Table 1 indicated that the T-T form was nearly prolate symmetric top with Ray's asymmetric parameter of −0.989. A large component of the dipole moment in this molecule was expected to lie close to the a axis. Consequently, strong a-type R-branch absorption lines were expected.

Many groups of relatively strong absorption lines were observed at intervals of about 4600 MHz. The strong

TABLE 1. STRUCTURAL PARAMETERS ASSUMED FOR 1-PROPANETHIOL

r(C–C)	1.534 Å	∠CCS	111.0°
r(C–S)	1.819	∠CSH	96.5°
r(S–H)	1.336	$\angle C_2C_1H$	110.1°
r(C–H)	1.094	$\angle C_2C_3H$	109.6°
∠CCC	110.5°	∠HCH	108.8°

TABLE 2. OBSERVED FREQUENCIES OF 1-PROPANETHIOL

Transition	Normal species				D species	
	Ground state		Excited state		Ground state	
	Obsd	$\Delta\nu^{a)}$	Obsd	$\Delta\nu^{a)}$	Obsd	$\Delta\nu^{a)}$
2_{02}-1_{01}	9191.36	0.08	9200.31	0.17	9048.81	0.10
2_{11}-1_{10}	9286.88	−0.07	9292.76	−0.06		
2_{12}-1_{11}	9096.26	0.13	9108.14	0.10	8960.02	−0.07
3_{03}-2_{02}	13786.41	0.39	13799.05	−0.44	13572.58	0.28
3_{12}-2_{11}	13930.31	0.08	13939.16	0.11	13706.65	−0.06
3_{13}-2_{12}	13644.39	0.39	13662.10	0.22	13440.20	0.25
3_{21}-2_{20}	13789.57	0.96	13801.64	−0.16		
3_{22}-2_{21}	13787.77	0.46	13799.95	−0.70		
4_{04}-3_{03}	18379.98	0.11	18398.26	0.28	18095.03	0.05
4_{13}-3_{12}	18573.19	−0.07	18584.58	−0.49	18275.27	0.03
4_{14}-3_{13}	18191.78	0.16	18215.70	0.20	17919.69	0.11
4_{22}-3_{21}	18385.97	−0.10	18403.49	−0.03		
4_{23}-3_{22}	18383.10	0.26	18401.12	0.48		
4_{31}-3_{30}	18383.79	0.06	18401.93	0.49		
4_{32}-3_{31}						
5_{05}-4_{04}	22972.57	0.17	22995.28	−0.03	22616.49	0.04
5_{14}-4_{13}	23215.84	−0.12	23230.95	0.16	22843.44	−0.05
5_{15}-4_{14}	22738.79	−0.14	22768.94	0.10	22398.93	0.02
5_{23}-4_{22}	22984.45	−0.15	23006.66	0.41		
5_{24}-4_{23}	22978.46	0.32	23001.52	1.08		
5_{32}-4_{31}	22979.66	−0.32	23003.22	1.14		
5_{33}-4_{32}		−0.30		1.16		
5_{41}-4_{40}		0.08		1.50		
5_{42}-4_{41}						
6_{06}-5_{05}	27563.42	0.08	27590.92	−0.28	27136.40	0.00
6_{15}-5_{14}	27858.24	−0.03	27876.14	−0.01	27411.48	0.13
6_{16}-5_{15}	27285.81	−0.04	27321.77	−0.05	26877.66	−0.20
6_{24}-5_{23}	27584.18	−0.30	27610.57	0.48		
6_{25}-5_{24}	27573.22	0.04	27600.17	0.18		
6_{33}-5_{32}	27576.04	−0.39	27603.14	0.24		
6_{34}-5_{33}		−0.35		0.28		
6_{42}-5_{41}		0.31	27602.51	0.24		
6_{43}-5_{42}						
6_{51}-5_{50}		0.60	27602.25	0.24		
6_{52}-5_{51}				0.23		
7_{07}-6_{06}	32152.28	−0.04	32185.52	0.16	31654.55	0.03
7_{16}-6_{15}	32499.99	−0.07	32521.24	0.18	31978.55	−0.18
7_{17}-6_{16}	31831.90	−0.37	31874.15	−0.23	31356.26	−0.11
7_{25}-6_{24}	32185.52	−0.45	32216.35	0.93		
7_{26}-6_{25}	32167.83	−0.06	32199.58	0.32		
7_{34}-6_{33}	32172.90	−0.23	32203.67	−0.27		
7_{35}-6_{34}		−0.14		−0.20		
7_{43}-6_{42}	32171.89	−0.12		−0.62		
7_{44}-6_{43}						
7_{52}-6_{51}		0.34		1.14		
7_{53}-6_{52}						
7_{61}-6_{60}		0.58		1.35		
7_{62}-6_{61}						

Only the frequencies of the transitions with $K_{-1}=1,0$ were fitted to the rigid rotor Hamiltonian. a) Obsd−Calcd. The calculated frequencies were obtained using the constants in Table 3.

Table 3. Rotational constants of 1-propanethiol (MHz)

	Normal species		D species
	Ground state	Excited state	Ground state
A	23429 (649)	24483 (934)	21758 (461)
B	2345.591 (35)	2346.314 (43)	2306.713 (25)
C	2250.181 (35)	2253.911 (42)	2217.793 (25)
Δ (amu Å^2)[a]	12.43 (61)	11.81 (79)	14.44 (49)

Values in parentheses denote the standard deviations and apply to the last significant digits. a) $I_a+I_b-I_c$.

lines in a group were preliminarily assigned to the T-T isomer in the ground vibrational state and fitted to the rigid rotor Hamiltonian by the least-squares method. These assigned absorption lines are accompanied by the several satellite lines. It seems reasonable to ascribe some of these satellite lines to the excited vibrational states. One set of the absorption lines, picked up from the bushes of the satellite lines, could be fitted to the rigid rotor Hamiltonian by the least-squares method and assigned to the first excited vibrational state. The observation of the temperature dependence of the lines led to the confirmation of the assignments of the sets of lines to the ground and excited vibrational states. The other sets of satellite lines were partly observed. The observed and calculated frequencies of the transition lines, assigned to the ground and excited states, are given in Table 2 and are in good agreement. The rotational constants obtained by the least-squares fit are given in Table 3.

The $\Delta(=I_a+I_b-I_c)$ value of 12.4 amu Å^2 calculated from the rotational constants for the ground states is very different from that of 9.569 amu Å^2 predicted from the T-T model. This indicates that the molecular structure in question deviates from the T-T form which has a plane of symmetry.

Table 4 shows a comparison of the observed rotational constants, Ray's asymmetry parameters, and the values of $\Delta(I_a+I_b-I_c)$ with those calculated from the assumed structural parameters for the five possible rotational isomers. A comparison of the observed constants with the calculated ones in Table 4 reveals that the observed spectrum assigned to the ground vibrational state can reasonably be attributed to the T-G rotational isomer. Although the existence of the T-T and G-T forms has been confirmed in the gaseous and liquid states,[2] that of the T-G rotational isomer has not yet been reported. The exsitence of the T-G isomer of 1-propanethiol in the gas phase is consistent with the following facts: the *trans* form of 1-propanethiol around the central C–C bond is more stable than the *gauche* form in the gas phase[1,2] and the *gauche* isomer of ethanethiol with respect to the C–S bond is more stable than the *trans* isomer in the gaseous state.[6]

There are two possible equivalent configurations in the T-G form which can interchange with each other through thiol internal motion. The spectrum of the T-G form, therefore, can be expected to be split into doublets due to the tunneling effect of the thiol internal rotation, as is observed in the spectrum of ethanethiol.[6] Therefore, the counterpart lines of the doublets were searched for in the vicinity of the lines assigned to the rigid T-G rotor, but there was no absorption line to be assigned as a counterpart line. Consequently, the analysis of the spectrum was done assuming the rigid T-G form.

Deuterated Species. The transitions of the deuterated species were predicted from the assumed T-G model with the same structural parameters as for the normal species. The observed transition lines in Table 2 were identified by measurements of their Stark effects and fitted to the rigid rotor Hamiltonian in order to obtain the rotational constants in Table 3. Table 2 indicates that the observed and calculated transition frequencies are in good agreement. Table 4 shows that the observed Δ value of 14.44 amu Å^2 is in good agreement with the value of 14.016 amu Å^2 calculated from the T-G model.

Conformation of 1-Propanethiol. The r_s coordinates of the thiol hydrogen atom were calculated from the observed rotational constants of the normal and deuterated species in Table 3, using the expressions given by Kraitchman.[7] Table 5 shows that the r_s coordinates obtained from the observed rotational constants are in good agreement with the coordinates calculated from the T-G model. This is consistent with the result ob-

Table 4. Observed and calculated rotational constants (MHz) of 1-propanethiol

	A	B	C	κ	Δ[a] (amu Å^2)
Model			Normal species		
G-T	11222	3448.28	2915.87	−0.87180	18.273
G-G′	10869	3500.00	2980.33	−0.86826	21.316
G-G	10867	3571.76	2971.11	−0.84748	17.983
T-T	24153	2374.03	2253.81	−0.98902	9.569
T-G	23341	2393.03	2288.57	−0.99008	12.012
Obsd (Ground state)	23429	2345.59	2250.18	−0.99099	12.43
			D species		
T-T	23004	2316.74	2316.74	−0.99393	9.570
T-G	21580	2354.90	2256.05	−0.98977	14.016
Obsd (Ground state)	21758	2306.71	2217.79	−0.99089	14.44

The calculations of the rotational constants for the models were based upon the assumption that the *gauche* form has the dihedral angle of 120°. a) $I_a+I_b-I_c$.

TABLE 5. r_s COORDINATES OF THE THIOL HYDROGEN ATOM (Å)

Coordinate	Obsd	Calcd T-G	Calcd T-T
a	1.585 (85)	1.553	2.296
b	0.83 (15)	0.836	1.040
c	1.11 (13)	1.050	0

Values in parentheses denote the uncertainties estimated from the standard deviations of the rotational constants.

tained above from Table 4.

Dipole Moment. The dipole moments of the molecules were determined from the measurements of the Stark effect of the absorption lines for the ground and excited vibrational states of the normal species and for the ground state of the deuterated species. The observed Stark coefficients are listed in the third, sixth, and eighth columns in Table 6 for the ground and excited vibrational states of the normal species, and for the ground state of the deuterated species, respectively. The electric field inside the absorption cell was calibrated by observing the Stark shifts of the transitions, $1\leftarrow 0$ and $2\leftarrow 1$, of OCS, whose dipole moment is 0.71521 D.[8)]

In the T-T form, the component of μ_c along the *c* principal axis should be zero due to the plane of symmetry. The T-G rotational isomer, however, has no electronic plane of symmetry, and it is expected that all three components of μ will be nonzero. Schmidt and Quade[6)] have reported that, in the *gauche* isomer of ethanethiol, the inclusion of the tunneling energy in the denominator of the Stark coefficient of μ_c^2 gave the correct variation of $\Delta\nu/E^2$ for the doublet split due to the tunneling motion of the thiol hydrogen in the normal spectrum. We proceeded, however, to analyze the observed Stark coefficients without taking account of the tunneling motion of the thiol hydrogen atom, because we could not observe the doublet lines split due to the tunneling effect described above.

The least-squares fit to obtain μ_a and μ_b, assuming $\mu_c=0$, for the ground state gave the results presented in the fourth column (Calcd I) of Table 6. The calculated Stark coefficients for the M=0 components of the transitions, $3_{12}\leftarrow 2_{11}$, $4_{04}\leftarrow 3_{03}$, and $4_{13}\leftarrow 3_{12}$, are very different from the observed ones. These deviations may be attributed to the assumption of the μ_c component being zero, since the μ_c component of the dipole moment in this molecule, if there is one, should give rise to a large effect on the Stark coefficients of these transitions. This fact indicates that the molecule in question is not in the T-T form. This result is consistent with the one deduced from the observed and calculated rotational constants.

Since the T-G isomer was likely to exist in the gaseous state, as has been described above, the observed Stark coefficients were fitted to obtain all three components of the dipole moment by the following procedures. First, since the μ_b and μ_c components have a smaller

TABLE 6. STARK COEFFICIENTS ($\Delta\nu/E^2$[MHz/(V/cm)^2]$\times 10^{-5}$) AND DIPOLE MOMENTS OF 1-PROPANETHIOL

Transition	|M|	Normal species, Ground state, Obsd	Normal species, Ground state, Calcd I	Normal species, Ground state, Calcd II	Normal species, Excited state, Obsd	Normal species, Excited state, Calcd	D species, Ground state, Obsd	D species, Ground state, Calcd
2_{02}-1_{01}	0	−2.19	−2.05	−1.99	−2.05	−2.06		
	1	2.04	1.67	1.64	2.07	1.68		
2_{12}-1_{11}	0	1.89	1.68	1.61	1.83	1.68		
2_{11}-1_{10}	0	1.46	1.65	1.56	1.41	1.64		
3_{03}-2_{02}	0	−0.40	−0.35	−0.39	−0.42	−0.36	−0.40	−0.38
	1	−0.14	−0.10	−0.13	−0.11	−0.11	−0.13	−0.13
	2	0.63	0.64	0.62	0.50	0.65	0.63	0.63
3_{13}-2_{12}	0	−0.10	−0.07	−0.08	−0.10	−0.09	−0.10	−0.10
	1	5.02	5.33	5.02	5.15	5.47	5.75	5.49
	2	19.9	21.5	20.3	20.1	22.2	23.1	22.2
3_{12}-2_{11}	0	0.18	−0.10	0.12			0.19	0.19
	1	−5.27	−5.18	−4.69	−4.38	−5.30	−5.20	−5.10
	2	−19.1	−20.4	−19.1			−19.9	−21.0
4_{04}-3_{03}	0	−0.39	−0.15	−0.35	−0.19	−0.19		
	2	−0.14	0.05	−0.10				
	3				0.34	0.29		
4_{14}-3_{13}	0	−0.12	−0.16	−0.10				
	1	0.52	0.47	0.48				
	2	2.23	2.36	2.24				
4_{13}-3_{12}	0	−1.37	−0.08	−1.68				
μ_a(D)			1.56	1.52±0.01		1.56±0.01		1.53±0.03
μ_b(D)			0.2	0.12±0.08		0.15±0.10		0 ±0.2
μ_c(D)			0(Assumed)	0.73±0.08		0.4 ±0.3		0.53±0.40
μ_{total}(D)			1.57	1.69±0.05		1.62±0.20		1.62±0.30

effect on the Stark coefficients for the a-type R-branch transitions than the μ_a component, the observed Stark coefficients of the $M=0$ components of the transitions, $3_{03} \leftarrow 2_{02}$, $3_{12} \leftarrow 2_{11}$, $3_{13} \leftarrow 2_{12}$, and $4_{14} \leftarrow 3_{13}$, all sensitive to the μ_b and μ_c components, were fitted to obtain all three components, μ_a, μ_b, and μ_c respectively. The values of μ_b and μ_c obtained are shown in the fifth column (Calcd II) of Table 6. Next, the values of μ_b and μ_c obtained above were kept fixed, and all the observed Stark coefficients were fitted to obtain the μ_a component. The results are listed in the fifth column of Table 6. The observed and calculated Stark coefficients are in good agreement, as a whole.

The observed Stark coefficients for the excited vibrational state of the normal species and for the ground state of the deuterated species were fitted to obtain all three components, μ_a, μ_b, and μ_c, by the same procedure as was used for the ground state of the normal species. The results are given in the seventh and last columns of Table 6 respectively.

The value of the total dipole moment of 1-propanethiol in the gas phase obtained in this work, 1.69 D, is considerably larger than the value of 1.33 D determined in a benzene solution.[9] This difference may be compared with that reported for ethanethiol; the dipole moments determined by microwave spectroscopic investigation, were 1.58 and 1.61 D in the gas phase for the *trans* form and for the *gauche* form respectively,[6] and 1.39 D in a benzene solution.[10]

The values of μ_a, μ_b, and μ_c for the T-G isomer of 1-propanethiol determined in this work can be compared with the values of μ_a (1.49 D), μ_b (0.19 D), and μ_c (0.59 D) for the *gauche* isomer of ethanethiol in the gas phase.[6]

Excited Vibrational State. Our measurements of the intensities of the transition lines, $J=2 \leftarrow 1$, $3 \leftarrow 2$, and $4 \leftarrow 3$, in the excited state relative to the lines in the ground state yielded the vibrational frequency of 136 ± 35 cm^{-1}. This value is very close to the $-CH_2-CH_2-$ torsional frequency of 130 cm^{-1} calculated using the Urey-Bradley force field.[2] Therefore, the assigned vibrational satellite can reasonably be ascribed to the excited state of the $-CH_2-CH_2-$ torsional mode.

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