The Microwave Spectrum, the r_s Structure and the Dipole Moment of the *TT* Isomer of Diethyl Ether

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The microwave spectra of six isotopic species of diethyl ether were measured in relation to the molecular form and dipole moment. Transitions of the *TT*(*trans-trans*) isomer could be assigned and the r_s structure of this isomer was obtained by the substitution method. The structural parameters of the *TT* isomer of diethyl ether are; r(CO) 1.408 Å, r(CC) 1.516 Å; α(COC) 112°25′, α(OCC) 108°37′ for the skeleton; r(CH) 1.093 Å, α(CCH) 110°11′, α(OCH) 110°10′, α(HCH) 107°29′ for the CH_2 group and r(CH) 1.090 Å, $\alpha(CCH_s)$ 110°35′, $\alpha(CCH_a)$ 110°15′, $\alpha(H_sCH_a)$ 108°48′, $\alpha(H_aCH_a)$ 108°4′ for the CH_3 group. The dipole moment was determined to be 1.061 ± 0.018 D from the Stark effect measurement for the *TT* isomer. A discussion was made on the structure and the dipole moment of the *TT* isomer of diethyl ether in comparison with those of the similar molecules.

Infrared and Raman spectra of diethyl ether were extensively studied by several authors.[1] They reported that at least two rotational isomers existed in the gaseous and liquid states, one of which was presumably in th *trans-trans* form (the *TT* form).

We measured the microwave spectra of diethyl ether in order to confirm the molecular forms of the isomers. As was already reported in a previous note,[2] the microwave spectra of the *TT* isomer of the normal species of diethyl ether were easily assigned, though the spectra were not so strong and their Stark patterns were not clearly resolved. The measurements were extended to its five isotopic species and the r_s structure of the *TT* isomer could be determined by the substitution method.

The dipole moment of this isomer was determined by the Stark effect measurements of the spectra.

We found very many weak spectra all over the frequency region, which may belong to other isomers. However, they are so complicated that the analysis was abandoned for them.

In the present paper, the r_s structure and the dipole moment of the *TT* isomer of diethyl ether will be given and discussed in comparison with those of the similar molecules such as dimethyl ether and ethyl halides.

Experimental

A commercial product was used for the normal species of diethyl ether. One of the deuterated species ($CH_3CHDOEt$) was prepared by the reaction of a mixture of acetaldehyde and ethanol with hydrogen chloride followed by the reduction of the resultant $CH_3CHClOEt$ with $LiAlD_4$ in *n*-butyl ether.[3] The other deuterated species (CH_2DCH_2OEt) was prepared by the Williamson method, *i.e.*, by treating sodium ethoxide with CH_2DCH_2Br which was prepared by the reaction of ethylene and DBr with $AlBr_3$ as a catalyst.[4] The ^{13}C species were prepared by the Williamson method using $^{13}CH_3CH_2I$ and $CH_3{}^{13}CH_2I$ (90 atom% ^{13}C, Merck Sharp & Dohme, Canada), respectively.

The microwave spectra were measured in the region from 8500 to 34000 MHz with conventional sinusoidal- and square-wave Stark modulation spectrometers at the temperature of dry ice.

The r_s Structure

The *b*-type transition are expected for the *TT* isomer of diethyl ether. The observed transition frequencies with $J\leqq10$ are shown in Table 1.

The rotational constants were determined by the least-squares technique from all the observed frequencies in the table so as to fit in with a modified rigid rotor expression which was including only the $D_J(J(J+1))^2$ term of the centrifugal distortion contributions. The rotational constants and the moments of inertia are in Table 2. The quantities $P_c(=(I_a+I_b-I_c)/2)$ and and $\Delta P_c(=P_c(\text{isotopic})-P_c(\text{parent}))$ in the table are quite reasonable when comparing with the reported values of other molecules.[5]

Since the moments of inertia in the ground state are available for the normal and each of its singly substituted isotopic species, it is possible to calculate the coordinates of each atom directly from Kraitchman's equations[6] except the x_b coordinate of the oxygen atom which can be solved by the use of the first moment equation. However, the x_b coordinate of the in-plane hydrogen (H_s) is small so that zero-point energy contributions of the vibrations to $\Delta I_a(=I_a(\text{isotopic})-I_a(\text{parent}))$ reduce the reliability of the calculated value from Kraitchman's equation for the x_b coordinate. On the other hand, all the coordinates for the out-of-plane hydrogen (H_a) and the x_a coordinate for the H_s atom are large and Karitchman's equations reliably fix their values. Thus one assumption is required to completely determine the structure of the *TT* isomer from the present data. We chose to assume the CH_a and CH_s bond distances to be equal.

Table 3 lists the coordinates of each atom of the *TT* isomer of diethyl ether. The moments of inertia as calculated from the coordinates are compared with the experimental moments of inertia as shown in Table 2. The deviations $\delta I_g(=I_g(\text{obsd})-I_g(\text{calcd}))$ are sizable and always positive, but this is to be expected for the r_s structure.

The structural parameters as derived from the coordinates are shown in Table 3. The assumption imposed on the CH bond distances of the methyl group has little influence on the structural parameters except $r(CH_s)$ and $\alpha(H_sCC)$. That is, the x_b coordinate of the H_s atom calculated directly from Kraitchman's equation is 0.2020 ± 0.0053 Å which gives the value of -0.2576 ± 0.0023 Å for the x_b coordinate of the oxygen atom. These values give the parameters of 1.409 ± 0.003 Å, 112°13′±16′, 108°31′±10′, 110°13′±20′ and 109°20′±30′ for r(CO), α(COC), α(OCC),

Table 1. Observed frequencies[a] for the *TT* isomer of diethyl ether (MHz)

Transition	$(CH_3CH_2)_2O$	$CH_3CHDOEt$	*s*-CH_2DCH_2OEt[b]	*a*-CH_2DCH_2OEt[b]	$^{13}CH_3CH_2OEt$	$CH_3{}^{13}CH_2OEt$
$1_{10} \leftarrow 1_{01}$	15854.38(0.00)	14607.30(0.01)	15920.33(−0.04)	14835.95(−0.14)	15806.98(−0.12)	15695.17(0.00)
$2_{11} \leftarrow 2_{02}$	15997.67(−0.09)	14754.45(0.01)	16051.41(0.06)	14974.92(−0.38)	15945.01(−0.10)	15839.27(−0.03)
$3_{12} \leftarrow 3_{03}$	16214.55(−0.08)	14976.75(−0.48)	16249.21(−0.10)	15186.02(0.10)	16153.72(−0.07)	16057.43(0.09)
$4_{13} \leftarrow 4_{04}$	16507.16(0.00)	15278.10(−0.01)	16516.13(0.07)	15470.17(0.02)	16435.21(0.05)	16351.54(0.05)
$5_{14} \leftarrow 5_{05}$	16878.22(0.02)	15660.35(−0.00)	16853.90(−0.07)	15830.77(−0.08)	16791.97(0.09)	16724.68(0.01)
$6_{15} \leftarrow 6_{06}$	17331.21(−0.10)	16128.08(0.08)	17266.02(0.01)	16271.66(0.07)	17227.27(0.02)	17180.50(−0.01)
$7_{16} \leftarrow 7_{07}$	17870.70(0.02)	16685.85(0.03)	17755.61(−0.08)	16796.68(0.07)	17745.09(−0.09)	17723.26(−0.02)
$8_{17} \leftarrow 8_{08}$	18501.18(0.05)	17339.28(0.00)	18327.16(0.13)	17410.73(0.00)	18350.17(0.01)	18357.87(−0.03)
$9_{18} \leftarrow 9_{09}$	19228.15(0.11)	18094.42(0.03)	18984.71(0.16)	18119.31(−0.03)	—[c]	19089.85(0.07)
$10_{19} \leftarrow 10_{010}$	20057.13(−0.08)	18957.72(0.05)	19733.05(−0.12)	18928.29(0.04)	19841.74(0.00)	19924.96(−0.04)
$1_{11} \leftarrow 0_{00}$	—[c]	18761.60(0.00)	19942.70(−0.26)	—[c]	19913.20(0.32)	19870.49(0.13)
$2_{12} \leftarrow 1_{01}$	24261.37(−0.09)	22915.80(−0.09)	23965.40(−0.15)	23017.06(−0.05)	24018.80(0.15)	24045.58(0.05)
$3_{13} \leftarrow 2_{02}$	28394.31(0.17)	26997.64(0.08)	27923.55(0.22)	27039.03(0.20)	28056.05(−0.13)	28149.45(−0.04)
$4_{14} \leftarrow 3_{03}$	32457.18(−0.01)	31008.02(0.04)	31817.42(0.10)	30993.05(0.05)	32026.50(−0.09)	32183.32(−0.13)
$5_{15} \leftarrow 4_{04}$		34949.48(0.12)				
$6_{06} \leftarrow 5_{15}$	11299.54(−0.30)	12293.53(−0.05)		11580.72(−0.09)	10690.37(0.06)	11297.72(0.00)
$7_{07} \leftarrow 6_{16}$	16027.00(0.27)	16979.00(−0.12)	14491.73(0.21)	16177.47(−0.03)	15301.35(0.01)	15998.12(−0.01)
$8_{08} \leftarrow 7_{17}$	20802.82(−0.02)	21712.56(−0.03)	19042.47(−0.47)	20821.05(−0.07)	19960.39(−0.05)	20747.73(0.10)
$9_{09} \leftarrow 8_{18}$	25622.27(−0.01)	26487.32(0.03)	23636.31(0.13)	25505.78(0.03)	24662.06(−0.04)	25540.24(0.03)
$10_{010} \leftarrow 9_{19}$	30478.54(−0.02)	31295.96(0.03)	28265.85(0.06)	30224.93(0.04)	29400.31(0.04)	30369.21(−0.06)

a) Figures in parentheses indicate the differences of the observed and calculated frequencies. $\delta\nu = \nu(\text{obsd}) - \nu(\text{calcd})$. b) "*s*-" and "*a*-" refer to the symmetric and asymmetric forms, respectively, with respect to the molecular plane. c) Overlapped with the other transition.

Table 2. Observed rotational constants (MHz) and moments of inertia (amu·Å^2)[a]

	$(CH_3CH_2)_2O$	$CH_3CHDOEt$	*s*-CH_2DCH_2OEt	*a*-CH_2DCH_2OEt	$^{13}CH_3CH_2OEt$	$CH_3{}^{13}CH_2OEt$
A	17956.15 (29)	16684.45 (30)	17931.67 (43)	16881.35 (30)	17859.99 (27)	17782.77 (15)
B	2244.19 (2)	2223.20 (2)	2141.47 (3)	2183.50 (2)	2190.00 (2)	2230.74 (1)
C	2101.77 (2)	2077.15 (2)	2011.30 (3)	2045.26 (2)	2052.89 (2)	2087.59 (1)
D_J[b]	−1.58	−3.56	−3.00	−4.55	−4.06	−3.82
δ[c]	0.12	0.12	0.17	0.12	0.11	0.06
I_a	28.1450(5)	30.2721(5)	28.1834(7)	29.9370(5)	28.2965(4)	28.4194(2)
δI_a[d]	0.3943	0.3944	0.4029	0.3945	0.3943	0.3943
I_b	225.1935(18)	227.3192(20)	235.9950(30)	231.4527(19)	230.7655(19)	226.5507
δI_b[d]	1.0653	1.0655	1.0657	1.0654	1.0653	1.0653
I_c	240.4525(26)	243.3024(28)	251.2688(42)	247.0965(28)	246.1778(29)	242.0855(14)
δI_c[d]	1.1258	1.1256	1.1112	1.1256	1.1276	1.1272
P_c[e]	6.4430(16)	7.1445(18)	6.4548(26)	7.1466(17)	6.4421(17)	6.4423(8)
ΔP_c[f]	—	0.7015(24)	0.0118(31)	0.7036(23)	−0.0009(24)	−0.0007(18)

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviation. b) 10^4 times the coefficient of $[J(J+1)]^2$ term of the centrifugal distortion contribution. c) Standard deviation of the observed frequencies from the calculated frequencies. d) $\delta I_g = I_g(\text{obsd}) - I_g(\text{calcd})$, (g=a, b and c). I_g(calcd) was calculated from the r_s structural parameters listed in Table 3. Since the x_b coordinate of the H_s atom was calculated by assuming $r(CH_a) = r(CH_s)$, δI_a and δI_c of *s*-CH_2DCH_2OEt species which are related to this coordinate, make slight differences from those of the other species. e) $P_c = (I_a + I_b - I_c)/2$. f) $\Delta P_c = P_c(\text{isotopic}) - P_c(\text{parent})$.

TABLE 3. ATOM COORDINATES (Å) AND STRUCTURAL PARAMETERSa)

Atom	x_a	x_b	x_c
O	0	−0.2546 (21)b)	0
C (CH_2)	±1.1699 (22)	0.5282 (12)	0
C (CH_3)	±2.3712 (14)	−0.3967 (20)	0
H (CH_2)	±1.1913 (25)	1.1745 (25)	±0.8818 (38)
H_s (CH_3)	±3.2977 (13)	0.1782 (75)c)	0
H_a (CH_3)	±2.3548 (12)	−1.0368 (28)	±0.8825 (37)

CH_3 group		CH_2 group		Skeleton	
$r(CH_s)$	1.090 Å (0.004)	r(CH)	1.093 Å (0.003)	r(CO)	1.408 Å (0.002)
$r(CH_a)$	1.090 Å (0.004)	α(CCH)	110°11′ (19′)	r(CC)	1.516 Å (0.003)
$\alpha(CCH_s)$	110°35′ (19′)	α(OCH)	110°10′ (19′)	α(COC)	112°25′ (16′)
$\alpha(CCH_a)$	110°15′ (19′)	α(HCH)	107°29′ (32′)	α(OCC)	108°37′ (10′)
$\alpha(H_sCH_a)$	108°48′ (37′)				
$\alpha(H_aCH_a)$	108° 4′ (33′)				

a) The figures in parentheses indicate the 99% reliability intervals. b) Calculated by the use of the first moment equation from the x_b coordinaties of the other atoms. c) Calculated from the x_a coordinate of the H_s atom and the coordinates of the C and H_a atoms, assuming that $r(CH_s)=r(CH_a)$.

TABLE 4. THE STARK COEFFICIENTS OF THE *TT* ISOMER OF DIETHYL ETHER

Transition	$\Delta\nu/E^2$ [$\times 10^{-4}$ MHz/(V/cm)^2] Obsd	Calcd
$1_{10} \leftarrow 1_{11}$ $M=1$	0.399±0.006	0.395
$2_{11} \leftarrow 2_{02}$ $M=2$	0.469±0.007	0.463
$3_{12} \leftarrow 3_{03}$ $M=3$	0.498±0.010	0.492
$2_{12} \leftarrow 1_{01}$ $M=1$	0.626±0.020	0.633
$3_{13} \leftarrow 2_{01}$ $M=0$	−0.308±0.010	−0.329
	$\mu=1.061\pm0.018$D	

α(OCH) and $\alpha(H_sCH_a)$, respectively. They are essentially equal to those given in Table 3 within the experimental error limit. On the other hand, the values of 1.103±0.004 Å and 109°32′±17′ are obtained for $r(CH_s)$ and $\alpha(H_sCC)$. However, an asymmetric CH_3 structure derived from these values is less believable than the nearly symmetric CH_3 structure given in Table 3.

Dipole Moment

The dipole moment of the *TT* isomer of diethyl ether was quantitatively determined by Stark-effect measurements of five transitions for the normal species. The spectrometer was calibrated with OCS7) before and after measurements on diethyl ether.

For the *TT* isomer, the dipole moment has to be parallel to the b-inertial axis from the symmetry. The observed and calculated Stark coefficients8) are shown in Table 4. By the least-squares technique, the dipole moment was determined to be $\mu=1.061\pm0.018$ D. A value of 1.16 D based on dielectric constant measurements was reported in the literature.9)

Discussion

A comparison of the r_s structure of the *TT* isomer of diethyl ether with that of *trans*-ethyl alcohol is of primary interest. Unfortunately, this is impossible at present, since the reported structure of *trans*-ethyl alcohol is not the r_s structure but the r_0 structure obtained with several assumptions.10)

However, a comparison is possible with those of the molecules, of which the r_s structures were reported in the literatures. First, the CO bond distance of the *TT* isomer is essentially equal to that of dimethyl ether11) while the COC angle is slightly larger than that of dimethyl ether. Second, the CC bond distance is about 0.01 Å shorter than that of propane,12) slightly shorter than those of ethyl chloride13) and bromide14) and about 0.01 Å longer than that of ethyl fluoride,15) though it is difficult to interprete the significance of this fact.

Third, and most noticeable, both the CCO and HCH angles of the CH_2 group for the *TT* isomer are abnormally smaller than tetrahedral. This anomalous feature of the angles of the CH_2 group may be explained by the tilted ethyl group towards the lone pair electrons of the oxygen atom in the similar manner as the tilted methyl group in dimethyl ether.11,16)

The dipole moment of the *TT* isomer of diethyl ether is 1.061 D which is smaller than that of dimethyl ether (1.310 D).11) From the observed dipole moments, the apparent bond moment on the CO bond can be calculated to be 1.167 and 0.952 D for dimethyl ether and diethyl ether, respectively. The decrease of the apparent bond moment for diethyl ether may be interpreted as due to the induction effect17) of the CO bond moment on the CC bond.

References

1) R. G. Synder and G. Zerbi, *Spectrochim. Acta,* **23A**, 291 (1967); H. Wieser, W. G. Laidlaw, P. J. Krueger, and H. Fuhrer, *ibid.,* **24A**, 1055 (1968); A. D. H. Clague and A. Danti, *ibid.,* **24A**, 439 (1968).

2) M. Hayashi, H. Iamishi, K. Ohno, and H. Murata, This Bulletin, **44**, 299 (1971).

3) C. S. Marvel and P. K. Porter, "*Organic Syntheses,*" Coll. Vol I, p. 377 (1941).

4) A. Murrey, III and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience, New York (1958), p. 1471.

5) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **40**, 3142 (1964).

6) J. Kraitchman, *Amer. J. Phys.*, **21**, 117 (1953).

7) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

8) S. Golden and E. B. Wilson, Jr., *ibid.*, **16**, 669 (1948).

9) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York (1955), p. 298.

10) Y. Sasada, M. Takano, and T. Satoh, *J. Mol. Spectrosc.*, **38**, 33 (1971).

11) U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).

12) D. R. Lide, Jr., *ibid.*, **33**, 1514 (1960).

13) R. H. Schwendeman and G. D. Jacobs, *ibid.*, **36**, 1245 (1962).

14) C. Flanagan and L. Pierce, *ibid.*, **38**, 2963 (1963).

15) L. Nygaard, *Spectrochim. Acta*, **22A**, 1261 (1966).

16) L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961).

17) I. Miyagawa, *Nippon Kagaku Kaishi*, **75**, 1061 (1954).