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DOUBLE MINIMUM SPLITTING IN gauche 1-PROPANETHIOL BY MICROWAVE SPECTRUM

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Torsional splitting of the thiol group in gauche 1-propanethiol was directly observed by microwave spectroscopy. From the splitting, the Fourier component of the internal rotation potential function was determined to be V_3=1302 cal/mol on the assumption that V_1 and V_2 were equal to those of ethanethiol. The dipole moments were also determined.

The direct observation of the torsional splitting in a molecule containing an asymmetric internal rotor such as the SH group is an interesting subject in the microwave investigations. As an extention of the previous work on the analysis of gauche ethanethiol,$^{1)}$ we studied the microwave spectrum of gauche 1-propanethiol and its deuterated compound. Though Ohashi et al.$^{2)}$ have partially assigned a-type transitions whose frequencies can be fitted by an ordinary rigid rotor expression, they have not given any comment on the assignment of c-type transitions and the splittings in some of the a-type transitions.

Microwave spectra of a- and c-types were measured for the normal and SD species. As is well known, the tunneling effect between two gauche minima in the thiol internal rotation potential produces two different energy states which are hereafter referred to as (+) and (-) states.

For the normal species, the c-type transitions exhibited doublet structures of about 3200 MHz, while the a-type transitions except k_a=1 showed no splittings within the resolution limit of our spectrometer (∿0.3 MHz). Some of the a-types with k_a=1 showed doublet structures whose spacings depended on the J-quantum number, i.e., the transitions with $J \leq 4$ had no splittings, while those of J=5-4, 6-5, and 7-6 exhibited splittings of 2 MHz, 4 MHz, and 0.5 MHz, respectively. These splittings are due to the accidental degeneracy between the (+) and (-) states, which are connected by the off-diagonal matrix elements of the thiol internal rotation.$^{1)}$

Table I. Obtained Spectroscopic Constants (in MHz)$^{a)}$

	A	B	C	$\Delta\nu^{b)}$	$D_J\times10^3$	$D_{JK}\times10^3$	D	$E^{c)}$
normal	23907.47(9)	2345.597(6)	2250.338(9)	1613.01(4)	0.22(8)	-5.7(15)	1.32(2)	58
SD	22082.94(10)	2306.716(7)	2217.804(11)	58.30(5)	0.21(10)	-6.8(19)	-	-

a) Figures in the parentheses indicate 99 % reliability intervals attached to the last significant figures.

b) The energy difference between (+) and (-) states.

c) Fixed value so as to obtain the smallest standard deviation.

For the SD species, the c-type transitions exhibited doublet structures of 116 MHz, whereas the a-types showed no splittings at all.

The procedure for the analysis of the observed spectra was essentially the same as described previously.[1] The rotational constants of the (+) and (-) states were assumed to be equal, since there was no splitting observed in the a-type transitions except those concerned with accidentally degenerate levels. Although the effective off-diagonal Hamiltonian between (+) and (-) states consists of the following four terms,

$$\langle +|H|-\rangle = D(P_xP_y + P_yP_x) + E(P_xP_z + P_zP_x) + NP_y + QP_z, \qquad (1)$$

we were not able to determine these four parameters independently. D and E are highly correlated with Q and N, respectively. Thus, N and Q were neglected and D was adjusted as a parameter. Since the simultaneous adjustment of E caused the divergence in the least squares fit, E was fixed to the value so as to obtain the minimum standard deviation, which was 4.4 times smaller than that for E=0. The constants obtained are tabulated in Table I. For the SD species, the parameters in Eq. (1) were not able to be determined, because of the lack of an accidental degeneracy.

As there were not sufficient data to determine the r_s structure of this isomer, a plausible structure was estimated from the r_s structures of gauche ethanethiol[1] and propane.[3] The bond lengths and angles in the skeletal part are; $r(CH_3\text{-}C)=1.533$ Å, $r(CH_2\text{-}CH_2)=1.528$ Å, $r(C\text{-}S)=1.814$ Å, $r(S\text{-}H)=1.336$ Å, $\alpha(C\text{-}C\text{-}C)=112°0'$, $\alpha(C\text{-}C\text{-}S)=113°37'$, $\alpha(C\text{-}S\text{-}H)=96°0'$, and $\tau(C\text{-}C\text{-}S\text{-}H)=61°45'$. The rotational constants calculated from this structure were in an excellent agreement with the observed ones. The maximum difference between the observed and calculated ones was 0.25 %.

The thiol internal rotation potential function was determined from the observed (+)-(-) energy differences of the normal and SD species. Since the V_3 term in the Fourier components of the potential function plays the predominant role for these splittings, V_1 and V_2 values were fixed to those of ethanethiol. The kinetic part was calculated from the plausible structure mentioned above. The result was; $V_3=1302 \pm 10$ cal/mol, $V_1=-207$ cal/mol, and $V_2=-386$ cal/mol. In comparison with $V_3=1305$ cal/mol for ethanethiol, this result shows that the thiol internal rotation potential function has a good transferability between ethanethiol and 1-propanethiol.

The dipole moments and their components listed in Table II were obtained by the Stark effect measurements of several low J transitions. The Stark coefficients were calculated from the observed energy levels and the rigid rotational transition probabilities. The previous calculation in Ref. (2) was based on the rotational constants obtained without any consideration of the tortional splitting. This makes fairly large discrepancy for μ_c component.

Table II. Dipole Moments and Their Components (Debye)

	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\langle\mp\lvert\mu_c\rvert\pm\rangle\rvert$	$\lvert\mu_{total}\rvert$
normal	1.575 ± 0.007	0.115 ± 0.082	0.580 ± 0.009	1.683 ± 0.010
SD	1.577 ± 0.011	0.067 ± 0.040	0.594 ± 0.013	1.677 ± 0.011

references

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