Vibration Spectra and Rotational Isomerism of Chain Molecules. I. Methyl Propyl Ether, Ethyl Propyl Ether, and Butyl Methyl Ether

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The Raman and infrared spectra of methyl propyl ether, ethyl propyl ether, and butyl methyl ether were measured for the gaseous, liquid, glassy and crystalline states. The normal vibration frequencies were calculated, a consistent set of force constants explaining the frequencies of basic aliphatic ethers being assumed. The rotational isomerism was studied and the following conclusions were obtained. (1) Only the all-*trans* form exists in the crystalline state. (2) Another form which takes the *gauche* conformation about the OC–CC axis and the *trans* conformation about the CC–CC and CO–CC axes exists in the glassy state. (3) Other forms also exist in the liquid state. These results confirmed that the repulsive force between nonbonded hydrogen atoms was one of the important factors influencing the stability of molecular conformations. The stable conformations of the ether molecules were correlated with those of polyether chains.

The existence of rotational isomers has been clearly shown from the observation of Raman spectral changes on crystallization of 1,2-dichloroethane[1] and the rotational isomerism of small molecules has been studied in detail for various compounds.[2–4] The quantum mechanical treatment has also shown that the approximation of rotational isomerism can be practically applied.[5]

The rotational isomers of longer chain molecules have not yet been fully explored, since infrared and Raman spectra show too many bands to be assigned to each of possible rotational isomers. Recently we succeeded in estimating the force constants of chain molecules consisting of the CH_3, CH_2, O, S, F, Cl, Br, and I units and in calculating the vibrational frequencies of possible rotational isomers accurately enough to give reliable band assignments for longer chain molecules.[6]

This procedure provides us with a reliable method of determining the rotational isomers existing in the solid, liquid and other states. Accordingly, we started a series of research in which the rotational isomerism of longer chain molecules was studied. This paper is the first of this series and deals with the isomerism of methyl propyl ether $CH_3OCH_2CH_2CH_3$, ethyl propyl ether $CH_3CH_2OCH_2CH_2CH_3$ and butyl methyl ether $CH_3OCH_2CH_2CH_2CH_3$ and the results are correlated with those of other ethers[7–11] and the stable conformations of polyether chains.[12,13]

Notation

The conformation of a chain molecule is expressed with respect to the backbone axes and the symbols c, g^+, s^+, t, s^-, and g^- are used for the approximate internal-rotation angles of 0, 60, 120, 180, 240, and 300°, respectively,[3,14,15] where c, g, s, and t are the abbreviations of *cis*, *gauche*, *skew*, and *trans*. For saturated compounds, t, g^+, and g^- are stable.[2,4,16] In this series of papers, we use the generic symbols T, G, and G′ to represent the conformation of rotational isomers, since some of the molecular conformations expressed by t, g^+ and g^- are indistinguishable by vibrational spectroscopy. The symbol T corresponds simply to t, and G and G′ correspond to one and the other of g^+ and g^-. Thus, for example, g^+g^+ and g^-g^- are represented generically as GG, and g^+g^- and g^-g^+ as GG′. The conformations of longer chain molecules are defined by arranging the conformation symbols, T, G, and G′. Table 1 shows the generic names for accessible rotational isomers of the molecules which are studied in this series of papers.

Experimental

Samples of methyl propyl ether, ethyl propyl ether, and butyl methyl ether were purchased from Tokyo Kasei Kogyo Co., Ltd. and were distilled prior to the measurements. The Raman and infrared spectra were measured for the gaseous, liquid, glassy and crystalline states.

The Raman spectra were recorded on a JEOL JRS-400D spectrophotometer with a Coherent Radiation CR-3 argon ion laser in the region below 1600 cm^{-1}. A multireflection accessory and a gas cell with a heater were used for the measurements of the spectra in the gaseous state. The Raman spectra in the liquid state were measured at room and lower temperatures. The glassy state was obtained by putting into liquid nitrogen the sample enclosed in an ampoule and cooling it rapidly, and the crystalline state by inserting a copper wire in the sample and cooling it slowly with liquid nitrogen.

The infrared spectra were recorded on a Hitachi EPI-G2 double beam grating spectrometer in the region 1600—400 cm^{-1} and on a Hitachi EPI-L double beam grating spectrometer in the region 700—250 cm^{-1}. For the measurements in the region 700—250 cm^{-1}, the spectrometer was flushed with dry air to get rid of the interference of water vapor absorptions. The spectra in the gaseous state were measured with a 10 cm gas cell with KBr windows in the region 1600—400 cm^{-1}. For the measurements of the spectra in the liquid state, a 0.025 mm fixed cell with KBr windows and a variable cell with KRS-5 windows were used. The infrared spectra in the glassy and crystalline states were measured by the method previously reported.[17]

Normal Coordinate Treatment

The normal coordinate treatment of the unbranched ethers (see Table 2) was carried out with a computer program NCTB2[6] and a HITAC 8700/8800 computer system at the Computer Center of the University of Tokyo. The calculation made it possible to assign the observed Raman and infrared bands to individual rotational isomers and to determine a consistent set of

TABLE 1. GENERIC NAMES OF ROTATIONAL ISOMERS

Molecule[a)]	Generic name	Conformations
CH_3CH_2-CH_2X	T	t
XCH_2-CH_2X	G	g^+, g^-
XCH_2-CH_2Y		
CH_3Z-CH_2CH_3		
CH_3CH_2-Z-CH_2CH_3	TT	tt
XCH_2-CH_2-CH_2X	TG	tg^+, tg^-, g^+t, g^-t
	GG	g^+g^+, g^-g^-
	GG′	g^+g^-, g^-g^+
CH_3CH_2-CH_2-CH_2X	TT	tt
XCH_2-CH_2-CH_2Y	TG	tg^+, tg^-
CH_3W-CH_2-CH_2CH_3	GT	g^+t, g^-t
CH_3W-CH_2-CH_2X	GG	g^+g^+, g^-g^-
	GG′	g^+g^-, g^-g^+
XCH_2-CH_2-CH_2-CH_2X	TTT	ttt
CH_3Z-CH_2-CH_2-ZCH_3	TTG	$ttg^+, ttg^-, g^+tt, g^-tt$
	TGT	tg^+t, tg^-t
	TGG	$tg^+g^+, tg^-g^-, g^+g^+t, g^-g^-t$
	GTG	g^+tg^+, g^-tg^-
	TGG′	$tg^+g^-, tg^-g^+, g^+g^-t, g^-g^+t$
	GTG′	g^+tg^-, g^-tg^+
	GGG	$g^+g^+g^+, g^-g^-g^-$
	GGG′	$g^+g^+g^-, g^-g^-g^+, g^+g^-g^-, g^-g^+g^+$
	GG′G	$g^+g^-g^+, g^-g^+g^-$
CH_3CH_2-CH_2-CH_2-CH_2X	TTT	ttt
XCH_2-CH_2-CH_2-CH_2Y	TTG	ttg^+, ttg^-
CH_3CH_2-W-CH_2-CH_2CH_3	TGT	tg^+t, tg^-t
CH_3W-CH_2-CH_2-CH_2CH_3	GTT	g^+tt, g^-tt
CH_3O-CH_2-CH_2-SCH_3	TGG	tg^+g^+, tg^-g^-
	GTG	g^+tg^+, g^-tg^-
	GGT	g^+g^+t, g^-g^-t
	TGG′	tg^+g^-, tg^-g^+
	GTG′	g^+tg^-, g^-tg^+
	GG′T	g^+g^-t, g^-g^+t
	GGG	$g^+g^+g^+, g^-g^-g^-$
	GGG′	$g^+g^+g^-, g^-g^-g^+$
	GG′G	$g^+g^-g^+, g^-g^+g^-$
	GG′G′	$g^+g^-g^-, g^-g^+g^+$

a) X, Y=F, Cl, Br, or I; Z=CH_2, O, or S; W=O or S.

force constants of ethers. Structural parameters and symmetry coordinates used in the calculation and a final set of the force constants are reported in a separate paper.[6)]

The force constants of the ethers were determined in the following way. The force constants associated with a methyl or methylene group which is not bound directly to an oxygen atom were assumed to be the same as those for the paraffin molecules.[18)] The force constants associated with the ether group, including those of neighboring methyl and methylene groups, were refined in the least-squares adjustment with initial values transferred from the results by Shimanouchi *et al.*,[19)] Snyder and Zerbi,[7)] and Matsuura and Miyazawa.[20)] Some of the ether force constants, which were unestimable from the observed frequencies, were assumed to have the same values as those for the corresponding paraffin force constants.

Table 2 shows the procedure of the least-squares calculation. The calculation began with the simplest ethers in the extended form, and then the molecules to be treated were extended to the longer ethers and the non-extended forms. The various deuterated derivatives of ethyl methyl ether and diethyl ether were also included in the force constants refinement. A total of 83 force constants associated with the ether group were determined from 690 Raman and infrared frequencies of 46 forms of 19 molecular species.

Results

Figures 1—9 show the Raman and infrared spectra in the gaseous, liquid, glassy and crystalline states. The observed frequencies and the assignment based on the calculated potential-energy distributions are listed in Tables 3—5. The observed spectra were analyzed with reference to the results of the normal coordinate treatment.

Table 2. Procedure of the least-squares calculation

Step	$CH_3OC_2H_5$[a]	$C_2H_5OC_2H_5$[b]	$CH_3OC_3H_7$[c]	$C_2H_5OC_3H_7$[c]	$CH_3OC_4H_9$[c]	$CH_3OC_2H_4OCH_3$[d]
1	T(22)	TT(27)				
2			TT(27)	TTT(33)	TTT(31)	
3	G(10)	TG(8)				
4			TG(14)	TTG(17)	TGT(18)	
5			GT(5)	TGT(8)	TTG(9)	
			GG(7)	TGG(4)	GTT(5)	
				GTG(4)	GTG(6)	
6						TGT(29)
						TTT(10)
7						TGG(15)
						TTG(12)
8	$CD_3OC_2H_5$[e] T(22) G(7)			$CH_3OCHDCH_3$[f] T(20) G(5)		
	$CH_3OCD_2CH_3$[g] T(21) G(7)			$CH_3OCH_2CD_3$[e] T(21) G(6)		
	$CD_3OCH_2CD_3$[f] T(19) G(5)			$CD_3OCHDCD_3$[f] T(21) G(4)		
	$CH_3OC_2D_5$[e] T(22) G(5)					
	$CD_3CH_2OCH_2CD_3$[h] TT(25) TG(12)			$CH_3CD_2OCD_2CH_3$[h] TT(25) TG(13)		
	$C_2D_5OC_2D_5$[i] TT(24) TG(8)			$C_2H_5OC_2D_5$[j] TT(22) TG(5)		
9	$(-OCH_2CH_2-)_n$[k] TGT (30)			$(-OCD_2CD_2-)_n$[j] TGT (20)		

The least-squares calculation begins with the simplest ethers given in the first step and the first set of force constants is determined so as to give the best fit between the observed and calculated frequencies. This set of force constants gives the definite vibrational assignments of the ethers given in the second step and the second set of force constants is subsequently determined from the observed frequencies in this step in addition to those in the first step. By repeating this procedure, the final set of force constants is obtained. The figures in parentheses give the numbers of observed frequencies used for the least-squares calculation.

The observed frequencies of the CH and CD stretching vibrations are not included in the calculation and accordingly the force constants associated with these vibrations are not refined.

a) Refs. 7, 10a, 10b, 11, and 21. b) Refs. 7, 9, 10b, 10c, and 22. c) This study. d) This study and Ref. 7. e) Refs. 10a, 10b, and 11. f) Refs. 10a and 10b. g) Refs. 10a and 11b. h) Refs. 9 and 10c. i) Refs. 9, 10b, and 10c. j) Refs. 10b and 10c. k) Refs. 12, 13, 24, and 25. l) Ref. 13.

The following spectral features are observed for the three ethers in common. (1) The spectra in the various states are distinctly different, especially in the 600—200 cm^{-1} region of the skeletal deformation and torsional vibrations and in the 1200—800 cm^{-1} region of the skeletal stretching and the methyl and methylene rocking vibrations. (2) The spectral pattern of the crystalline state is the simplest and the smallest number of bands is observed. (3) In the glassy state, more bands appear in addition to those which persist in the crystalline state. (4) The liquid-state spectra have further more bands. As temperature is lowered, the intensities of the additional bands decrease rapidly relative to those of the bands which persist in the glassy state. (5) The gaseous-state spectra are essentially the same as the corresponding liquid-state spectra at room temperature.

In the following subsections, the rotational isomerism of the individual ethers is described.

Methyl Propyl Ether. Since this molecule has two internal-rotation axes associated with the rotational isomerism, there are five possible isomers, TT, TG, GT, GG, and GG′, as given in Table 1. The observed and calculated frequencies in the 600—250 cm^{-1} region are compared in Fig. 3.

The spectra in the crystalline state show that only the TT form exists. The number of the observed bands is just what is expected for one form. The frequencies, especially in the region below 600 cm^{-1}, can only be explained by the TT form.

The glassy-state spectra show that the TT and TG forms coexist. The bands at 506, 357, and 308 cm^{-1} which appear newly in the glassy state can only be explained by the TG form.

In the liquid and gaseous states, the observed spectra are explained by the coexistence of the TT, TG, GT and GG forms. The Raman band at 375 cm^{-1} and the infrared band at 495 cm^{-1} are assigned to the GT form, while the weak Raman band at 530 cm^{-1} in the gaseous state and the Raman and infrared bands at 285—292 cm^{-1} in the liquid and gaseous states are assigned to the GG form. The existence of the GG form is also confirmed by the observation of the Raman and infrared bands at 852 cm^{-1} which are assigned only to this form.

It is not likely that the GG′ form exists, since no Raman or infrared bands to be assigned to this form are detected. Furthermore, the distance between the two terminal methyl groups is too short for the GG′ form to be stable.

Ethyl Propyl Ether. This molecule has two C–O axes and a C–C axis which determine the molecular conformation. Accordingly, fourteen rotational isomers listed in Table 1 are derived as possible. Of these, the forms with a sequence of GG′ conformation, *i.e.* TGG′, GG′T, GGG′, GG′G, and GG′G′ are rejected because of the same reason as stated above for the GG′ form of methyl propyl ether.

Figure 6 indicates that the Raman and infrared

TABLE 3. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF METHYL PROPYL ETHER

Observed frequency (cm^{-1})[a]								Assignment[b]
Gas		Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	R	IR	
						1533VW		Origin unknown
	1475M, b	1480W, sh	1478M, sh	1486W	1480M	1498S	1482M	$\mathrm{CH_2}$ scis
				1475VW, sh		1476M	1473M, sh	$\mathrm{CH_2}$ scis
							1469VS	$\mathrm{CH_3}$ ip-d-deform
1462M, vb			1463S, b	1465W, sh	1460M	1463W	1463VS	$\mathrm{CH_3}$ s-deform
	1460M, vb	1451S, vb				1460W	1457VS, sh	$\mathrm{CH_3}$ op-d-deform
			1452S	1454M	1449M	1450VS	1448W, sh	$\mathrm{CH_3}$ op-d-deform
			1438M, sh	1439W, sh	1438M, sh	1443VW, sh	1440VW, sh	$\mathrm{CH_3}$ ip-d-deform
	1396M	1389VW	1389S	1396VW	1388M	1403VW	1390VS	$\mathrm{CH_2}$ wag (**TT**, TG)
	1386M		1381M, sh	1389VW	1381W, sh	1385VW	1381W	$\mathrm{CH_3}$ s-deform (**TT**), $\mathrm{CH_2}$ wag (GT, GG)
	1373VW, sh	1376VW	1374W, sh	1374VW	1371W			$\mathrm{CH_3}$ s-deform (**TG**, GT, GG)
	1345VW	1343VW	1345W	1343VW	1344VW			$\mathrm{CH_2}$ wag (**TG**, GG)
1312VW, sh	1308VW, sh	1305VW, sh	1309VW	1305VW	1307W	1307VW	1308W	$\mathrm{CH_2}$ wag (**TT**, GT), $\mathrm{CH_2}$ twist (GT)
1292VW	1292VW	1284W	1287W	1288W	1286W	1289S	1288VW	$\mathrm{CH_2}$ twist (**TT**, TG, GG)
1272VW, sh	1268VW		1268VW					$\mathrm{CH_2}$ twist (GT, GG)
							1263VW	Origin unknown
1249VW, sh	1251VW	1249VW	1251W	1249VW	1249W	1249VW	1251M	$\mathrm{CH_2}$ twist (**TT**, TG)
1212VW	1212M					1212VW	1214VS	$\mathrm{CH_3}$ ip-rock (**TT**)
	1204M	1204VW	1204VS	1205VW	1205S			$\mathrm{CH_3}$ ip-rock (**TG**, GT, GG)
1178VW, sh	1178VW, sh	1174VW, sh	1174M, sh	1174VW, sh	1174VW, sh	1173VW	1175W	$\mathrm{CH_3}$ op-rock (**TT**), $\mathrm{CH_2}$ rock (GT)
1167VW, sh	1168VW, sh	1163VW	1165S	1166VW	1166W			$\mathrm{CH_3}$ op-rock (**TG**, GT, GG)
1152VW, sh		1150VW, sh		1151VW, sh		1152VW	1152VW, sh	$\mathrm{CH_3}$ op-rock (**TT**)
1147W	1148VS, sh	1141VW, sh	1144VS, sh	1144VW	1144M			$\mathrm{CH_3}$ op-rock (**TG**)
1135VW, sh	1134VS	1131W	1132VS	1131W	1130VS	1126S	1132VS	CC stretch (**TT**)
1115VW	1118VS, sh	1116VW	1119VS	1114VW	1114VS			CO stretch (**TG**), $\mathrm{CH_3}$ ip-rock (GT)
	1110VS	1103VW	1104VS, sh					$\mathrm{CH_3}$ ip-rock (**GG**)
1096VW, sh	1098W, sh	1096VW, sh	1096VS, sh	1100VW	1100VS	1096W	1098VS	CO stretch (**TT**), $\mathrm{CH_3}$ ip-rock (TG)
		1077VW, sh	1077VW, sh					CC stretch (**GG**)
	1062W							CO stretch (**GT**)
1058VW	1052M	1050VW, sh	1050S	1050VW, sh	1050S			CC stretch (**TG**)
1047W	1038VW, sh	1040W	1040W, sh	1042W	1042W, sh	1039VS	1042M	CC stretch (**TT**, GT)
1030VW, sh	1030VW, sh	1026VW	1026W					CO stretch (**GG**)
965VW, sh		958VW	959M	960VW	960S	961M	960VS	CO stretch (**TT**)
			942M, sh					CO stretch (**GT**)
938VW	938M, vb	933W	935S	935W	935S			CO stretch (**TG**), $\mathrm{CH_3}$ ip-rock (GG)
		911VW, sh	913M	913VW, sh	912S			$\mathrm{CH_2}$ rock (**TG**)
			903M, sh		905M, sh	911VW, sh	909VW	$\mathrm{CH_2}$ rock (**TT**)
905W		902W	897W, sh	904W	897VW, sh	902VS	897S	$\mathrm{CH_3}$ ip-rock (**TT**), $\mathrm{CH_3}$ op-rock (GT), $\mathrm{CH_2}$ rock (GG)
879VS		876VS	879W	879VS	879M			CC stretch (**TG**, GT)
855W		852W	852VW					CC stretch (**GG**)
759VW	760VW	756VW	759VW	758VW	760W	764VW	764M	$\mathrm{CH_2}$ rock (**TT**, TG, GT, GG)
530VW								OCC deform (**GG**)
508M		505W	505VW, sh	506W	505VW			CCC deform (**TG**)
			495VW					OCC deform (**GT**)
447M		443W	441VW	442M	441VW	443M	442VW	COC bend (**TT**)
422W		418VW	414VW	416VW	414VW	424M	409VW	CCC deform (**TT**), COC bend (GG)
375VW, sh		375VW, sh						COC bend (**GT**)
355M		358VW	358VW	357W	357VW			COC bend (**TG**)
		312VW	305VW, sh	308VW	305VW			OCC deform (**TG**), CCC deform (GT)
287VW		292VW	285VW					CCC deform (**GG**)
223VW						223VW		$\mathrm{CH_3}$ torsion (**TT**)
		195VW, b		205VW, b		205VW		OCC deform (**TT**), $\mathrm{CH_3}$ torsion (TG)
						131VW		Torsions (**TT**) and lattice vibrations
						123W		
						110W		
						87VW		
						76W		
						68VW		
						55M		

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a) VS: very strong, S: strong, M: medium, W: weak, VW: very weak, vb: very broad, b: broad, sh: shoulder. The broadness of the band shapes in the gaseous state does not always allow us to correlate the individual bands in the liquid state to those in the gaseous state. Only approximate correlations are made in such cases and in other cases of similar situations. b) The band is assigned preferentially to the isomer(s) given by boldface. For the notation and definition of the local symmetry coordinates, see Ref. 26.

TABLE 4. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF ETHYL PROPYL ETHER

Observed frequency (cm^{-1})[a)								
Gas		Liquid		Glass		Crystal		Assignment[b)
R	IR	R	IR	R	IR	R	IR	
		1490W	1490W, sh	1492W	1490W, sh	1497W	1484W, sh	CH$_2$ scis
			1487W		1486W		1480M	CH$_2$ scis
			1473M	1473VW, sh	1472W, sh	1478VW, sh	1476W, sh	CH$_2$ scis
			1464M, sh	1460M, sh	1462W, sh	1468VW	1464M	CH$_3$ ip-d-deform
1462M, vb	1465M, vb	1458M, vb	1460M	1457M	1457W	1457M	1457M	CH$_3$ op-d-deform
			1452M, sh	1450M, sh	1449W, sh	1452W, sh	1456M	CH$_3$ ip-d-deform
			1443M	1439W, sh	1438W	1447W, sh	1442W	CH$_3$ op-d-deform
		1415VW, sh	1408W	1415VW	1418VW	1415VW	1416VW	CH$_2$ wag (**TTT**)
					1408W			CH$_2$ wag (**TTG**, TGT, TGG, GTG)
	1382M	1380VW	1379S	1379VW	1378M		1378M	CH$_3$ s-deform (**TTT**, TTG, TGT, TGG, GTG), CH$_2$ wag (TGT, TGG, GTG)
	1366M		1370M, sh	1372VW	1368M, sh	1371VW	1370M	CH$_3$ s-deform (**TTT**, TGT, TGG, GTG)
	1356M		1356M	1356VW	1354W	1355VW	1357W	CH$_2$ wag (**TTT**, TTG)
	1344VW, sh	1345VW	1345W	1344VW	1344W			CH$_2$ wag (**TTG**, TGG, GTG)
	1303W, b	1303VW, sh	1304W	1304VW	1303W	1308VW	1308W	CH$_2$ wag (**TTT**, TGT), CH$_2$ twist (TGT)
			1283W	1292VW, sh	1292VW, sh	1292W	1295VW	CH$_2$ twist (**TTT**, TGG, GTG)
				1285W, sh	1282W			CH$_2$ twist (**TTG**)
1284W, vb	1279W	1277W, b	1275W, sh	1276W	1274W, sh	1276W	1274VW	CH$_2$ twist (**TTT**, TTG, TGG)
			1265W					CH$_2$ twist (TGT, GTG)
	1264W, b	1250VW	1252W	1252VW, sh	1254VW, sh			CH$_2$ twist (**TTG**, TGT, TGG, GTG)
				1246VW	1246W	1245VW	1247W	CH$_2$ twist (**TTT**)
	1180W, sh		1182M, sh					CH$_2$ rock (**TGT**)
1170VW, sh	1168M, sh	1170VW, sh	1168M, sh	1170VW, sh	1172W, sh	1172VW	1172W	CH$_2$ rock (**TTT**)
		1165VW, sh			1165W			CH$_2$ rock (**TTG**, TGG), CH$_3$ op-rock (GTG)
1156W		1154W	1154S	1155M	1152M	1152M	1155S	CH$_3$ ip-rock (**TTT**, GTG), CH$_2$ rock (GTG), CH$_3$ op-rock (**TTT**, TTG, TGT, TGG)
1133W			1133VS	1133VW	1131M, sh			CH$_3$ ip-rock (**TTG**),CO stretch (TGT, TGG)
	1135VS, b	1124VW, b	1118VS	1119VW	1117VS			CO stretch (**TTG**), CH$_3$ ip-rock (TGT, TGG)
1110VW			1110VS, sh	1110VW, sh	1109W, sh	1110W	1112VS	CO stretch (**TTT**), CC stretch (TGT)
1098VW, sh	1090M, b	1099VW	1096S	1098VW	1098W	1101VW, sh	1098VS	CC stretch (**TTT**), CO stretch (GTG)
1085W		1085W	1086S	1085W	1087W			CC stretch (**TTG**, GTG)
1075VW, sh		1075VW, sh	1074M, sh					CC stretch (**TGG**)
			1062M	1062VW	1063M			CC stretch (**TTG**)
1050VW, b	1059W, sh	1048VW	1051M	1048VW	1051W	1050VW	1050S	CC stretch (**TTT**, TGG, GTG)
		1040VW, sh	1042VW, sh					CC stretch (**TGT**)
1017VW	1017W	1017VW	1017W	1017VW	1018W	1020M	1020S	CC stretch (**TTT**, TGT)
990VW, b	986W	985VW	986M	985VW	985M			CC stretch (**TTG**), CO stretch (TGG)
	962VW, sh	961VW	962W					CO stretch (**GTG**)
918VW, sh		918VW, sh	920VW, sh	918VW, sh	918VW			CH$_2$ rock (**TTG**, TGG, GTG), CH$_3$ op-rock (TGT)
908W, sh		908VW, sh	908VW, sh	908VW, sh	908VW, sh	908VW, sh	906W, sh	CH$_3$ ip-rock (**TTT**)
902W, sh		902W	902W	903VW	902W	901W	900M	CH$_3$ op-rock (**TTT**)
884VS	885W, vb	883VS		885VS	896W, sh			CO stretch (**TTG**), CH$_3$ ip-rock (TGT, GTG)
			883M		884M	885W	883M	CO stretch (**TTT**), CC stretch (**TTG**, GTG)
871W, sh		871VW, sh	873W, sh					CC stretch (**TGG**)
849W		844W	846W					CO stretch (TGT), CH$_3$ ip-rock (TGG)
820VW, sh	820VW	820VW, sh	818VW	819VW	818VW	826VW	826VW	CH$_2$ rock (**TTT**, TGT), CH$_3$ op-rock (TTG, TGG, GTG)
761VW	760VW, b	761VW	762VW	763VW	768VW, sh	769VW	767W	CH$_2$ rock (**TTT**, TGG, GTG)
					762W			CH$_2$ rock (**TTG**)
753VW, sh		753VW, sh	753VW, sh					CH$_2$ rock (**TGT**)
		546VW, sh	545VW					COC bend (TGT), CCC deform (TGG)
520VW		518VW	518VW					OCC deform (**GTG**)
496VW, sh	490VW	496VW, sh	494VW	498VW, sh	495VW	498VW	494VW	OCC deform (**TTT**)
488VW		489VW	486VW, sh	490VW	488VW, sh			OCC deform (**TTG**)
439M	439VW	439M	438VW	439M	438VW			COC bend (**TTG**, TGG)
408M	408VW	410M	409VW	410M	408VW	410VS	409VW	COC bend (**TTT**), OCC deform (GTG)
360W		363VW	361VW					OCC deform (**TGT**)
				335VW	331VW			CCC deform (**TTG**), OCC deform (TGG), COC bend (GTG)
328W		330VW	328VW					CCC deform (**TGT**)
				314VW	315VW	314VW	315VW	CCC deform (**TTT**), OCC deform (GTG)
						266VW	266VW	CH$_3$ torsion (**TTT**)
				257VW				CH$_3$ torsion (**TTG**)
						237VW		CH$_3$ torsion (**TTT**)
				195VW, sh		199VW		CH$_2$CH$_2$ torsion (**TTT**)
				165VW		160VW		OCC bend (**TTT**), torsions (**TTT**), and lattice vibrations
						147VW, sh		
						121VW, sh		
						103VW		
						80W, sh		
						78M		
						60VW		
						43VW		

a), b) See a) and b), respectively, of Table 3.

TABLE 5. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF BUTYL METHYL ETHER

Observed frequency (cm^{-1})[a]								
Gas		Liquid		Glass		Crystal		Assignment[b]
R	IR	R	IR	R	IR	R	IR	
		1480W, b	1480M, sh	1486W	1484W, sh	1498VW	1482M	CH$_2$ scis
					1480M	1486W	1475W, sh	CH$_2$ scis
			1474M, sh	1470W, sh	1474W, sh	1477W	1471S	CH$_3$ ip-d-deform
1457M, vb	1460M, vb		1467S, sh	1461S, sh	1464S, sh	1463VW, sh	1462S	CH$_2$ scis
			1461S		1460S	1460W, sh	1458S, sh	CH$_3$ s-deform, CH$_3$ op-d-deform
		1452S, b	1452S	1452S	1452S	1452W	1452W, sh	CH$_3$ op-d-deform
			1444M, sh		1447M, sh	1448W, sh	1442W, sh	CH$_3$ ip-d-deform
			1432W	1434W	1430W, sh			Origin unknown
		1395VW	1395W, sh	1395VW	1395W, sh	1395VW	1395S	CH$_2$ wag (**TTT**, TTG)
1390VW, b	1385M, b	1385VW, sh	1387S	1385VW	1385M			CH$_2$ wag (**TGT**, GTT, GTG)
		1378VW, sh	1379M, sh	1378VW	1376M, sh	1381VW	1377M	CH$_3$ s-deform (**TTT**, TGT, TTG, GTT, GTG)
1367VW		1367VW	1367VW, sh	1368VW	1367VW, sh	1364VW	1366VW	CH$_2$ wag (**TTT**, TGT)
	1345VW	1342VW, sh	1342VW					CH$_2$ wag (TTG, GTT, GTG)
1300W	1312VW	1318VW, sh	1313VW, sh					CH$_2$ wag (TTG, GTG), CH$_2$ twist (GTT)
	1304VW	1304W	1305VW	1305M	1304W	1305VW		CH$_2$ twist (**TTT**, TGT, GTG)
		1286VW, sh		1286VW, sh	1287VW, sh	1284VW	1290VW	CH$_2$ twist (**TTT**, GTT), CH$_2$ wag (TGT)
1265VW, sh	1260W	1270VW, sh	1271VW, sh		1271W, sh	1272VW, sh	1276W	CH$_2$ wag (**TTT**, GTT), CH$_2$ twist (TTG)
		1260VW	1260W	1259VW	1261W			CH$_2$ twist (**TGT**, TTG, GTG)
1231VW, sh	1230W	1233VW	1237W	1236VW	1236M			CH$_2$ twist (**TGT**, TTG, GTT, GTG)
		1225VW, sh	1227VW, sh	1225VW, sh	1227W, sh	1227VW	1231VW	CH$_2$ twist (**TTT**)
1204VW	1208M					1206VW	1214S	CH$_3$ ip-rock (**TTT**)
	1200M	1200VW	1200S	1202VW	1202VS			CH$_3$ ip-rock (**TGT**, TTG, GTT, GTG)
1172VW, sh	1172M, sh	1171VW, sh	1172M, sh	1172VW, sh	1172W, sh	1172VW	1173W	CH$_2$ rock (**TTT**, GTT, GTG), CH$_3$ op-rock (TTG)
1162VW, sh	1162M, sh	1162VW, sh	1163S, sh	1165VW	1164M			CH$_3$ op-rock (**TGT**, GTT, GTG)
1150W, sh	1150S, sh	1148VW, sh	1149S, sh	1149VW, sh	1149W, sh	1149VW	1151VW, sh	CH$_3$ op-rock (**TTT**, TTG)
1142W		1142W	1144S, sh	1145W	1143S			CH$_2$ rock (**TGT**), CH$_3$ op-rock (TTG)
1131W, sh	1135VS	1130W	1132VS	1130W	1132VS, sh	1126W	1132VS	CC stretch (**TTT**)
1120W, sh		1121W, sh	1120VS	1120W	1122VS			CC stretch (**TGT**, TTG), CH$_3$ ip-rock (GTT)
1115W	1112S, sh	1115W	1112VS	1112W	1112VS			CO stretch (**TGT**)
1103VW, sh	1104M, sh	1103VW, sh	1103S, sh	1103VW, sh	1103VS, sh	1103VW	1107VS	CO stretch (**TTT**), CH$_3$ ip-rock (GTG)
1095VW, sh	1095M, sh	1098VW, sh	1098S, sh					CO stretch (**TTG**)
1067VW	1061M	1065VW	1066M	1063VW	1065W	1065W	1067VW	CC stretch (**TTT**, TTG, GTG), CO stretch (GTT, GTG)
1055VW		1054VW	1055W	1053VW	1053S			CC stretch (**TGT**, GTT)
1028VW	1024VW, sh	1022VW, sh	1024VW, sh	1025VW, sh	1026W, sh	1024W	1026M	CC stretch (**TTT**)
1019W	1016W	1016W	1017W	1019W	1019S			CC stretch (**TGT**, GTT)
		991VW	990W	991VW	989VW			Origin unknown
973W, sh		970W, sh		970VW, sh				CH$_3$ ip-rock (**TGT**, TTG), CH$_3$ op-rock (GTG) CC stretch (GTG)
966W		962W	960M	963VW	961S	962M	962VS	CO stretch (**TTT**), CH$_2$ rock (TTG)
955VW, sh	954W, b	952W, sh	952M, sh					CO stretch (TTG), CH$_3$ op-rock (GTT)
						945VW, sh	947W	CH$_3$ op-rock (**TTT**)
945W		942W	941M	940W	938S			CH$_3$ op-rock (**TGT**)
926VW, sh		924VW	920W					CO stretch (GTT, GTG)
898VW	895VW	897VW	896W	899VW	895W	900VW	895S	CH$_3$ ip-rock (**TTT**), CC stretch (GTT, GTG)
880VW		879VW	877VW, sh					CC stretch (**TTG**)
840VS	838W	839VS	838W, sh	841VS	838W			CO stretch (**TGT**)
831W, sh	828W	829M, sh	828W	828W	827S			CH$_2$ rock (**TGT**)
820W, sh		818W						CH$_2$ rock (**TTG**)
	813VW, sh	810W	813VW, sh	813VW, sh	813VW	813VW	813VW	CH$_2$ rock (**TTT**, TTG, GTT, GTG)
791VW, sh		791VW, sh						Other isomers
	753VW		756VW					CH$_2$ rock (GTG, TTG)
						747VW	745M	CH$_2$ rock (**TTT**, GTT)
739VW	740VW	740VW	738VW	740VW	739W			CH$_2$ rock (**TGT**)
550VW, sh		549VW	545VW	551VW	549VW			CCC deform (**TGT**)
525VW		525VW	529VW					Other isomers
509VW		509VW	505VW, sh					COC bend (**GTG**)
494VW		496VW	492VW	495VW	494VW	497VW	494VW	COC bend (**TTT**), OCC deform (GTT)
						485VW		Origin unknown
460VW, sh		460VW	459VW					CCC deform (**TTG**)
449VW		449VW						COC bend (**TTG**)
			425VW					Other isomers
		408VW	410VW					CCC deform (GTT, GTG)
383W		387W	386VW	385W	383VW	391VS	382VW	OCC deform (**TTT**)
349S		352M	352VW, sh	352W	352VW			COC bend (**TGT**, GTT), OCC deform (GTG)
323W		326W	322VW	323VW	324VW, sh	324W	322VW	CCC deform (**TTT**, TTG)
				315VW, sh	315VW			OCC deform (**TGT**)
				275VW	275VW			CCC deform (**TGT**)
		250VW, vb		250VW		247VW	252VW	CH$_3$ torsion (**TTT**, TTG)
						184VW		CCC deform (**TTT**), torsions (**TTT**), and lattice vibrations
						170VW		
						108VW		
						90M, sh		
						86M		
						57VW		
						49VW		

a), b) See a) and b), respectively, of Table 3.

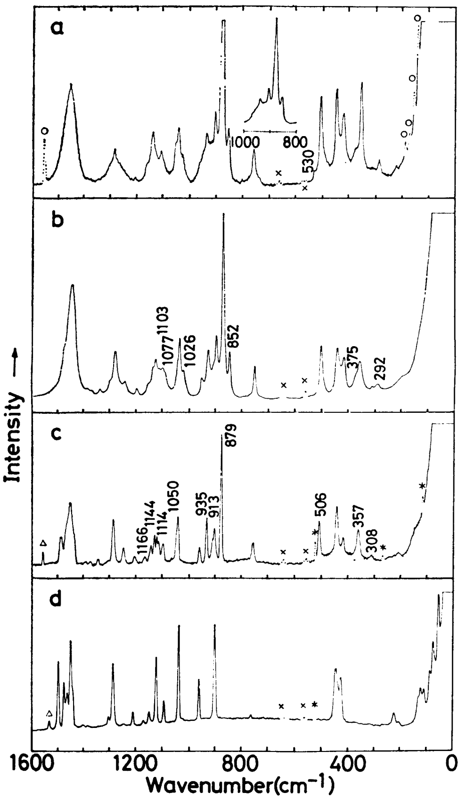

Fig. 1. Raman spectra of methyl propyl ether.
a: Gas (room temperature),
b: liquid (room temperature),
c: glass (liquid nitrogen temperature),
d: crystal (liquid nitrogen temperature).
Following symbols are used in Figs. 1—9. ＊: emission line of Ar$^+$, ○: rotational or vibrational Raman band of O_2 or N_2, □: librational infrared band of H_2O, × : impurity, △: origin unknown.

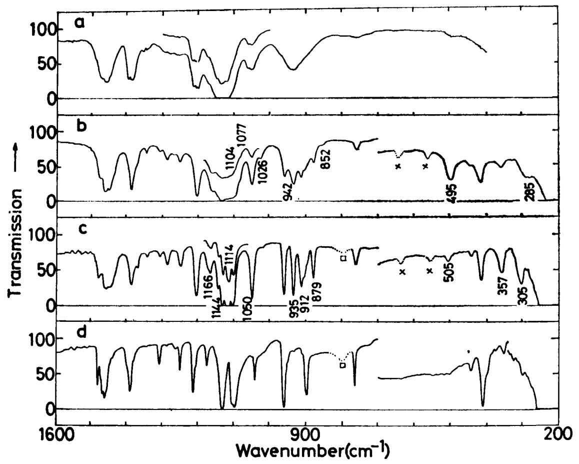

Fig. 2. Infrared spectra of methyl propyl ether.
a: Gas, b: liquid, c: glass, d: crystal.
The symbols are explained in the caption of Fig. 1.

bands observed in the crystalline state are explained only by the calculated result for the TTT form. The additional bands observed in the glassy state are assigned to the TTG form on the basis of the calculated frequencies.

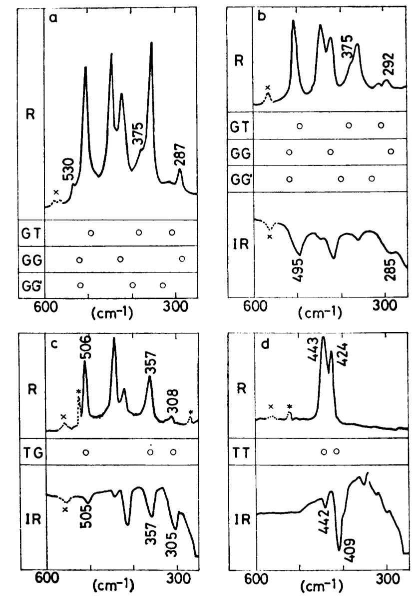

Fig. 3. Observed and calculated frequencies of methyl propyl ether in the 600—250 cm^{-1} region.
a: Gas, b: liquid, c: glass, d: crystal.
The symbols are explained in the caption of Fig. 1.

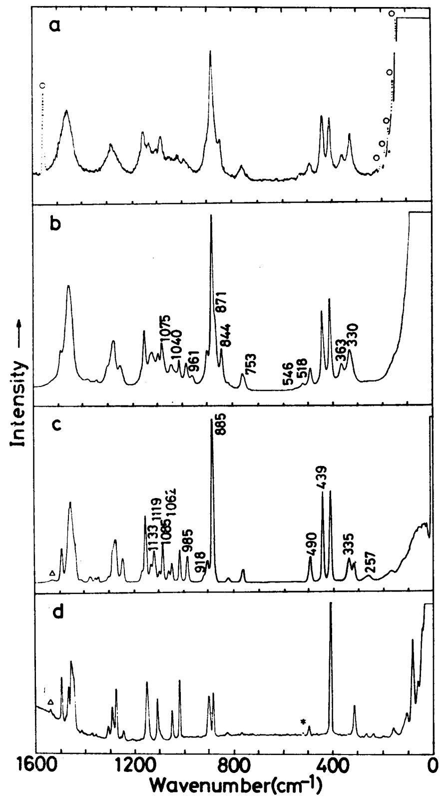

Fig. 4. Raman spectra of ethyl propyl ether.
a: Gas (room temperature),
b: liquid (room temperature),
c: glass (liquid nitrogen temperature),
d: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

In the liquid state, several new Raman and infrared bands appear. The temperature dependence of the

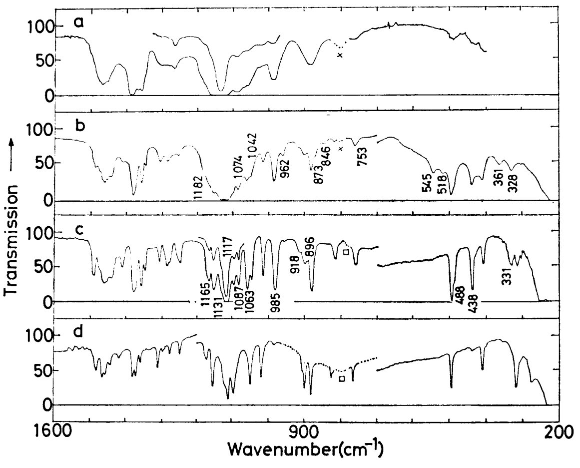

Fig. 5. Infrared spectra of ethyl propyl ether.
a: Gas, b: liquid, c: glass, d: crystal.
The symbols are explained in the caption of Fig. 1.

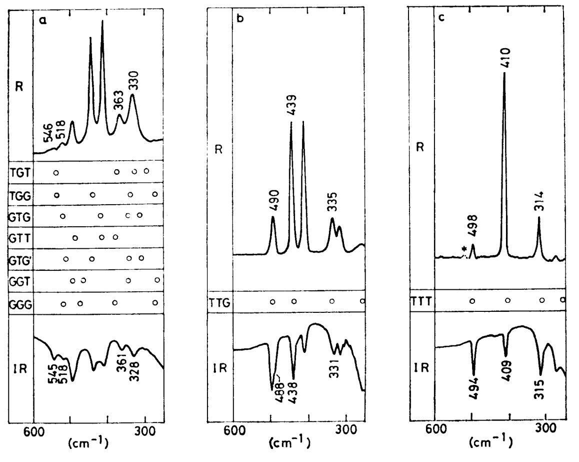

Fig. 6. Observed and calculated frequencies of ethyl propyl ether in the 600—250 cm^{-1} region.
a: Liquid, b: glass, c: crystal.
The symbols are explained in the caption of Fig. 1.

spectra and the calculated results show that the liquid-state spectra are explained by the TGT, TGG, and GTG forms in addition to the TTT and TTG forms which persist in the glassy state.

Existence of the GTT and GTG′ forms is uncertain, since all of their calculated frequencies are almost coincident with those of the other forms mentioned above. The GGT and GGG forms do not seem to exist in the liquid state, since no bands are observed around their characteristic frequencies of about 470 cm^{-1}.

Butyl Methyl Ether. This molecule has two C–C axes and a C–O axis associated with the rotational isomerism. Accordingly, fourteen isomers listed in Table 1 are derived as possible. The GG′T, GG′G and GG′G′ forms are unlikely because of the same reason as stated for methyl propyl ether. However, the TGG′ and GGG′ forms are not ruled out, since unlike the GG′ sequence of the CO–C–CC part in methyl propyl ether or ethyl propyl ether, the GG′ sequence of the OC–C–CC part is not expected to give rise to very large steric hindrance.

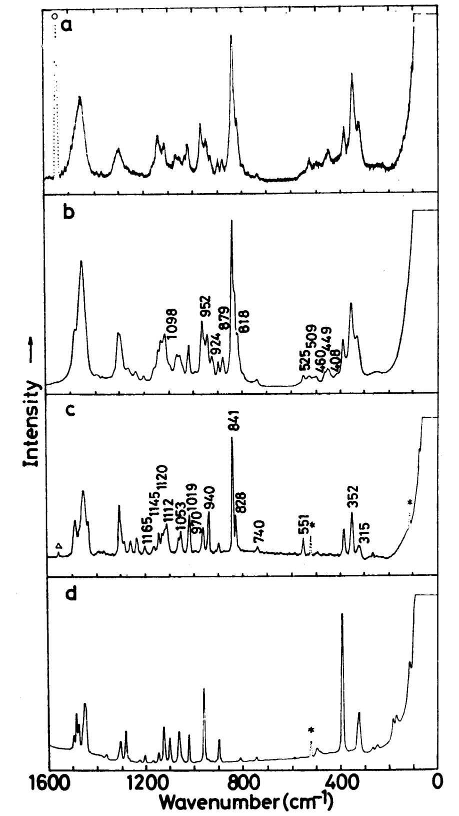

Fig. 7. Raman spectra of butyl methyl ether.
a: Gas (room temperature),
b: liquid (room temperature),
c: glass (liquid nitrogen temperature),
d: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

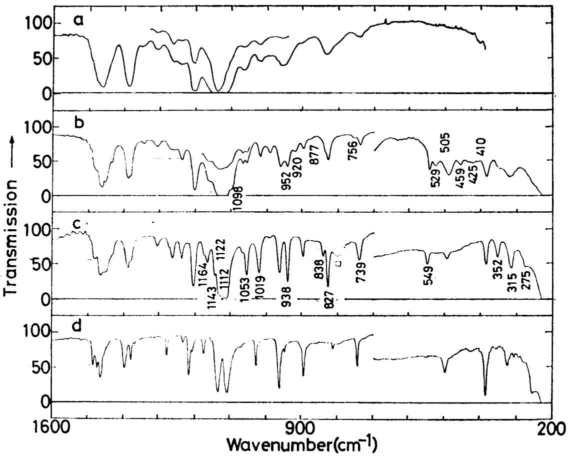

Fig. 8. Infrared spectra of butyl methyl ether.
a: Gas, b: liquid, c: glass, d: crystal.
The symbols are explained in the caption of Fig. 1.

The comparison with the calculated results (Fig. 9) shows that the crystalline-state spectra can be explained only by the TTT form and the glassy-state spectra by the TTT and TGT forms. The spectra in the liquid state have several new bands. Their frequencies are close to the frequencies calculated for the TTG, GTT, and GTG forms. In the liquid-state infrared spectrum,

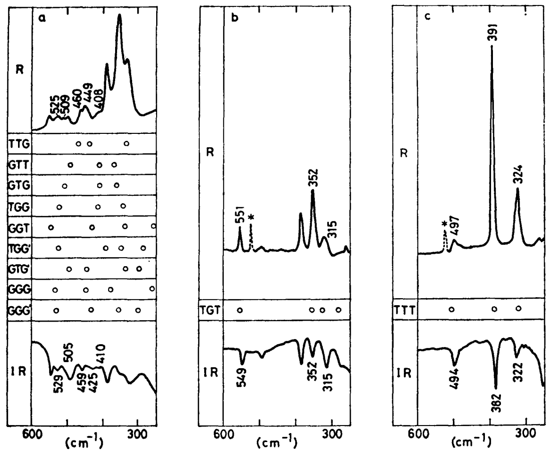

Fig. 9. Observed and calculated frequencies of butyl methyl ether in the 600—250 cm^{-1} region.
a: Liquid, b: glass, c: crystal.
The symbols are explained in the caption of Fig. 1.

several weak bands are observed in the region 450—400 cm^{-1}, which are not assignable to the isomers mentioned above. Accordingly, there are possibilities that other forms such as TGG, GGT, TGG′ ,GTG′, GGG, and GGG′ isomers exist in the liquid state. The Raman band at 525 cm^{-1} and the infrared band at 529 cm^{-1} are assigned to either one or both of the TGG and TGG′ forms.

Rotational Isomerism. In Table 6, the rotational isomerism of the ethers studied in this work is summarized, together with that of ethyl methyl ether and diethyl ether which has been established in earlier studies.[7,9–11] The symbol G̃ is used to specialize the *gauche* conformation about the C–C axis directly adjoining the O–C axis.

Discussion

The following results were obtained for the three ethers in common. (1) Only the all-*trans* form exists in the crystalline state. (2) An additional form coexists in the glassy state. This form takes the *gauche* conformation (G̃) about the OC–CC axis and the *trans* conformation about other axes. (3) More forms exist in the liquid state than in the glassy state. The temperature dependence of the Raman intensities indicates that the additional forms are much less stable than the two forms which persist in the glassy state, while the energy difference between the latter two is not appreciable. (4) It is likely that the molecules in the gaseous state take the same conformations as in the liquid state.

The stability of the *trans* conformation over the *gauche* conformation may be explained, in a way similar to the case of paraffins, in terms of the weaker nonbonded interactions. In fact, it has been shown that the *trans* conformation about the CO–CC axis is more stable than the *gauche* conformation by 1.1—1.5 kcal/mol as obtained for ethyl methyl ether[10a,11a,11c] and diethyl ether.[9,10c] The existence of the all-*trans* form in the crystal is ascribable also to the requirement of the molecular packing which is determined primarily by intermolecular forces.

In addition to the all-*trans* form, the second isomer with the G̃ conformation exists in the glassy state of the three ethers at liquid nitrogen temperature. This isomer was found to be as stable as the all-*trans* form in the liquid state. The stability of the G̃ conformation is also shown by the fact that ethylene glycol dimethyl ether $CH_3O–CH_2–CH_2–OCH_3$ takes the TG̃T conformation in the crystalline state.[7,23] Thus, it is now established that the G̃ conformation (*gauche* about the OC–CC or OC–CO axis) is much more stable than the *gauche* conformation about other axes such as CC–CC and CO–CC.

The stability of the G̃ conformation is understood in the following way by taking the case of the $C_1–O–C_2–C_3–C_4–C_5$ bond system. When the $C_1O–C_2C_3$ or $C_2C_3–C_4C_5$ axis takes the G conformation, appreciable repulsive forces are expected between the nonbonded hydrogen atoms attached to C_1 and C_3, or between those attached to C_2 and C_5. On the other hand, the G̃ conformation about the $OC_2–C_3C_4$ axis does not give rise to such forces, since the hydrogen atoms attached to C_4 have no counterpart hydrogen atoms. The absence of this type of nonbonded interaction is suggested to be one of the principal factors to stabilize the G̃ conformation.

In connection with the stable G̃ conformation, it is important to examine the structure of polyethers.[12,13]

Table 6. Rotational isomers of the ethers

	CH_3OCH_2- CH_3[a]	$CH_3CH_2OCH_2$- CH_3[b]	CH_3OCH_2- CH_2CH_3	$CH_3CH_2OCH_2$- CH_2CH_3	$CH_3OCH_2CH_2$- CH_2CH_3
Gas	**T G**	**TT TG**	**TT TG̃ GT** **GG̃**	**TTT TTG̃** TGT TGG̃ GTG̃ (GTT) (GTG̃′)	**TTT TG̃T** TTG GTT GTG (TG̃G) (GG̃T) (TG̃G′) (GTG′) (GG̃G) (GG̃G′)
Liquid	**T G**	**TT TG**	**TT TG̃ GT** **GG̃**	**TTT TTG̃** TGT TGG̃ GTG̃ (GTT) (GTG̃′)	**TTT TG̃T** TTG GTT GTG (TG̃G) (GG̃T) (TG̃G′) (GTG′) (GG̃G) (GG̃G′)
Glass	—	—	**TT TG̃**	**TTT TTG̃**	**TTT TG̃T**
Crystal	**T**	**TT**	**TT**	**TTT**	**TTT**

The isomers given by boldface are confirmed to exist. The existence of the isomers in parentheses is uncertain. For more details, see text.
a) Refs. 7, 10a, 10b, 11, and 21. b) Refs. 7, 9, 10b, 10c, and 22.

It has been shown that poly(oxyethylene) ($-OCH_2-CH_2-)_n$ and poly(oxytrimethylene) $(-OCH_2CH_2CH_2-)_n$ have several crystal modifications. In the most stable modification, the molecule takes the $\mathrm{T\tilde{G}T}$ conformation for the series of O–C–C–O bonds in the former polymer and the $\mathrm{T\tilde{G}\tilde{G}T}$ conformation for the series of O–C–C–C–O bonds in the latter polymer. In other modifications, the poly(oxyethylene) molecule takes the TTT conformation, and the poly (oxytrimethylene) molecule takes the $\mathrm{TT\tilde{G}TTT\tilde{G}'T}$ and $(\mathrm{TTTT})_2$ conformations for the series of O–C–C–C–O–C–C–C–O bonds. These facts suggest that the $\mathrm{\tilde{G}}$ conformation plays an important role in stabilizing molecular conformations of crystalline polymers.

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