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MICROWAVE SPECTRA OF THE TRANS-TRANS ISOMER OF METHYLPROPYLETHER

Michiro HAYASHI, Misako IMACHI, Jun NAKAGAWA, and Akane OZAKI
Department of Chemistry, Faculty of Science, Hiroshima University
Higashi-sendamachi, Hiroshima 730

Microwave spectra of the trans-trans isomer of methylpropylether and its four deuterated species were measured. A plausible structure was estimated from the observed rotational constants. The dipole moment was determined to be 1.107 ± 0.005 D by Stark effect measurements. From the observed splittings of the spectra in the excited torsional state, the barrier to internal rotation of the CH_3C group was obtained as 3280 ± 60 cal/mol.

Recently we studied the microwave spectra of methylpropylether and its four deuterated species ($CD_3OCH_2CH_2CH_3$, $CH_3OCD_2CH_2CH_3$, $CH_3OCH_2CD_2CH_3$, and $CH_3OCH_2CH_2CD_3$) in order to compare the molecular structure, dipole moment and barrier to internal rotation with the results for the other ethers such as dimethylether,[1] ethylmethylether,[2] and diethylether.[3]

For methylpropylether, though five different rotational isomers were expected, we assigned about twenty of the b-type transitions belonging to the trans-trans isomer. For each species, all the observed frequencies were used in a least squares fit of the four parameters in a modified rigid rotor expression which included the $D_J[J(J+1)]^2$ term of the centrifugal distortion formula. They are given in Table 1.

As the r_s structure cannot be solved from the present data, a plausible structure was estimated from the observed rotational constants. The rotational constants of five isotopic species were calculated from a model which had a set of the structural parameters transferred from those of ethylmethylether and propane.[4] The deviations of the calculated rotational constants were more than 1.3 % from the observed. In order to reduce the deviations, seven skeletal structural parameters were adjusted. The deviations have been reduced to less than 0.15 %, as shown in Table 1, and the skeletal structural parameters are shown in the footnote of Table 1. This adjusted model is proposed as a plausible structure.

The dipole moments were determined by Stark effect measurements of six low J transitions for the normal and $CD_3OCH_2CH_2CH_3$ species. They are given in Table 1. The magnitude of the dipole moment of methylpropylether is smaller than that of trans-ethylmethylether (1.174 D) but larger than that of the trans-trans isomer of diethylether (1.061 D).

For the normal species, two sets of weak Q-branch spectra were assigned. One of them exhibited doublet structures and hence was attributed to the set of spectra due to the first excited methyl torsional state. The quantities of $Y = A - (B + C)/2$

Table 1. Rotational Constants (MHz) and Dipole Moment (D)[a)]

Species	A	$\delta A^{b)}$	B	$\delta B^{b)}$	C	$\delta C^{b)}$	$D_J \times 10^3$
$CH_3OCH_2CH_2CH_3$	19755.36(14)	0.10	2125.45(1)	0.00	2017.60(1)	0.08	0.35(10)
$CD_3OCH_2CH_2CH_3$	17418.82(24)	0.07	1939.01(2)	-0.02	1847.38(2)	0.05	0.29(18)
$CH_3OCD_2CH_2CH_3$	17324.33(19)	-0.06	2111.88(1)	0.03	2002.22(2)	0.09	0.31(14)
$CH_3OCH_2CD_2CH_3$	16953.13(14)	0.13	2087.56(1)	0.03	1974.80(1)	0.11	0.24(11)
$CH_3OCH_2CH_2CD_3$	17431.38(15)	0.11	1921.60(1)	0.00	1831.33(1)	0.07	0.30(12)

Species	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	$\lvert\mu_{total}\rvert$	$\alpha(\mu \times a)^{c)}$	$\alpha(\mu \times bisect)^{d)}$
$CH_3OCH_2CH_2CH_3$	0.082(4)	1.104(5)	0	1.107(5)	85°43'	2°30'
$CD_3OCH_2CH_2CH_3$	0.052(3)	1.112(6)	0	1.113(6)	87°19'	1°45'

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviations.

b) $\delta R = 100 \times (R_{obsd} - R_{calctd})/R_{obsd}$, R = A, B, and C. R_{calctd} was calculated from the skeletal structural parameter values of $r(CH_3\text{-}C)=1.536$, $r(CH_2\text{-}CH_2)=1.529$, $r(CH_2\text{-}O)=1.408$, $r(CH_3O)=1.415$ Å, $\alpha(CCC)=112°9'$, $\alpha(CCO)=108°47'$, and $\alpha(COC)=110°39'$ and the other parameter values transferred from those of trans-ethylmethylether and propane.

c) The angle between the dipole moment and the a-inertial axis.

d) The angle between the dipole moment and the bisector of the COC angle in the proposed structure. The dipole moment exists along a line inclining towards the $CH_2\text{-}O$ bond.

and $Z = (B - C)/2$ for this set of spectra were 17569.60(29) and 52.08(1) MHz, respectively. From the observed splittings of the spectra, the barrier to methyl internal rotation was calculated to be 3280 ± 60 cal/mol in the one top approximation where the coupling terms of the two methyl groups were entirely neglected. The following parameters obtained from the proposed structure were used in the calculation by the standard principal axis method:[5)] $I_\alpha = 3.1441$ amu·Å^2, $\lambda_a = 0.8402$, $\lambda_b = 0.5422$, $\lambda_c = 0$. From the barrier height, this set of the spectra was regarded as that due to the first excited methyl torsional state of the CH_3C group.

The spectra belonging to the other set were singlets and may be due to the first excited skeletal torsional state. The quantities of Y and Z for this set were 18048.13(79) and 54.83(6) MHz, respectively. Search of the spectra due to the excited CH_3O torsional state was attempted but we could not find them at present.

We are working on the other isotopic species of the trans-trans isomer in order to get more reliable structural parameters and on the excited vibrational states in order to find the barrier to internal rotation of the CH_3O group.

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