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Vibration Spectra and Rotational Isomerism of Chain Molecules. V.[1)] 2,5-Dioxahexane, 2,5-Dithiahexane, and 2-Oxa-5-thiahexane

Yoshiki Ogawa, Masahiro Ohta, Masaaki Sakakibara,
Hiroatsu Matsuura, Issei Harada, and Takehiko Shimanouchi
Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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The Raman and infrared spectra of 2,5-dioxahexane $CH_3OCH_2CH_2OCH_3$, 2,5-dithiahexane $CH_3SCH_2CH_2SCH_3$ and 2-oxa-5-thiahexane $CH_3OCH_2CH_2SCH_3$ were measured for the gaseous, liquid, glassy and crystalline states and were correlated with the normal-vibration calculations. The rotational isomerism was studied and the following conclusions were obtained. (1) The molecular form existing in the crystalline state is a non-extended form, in contrast with the cases of the unbranched ethers or sulfides containing one oxygen or sulfur atom which take the extended all-*trans* form. (2) Many forms coexist in the gaseous, liquid and glassy states. (3) The form existing in the crystalline state is the most stable in the liquid state. It was found that the repulsive force between non-bonded hydrogen atoms is one of the important factors influencing the conformational stabilities and for 2,5-dioxahexane the dipole-dipole interaction is another important factor. The stable conformations of these molecules were correlated with those of the polyether and polythioether chains. The stable isomers of 2-oxa-5-thiahexane could be explained on the basis of the knowledge of the conformational stabilities of the unbranched ethers and sulfides. The force constants of the ethers and sulfides were satisfactorily transferred to 2-oxa-5-thiahexane.

In previous papers,[1,2)] we reported the vibration spectra and the rotational isomerism of the unbranched ethers and sulfides which contain one oxygen or sulfur atom, and obtained information on the conformational stability for these molecules. In the present paper, we extended our studies to 2,5-dioxahexane (ethylene glycol dimethyl ether) $CH_3OCH_2CH_2OCH_3$, 2,5-dithiahexane $CH_3SCH_2CH_2SCH_3$, and 2-oxa-5-thiahexane $CH_3OCH_2CH_2SCH_3$. The Raman and infrared spectra of these molecules in various states were analyzed and the rotational isomers existing in each state were determined on the basis of normal-vibration calculations.

The present results on the rotational isomerism will be discussed together with those previously obtained for the unbranched ethers and sulfides.[1—6)] Discussions will also be made in relation to the stable conformations of polyethers[7,8)] and polythioethers.[9)]

Experimental

2,5-Dioxahexane was purchased from Tokyo Kasei Kogyo Co., Ltd. and was distilled prior to the measurements. 2,5-Dithiahexane was synthesized by the reaction

$$\mathrm{BrCH_2CH_2Br + 2CH_3SNa\ (aq) \xrightarrow{60\,^\circ C,\ 6\,h} CH_3SCH_2CH_2SCH_3 + 2NaBr.}$$

After the organic layer was dried over anhydrous sodium sulfate, 2,5-dithiahexane was obtained by the distillation under reduced pressure. 2-Oxa-5-thiahexane was synthesized by the following reactions

$$\mathrm{2HOCH_2CH_2Cl + (CH_3)_2SO_4 \xrightarrow[120\,^\circ C,\ 5\,h]{CaCO_3} 2CH_3OCH_2CH_2Cl + H_2SO_4}$$

and

$$\mathrm{CH_3OCH_2CH_2Cl + CH_3SNa\ (aq) \xrightarrow[60\,^\circ C,\ 30\,h]{NaOH} CH_3OCH_2CH_2SCH_3 + NaCl.}$$

After the organic layer was dried over anhydrous sodium sulfate, 2-oxa-5-thiahexane was obtained by the distillation (bp 134—135 °C).

The Raman and infrared spectra were measured for the gaseous, liquid, glassy, and crystalline states by the methods reported previously.[1,2)] The glassy state for the Raman measurements was obtained by putting into liquid nitrogen the sample enclosed in an ampoule and cooling it rapidly, and that for the infrared measurements by depositing the sample onto a cooled window of KBr or KRS-5.

Normal Coordinate Treatment

Normal coordinate treatment was carried out with a computer program NCTB2[10)] and a HITAC 8700/8800 computer system at the Computer Center of the University of Tokyo. The data of 2,5-dioxahexane and 2,5-dithiahexane were included in the least-squares refinement of the force constants of the unbranched ethers and sulfides.[1,2)]

For 2-oxa-5-thiahexane, the force constants were transferred from the unbranched ethers and sulfides[1,2)] except those for the OCH_2CH_2S part. The force constants for this part were initially transferred from the OCH_2CH_2O part and the stable forms of the rotational isomers were determined. The nine important force constants, the CC stretching and methylene-methylene interactions, were subsequently refined by the least-squares method from 56 Raman and infrared frequencies.

Detailed results of the calculations and the force constants are reported in a separate paper.[10)]

Results

Figures 1—10 show the Raman and infrared spectra obtained. The observed frequencies and the vibrational assignments based on the calculated potential-energy distributions are listed in Tables 1—3. The observed spectra were analyzed with reference to the results of the normal coordinate treatment.

In the following subsections, the rotational isomerism

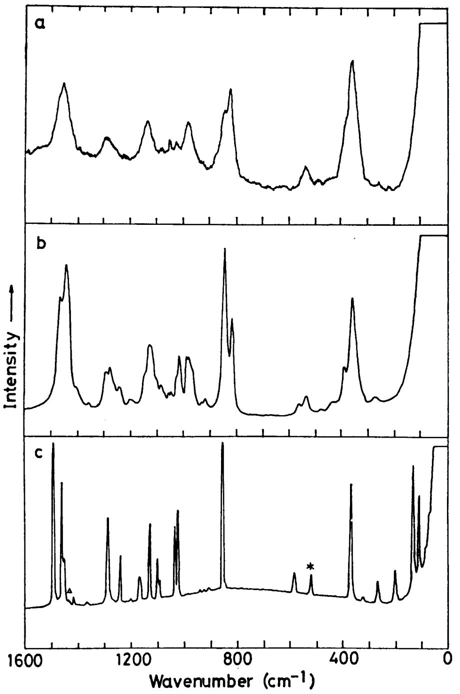

Fig. 1. Raman spectra of 2,5-dioxahexane.
a: Gas (60 °C), b: liquid (room temperature), c: crystal (liquid nitrogen temperature).
Following symbols are used in Figs. 1—10.
*: Emission line of Ar^+, □: librational infrared band of H_2O, × : impurity, △: origin unknown.

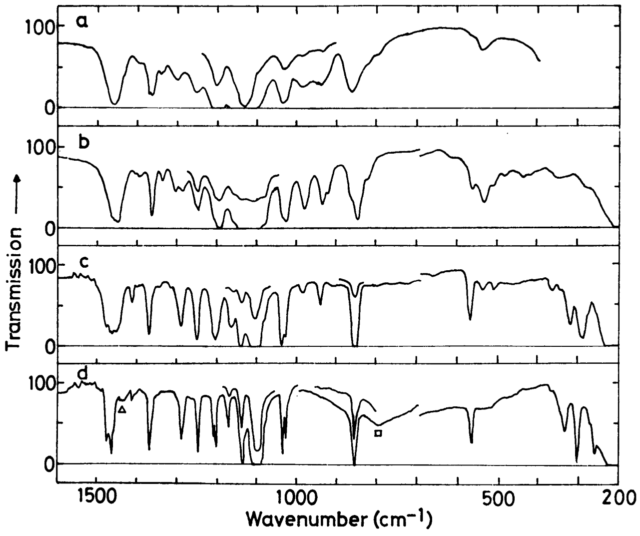

Fig. 2. Infrared spectra of 2,5-dioxahexane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.
The symbols are explained in the caption of Fig. 1.

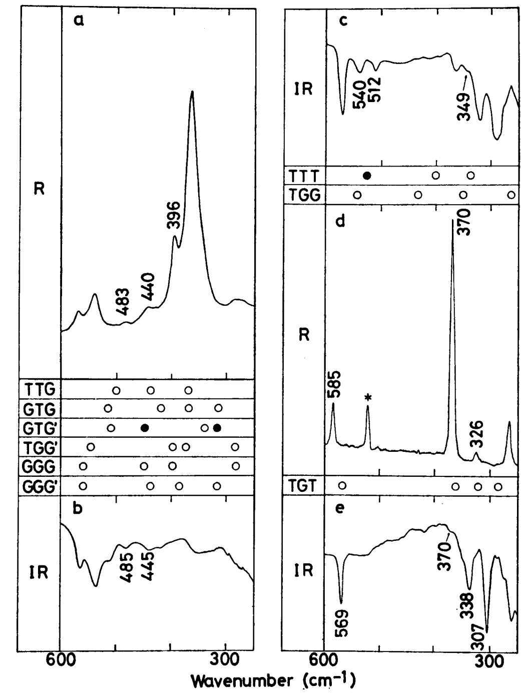

Fig. 3. Comparison of the observed and calculated frequencies of 2,5-dioxahexane in the 600—250 cm^{-1} region.
a: Liquid (R), b: liquid (IR), c: glass (IR), d: crystal (R), e: crystal (IR).
The symbol is explained in the caption of Fig. 1. For the forms which have the center of symmetry, the open and filled circles denote the Raman and infrared active vibrations, respectively.

of the individual molecules is described.

2,5-Dioxahexane $CH_3OCH_2CH_2OCH_3$. Since this molecule has two C–O axes and one C–C axis associated with the rotational isomerism, there are ten possible rotational isomers as given in Table 1 of Part I of this series.[2] Of these, the GG'G form is rejected, because the distance between the two terminal methyl groups is too short for this form to be stable. However, the TGG' and GGG' forms are not simply ruled out, since the steric hindrance in the GG' sequence of the OC–C–OC part is expected to be smaller than that in the former case. The observed and calculated frequencies in the 600—250 cm^{-1} region are compared in Fig. 3.

A comparison between the observed spectra and the calculated frequencies indicates that the TGT form exists in the crystalline state. It should be noted that some of the low-frequency vibrations give frequencies depending to some extent on the state and the spectroscopic measurement. Namely, the infrared bands at 338 and 307 cm^{-1} in the crystalline state correspond to the infrared bands at 325 and 295 cm^{-1}, respectively, in the glassy state and the Raman bands at 585 and 326 cm^{-1} in the crystalline state correspond to the infrared bands at 569 and 338 cm^{-1}, respectively.

The infrared spectrum in the glassy state shows that the TGT, TTT, and TGG forms coexist in this state. The glassy state for Raman measurements could not be obtained, since the liquid sample enclosed in an ampoule cell turns quickly into crystal even when it is put into liquid nitrogen for rapid cooling. In the glassy-state infrared spectrum, many bands appear in addition to the bands which have been assigned to the TGT form. Of these, the infrared band at 512 cm^{-1} is also observed in the infrared spectrum of the liquid state, but not observed in the Raman spectrum of this state. On the other hand, the Raman band observed at 396 cm^{-1} in the liquid state is missing in the infrared spectrum of this state. These bands are reasonably assigned to the

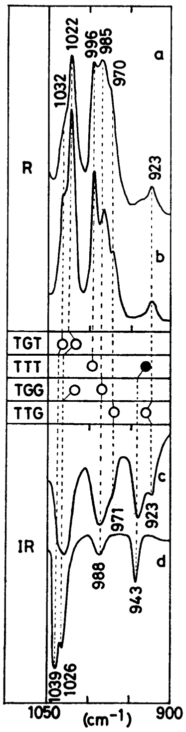

Fig. 4. Liquid-state Raman spectra at room and lower temperatures and liquid- and glassy-state infrared spectra of 2,5-dioxahexane in the 1050—900 cm^{-1} region.
a: Liquid (R, room temperature), b: liquid (R, −60°C), c: liquid (IR, room temperature), d: glass (IR, near liquid nitrogen temperature).
For the TTT form, the open and filled circles denote the Raman and infrared active vibrations, respectively.

TTT form which has the center of symmetry. Other additional frequencies such as 540 and 349 cm^{-1} are well explained by the calculated frequencies of the TGG form.

In the liquid state, the observed spectra are explained by the coexistence of the TGT, TTT, TGG, and TTG forms. The Raman bands at 483 and 440 cm^{-1} and the corresponding infrared bands at 485 and 445 cm^{-1} appear in the liquid state. These frequencies agree well with the calculated frequencies of the TTG form. The existence of other forms is not proved, since their frequencies and the Raman and infrared activities are not consistent between the calculated results and the spectral observations.

The liquid-state Raman spectra at room and lower temperatures and the liquid- and glassy-state infrared spectra in the 1050—900 cm^{-1} region are shown in Fig. 4. These spectra also prove the coexistence of the TGT, TTT, and TGG forms in the glassy state and of the TGT, TTT, TGG, and TTG forms in the liquid state. The Raman bands at 1032 and 1022 cm^{-1} and the infrared bands at 1039 and 1026 cm^{-1} in the glassy state are assigned to the TGT form, the Raman band at 996 cm^{-1} and the infrared band at 943 cm^{-1} in the glassy state to the TTT form, the Raman band at 985 cm^{-1} and the infrared band at 988 cm^{-1} to the TGG form, and the Raman bands at 970 and 923 cm^{-1} and the additional infrared bands at 971 and 923 cm^{-1} in the liquid state to the TTG form. The temperature dependence of the liquid-state Raman spectra and the non-existence of the TTG form in the glassy state near the liquid nitrogen temperature indicate that the rotational isomers become less stable in the order of the TGT, TTT, TGG, and TTG forms.

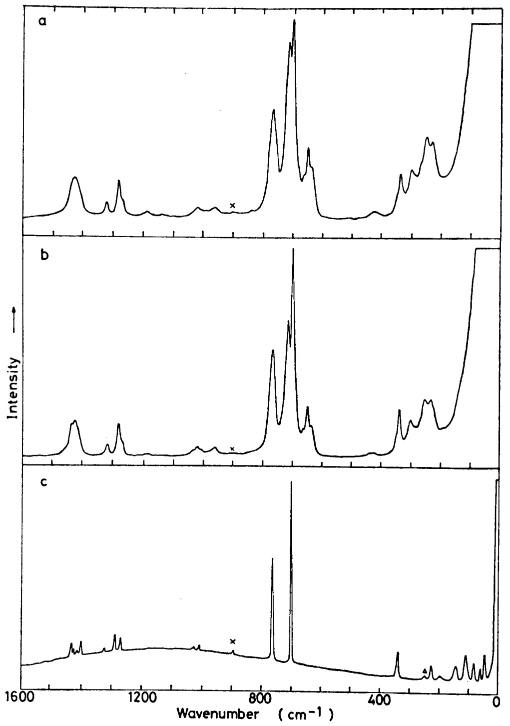

Fig. 5. Raman spectra of 2,5-dithiahexane.
a: Liquid (80 °C), b: liquid (room temperature), c: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

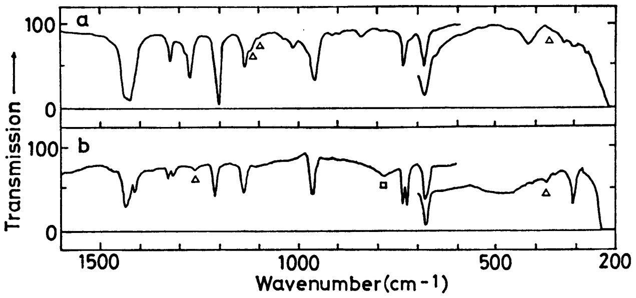

Fig. 6. Infrared spectra of 2,5-dithiahexane.
a: Liquid (room temperature), b: crystal.
The symbols are explained in the caption of Fig. 1.

In the gaseous state, the spectra have essentially the same number of bands as in the liquid state (Figs. 1 and 2). However, in contrast with the liquid-state spectra, the Raman intensity of the 822 cm^{-1} band is stronger than that of the 848 cm^{-1} band in the gaseous state. The infrared intensity of the 868 cm^{-1} band, which is observed as a shoulder of the 852 cm^{-1} band in the liquid state, increases in the gaseous state. These spectral changes are related to the polarity of the molecules as will be mentioned later. The gaseous-state spectra are explained by the coexistence of the TGT,

TABLE 1. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 2,5-DIOXAHEXANE

Observed frequency (cm^{-1})a)							
Gas		Liquid		Glass	Crystal		Assignmentb)
R	IR	R	IR	IR	R	IR	
			1490 VW, sh	1485 W, sh	1492 VS		CH_2 scis
		1470 M, b	1479 W, sh	1478 M	1472 VW	1475 M	CH_2 scis
			1468 M, sh	1468 M		1464 S	CH_3 ip-d-deform
1460 M, vb	1460 M, vb		1460 M, sh	1462 M	1461 S		CH_3 ip-d-deform
			1459 M	1459 M, sh		1458 M, sh	CH_3 s-deform
		1450 VS, b		1457 M	1453 W, sh		CH_3 s-deform
			1451 M, sh	1451 M, sh		1450 VW, sh	CH_3 op-d-deform
			1439 W, sh	1440 W, sh	1438 VW	1435 VW	Origin unknown
	1396 VW, b	1410 VW, sh	1407 VW	1415 W	1417 VW	1411 VW	CH_2 wag (**TGT**, TTT)
		1395 VW, sh	1393 VW				CH_2 wag (TGG, TTG)
	1372 W						CH_2 wag (**TGG**)
	1365 W	1365 VW	1365 M	1370 M	1370 VW	1366 S	CH_2 wag (**TGT**)
	1340 VW		1338 VW	1347 VW			CH_2 wag (**TTT**, TTG)
1309 W		1301 W	1306 W	1313 VW			CH_2 twist (**TGG**, TTG)
1285 W	1300 W, b	1285 W	1286 W	1290 M	1288 M	1286 M	CH_2 twist (**TGT**)
1270 VW, sh		1270 VW, sh					CH_2 twist (TTT, TTG)
1255 VW, sh	1256 W	1250 VW	1256 W, sh				CH_2 twist (**TGG**)
			1247 M	1250 S	1244 W	1247 S	CH_2 twist (**TGT**)
	1204 M	1208 VW	1210 S, sh	1204 S	1202 VW	1208 M 1202 S	CH_3 ip-rock (**TGT**, TTT, TGG, TTG)
	1192 W, sh	1195 VW, sh	1195 VS				CH_3 ip-rock (**TGG**)
1160 VW, sh	1155 W, sh	1155 VW, sh	1160 S, sh	1164 M	1171 W	1174 W	CH_3 op-rock (**TGT**, TTT, TGG, TTG)
						1171 W	CH_3 op-rock (**TGT**, TTT, TGG, TTG)
1145 W	1142 VS, sh	1138 W	1140 VS, sh	1140 VS			CC stretch (**TTG**, TTT)
1125 VW, sh	1132 VS	1131 W	1130 VS, sh		1131 M	1137 S	CC stretch (**TGT**, TGG)
	1118 VS, sh		1122 VS, sh	1122 W, sh			CO stretch (**TTT**)
	1108 M, sh	1108 VW, sh	1106 VS	1106 VS			CH_2 rock (**TGG**, TTG)
	1095 M, sh	1092 VW	1092 S, sh		1102 W 1095 VW	1100 VS	CO stretch (**TGT**)
	1080 W, sh	1078 VW, sh	1080 M, sh	1080 W, sh		1080 W	CH_2 rock (**TGT**, TTT), CO stretch (TTG)
		1063 VW					CO stretch (**TTT**)
1058 VW	1038 M, b	1053 VW	1055 VW, sh				CO stretch (TGG, TTG)
1035 VW		1032 VW, sh	1037 M, sh	1039 S	1036 M	1037 M	CO stretch (**TGT**)
1020 VW		1022 W	1028 S	1026 M	1026 M	1028 M	CO stretch (**TGT**, **TGG**)
990 M, b	990 W, b	996 W					CO stretch (**TTT**)
		985 W	985 M	988 VW			CO stretch (**TGG**)
		970 W, sh	971 W, sh				CO stretch (**TTG**)
	940 W		938 M	943 VW			CO stretch (**TTT**)
		936 VW					(365 cm^{-1}+ 568 cm^{-1})
		923 VW	923 W				CO stretch (**TTG**)
	868 M		868 M, sh				CO stretch (**TGG**)
848 M	852 W, sh	848 VS	852 S	858 VS	857 VS	858 VS	CO stretch (**TGT**), CH_2 rock (**TGT**, TGG)

Table 1. (Continued)

Observed frequency (cm^{-1})[a]							
Gas		Liquid		Glass	Crystal		Assignment[b]
R	IR	R	IR	IR	R	IR	
822 M	823 W, sh	822 W	823 W	822 VW			CH$_2$ rock (**TTG**, TTT)
565 VW, sh		568 VW	568 VW	571 VW	585 VW	569 VW	OCC deform (**TGT**)
540 VW	540 VW, b	540 W	539 VW	540 VW			OCC deform (**TGG**)
			513 VW	512 VW			COC bend (**TTT**)
490 VW		483 VW	485 VW				COC bend (**TTG**)
451 VW		440 VW	445 VW				OCC deform (**TTG**)
425 VW, sh		420 VW, sh	420 VW				COC bend (**TGG**)
390 M, sh		396 W					OCC deform (**TTT**)
365 VS		365 S	360 VW	368 VW	370 M	370 VW	COC bend (**TGT**, TTG)
		352 W, sh	352 VW, sh	349 VW			COC bend (**TGG**)
		326 VW, sh		325 VW	326 VW	338 VW	COC bend (**TGT**)
		280 VW, b		295 VW		307 VW	OCC deform (**TGT**)
				275 VW, sh			OCC deform (**TGG**)
					267 VW	262 VW	Torsions (**TGT**) and lattice vibrations
					205 W		
					136 S		
					115 S		
					90 VW		
					76 VW		

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. 11.

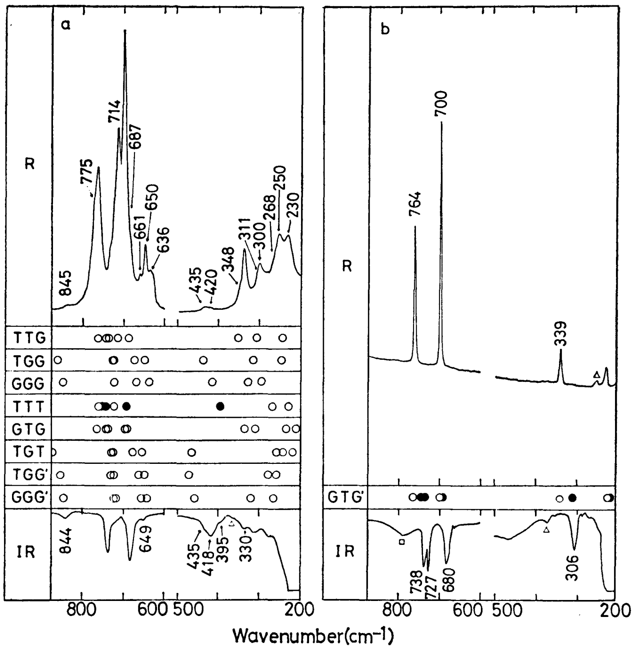

Fig. 7. Comparison of the observed and calculated frequencies of 2,5-dithiahexane in the 875—200 cm^{-1} region.
a: Liquid, b: crystal.
The symbols are explained in the caption of Fig. 1. For the forms which have the center of symmetry, the open and filled circles denote the Raman and infrared active vibrations, respectively.

TTT, TGG, and TTG forms similar to the liquid state.

2,5-Dithiahexane $CH_3SCH_2CH_2SCH_3$. This molecule has ten possible rotational isomers like the case of 2,5-dioxahexane. Of these, the GG'G form is rejected because of the reason stated for 2,5-dioxahexane. The observed and calculated frequencies in the 900—200 cm^{-1} region are shown in Fig. 7.

In the crystalline state, the Raman and infrared spectra are quite different from each other and the mutual exclusion rule holds as shown in Fig. 7. The TTT and GTG' forms are the possible candidates, since they possess the center of symmetry. Figure 7 shows that the calculated frequencies of the GTG' form are in good agreement with the observed frequencies of the crystalline state. The Raman and infrared activities expected for each vibration of this molecular form are also consistent with the spectral observations.

In the liquid state, the observed spectra are explained by the coexistence of the GTG', TTT, TTG, TGG, and GGG forms. Many bands appear in this state in addition to those existing in the crystalline state. As seen from Fig. 7, the Raman band at 268 cm^{-1} and the infrared band at 395 cm^{-1} are assigned to the TTT form, the Raman bands at 714, 348, and 300 cm^{-1} to the TTG form, the Raman bands at 650, 435 and 250 cm^{-1} and the infrared band at 435 cm^{-1} to the TGG form, and the Raman bands at 636 and 420 cm^{-1} and the infrared bands at 418 and 330 cm^{-1} to the GGG form.

The existence of the GTG form is uncertain, since all of its calculated frequencies are almost coincident

TABLE 2. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 2,5-DITHIAHEXANE

Observed frequency (cm^{-1})[a]				
Liquid		Crystal		Assignment[b]
R	IR	R	IR	
1439 VW, sh	1436 VS, sh		1437 VS	CH_3 ip-d-deform
		1436 VW, sh		CH_3 ip-d-deform
			1432 VS, sh	CH_3 op-d-deform
1428 VW	1432 VS	1432 VW 1425 VW		CH_3 op-d-deform
	1425 VS		1424 M, sh 1412 M	CH_2 scis
1415 VW, sh		1415 VW 1402 VW		CH_2 scis
		1325 VW		CH_3 s-deform
1322 VW	1323 W		1326 VW 1316 VW	CH_3 s-deform, CH_2 wag (TGG, GGG)
1284 VW		1290 VW		CH_2 twist (**GTG′**, TTT)
	1286 W, sh			CH_2 twist (**TTG**)
1270 VW, sh		1270 VW		CH_2 wag (**GTG′**, TTT)
	1272 S			CH_2 wag (TTG), CH_2 twist (TGG, GGG)
			1262 VW	Origin unknown
	1206 VS		1210 S	CH_2 wag (**GTG′**, TTT)
1209 VW				CH_2 wag (**GTG**)
1190 VW				CH_2 wag (**TTG**)
1181 VW	1181 VW, sh			CH_2 wag (TGG, GGG)
	1134 M		1136 M	CH_2 twist (**GTG′**, TTT)
1135 VW				CH_2 twist (TTG, TGG, GGG)
	1120 W, sh			Origin unknown
	1096 VW, sh			Origin unknown
1045 VW, sh				CC stretch (**TTT**)
1036 VW, sh	1034 VW, sh			CC stretch (**TTG**)
1024 VW		1026 VW 1010 VW		CC stretch (**GTG′**)
	1024 VW, sh			CC stretch (**TGG**)
1010 VW	1010 W			CC stretch (**GGG**)
976 VW, sh	976 W, sh			CH_2 rock (TTG, TTT), CH_3 ip-rock (TGG, GGG)
970 VW, sh			968 S	CH_3 ip-rock (**GTG′**, TTG, TTT)
	960 S	965 VW		CH_3 ip-rock (**GTG′**, TTG, TGG, GGG, TTT)
960 VW			964 S	CH_3 op-rock (**GTG′**, TTG, TGG, GGG, TTT)
		958 VW		CH_3 op-rock (**GTG′**, TTG, TGG, GGG, TTT)
	915 VW			CH_2 rock (**GGG**)
845 VW	844 VW			CH_2 rock (TGG, GGG)
775 VW, sh				CS stretch (**TTG**)
765 M		764 M, sh		CS stretch (**GTG′**, TTT), CH_2 rock (TTT)
	736 M		738 S	CS stretch (**GTG′**, TTT), CH_2 rock (TTG)
735 W, sh				CS stretch (**TTG**)
	727 VW, sh		727 S	CH_2 rock (**GTG′**)
725 M, sh				CS stretch (TGG, GGG, TTT)
714 S				CS stretch (**TTG**)
700 VS		700 VS		CS stretch (**GTG′**)
687 W, sh	684 M			CS stretch (**TTG**)
			680 S	CS stretch (**GTG′**, TTT)
661 VW				CS stretch (TGG, GGG)
650 W	649 VW			CS stretch (**TGG**)
636 VW				CS stretch (**GGG**)
435 VW	435 VW			SCC deform (**TGG**)
420 VW	418 VW			SCC deform (**GGG**)
	395 VW, sh			CSC bend (**TTT**)
	372 VW, sh		372 VW	Origin unknown
348 VW, sh				CSC bend (**TTG**)

Table 2. (Continued)

Observed frequency (cm^{-1})$^{a)}$				Assignment$^{b)}$
Liquid		Crystal		
R	IR	R	IR	
339 VW		339 VW		CSC bend (**GTG′**)
	330 VW			CSC bend (**GGG**)
311 VW, sh	309 VW			CSC bend (**TGG**)
			306 VW	CSC bend (**GTG′**)
300 VW				CSC bend (**TTG**)
295 VW, sh	278 VW			CSC bend (**GGG**)
268 VW, sh				SCC deform (**TTT**)
250 W				CSC bend (**TGG**)
		250 VW		Origin unknown
245 VW, sh				SCC deform (**TTG**)
230 W		228 W		SCC deform (**GTG′**), CSC bend (TTT)
		199 VW		
		145 VW		Torsions (**GTG′**) and lattice vibrations
		112 VW		
		105 VW, sh		
		84 VW		
		61 VW		
		46 VW		

a), b) See a) and b), respectively, of Table 1.

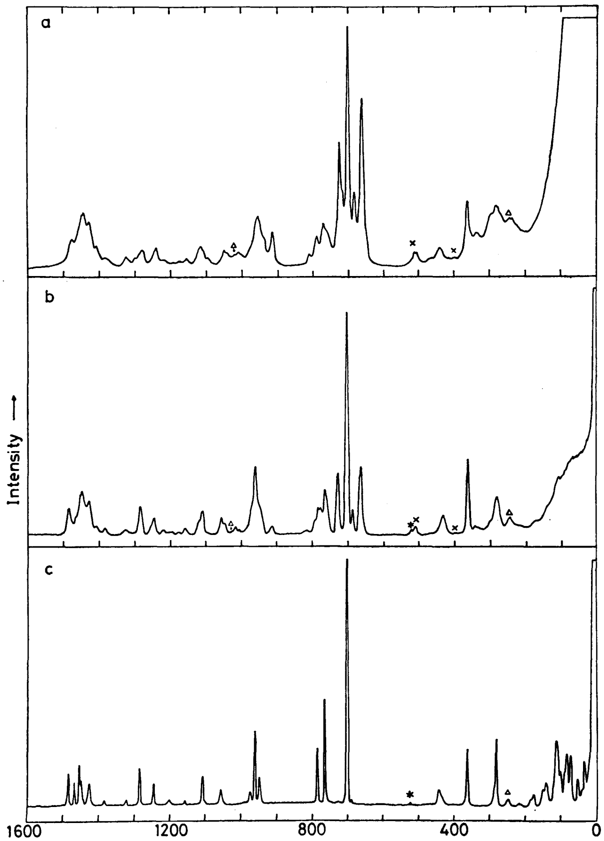

Fig. 8. Raman spectra of 2-oxa-5-thiahexane.
a: Liquid (room temperature), b: glass (liquid nitrogen temperature), c: crystal (liquid nitrogen temperature). The symbols are explained in the caption of Fig. 1.

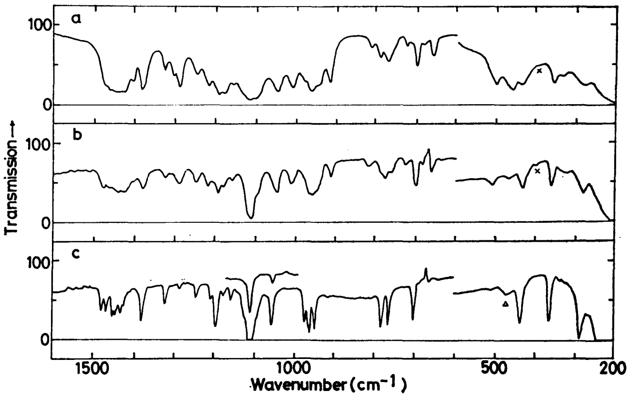

Fig. 9. Infrared spectra of 2-oxa-5-thiahexane.
a: Liquid (room temperature), b: glass, c: crystal. The symbols are explained in the caption of Fig. 1.

with those of the GTG′ form. However, the existence of the GTG form may not be ruled out, since the spacial steric repulsions in this form are not much larger than those in the GTG′ form. It is not probable that the TGT, TGG′, and GGG′ forms exist in the liquid state, since no bands are observed around their characteristic frequencies in the region 460—475 cm^{-1}.

As temperature is lowered in the liquid state, the Raman intensities of the bands assigned to the GTG′ form increase relative to those of other bands (Fig. 5). Thus the GTG′ form is found to be the most stable in the liquid state.

2-Oxa-5-thiahexane $CH_3OCH_2CH_2SCH_3$. This molecule has fourteen possible rotational isomers as listed in Table 1 of Part I of this series.[2] The existence of the GG′G form can be again rejected because of the very large steric hindrance. Figure 10 shows the observed and calculated frequencies in the 1000—200 cm^{-1} region.

The spectra in the crystalline state show that the

Table 3. Observed frequencies and vibrational assignments of 2-oxa-5-thiahexane

Observed frequency (cm^{-1})[a]						Assignment[b]
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
1480 VW	1480 S, sh	1484 W	1477 W	1484 VW	1480 W	CH_2 scis
1465 VW, sh	1465 S, sh	1465 VW, sh	1465 VW	1466 VW	1467 W	CH_3 ip-d-deform
1455 W, sh	1460 VS	1460 VW, sh	1460 W	1453 VW	1453 W	CH_3 s-deform
	1455 VS, sh	1449 W	1449 W, sh	1450 VW, sh	1449 W	CH_3 op-d-deform
1449 M	1449 VS	1444 W, sh	1444 W	1444 VW, sh	1444 VW, sh	CH_3 ip-d-deform
1431 M	1432 VS	1427 VW	1435 W	1431 VW, sh	1432 W	CH_3 op-d-deform
	1420 S, sh		1420 W, sh	1426 VW	1424 VW	CH_2 scis
1410 W	1405 S	1405 VW, sh	1405 VW, sh			CH_2 wag (TGG, TGT)
1390 VW	1382 S	1380 W	1380 W	1383 VW	1381 M	CH_2 wag (**TTG**, TTT)
1375 VW, sh	1373 M, sh		1373 VW, sh			CH_2 wag (GTG or GTG′)
1327 VW	1325 M	1324 VW	1324 W	1322 VW	1321 W	CH_3 s-deform (**TTG**, TGG, TGT, TTT)
1305 VW	1304 M	1301 VW	1307 VW			CH_2 twist (GTG or GTG′)
1290 VW, sh	1290 S	1290 VW, sh	1290 W			CH_2 twist (TGG, TGT)
1283 VW	1281 W, sh	1283 VW	1283 W, sh	1284 W	1286 VW	CH_2 twist (**TTG**, TTT)
1255 VW, sh	1247 M	1249 VW	1246 W			CH_2 wag (**TGG**)
1245 VW				1245 VW	1246 VW	CH_2 wag (**TTG**, TGT, TTT)
1215 VW, sh	1218 S	1218 VW	1218 M	1208 VW, sh	1209 VW	CH_2 twist (**TTG**, TTT), CH_3 ip-rock (TGG, TGT)
1190 VW, sh	1196 VS	1195 VW	1193 M	1198 VW	1196 M	CH_3 ip-rock (**TTG**, TTT)
1180 VW	1180 VS	1176 VW	1178 W			CH_2 twist (TGG, TGT)
1158 VW	1156 VS	1158 VW	1156 W	1160 VW	1158 W	CH_3 op-rock (**TTG**, TTT)
1130 VW, sh	1135 VS		1135 W, sh			CH_3 op-rock (TGG, TGT)
1120 VW	1122 VS	1120 VW, sh	1120 S, sh			CO stretch (TGG, TGT, TTT)
1110 VW, sh	1113 VS	1110 VW	1110 VS	1107 VW	1111 VS	CO stretch (**TTG**)
1100 VW, sh	1098 S	1096 VW, sh	1092 M, sh			CO stretch (GTG or GTG′)
1055 VW	1055 M, sh	1055 VW	1055 W, sh	1056 VW	1055 M	CC stretch (**TTG**, TGT, TTT)
1045 VW, sh	1046 S	1045 VW	1047 M			CC stretch (**TGG**)
1028 VW, sh		1028 VW, sh				Origin unknown
1015 VW	1012 S	1015 VW	1013 M			CH_2 rock (**TGT**)
1005 VW, sh	1000 M, sh	1005 VW	1005 M, sh			CH_2 rock (**TGG**)
980 VW, sh	980 S, sh	980 VW, sh	980 M, sh	974 VW	973 M	CH_2 rock (**TTG**, TTT)
968 VW, sh	968 S	968 VW, sh	970 M, sh			CH_3 ip-rock (TGT), CO stretch (TTT)
961 VW	964 S	959 W	964 S	961 M	962 M, sh	CO stretch (**TTG**, TGT), CH_3 ip-rock (TGG, TTT)
	959 S		956 S		960 M	CH_3 ip-rock (**TTG**, TGT, TTT), CO strech (TGG)
945 VW, sh	945 S	945 VW, sh	945 M, sh	948 VW	948 M	CH_3 op-rock (**TTG**, TGG)
920 W	918 S	914 VW	915 W			CO stretch (GTG or GTG′)
815 VW	814 VW	818 VW	816 VW			CH_2 rock (TGT, TTT)
793 VW	792 W	793 VW, sh	792 W, sh	785 W	783 M	CH_2 rock (**TTG**, TGG)
778 VW, sh	773 W	778 VW	778 W			CS stretch (GTG or GTG′)
765 VW, sh	760 VW, sh	762 VW	760 W	764 M	764 M	CS stretch (**TTG**)
758 VW, sh		758 VW, sh				CS stretch (**TTT**)
729 S	727 VW	728 W	726 VW			CS stretch (TGG, TGT)
720 VW	720 VW, sh	720 VW, sh	719 VW, sh			CS stretch (**TTT**)
703 VS	702 W	702 VS	700 W	701 VS	701 M	CS stretch (**TTG**)
685 W	682 VW	687 VW	683 VW			CS stretch (**TGT**)
664 S	661 W	665 W	660 VW			CS stretch (**TGG**)
520 VW	520 VW, sh	520 VW	519 VW, sh			OCC deform (**TGT**)
509 VW	503 VW	509 VW	509 VW			OCC deform (**TGG**)
468 VW	464 VW	470 VW	465 VW			COC bend (**TTT**)
441 VW	438 VW	435 VW	433 VW	441 VW	436 VW	COC bend (**TTG**)
363 W	359 VW	364 W	360 VW	363 W	363 VW	OCC deform (**TTG**)
340 VW, sh	340 VW	340 VW, sh	340 VW, sh			OCC deform (**TTT**)
335 VW	335 VW, sh	335 VW	335 VW			COC bend (TGG, TGT), CSC bend (TGG)

Table 3. (Continued)

Observed frequency (cm^{-1})[a]						Assignment[b]
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
303 VW	300 VW, sh	303 VW, sh	300 VW, sh			CSC bend (GTG or GTG′)
290 VW, sh						CSC bend (**TGT**)
281 W	285 VW	285 VW	280 VW	281 W	285 VW	CSC bend (**TTG**)
265 VW, sh						CSC bend (**TTT**)
243 W		245 VW		248 VW		Origin unknown
228 VW, sh						CH_3 torsion (TGG, TGT, TTT)
				218 VW		
				184 VW, sh		
				176 VW		
				152 VW, sh		
				144 VW		
				113 W		SCC deform (**TTG**), torsions (**TTG**) and lattice vibrations
				103 VW, sh		
				90 VW, sh		
				85 W		
				73 W		
				54 VW		
				33 VW		

a), b) See a) and b), respectively, of Table 1.

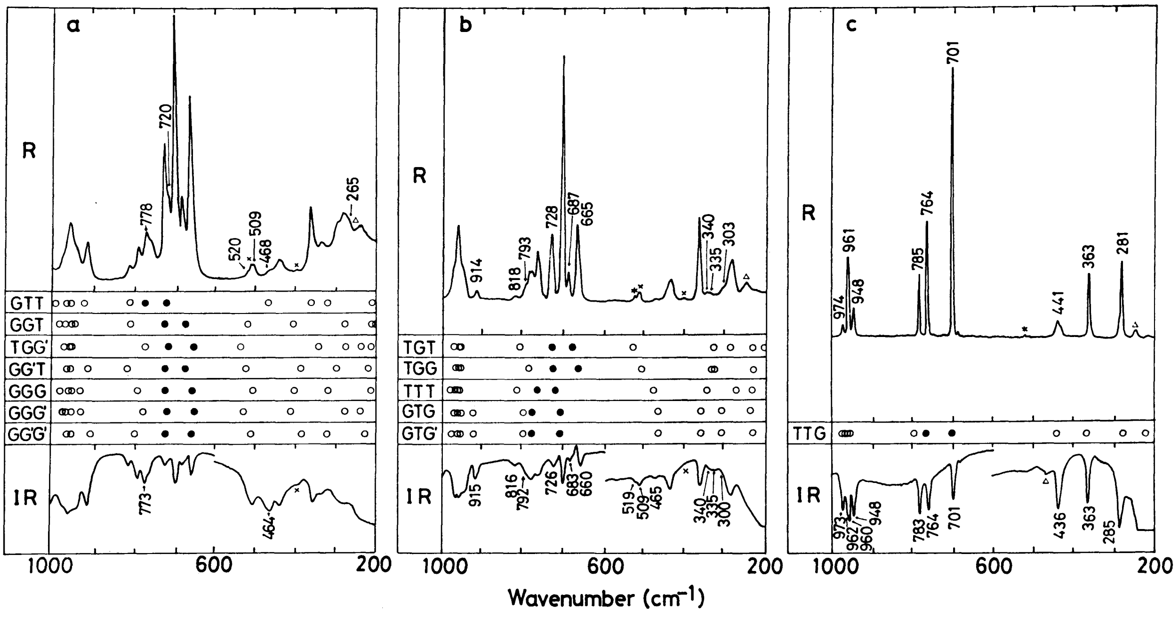

Fig. 10. Comparison of the observed and calculated frequencies of 2-oxa-5-thiahexane in the 1000—200 cm^{-1} region.
a: Liquid, b: glass, c: crystal.
The symbols are explained in the caption of Fig. 1. The filled circles denote the CS stretching vibrations.

TTG form exists. In the liquid state, the spectra have essentially the same number of bands as in the glassy state. The glassy- and liquid-state spectra are explained by the coexistence of the TTG, TTT, TGT, and TGG forms. One or both of the GTG and GTG′ forms also exist in these states. In the liquid and glassy states, many bands appear in addition to those existing in the crystalline state. Of these bands observed in the liquid state, the Raman bands at 720, 468, and 265 cm^{-1} and the infrared band at 464 cm^{-1} are assigned to the TTT form, the Raman bands at 687 and 520 cm^{-1} and the infrared bands at 683 and 519 cm^{-1} to the TGT form, the Raman bands at 665 and 509 cm^{-1} and the infrared bands at 660 and 509 cm^{-1} to the TGG form, and the Raman bands at 914 and 303 cm^{-1} and the infrared bands at 915 and 300 cm^{-1} to one or both of the GTG and GTG′ forms.

Each of the GGT, GGG, GG′T, GGG′, and GG′G′ forms has a characteristic frequency in the region 385—410 cm^{-1}. The weak Raman band at 400 cm^{-1} and the

TABLE 4. ROTATIONAL ISOMERISM OF THE MOLECULES TREATED IN THIS WORK

	$CH_3OCH_2CH_2OCH_3$	$CH_3SCH_2CH_2SCH_3$	$CH_3OCH_2CH_2SCH_3$
Gas	**TGT TTT TGG TTG**	—[a]	—[a]
Liquid	**TGT TTT TGG TTG**	**GTG′ TTG TGG GGG TTT** GTG	**TTG TGT TGG TTT** GTG or GTG′ (GTT) (GGT) (TGG′) (GG′T) (GGG) (GGG′) (GG′G′)
Glass	**TGT TTT TGG**	—[a]	**TTG TGT TGG TTT** GTG or GTG′ (GTT) (GGT) (TGG′) (GG′T) (GGG) (GGG′) (GG′G′)
Crystal	**TGT**	**GTG′**	**TTG**

The isomers given by boldface are confirmed to exist. The existence of the isomers in parentheses is uncertain. For more details, see text. a) Spectral measurements were not made.

weak infrared band at 395 cm^{-1} are observed in the liquid-state spectra. However, these bands are attributed at least in part, to an impurity, because the Raman intensity of this band in the liquid state of the distillate with bp 135—136 °C is much stronger than that of the distillate with bp 134—135 °C. Since these bands are much weaker than those assigned to the TTG, TTT, TGT, TGG, and GTG or GTG′ forms, the populations of the GGT, GGG, GG′T, GGG′, and GG′G′ forms, if they exist, are much smaller than those of the former ones. The existence of the GTT and TGG′ forms is uncertain, since all of their calculated frequencies are almost coincident with those of the other forms mentioned above.

As temperature is lowered in the liquid state, the Raman intensities of the bands assigned to the TTG form increase relative to those of the bands assigned to the other forms. Accordingly, the TTG form is the most stable in the liquid state.

Rotational Isomerism. In Table 4, the rotational isomerism of the three compounds treated in this work is summerized.

The vibration spectra of 2,5-dioxahexane have been studied by several investigators.[3—5] Snyder and Zerbi[4] concluded that the TGT form exists in the crystalline state and the TGT, TTT, and other forms in the glassy and liquid states. Iwamoto[5] indicated the existence of the TGG and TTG forms in addition to that of the TGT and TTT forms in the liquid state on the basis of the comparison of the infrared spectra of pure liquid, liquid containing HgCl$_2$ and crystalline complex with HgCl$_2$. In the present work, these conclusions were further confirmed and the relative stabilities among the rotational isomers were determined.

The rotational isomerism of 2,5-dithiahexane has been discussed by Hayashi *et al.*[6] They found that the GTG′ form exists in the crystalline state and the GTG′ and GGG forms in the liquid state. The present work shows that in addition to these two forms the TTT, TTG, and TGG forms also exist in the liquid state. The isomerism of 2-oxa-5-thiahexane has first been studied in the present work.

The following results were obtained for the three compounds studied in this work in common. (1) The molecular form existing in the crystalline state is a non-extended form, in contrast with the cases of the unbranched ethers or sulfides containing one oxygen or sulfur atom which take the extended all-*trans* form.[1,2] (2) Many forms coexist in the gaseous, liquid and glassy states. (3) The form existing in the crystalline state is the most stable in the liquid state.

Discussion

In a previous paper,[2] the following results were reported for unbranched ethers containing one oxygen. (1) About the CO–CC axis, the *trans* conformation is more stable than the *gauche* conformation. (2) About the OC–CC axis, the *gauche* conformation is as stable as the *trans* conformation. (3) The repulsive force between nonbonded hydrogen atoms is one of the important factors influencing the stability of these conformations.

In the crystalline state, 2,5-dioxahexane exists in the TGT form which has the *gauche* conformation about the OC–CO axis. This form is also the most stable in the liquid state. These results are consistent with those obtained for the one-oxygen containing ethers mentioned above.

In addition to the stabilizing factor with regard to the repulsive force between the nonbonded hydrogen atoms in the TGT form, the dipole moment is suggested to be another important factor to stabilize this form in the crystalline and liquid states. For 2,5-dioxahexane, the observed frequencies for the same molecular vibrations are appreciably different between the Raman and infrared spectra in the crystalline state and between the infrared spectra in the crystalline and glassy states. The magnitudes of these frequency differences are much larger than those for the one-oxygen containing ethers.[2] These spectral observations may be due to the effect of dipole moment.

In the liquid state, as compared with the case in the gaseous state, polar molecular forms are more stabilized than non-polar forms.[12] In fact, as shown in Fig. 1, the intensities of the bands assigned to the TGT form (polar form) increase in the liquid state as compared with the gaseous state. However, the details in this point are left to be studied.

In connection with the TGT form of 2,5-dioxahexane in the crystalline state, it is important to examine the structure of polyether.[7,8] 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 crystal modification, the molecule takes the TGT conformation for the series of O–C–C–O bonds in the former polymer and the TGGT 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 TTGTTTG′T and $(TTTT)_2$ conformations for the series of O–C–C–C–O–C–C–C–O bonds. The stabilizing factors for the TGT conformation of 2,5-dioxahexane are thus found to be strongly correlated to those of the TGT conformation of poly(oxyethylene) and the TGGT conformation of poly(oxytrimethylene).

In a previous paper,[1] the following results were reported for the one-sulfur containing sulfides. (1) About the CS–CC axis, the *gauche* conformation is slightly more stable than the *trans* conformation. (2) About the SC–CC axis, the *gauche* conformation is as stable as the *trans* conformation. (3) The repulsive force between nonbonded hydrogen atoms is an important factor influencing the conformational stability.

In the crystalline state, 2,5-dithiahexane exists in the GTG′ form which has the *gauche* conformation about the two CS–CC axes. This form is also the most stable in the liquid state. These results are consistent with those obtained for the one-sulfur containing sulfides mentioned above.

The 2,5-dithiahexane molecule corresponds to the monomer unit of poly(thioethylene) $(-SCH_2CH_2-)_n$. Accordingly, the conformation of 2,5-dithiahexane in the crystalline state must be closely related to the chain conformation of poly(thioethylene). In fact, the poly(thioethylene) molecule takes the GTG′G′TG conformation for the series of S–C–C–S–C–C–S bonds according to the X-ray diffraction studies by Tadokoro *et al.*[9]

From the results for the unbranched ethers and sulfides stated above, the stable conformations of 2-oxa-5-thiahexane are expected to have the following factors. (1) About the CO–CC axis, the *trans* conformation is more stable than the *gauche* conformation. (2) About the OC–CS axis, the *gauche* conformation is as stable as the *trans* conformation. (3) About the CC–SC axis, the *gauche* conformation is slightly more stable than the *trans* conformation.

In the present study, 2-oxa-5-thiahexane was found to take the TTG form in the crystalline state. Most of the bands observed in the liquid state are explained by the existence of the four forms of TTG, TTT, TGT, and TGG, of which the TTG form is the most stable. These results are in good agreement with the above points for the stable conformations of this molecule.

In the present normal vibration calculations, 107 force constants were used for 2-oxa-5-thiahexane. However, the majority of the force constants was assumed to be the same as the corresponding force constants for the unbranched ethers and sulfides treated previously,[1,2] and only nine force constants characteristic of this molecule were determined by the least-squares method. The vibrational frequencies calculated from these force constants were indeed accurate enough to predict the rotational isomerism of this molecule.

Through the previous[1,2] and present studies on the vibration spectra and rotational isomerism of the unbranched ethers and sulfides, the following conclusions are drawn. (1) The force constants determined in these studies are satisfactorily transferable to similar molecules. (2) The conformational stabilities of the ethers and sulfides are consistently explained and it may be possible to predict stable isomers of similar molecules on the basis of the knowledge obtained in these studies. (3) The combined method of the systematic measurements of vibration spectra and the systematic normal vibration calculations is useful for the studies of the rotational isomerism of chain molecules. The measurement of Raman spectra is more important than that of infrared spectra. The former offers, without much difficulty, information on the low-frequency vibrations which are closely associated with the rotational isomerism. In addition, the temperature dependence of band intensities is more easily measured by the method of Raman spectroscopy.

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