Vibration Spectra and Rotational Isomerism of Chain Molecules. IV.[1)] Diethyl Sulfide, Ethyl Propyl Sulfide, and Butyl Methyl Sulfide

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The Raman and infrared spectra of diethyl sulfide, ethyl propyl sulfide and butyl methyl sulfide 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 sulfides 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) Many forms coexist in the liquid state and most of them persist in the glassy state even at the liquid nitrogen temperature. (3) In the liquid state, the *gauche* conformation about the S–C axis is more stable than the *trans* conformation, and the *gauche* conformation about the C–C axis directly adjoining the S–C axis is as stable as the *trans* conformation. These results confirm that the repulsive force between nonbonded hydrogen atoms is one of the important factors influencing the stability of molecualr conformations. The stable conformations of the sulfide molecules were correlated with those of polythioether chains.

In previous papers,[1–3)] we compared the Raman and infrared spectra of unbranched ethers, paraffins and ethyl methyl sulfide in the crystalline, glassy, liquid and gaseous states with the results of normal vibration calculations and determined the rotational isomers existing in each state.

In the present paper, the same method is applied to unbranched sulfide molecules. The results also show that the method is useful in the study of rotational isomerism. The stable forms of these sulfide molecules do not always correspond to those of the ethers. The factors stabilizing the isomers will be discussed.

The stable conformations of some sulfides[1,4–12)] and polythioethers[13–15)] have already been studied. The present results will be correlated with the former conclusions.

Experimental

Diethyl sulfide, ethyl propyl sulfide and butyl methyl sulfide were purchased from Tokyo Kasei Kogyo Co., Ltd. and were distilled prior to the measurements. The Raman spectra were measured for the liquid, glassy and crystalline states and the infrared spectra for the gaseous, liquid, glassy and crystalline states. The spectrometers described in the previous study[2)] are used.

The Raman spectra were recorded in the region below 1600 cm^{-1}. The spectra in the liquid state were measured at room and lower temperatures. 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 the crystalline state by cooling the sample slowly with liquid nitrogen. The crystallization of diethyl sulfide was very rapid and the Raman spectra in the glassy state could not be measured.

The infrared spectra in the gaseous state were measured with a 10 cm gas cell in the region 1600—600 cm^{-1}. For the measurements of the infrared spectra in the liquid state, 0.05 and 0.025 mm fixed cells with KBr windows were used in the region 1600—400 cm^{-1}, and a variable thickness cell with KRS-5 windows in the region 700—250 cm^{-1}. The glassy state for the infrared measurements were obtained by depositing the sample onto a cooled window of KBr or KRS-5, and the crystalline state by annealing the glass several times. For the measurements in the region 700—250 cm^{-1}, the spectrometer was flushed with dry air to get rid of water vapor absorptions.

Normal Coordinate Treatment

The normal coordinate treatment of the unbranched sulfides was carried out in a way similar to the case of the ethers.[2)] Detailed results including structural parameters, symmetry coordinates and force constants are reported in a separate paper.[16)]

A total of 70 force constants associated with the sulfide group were determined from 446 Raman and infrared frequencies of 31 forms of 11 molecular species. Table 1 shows the procedure of the least-squares refinement of the force constants.

Results

Figures 1—9 show the Raman and infrared spectra of the sulfides in the various states. The observed frequencies and the assignment based on the calculated potential-energy distributions are listed in Tables 2—4.

The observed spectra were analyzed with reference to the results of the normal coordinate treatment. The following spectral features are observed for the three sulfides studied in this work. (1) The spectra in the various states are distinctly different, especially in the 500—200 cm^{-1} region of the skeletal deformation vibrations and in the 800—600 cm^{-1} region of the C–S stretching and the methylene rocking vibrations. (2) The spectral pattern of the crystalline state is the simplest and the number of the observed bands is the smallest. (3) In the glassy state, many bands are observed in addition to those which persist in the crystalline state. (4) The liquid-state spectra have essentially the same numbers of bands as those in the glassy-state spectra. However, their relative band intensities and widths are considerably different between the two states.

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

Diethyl Sulfide. Since this molecule has two C–S axes associated with the rotational isomerism, there are four possible isomers, TT, TG, GG, and GG′, as given in Table 1 of Part I of this series.[2)] The observed and calculated frequencies in the 900—200 cm^{-1} region are compared in Fig. 3.

The spectra in the crystalline state show that only

Table 1. Procedure of the least-squares calculation

Step	$CH_3SC_2H_5$ a)	$C_2H_5SC_2H_5$ b)	$CH_3SC_3H_7$ c)	$C_2H_5SC_3H_7$ b)	$CH_3SC_4H_9$ b)	$CH_3SC_2H_4SCH_3$ d)
1	T (7) G (20)	TT (27)	TT (25)	TTT (32)	TTT (30)	
2		TG (8) GG (4)	TG (4) GT (25) GG (16)			
3				TGT (17)	GTT (9)	
4						GTG′(26)
5				GTT (5) GGT (9) GGG (7)	TGT (9) GGT (9)	TTT (3) TTG (9) TGG (7) GGG (8)
6	$CD_3SC_2H_5$ e) T (5), G (20) $CH_3SC_2D_5$ f) T (5), G (20)			$CH_3SCH_2CD_3$ e) T (7), G (20)		
7	$(\text{-}SCH_2CH_2SCH_2CH_2\text{-})_n$ g) GTG′G′TG (28)			$(\text{-}SCD_2CD_2SCD_2CD_2\text{-})_n$ g) GTG′G′TG (25)		

The least-squares calculation begins with the simplest sulfides 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 sulfides 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. The results of the following references are utilized in the least-squares calculation. a) Refs. 1, 5, and 17. b) This study. c) Refs. 8 and 12. d) Ref. 18. e) Ref. 1. f) Refs. 1 and 6. g) Ref. 13.

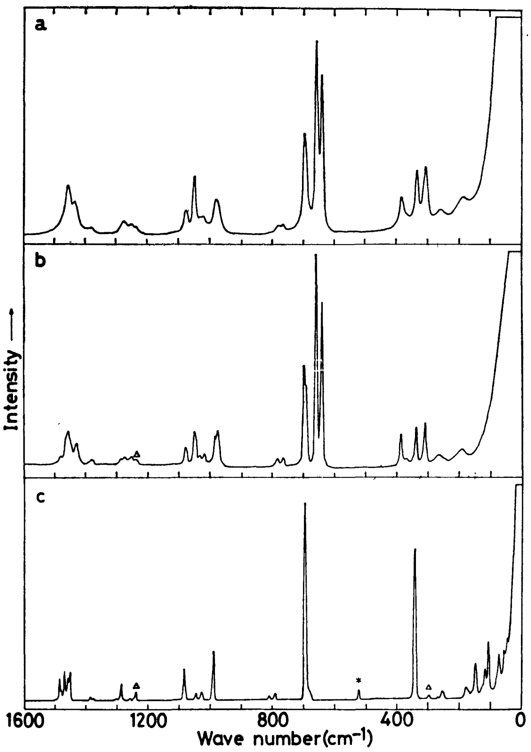

Fig. 1. Raman spectra of diethyl sulfide.
a: Liquid (room temperature), b: liquid (−100 °C), c: crystal (liquid nitrogen temperature).
Following symbols are used in Figs. 1—9.
*: Emission line of Ar⁺, □: librational infrared band of H_2O, ×: impurity, △: origin unknown.

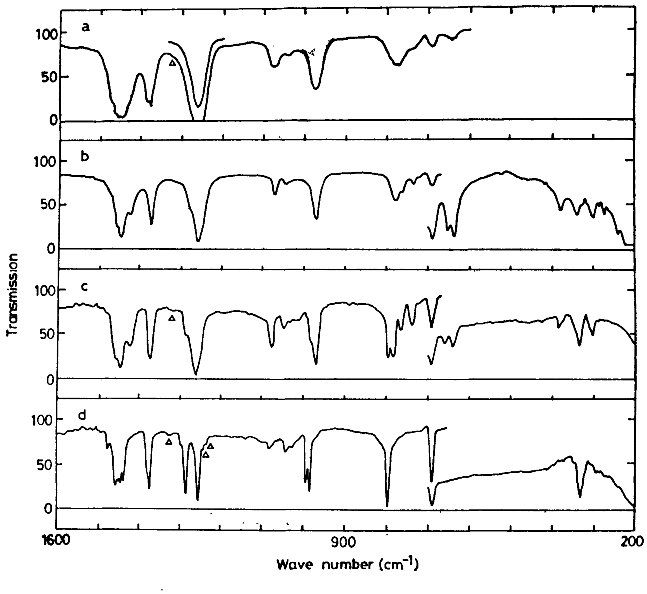

Fig. 2. Infrared spectra of diethyl sulfide.
a: Gas, b: liquid, c: glass, d: crystal.
The symbol is explained in the caption of Fig. 1.

the TT form exists. The number of the observed bands is just what is expected for one form. The frequencies of the skeletal deformation bands, 343 and 332 cm⁻¹, can only be explained by the TT form.

The glassy- and liquid-state spectra show that the TT, TG, and GG forms coexist. The temperature dependence of the liquid-state Raman spectra, combined with the results of the normal vibration calculations,

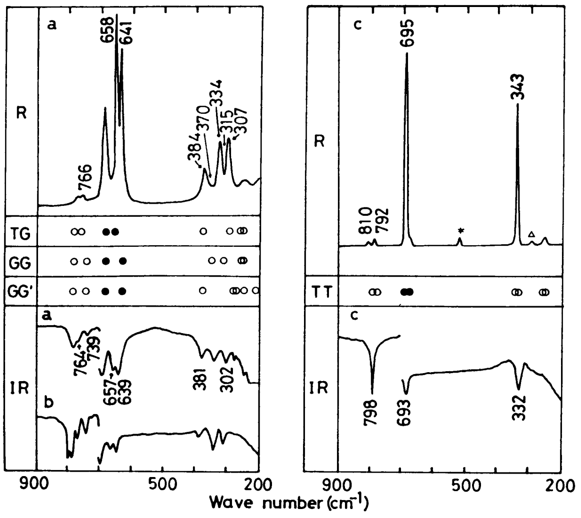

Fig. 3. Comparison of the calculated and observed frequencies of diethyl sulfide in the 900—200 cm^{-1} region.
a: Liquid, b: glass, c: crystal.
The filled circles denote the CS stretching vibrations. The symbols in the Raman spectrum of the crystalline state are explained in the caption of Fig. 1.

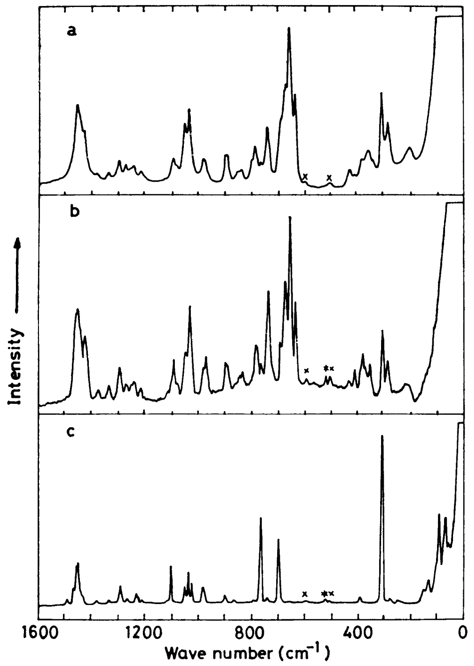

Fig. 4. Raman spectra of ethyl propyl sulfide.
a: Liquid (room temperature), b: glass (liquid nitrogen temperature), c: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

indicates that the bands at 766, 658, 384, and 307 cm^{-1} are assigned to the TG form and those at 739, 641, 370 (a shoulder of the 384 cm^{-1} band), and 315 cm^{-1} (a shoulder of the 307 cm^{-1} band) are assigned to the GG form. It should be noted that the assignment of the 739 cm^{-1} band, which has not been made clearly in previous studies, is now established.

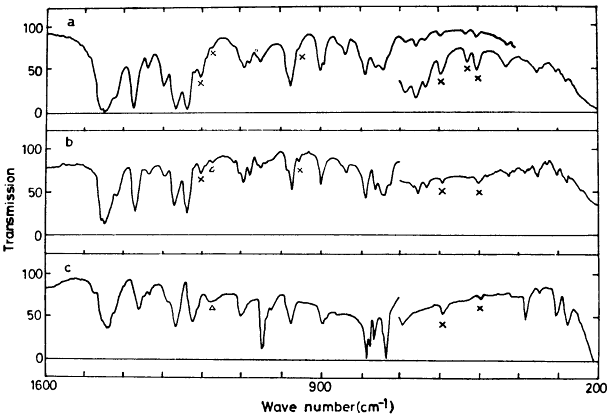

Fig. 5. Infrared spectra of ethyl propyl sulfide.
a: Liquid, b: glass, c: crystal.
The symbols are explained in the caption of Fig. 1.

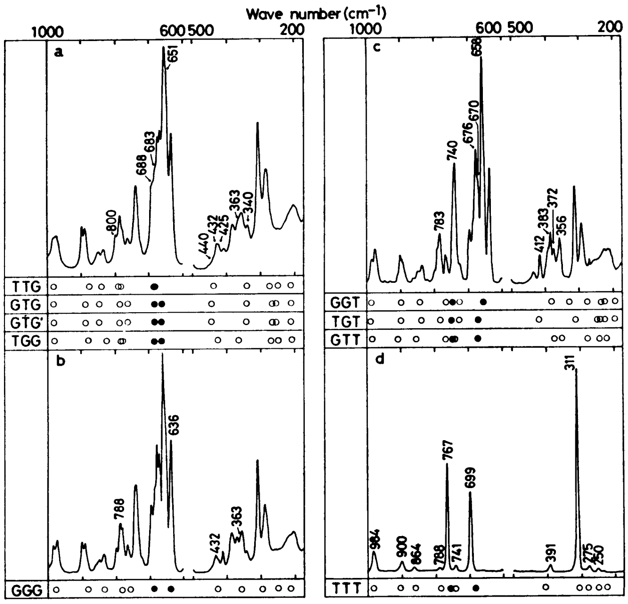

Fig. 6. Comparison of the calculated and observed Raman frequencies of ethyl propyl sulfide in the 1000—600 and 500—175 cm^{-1} regions.
a: Liquid (room temperature), b: liquid (−90 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).
The filled circles denote the CS stretching vibrations.

Existence of the GG′ form is uncertain, since all of the calculated frequencies of this form are almost coincident with those of the other forms, TT, TG, and GG. However, the distance between the two terminal methyl groups seems to be too short for this form to be stable. In fact, for methyl propyl sulfide, the GG′ form is found to be very unlikely as will be described later.

The enthalpy differences between the GG and TG forms and between the TT and TG forms in the liquid state were determined from the relative Raman intensities at eight different temperatures between −90 and 23 °C. The intensity ratios of the 641 and 658 cm^{-1} bands and of the 334 and 384 cm^{-1} bands gave the enthalpy differences $\Delta H_{GG-TG}=40\pm50$ cal/mol and

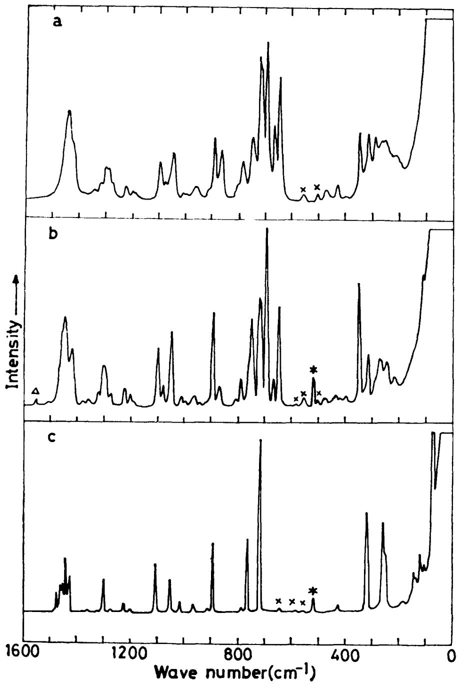

Fig. 7. Raman spectra of butyl methyl sulfide.
a: Liquid (room temperature), b: glass (liquid nitrogen temperature), c: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

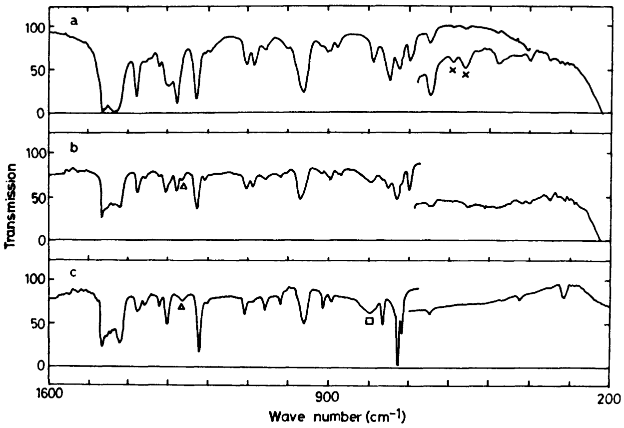

Fig. 8. Infrared spectra of butyl methyl sulfide.
a: Liquid, b: glass, c: crystal.
The symbols are explained in the caption of Fig. 1.

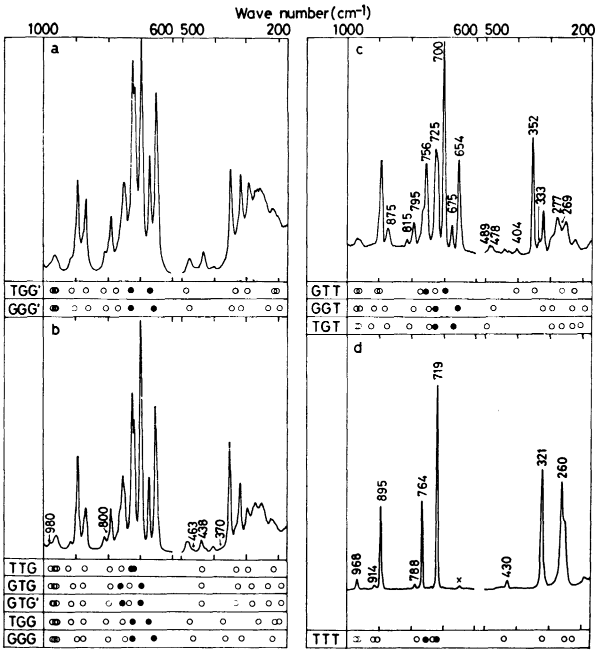

Fig. 9. Comparison of the calculated and observed Raman frequencies of butyl methyl sulfide in the 1000—600 and 500—175 cm^{-1} regions.
a: Liquid (room temperature), b: liquid (−90 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).
The filled circles denote the CS stretching vibrations. The symbol in the spectrum of the crystalline state is explained in the caption of Fig. 1.

$\Delta H_{\mathrm{TT-TG}}=460\pm100$ cal/mol, respectively.

The infrared spectrum of gaseous diethyl sulfide is essentially the same as that of the liquid. This observation suggests that the TT, TG, and GG forms coexist in the gaseous state.

Ethyl Propyl Sulfide. This molecule has fourteen possible rotational isomers as listed in Table 1 of Part I.[2] Of these, TGG′, GG′T, GGG′, GG′G, and GG′G′ are rejected because of the same reason as stated above for diethyl sulfide.

Figure 6 shows that the observed Raman spectrum in the crystalline state is explained by the TTT form only. The spectra in the glassy and liquid states exhibit much more bands than those in the crystalline state, suggesting the coexistence of many rotational isomers. The temperature dependence of the Raman intensities and the comparison with the calculated results indicate that the observed spectra in these states are explained by the TTT, GGT, TGT, GTT, GGG, TTG, and TGG forms and either one or both of the GTG, and GTG′ forms.

The comparison of the Raman spectrum in the glassy state and that in the liquid state at room temperature shows that the intensities of the bands at 783, 740, 658, 412, 383, 372, and 356 cm^{-1} are enhanced in the glassy state. In the liquid state, these bands are also stronger at lower temperatures. Examinations of the experimental and calculated results indicate that the bands at 658 and 383 cm^{-1} are assigned to the GGT form, those at 783 and 412 cm^{-1} to the TGT form, those at 372 and 356 cm^{-1} to the GTT form, and that at 740 cm^{-1} to the GGT, TGT, and GTT forms. The bands at 676 and 670 cm^{-1} are assigned to the TGT and GTT forms, respectively, on the basis of the facts that the intensity of the former band increases at lower temperatures relative to the intensity of the latter band and that corresponding intensity variations are observed for the band pair of the 412 cm^{-1} band (TGT form) and the 372 or 356 cm^{-1} band (GTT form).

The observed spectra show that the intensities of some other bands such as those at 800, 788, 688, 683, 651, 440, 432, 425, 363, and 340 cm^{-1} decrease in the glassy state as compared with the liquid state at room

TABLE 2. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF DIETHYL SULFIDE

Observed frequency (cm^{-1})[a]						
Gas[c]	Liquid		Glass	Crystal		Assignment[b]
IR	R	IR	IR	R	IR	
			1478 VW	1483 VW	1478 VW	CH_3 ip-d-deform
		1463 S, sh		1466 VW	1458 S	CH_3 ip-d-deform
1450 S, vb	1456 W, b	1456 VS, b	1459 VS, sh	1455 VW	1454 S, sh	CH_3 op-d-deform
			1448 VS	1449 VW	1450 S	CH_3 op-d-deform
					1444 S	CH_2 scis
	1431 VW	1436 M	1424 M		1438 S	CH_2 scis
1382 M, b	1382 VW			1382 VW	1380 S, sh	CH_3 s-deform
		1375 S	1372 S	1372 VW	1375 S	CH_3 s-deform
1324 VW, sh			1322 VW		1326 VW, b	Origin unknown
1287 M, sh	1273 VW, b	1278 M, sh	1285 W, sh	1298 VW	1299 VW	CH_2 wag (**TT**, TG, GG)
				1284 VW	1286 VS	CH_2 wag (**TT**, TG, GG)
1260 VS, b		1260 VS	1262 VS		1264 W, sh	CH_2 twist (**TT**, TG, GG)
	1252 VW	1248 M, sh	1254 S, sh	1255 VW	1256 VS	CH_2 twist (**TT**, TG, GG)
					1244 W	Origin unknown
1236 VW, sh	1236 VW, sh			1235 VW	1238 VW	Origin unknown
1076 W, b	1077 VW	1076 W	1079 M	1082 VW	1080 VW	CC stretch (**TT**, TG)
1044 VW, b	1047 W	1048 VW	1048 W	1044 VW	1042 VW	CH_3 ip-rock (**TT**, TG, GG), CH_3 op-rock (**TT**), CC stretch (GG)
			1032 VW			CH_3 op-rock (TG, GG)
				1026 VW	1028 VW	CH_3 op-rock (**TT**)
	1018 VW		1014 VW			CH_3 op-rock (TG, GG)
			994 VW, sh		993 S	CH_3 ip-rock (**TT**)
976 M, b	979 VW	980 M, sh	982 M, sh	988 W	986 S	CC stretch (**TT**, GG), CH_3 ip-rock (TG)
967 M, sh		973 S	971 VS			CC stretch (TG), CH_3 ip-rock (GG)
			797 VS	810 VW	798 VW	CH_2 rock (**TT**)
784 W	782 VW	783 M	784 VS	792 VW		CH_2 rock (**TT**, TG, GG)
773 W	766 VW	764 W	765 M			CH_2 rock (**TG**)
735 VW, sh		739 VW	739 W			CH_2 rock (**GG**)
698 VW, sh	695 M	695 VW	692 M	695 VS	693 S	CS stretch (**TT**, TG, GG)
691 VW	689 W, sh	689 VW, sh		683 VW, sh		CS stretch (**TT**)
648 VW	658 VS	657 VW	656 W			CS stretch (**TG**)
639 VW	641 VS	639 VW	639 W			CS stretch (**GG**)
	384 VW	381 VW	384 VW			SCC deform (**TG**)
	370 VW, sh					SCC deform (**GG**)
	349 VW, sh	342 VW	349 VW		348 VW	SCC deform (**TT**)
	334 W	328 VW	335 W	343 S	332 W	SCC deform (**TT**)
	315 VW, sh					SCC deform (**GG**)
	307 W	302 VW	303 VW			SCC deform (**TG**)
				294 VW	294 VW	Origin unknown
		275 VW		267 VW	273 VW	CH_3 torsion (**TT**, TG, GG)
	260 VW	263 VW		253 VW	262 VW	CH_3 torsion (**TT**)
		243 VW				CH_3 torsion (TG, GG)
	187 VW					CSC bend (TG, GG)
				178 VW		CSC bend (**TT**), torsions (**TT**) and lattice vibrations
				171 VW		
				147 VW		
				126 VW, sh		
				116 VW		
				104 W		
				72 VW		
				55 VW		
				48 VW		

TABLE 2. (Continued)

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 liquid state does not always allow us to correlate the individual bands in the glassy or crystalline state to those in the liquid state. Only approximate correlations are made in such cases. 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. 19. c) Some of the infrared bands in the gaseous state have rotational structures. However, only the frequencies of the band centers are listed in the table.

TABLE 3. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF ETHYL PROPYL SULFIDE

Observed frequency (cm^{-1})[a]						
Liquid		Glass		Crystal		Assignment[b]
R	IR	R	IR	R	IR	
	1473 W, sh		1472 VW, sh	1489 VW	1474 W	CH_2 scis
	1457 VS	1465 VW, sh	1464 VS, sh	1465 VW	1463 VS, sh	CH_3 ip-d-deform
1452 M, vb	1451 VS	1457 W, b	1457 VS	1452 W	1456 VS	CH_3 op-d-deform
		1449 W, sh	1446 VS	1449 W	1446 VS, sh	CH_3 ip-d-deform
	1440 S, sh			1440 VW, sh	1440 VS	CH_2 scis
1430 M, sh	1423 M, sh	1424 W, sh	1434 M, sh	1431 VW	1424 S, sh	CH_2 scis (**TTT**, GTT, GGG)
			1417 S			CH_2 scis (TGT, GGT)
1381 VW	1375 VS	1375 VW	1374 M, sh	1379 VW, sh		CH_3 s-deform
			1370 S	1376 VW	1366 S	CH_3 s-deform, CH_2 wag (**GGG**)
1335 VW	1339 W	1335 VW	1335 VW	1332 VW	1333 VW	CH_2 wag (**TTT**, TGT, GTT, GGT)
1298 W	1298 M	1293 VW	1295 VW	1290 VW	1286 W	CH_2 twist (**TTT**, TGT, GTT, GGT, GGG)
1270 VW	1269 S	1269 VW	1271 S			CH_2 wag (TGT, GTT, GGT, GGG)
1266 VW, sh				1263 VW	1266 VS	CH_2 twist (**TTT**, TGT, GTT, GGT, GGG), CH_2 wag (**TTT**)
1250 VW, sh		1248 VW				CH_2 wag (TGT, GGT)
1239 VW	1238 S	1237 VW	1237 VS	1231 VW 1225 VW, sh	1224 M	CH_2 wag (**TTT**, GTT)
	1219 W	1220 VW, sh	1222 VW, sh			CH_2 twist (TGT, GTT, GGT), CH_2 wag (GGG)
1213 VW		1213 VW		1210 VW	1212 VW, sh	CH_2 twist (**TTT**)
1120 VW, sh	1116 VW	1122 VW	1118 VW			CC stretch (**TTG**)
1100 VW, sh	1100 VW, sh	1100 VW, sh	1101 W	1100 W	1100 M	CH_3 ip-rock (**TTT**, GTT)
1092 VW	1090 VW	1093 W	1093 M			CH_3 ip-rock (TGT, GGT), CC stretch (GGG)
1080 VW	1076 VW	1079 VW	1078 W	1078 VW	1073 VW	CH_2 rock (**TTT**, TGT, GTT, GGT)
1056 VW, sh	1056 VW, sh	1056 VW, sh	1056 VW, sh			CH_3 ip-rock (TGT, GTT, GGT, GGG)
1047 M	1049 VW	1047 W	1050 VW	1047 VW	1049 VS	CH_3 ip-rock (**TTT**, GGG)
	1036 VW, sh		1038 VW	1036 VW	1039 W, sh	CC stretch (**TTT**), CH_3 op-rock (TGT)
1030 M	1030 VW, sh	1030 S	1030 VW, sh			CC stretch (TGT, GTT, GGT, GGG)
1022 VW, sh	1023 VW, sh	1020 VW, sh	1021 VW	1023 VW	1024 W	CH_3 op-rock (**TTT**, GTT, GGT, GGG)
981 VW, sh	981 VW, sh	982 W	982 M	984 VW	983 M, sh 976 M	CC stretch (**TTT**, TGT)
972 VW	972 M	972 W	972 S			CC stretch (GTT, GGT, GGG)
	954 VW, sh		954 VW			Origin unknown
899 VW	898 W	900 VW	899 S	900 VW	898 W	CC stretch (**TTT**, GTT, GGT)
892 VW	890 W, sh	892 VW, sh	890 VW, sh			CC stretch (TGT, GGG)
862 VW, sh		863 VW, sh	860 VW, sh	864 VW	860 VW	CH_3 op-rock (**TTT**)
852 VW	849 VW, sh	847 VW	846 VW, sh			CH_3 op-rock (**GTT**)
836 VW	835 VW	835 VW	833 W			CH_3 op-rock (TGT, GGT, GGG)
800 VW, sh	800 VW, sh	800 VW, sh	800 VW, sh			CH_2 rock (TTG, GTG or GTG′)
788 W	786 W	788 VW, sh	786 S	788 VW	788 VS	CH_2 rock (**TTT**, GGG)
780 VW, sh		783 W			778 S	CH_2 rock (**TGT**)
764 VW	760 VW	765 VW	762 M	767 M	766 S	CS stretch (**TTT**), CH_2 rock (GTT, GGT, GGG)

Table 3. (Continued)

Observed frequency (cm^{-1})[a)						
Liquid		Glass		Crystal		Assignment[b)
R	IR	R	IR	R	IR	
740 M	740 W	740 S	740 S, b	741 VW	747 M, sh 736 VS	CH_2 rock (**TTT**, GTT), CS stretch (TGT, GTT, GGT)
723 VW, sh	724 VW, sh	723 VW, sh	723 M			CH_2 rock (TGT, GGT)
693 M, sh		695 W	690 VW	699 M	694 W	CS stretch (**TTT**, GGG)
688 M, sh		688 W, sh				CS stretch (TTG, TGG, GTG or GTG′)
683 M, sh	685 VW, b	683 W, sh				CS stretch (**TTG**)
675 S		676 S	675 VW			CS stretch (**TGT**)
670 S		670 M				CS stretch (**GTT**)
658 VS	657 VW	658 VS	657 VW			CS stretch (**GGT**)
651 VS, sh		651 M, sh				CS stretch (TGG, GTG or GTG′)
636 S	634 VW	636 M	634 VW			CS stretch (**GGG**)
440 VW, sh	440 VW, sh	442 VW, sh				CCC deform (GTG or GTG′)
432 VW	428 VW, b	433 VW	424 VW, b			CCC deform (GGG, TTG)
425 VW, sh		425 VW, sh				CCC deform (**TGG**)
411 VW	411 VW, sh	412 VW				CSC bend (**TGT**)
392 VW, sh		392 VW, sh		391 VW	385 VW	CCC deform (**TTT**)
383 W	385 VW, sh	383 W	384 VW, b			CSC bend (**GGT**)
372 W, sh	366 VW, sh	372 VW				CSC bend (**GTT**)
363 W, sh		363 VW, sh				CSC bend (GGG, TGG)
355 W	351 VW	356 W	351 VW			CCC deform (**GTT**)
340 W		340 VW, sh				SCC deform (TTG, GTG or GTG′)
321 VW, sh		321 VW, sh				SCC deform (**GGT**)
307 S	302 VW	309 M	303 VW	311 VS	307 VW	SCC deform (**TTT**), CCC deform (TGT)
295 W, sh		295 W, sh				SCC deform (**GGG**)
285 M		288 W				CCC deform (GGT), SCC deform (GTT)
277 VW, sh	277 VW	277 VW, sh	277 VW	275 VW	279 VW	SCC deform (**TTT**)
		255 VW				CH_3 torsion (TGT, GGG)
		245 VW, sh	244 VW	250 VW	243 VW	CH_3 torsion (**TTT**, GTT), SCC deform (TGT)
		240 VW, sh				CH_3 torsion (**GGT**)
225 W, sh		225 VW, b				CH_3 torsion (**TTT**, TGT, GTT, GGT)
		213 VW, b				CH_3 torsion (**GGG**)
200 W, b		200 VW, sh				CH_3 torsion (TGT, GGT)
				148 VW 132 VW 107 VW, sh 92 M 70 W 58 VW		CSC bend (**TTT**), torsions (**TTT**) and lattice vibrations

a), b) See a) and b), respectively, of Table 2.

temperature. Of these, the band at 788 cm^{-1} is assigned to the GGG form, that at 683 cm^{-1} to the TTG form, that at 425 cm^{-1} to the TGG form, that at 440 cm^{-1} to either one or both of the GTG and GTG′ forms, that at 432 cm^{-1} to both of the GGG and TTG forms, and that at 363 cm^{-1} to both of the GGG and TGG forms. The existence of the GGG form is evident from the result that the band at 636 cm^{-1} is assigned exclusively to this form. The following bands are assigned to all or any of the molecular forms given in parentheses: 800 and 342 cm^{-1} (TTG, GTG, and GTG′), 688 cm^{-1} (TGG, GTG, GTG′, and TTG), and 651 cm^{-1} (TGG, GTG, and GTG′).

The relative stabilities of the rotational isomers existing in the liquid state are determined from the dependence of the band intensities on temperature (Fig. 6) and the band assignment mentioned above; (1) the GGT and TGT forms have almost the same stability and are the most stable, (2) the third stable isomer is the GTT form, which is followed by the TTT and GGG forms having nearly equal stability to each other, and (3) the TTG, GTG, GTG′, and TGG forms are less stable than the forms given above, but the relative stabilities among these forms are not clear.

The above conclusion obtained from the Raman spectra is also consistent with the change of the infrared

TABLE 4. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENT OF BUTYL METHYL SULFIDE

Observed frequency (cm^{-1})[a]						Assignment[b]
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
		1555 VW				Origin unknown
		1470 VW, sh		1476 VW	1476 VW, sh	CH_2 scis
1462 VW, sh	1464 VS	1457 W, sh	1465 VS	1461 VW	1464 M	CH_2 scis
	1458 VS, sh		1458 VS, sh	1454 VW	1458 M, sh	CH_3 op-d-deform
1445 M, sh	1452 VS, sh	1448 M	1452 VS	1446 VW, sh	1451 M	CH_3 ip-d-deform
	1435 VS	1443 W, sh	1436 S	1441 W	1442 M	CH_3 ip-d-deform
	1432 VS		1432 VS	1429 W	1432 W	CH_3 op-d-deform
1429 W, sh			1428 S			CH_3 op-d-deform (**GTT**)
	1424 VS	1422 W	1422 S			CH_2 scis (**GTT**)
	1418 S, sh		1419 S		1424 M, sh 1418 M	CH_2 scis
1381 VW	1378 S	1380 VW	1375 M	1380 VW	1376 W 1372 W, sh	CH_3 s-deform, CH_2 wag (TGT, GGT)
1360 VW	1354 VW	1360 VW	1356 VW	1359 VW	1356 VW	CH_2 wag (**TTT**, GTT)
1345 VW	1341 VW					CH_2 wag (TGG or GGG)
1324 VW	1321 VW	1323 VW	1323 VW	1325 VW	1320 VW	CH_3 s-deform, CH_2 wag (TGT)
1305 VW	1302 W	1305 VW	1304 M			CH_2 twist (**TTT**, GTT, TGT, GGT), CH_2 wag (GGT)
1296 VW	1296 W	1297 VW, sh	1297 W, sh	1301 VW	1302 W	CH_2 wag (**TTT**, GTT)
1278 VW	1276 S	1278 VW	1277 M	1276 VW		CH_2 twist (**TTT**, GTT, TGT, GGT)
			1264 W		1263 VW	Origin unknown
1228 VW	1227 S	1229 VW	1226 VS	1225 VW	1220 S	CH_2 wag (**TTT**, GTT)
1203 VW	1204 VW	1206 VW	1208 W	1201 VW	1201 VW	CH_2 rock (**TTT**, GTT, TGT)
1193 VW	1193 VW	1194 VW, sh				CH_2 rock (**GGT**)
1169 VW, sh	1169 VW					CH_2 wag (TGT, GGT)
1125 VW, sh		1126 VW				CC stretch (TGG or GGG)
	1108 VW, sh	1110 W, sh	1108 W, sh	1106 W	1107 W	CC stretch (**TTT**)
1101 W	1100 W	1104 W	1101 M			CC stretch (GTT, TGT, GGT)
1082 VW	1083 W	1086 VW	1086 M			CH_2 twist (**TTT**, GTT, TGT, GGT)
1058 VW, sh	1058 W	1061 VW, sh	1059 W			CC stretch (TTG, GTG or GTG′)
1053 W	1051 W	1053 W	1051 W	1054 VW	1056 W	CC stretch (**TTT**, GTT, TGT, GGT)
1012 VW	1012 VW, sh	1015 VW	1014 VW	1017 VW	1017 VW	CC stretch (**TTT**, GTT)
1001 VW, sh	998 VW	1002 W	995 VW			CC stretch (TGT, GGT)
980 VW, sh	980 W, sh	978 VW, sh	978 VW, sh			CH_3 ip-rock (TGG, GGG, TTG, GTG or GTG′)
966 VW, b	968 M, sh	970 VW	968 S	968 VW	964 W, sh	CH_3 ip-rock (**TTT**, GTT, TGT, GGT)
	959 S	962 VW	963 S		957 W	CH_3 op-rock (**TTT**, TGT, GGT)
			956 S			CH_3 op-rock (**GTT**)
918 VW, sh	916 VW	918 VW, sh	916 VW	914 VW	910 VW	CH_3 op-rock (**TTT**), CH_3 ip-rock (TGT, GGT)
903 VW, sh	901 W	903 VW, sh	899 W, sh			CH_3 op-rock (**GTT**)
897 W	894 W	896 M	894 W	895 M	892 VW	CH_3 ip-rock (**TTT**, GTT)
878 VW, sh	877 VW	875 VW	873 VW			CH_3 op-rock (**GGT**)
872 W	870 VW, sh		867 VW			CH_3 op-rock (**TGT**)
813 VW	812 VW	815 VW				CH_2 rock (**TGT**)
800 VW, sh	800 VW, sh	800 VW, sh				CH_2 rock (TTG, GTG, GTG′ or GGG)
793 VW	788 VW	795 VW	794 VW	788 VW		CH_2 rock (**TTT**, GGT)
		775 VW, sh	776 VW			CH_2 rock (**GTT**)
765 VW, sh		765 VW, sh	766 W	764 M	764 W	CS stretch (**TTT**)
753 M	756 VW, sh	756 M	756 W, sh			CS stretch (**GTT**)
	748 M		749 M			CH_2 rock (TGT, GGT)

Table 4. (Continued)

Observed frequency (cm^{-1})[a)						Assignment[b)
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
725 VS	729 W, sh	725 M	729 S			CS stretch (TGT, GGT)
	724 M			735 VW	726 VS	CH_2 rock (**TTT**, GTT)
719 VS, sh	718 W, sh	720 M, sh	720 M, sh	719 VS	716 M	CS stretch (**TTT**)
697 VS	697 W	700 VS	699 M			CS stretch (**GTT**)
672 M	671 VW	675 VW	672 VW			CS stretch (**TGT**)
654 S	650 VW	654 M	651 VW			CS stretch (**GGT**)
489 VW, sh	480 VW	489 VW				CCC deform (**TGT**)
481 VW		478 VW				CCC deform (GGT, TGG)
463 VW	460 VW	463 VW				CCC deform (**GGG**)
438 VW		443 W				CCC deform (TTG, GTG or GTG′)
425 VW, sh	430 VW	425 VW	420 VW	430 VW	426 VW	CCC deform (**TTT**)
406 VW	402 VW	404 VW	399 VW			CCC deform (**GTT**)
370 VW, sh	366 VW					CCC deform (TGG or GGG)
353 M	350 VW	352 M	352 VW			SCC deform (**GTT**)
333 W, sh	328 VW	333 VW, sh				CSC bend (**GGT**)
320 W	316 VW	319 W		321 M	316 VW	CCC deform (**TTT**)
295 W	303 VW	295 VW, sh				CCC deform (TGT, GGT)
277 W, sh		277 W				CSC bend (**GTT**)
267 W		269 VW, sh				CSC bend (**TGT**)
258 W		258 VW, sh				CSC bend (**TGG**)
250 W, sh		250 VW		260 M 253 W, sh		CSC bend (**TTT**)
220 VW		221 VW				CH_3 torsion
				205 VW		SCC deform (**TTT**), torsions (**TTT**) and lattice vibrations
				189 VW		
				159 VW, sh		
				147 VW		
				137 VW		
				124 VW		
				108 VW		
				75 VW		
				64 VW		

a), b) See a) and b), respectively, of Table 2.

spectra in the various states.

Butyl Methyl Sulfide. This molecule has fourteen possible rotational isomers. The existence of the GG′T, GG′G, and GG′G′ forms are unlikely, but the TGG′ and GGG′ forms are not ruled out, since unlike the GG′ sequence of the CS–C–CC part in ethyl propyl sulfide, the GG′ sequence of the SC–C–CC part is not expected to give rise to very large steric hindrance.

Figure 9 shows that only the TTT form exists in the crystalline state. In the glassy and liquid states, the spectra exhibit many bands to be assigned to various rotational isomers. It is evident, however, that the GTT and TTT forms exist in these states. The relative intensities of the bands at 756, 700, 404, 352, and 277 cm^{-1} increase in going from the liquid state at room temperature to the glassy state. These bands are all explained by the calculated frequencies of GTT form.

The remaining many bands in the glassy and liquid states imply the coexistence of additional isomers. However, the assignment of the observed bands to individual isomers is not always straightforward, because each of the observed Raman bands corresponds to calculated frequencies of two or more isomers. It is likely that the *trans* conformation about the CH_2CH_2–CH_2CH_3 axis in this molecule is appreciably more stable than the *gauche* conformation as suggested from the conformational stabilities of normal paraffin molecules.[3) The molecular forms with the *trans* conformation about this axis are the TGT and GGT form besides the TTT and GTT forms mentioned above Most of the bands which persist in the glassy state but are not assigned to the GTT and TTT forms are explained by the calculated frequencies of the TGT and GGT forms; namely the bands at 815, 675, 489, and 269 cm^{-1} are assigned to the TGT form, those at 795, 654, 478, and 333 cm^{-1} to the GGT form and those at 875 and 725 cm^{-1} to both of the TGT and GGT forms.

Table 5. Rotational isomerism of the sulfides

	$CH_3SC_2H_5$[a]	$C_2H_5SC_2H_5$	$CH_3SC_3H_7$[b]	$C_2H_5SC_3H_7$	$CH_3SC_4H_9$
Liquid	**G** **T**	**TT** **TG** **GG**	**TT** **GT** **TG** **GG**	**TTT** **GGT** **TGT** **GTT** **GGG** TTG TGG GTG GTG′	**TTT** **GTT** **TGT** **GGT** TTG TGG GGG GTG GTG′ (TGG′) (GGG′)
Glass	—	**TT** **TG** **GG**	**TT** **GT** **TG** **GG**	**TTT** **GGT** **TGT** **GTT** **GGG** TTG TGG GTG GTG′	**TTT** **GTT** **TGT** **GGT** TTG TGG GGG GTG GTG′ (TGG′) (GGG′)
Crystal	**G**	**TT**	**TT**[c] **GT**[c] **GG**[c]	**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. 1 and 7. b) Ref. 8. c) Three different crystal modifications have been identified. For more details, see Ref. 8.

In addition to the bands mentioned above, the liquid- and glassy-state Raman spectra have several other bands such as those at 980, 800, 463, 438, and 370 cm^{-1}. Spectral observations indicate that the intensities of these bands decrease more sharply than those of the above-mentioned bands when temperature is lowered. With reference to the calculated frequencies, the 463 cm^{-1} band is assigned to the GGG form, the 370 cm^{-1} band to either one or both of the TGG and GGG forms, the 800 and 438 cm^{-1} bands to all or any of the TTG, GTG and GTG′ forms, and the 980 cm^{-1} band to all or any of the TTG, TGG, and GTG forms. The calculated frequencies of the TGG′ and GGG′ forms are almost coincident with those of the other forms. This situation makes it difficult to confirm the existence of these forms in the liquid or glassy state.

As mentioned above, the examinations of the experimental and calculated results show that the relatively strong bands which retain most of their intensities in the low-temperature liquid and glassy states are reasonably explained by the isomers with the *trans* CH_2CH_2–CH_2CH_3 axis and the other bands which lose their intensities largely in these states are explained by the isomers with the *gauche* CH_2CH_2–CH_2CH_3 axis. These interpretations justify the statement made earlier that the *trans* conformation about this axis is more stable than the *gauche* conformation.

The relative stabilities of the rotational isomers existing in the liquid state are found from the temperature dependence of the Raman intensities; (1) the GTT form is the most stable, (2) the TTT, GGT, and TGT forms follow in order, and (3) the forms having the *gauche* CH_2CH_2–CH_2CH_3 axis are less stable than the above-mentioned forms.

The above conclusion is also consistent with the results of the infrared spectra.

Rotational Isomerism. In Table 5, the rotational isomerism of the three sulfides studied in this work and of ethyl methyl sulfide and methyl propyl sulfide is summarized.

Ethyl methyl sulfide has long been accepted to take the T form in the crystalline state and the T and G forms in the liquid state.[4–6,10] However, the recent studies by Nogami *et al.*[7] and by Sakakibara *et al.*[1] showed that the bands of the crystalline state are assigned to the G form but not to the T form.

The rotational isomerism of methyl propyl sulfide was studied by Nogami *et al.*[8] They found three crystal modifications with the molecular conformations of GT, TT, and GG, respectively. In the liquid and glassy states, an additional isomer of the TG form coexists with the three isomers. They obtained no experimental evidence for the existence of the GG′ form. The comparison of their spectra with the present results of the normal coordinate treatment indicates that the existence of this form may safely be ruled out.

The vibrational spectra of diethyl sulfide have been studied by several investigators.[6,9] Their conclusions on the rotational isomerism agree essentially with the present one, although the existence of the GG form in the liquid state has once been questioned.[10]

The rotational isomerism of ethyl propyl sulfide and butyl methyl sulfide has been discussed previously by Ohsaku.[11] He showed that these molecules in the crystalline state take the *trans* conformation about the C–C axis adjacent to the S–C axis, but did not determine whole molecular conformations.

Discussion

The following results were obtained for the three sulfides studied in this work. (1) Only the all-*trans* form exists in the crystalline state. (2) Many forms coexist in the liquid state. Most of them persist in the glassy state even at the liquid nitrogen temperature. (3) In the liquid state, the forms with the *gauche* C–S axes are more stable than those with the *trans* C–S axes. (4) The *gauche* conformation about the C–C axis directly adjoining the S–C axis is appreciably stable and is only slightly less stable than the corresponding *trans* conformation.

For the C–C and C–O axes in unbranched paraffins and ethers, the *trans* conformation has been found to be more stable than the *gauche* conformation.[2,3] However, the above results indicate that the conformational stability about the C–S axis is remarkably different from that of the C–C or C–O axis. For diethyl sulfide, the TG and GG forms were found to be more stable than the TT form by 400—450 cal/mol in the liquid state. The stability of the *gauche* conformation about the C–S axis over that of the *trans* conformation was also observed for ethyl propyl sulfide and butyl methyl sulfide. In addition to these experimental evidences, it has been found that the G form of ethyl methyl sulfide is more stable than the T form by 140±50 cal/mol in the liquid state[7] and by 30±50 cal/mol in the gaseous state,[1] and that the GT form of methyl propyl sulfide is the most stable isomer in the liquid state.[12] Thus, it is now established that the *gauche* C–S axis in unbranched sulfides is more stable than the *trans* C–S axis but the stability difference between them is not large.

The stable existence of the *gauche* C–S axis contrasts with the *gauche* C–O axis which is far less stable. One of the possible factors making this difference is the longer C–S bond length (about 1.8 Å) than the C–O bond length (about 1.4 Å), as has been discussed by Tadokoro *et al.*[13a] When the C_1S–C_2C_3 axis takes the *gauche* conformation, the distance between nonbonded hydrogen atoms attached to C_1 and C_3 is 2.1—2.2 Å, which is 0.4—0.5 Å longer than the corresponding distance in ethers. This fact suggests that the repulsive forces between the nonbonded hydrogen atoms in the sulfides are much weaker than those in the ethers and that this effect is responsible for making the *gauche* C–S conformation stable.

The relative stability of the *gauche* conformation about the SC–CC axis was found to be much higher than that of the *gauche* conformation about the CC–CC axis. This is explained by less significant nonbonded interactions as in the case of the *gauche* OC–CC axis in the ethers.[2] Indeed, methyl propyl sulfide takes the GG form in a metastable crystal modification.[8]

The above discussions on the conformational stability indicate that the S–C axis and the C–C axis adjacent to the S–C axis are susceptible of taking the *trans* and *gauche* conformations without large stability differences and accordingly the energy differences among various rotational isomers are small. These results are in accord with the experimental facts observed for all of the sulfides so far studied that many isomers coexist in the glassy state and that methyl propyl sulfide has the three crystal modifications with the molecular conformations of GT, TT, and GG.[8]

It is noticed for the three sulfides studied in this work that the most stable isomer in the liquid or glassy state does not exist in the crystalline state. This fact suggests that intermolecular forces play a more important role for stabilizing the molecular conformation in the crystal.

It is of interest to compare the molecular conformations of the unbranched sulfides with the chain conformations of polythioethers. According to the X-ray diffraction studies, poly(thioethylene)$(-SCH_2CH_2-)_n$ takes the GTG′G′TG conformation for the series of S–C–C–S–C–C–S bonds[13] and poly(thiotrimethylene)$(-SCH_2CH_2CH_2-)_n$ takes the GGGG conformation for the series of S–C–C–C–S bonds.[14] It should be noted that S–C axes in these polymers are all in the *gauche* conformation and the C–C axes adjacent to the S–C axes in the latter polymer are in the *gauche* conformation. These chain conformations are consistent with those of the shorter sulfides as described in this paper.

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Note added in proof

Erratum in Table 3 of Part II.[3] For 629 listed in the column of Raman (−100°C) of Liquid read 692.