Vibrational Spectra and Rotational Isomerism of 2-Chloro- and 2-Bromoethyl Methyl Sulfides

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The Raman and infrared spectra of 2-chloro- and 2-bromoethyl methyl sulfides $CH_3SCH_2CH_2X$ (X=Cl and Br) were measured for the liquid and crystalline solid states. The vibrational frequencies of these molecules were calculated by the use of the force constants transferred from unbranched alkyl sulfides and alkyl halides. The rotational isomerism was studied on the basis of the spectral observations and the calculations, and the following conclusions were obtained. (1) In the crystalline solid state, both the chloride and the bromide take the molecular form with the *gauche* conformation about the (C)S–C(C) axis and the *trans* conformation about the (S)C–C(X) axis. (2) In addition to this form (GT), three other forms (TG, GG, and TT) coexist in the liquid state, the GT form being the most stable. (3) The sulfur atom is suggested to lower the energy of the *trans* conformation of the (S)C–C(X) axis.

The vibrational spectra of unbranched alkyl halides have been studied extensively by many investigators. The rotational isomerism of these molecules was thoroughly examined in recent studies[1,2] by analyzing the spectra in conjunction with the systematic calculations of normal coordinates. These studies provided us with essential knowledge on the conformational stability of the halide molecules. In the present study, we deal with 2-halogenoethyl methyl sulfides $CH_3SCH_2CH_2X$ (X=Cl and Br), in which halogen and sulfur atoms are simultaneously involved, in order to examine the effect of the sulfur atom on the conformation of the halide part. Another interest is the reversed effect, namely the effect of the halogen atom on the conformation of the sulfide part. The rotational isomerism of alkyl sulfides has also been investigated systematically in a series of recent studies.[3–5]

Experimental

2-Chloroethyl methyl sulfide was purchased from Tokyo Kasei Kogyo Co., Ltd. and was distilled prior to the Raman and infrared measurements. 2-Bromoethyl methyl sulfide was prepared from 2-methylthioethanol (Tokyo Kasei Kogyo Co., Ltd.) and phosphorus tribromide and was distilled under reduced pressure (bp 64 °C at 25 mmHg).

The measurements of Raman spectra were made on a JEOL JRS-400D spectrophotometer with a Coherent Radiation CR-2 or CR-3 argon ion laser. The Raman spectra were obtained for the liquid state at various temperatures and the crystalline solid state at liquid nitrogen temperature. The infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer and Hitachi EPI-G2 and EPI-L spectrophotometers. The crystalline solid sample for the infrared measurements was obtained by depositing vapor of the substance onto a cooled window and annealing it repeatedly.

Normal Coordinate Treatment

The calculations of the normal coordinates for 2-chloro- and 2-bromoethyl methyl sulfides were carried out by an MVIB system,[6] which is a program system consisting of various program units combined functionally with one another to calculate vibrational frequencies, modes and other information on the normal vibrations from minimal input data of only a name of the molecule and its conformation. This program system is adapted for a HITAC 8800/8700 Computing System at the University of Tokyo.

The force constants associated with the sulfur and halogen parts were transferred from the unbranched alkyl sulfides[6] and alkyl halides.[7] The force constants for the (S)C–C(X) stretching and the methylene-methylene interactions were transferred from the corresponding alkyl halides. No further adjustment of the force constants was made. The transferred values were found to be accurate enough for determining the existing rotational isomers from their vibrational frequencies. Structural parameters used in the calculations were the same as those of the corresponding parts of the sulfides and halides.[6,7]

Results

The Raman spectra of 2-chloro- and 2-bromoethyl methyl sulfides are shown in Figs. 1—4, and the observed and calculated frequencies and the vibrational assignments based on the potential-energy distributions are listed in Tables 1 and 2. Considering possible molecular forms to be in the staggered conformations, we have for a 2-halogenoethyl methyl sulfide molecule five rotational isomers, TT, TG, GT, GG, and GG′, where the first and second conformation symbols in each isomer designation are those for the (C)S–C(C) and (S)C–C(X) axes, respectively. The symbols T and G imply *trans* and *gauche*, respectively, in accordance with the convention generally accepted.[8]

The following general spectral features are observed for the two halogeno sufildes. (1) As expected, the spectra have combined features of alkyl halides and sulfides. (2) The number of the bands observed in the crystalline solid state is less than that in the liquid state. The former corresponds to what is expected for one molecular form. (3) The relative intensities in the liquid-state Raman spectra vary with the change of temperature.

The rotational isomers existing in each state of aggregation and their relative stabilities will be considered below. The results are summarized in Table 3.

2-Chloroethyl Methyl Sulfide. The key bands for studying molecular conformations of this molecule are the bands due to the S–CH_2 stretching, C–Cl stretching and skeletal deformation vibrations.[1,4,5] The C–S stretching (CH_3–S and S–CH_2) and C–Cl stretching frequencies are expected to be in the range between 800 and 600 cm^{-1}, where the CH_2 rocking frequencies are also likely to be.

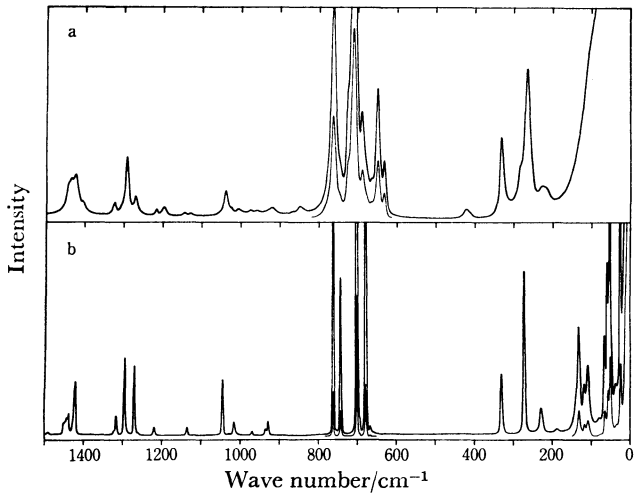

Fig. 1. Raman spectra of 2-chloroethyl methyl sulfide.
a: Liquid, b: crystalline solid.

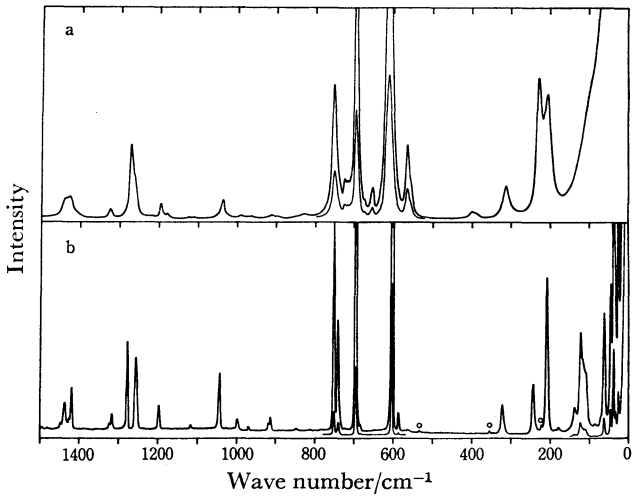

Fig. 3. Raman spectra of 2-bromoethyl methyl sulfide.
a: Liquid, b: crystalline solid.
○: Spurious emission line from the Ar^+ laser.

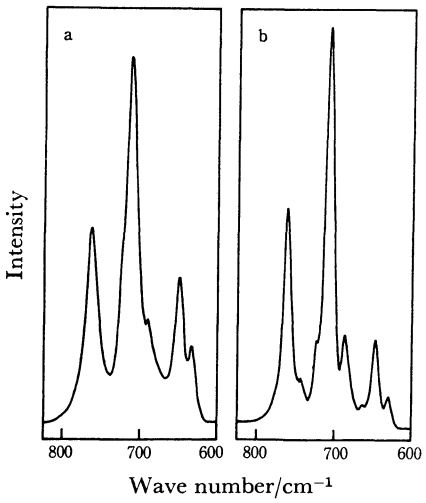

Fig. 2. Raman spectra of 2-chloroethyl methyl sulfide in the liquid state.
a: 110 °C, b: −55 °C.

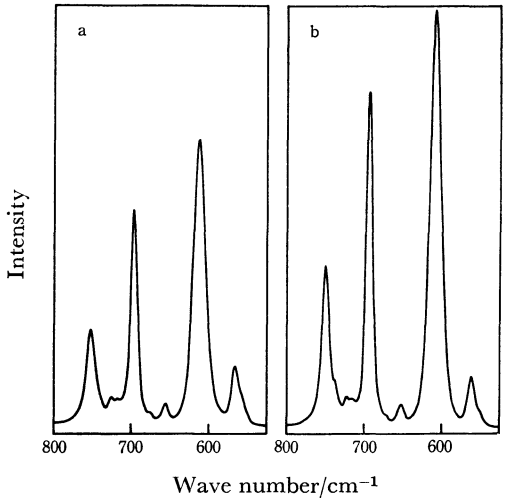

Fig. 4. Raman spectra of 2-bromoethyl methyl sulfide in the liquid state.
a: 25 °C, b: −30 °C.

Table 1. Observed and calculated frequencies and assignments of 2-chloroethyl methyl sulfide

Observed frequency (cm^{-1})[a]				Assignment[b]
Liquid		Crystalline solid		
Raman	Infrared[c]	Raman	Infrared[c]	
		1512 VW		Overtones
		1491 VW		
		1450 W	1451 W,sh	CH_2(Cl) scis (TG 1450, GG 1442, GT 1433, TT 1433), CH_3 ip-d-deform (TT 1444, GT 1442, GG 1441, TG 1440), CH_3 op-d-deform (GT 1432, TG 1432, GG 1432, TT 1432), (S) CH_2 scis (TG 1420, TT 1420, GG 1415, GT 1410)
		1447 W	1445 W,sh	
1442 W,sh	1443 S	1443 W		
1436 W	1438 S	1439 W	1439 M	
1425 W	1428 S	1427 W,sh		
		1423 M	1421 M	
1407 VW, sh	1406 W			

TABLE 1. Continued

Observed frequency (cm^{-1})[a]				Assignment[b]
Liquid		Crystalline solid		
Raman	Infrared[c]	Raman	Infrared[c]	
1322 VW	1327 W	1322 VW 1316 W	1324 W 1318 W	CH_3 s-deform (TG 1325, GG 1324, TT 1323, GT 1322)
	1306 M,sh			CH_2(Cl) wag (TG 1318, GG 1316)
1293 M	1296 M	1295 M	1301 M	CH_2(Cl) wag (GT 1307, TT 1306)
1271 VW	1280 M	1270 M 1260 VW	1272 W	(S)CH_2 twist (TT 1280, GT 1277), (S) CH_2 wag (TG 1277, GG 1277)
1218 VW	1219 S	1218 W	1221 M	(S)CH_2 wag (GT 1219, TT 1217)
1198 VW				(S)CH_2 twist (GG 1199, TG 1198)
1144 VW	1144 VW,sh			CH_2(Cl) twist (GG 1149)
1132 VW	1130 W	1135 VW	1135 M	CH_2(Cl) twist (GT 1147, TG 1147, TT 1147)
1038 W	1040 W	1046 M	1046 W	CC stretch (TT 1030, TG 1023, GT 1019)
1027 VW,sh	1028 W			CC stretch (GG 1008)
1006 VW	1008 W	1016 W	1016 M	CH_2(Cl) rock (TT 986, GT 975)
975 VW	977 W			CH_3 ip-rock (GG 972, TG 968, TT 965)
960 VW	961 W	969 VW	970 M	CH_3 ip-rock (GT 960), CH_3 op-rock (TG 958, GG 957, TT 956)
922 VW	927 W	933 VW 927 W	929 W	CH_3 op-rock (GT 957), CH_2(Cl) rock (TG 948, GG 941)
863 VW	866 VW			(S)CH_2 rock (TG 881)
845 VW	848 W			(S)CH_2 rock (GG 863)
763 S	764 W	763 S	764 W	SC(H_2) stretch (GT 773, TT 770)
745 W, sh	746 W	745 M	745 W	(S)CH_2 rock (TT 754, GT 742), C(H_3)S stretch (TT 736)
724 S, sh				C(H_3)S stretch (TG 726, GG 723)
710 VS	712 S	703 VS 695 VW	705 S	CCl stretch (GT 719)
688 M	688 S	680 S	686 S 679 S	C(H_3)S stretch (GT 697), CCl stretch (TT 697)
		667 VW	668 W	^{13}CCl stretch ? (GT)
663 W	667 W, sh			SC(H_2) stretch (TG 669)
648 S	651 W			SC(H_2) stretch (GG 659), CCl stretch (TG 651)
632 W	634 VW			CCl stretch (GG 643)
422 VW	415 W			SCC deform (TG 423)
412 VW, sh				CCCl deform (GG 387)
332 M	328 VW	333 M	329 W	CSC bend (GT 337, TT 335, GG 327)
282 W, sh				CCCl deform (TT 288)
265 S	258 VW	274 M	267 W	CCCl deform (TG 266, GT 257)
226 W				CSC bend (TG 216)
218 W, sh		228 W		SCC deform (GT 204, GG 200)
		188 VW		
		140 W,sh		
		132 M		
		120 W		
≈100 sh		107 W		
		78 VW		Torsions and lattice vibrations
		65 M		
		60 M		
		53 S		
		40 W		
		28 S		

a) VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder. b) All the calculated frequencies for the individual rotational isomers are given in parentheses except for those of the CH stretching and torsional vibrations and the lowest skeletal deformation frequency for the TT form (133 cm^{-1}, SCC deform) which are not included in the table. c) The infrared spectra in the region below 250 cm^{-1} were not measured.

The Raman and infrared spectra of the crystalline solid state exhibit four distinct bands at 763, 745, 703, and 680 cm^{-1}, the fourth being a doublet in the infrared spectrum. Since a single molecular form exists in this state as is evident from the number of the bands observed in the whole region, the four bands are assigned to the CH_3–S, S–CH_2, and C–Cl stretching, and one of the two CH_2 rocking vibrations. The least strong Raman band at 745 cm^{-1} is assignable to the CH_2 rocking vibration by considering that Raman intensities for the C–S or C–Cl stretching vibration are generally stronger than those for the rocking vibration. Previous studies indicated that the C–S stretching frequencies for the P_C conformation (the sulfur atom is *trans* to a carbon atom) and the P_H conformation (the sulfur atom is *trans* to a hydrogen atom) are 745—760 and 645—670 cm^{-1}, respectively,[9] and that the C–Cl stretching frequencies for the P_C conformation (the chlorine atom is *trans* to a carbon atom) and the P_H conformation (the chlorine atom is *trans* to a hydrogen atom) are 720—730

Table 2. Observed and calculated frequencies and assignments of 2-bromoethyl methyl sulfide

Observed frequency (cm^{-1})[a]				Assignment[b]
Liquid		Crystalline solid		
Raman	Infrared[c]	Raman	Infrared[c]	
		1503 VW		
≈1490 VW		1493 VW	1492 VW	Overtones
		1479 VW		
		1446 VW	1449 W	
1437 W	1433 S	1434 W	1435 M	CH_2(Br) scis (TG 1451, GG 1443, GT 1435, TT 1435), CH_3 ip-d-deform (TT 1444, GT 1442, GG 1442, TG 1441), CH_3 op-d-deform (GT 1432, GG 1432, TG 1432, TT 1432), (S)CH_2 scis (TG 1418, TT 1418, GG 1413, GT 1408)
1427 W		1424 W	1432 M,sh	
		1417 M	1419 M	
1408 VW,sh	1409 W,sh			
1323 W	1322 W	1323 VW 1316 W	1323 VW 1316VW,sh	CH_3 s-deform (TG 1323, TT 1323, GT 1322, GG 1322)
	1282 W,sh			(S)CH_2 wag (GG 1288, TG 1288)
1270 M	1268 M	1276 M	1277 M	(S)CH_2 wag (GT 1272, TT 1269)
1259 M, sh	1255 M	1256 M 1252 M,sh	1255 W	(S)CH_2 twist (GG 1267, TG 1267, TT 1265, GT 1262)
1193 W	1192 S	1197 W	1198 S	CH_2(Br) wag (GT 1200, TT 1199)
1177 VW				CH_2(Br) wag (GG 1179, TG 1179)
1121 VW				CH_2(Br) twist (TT 1127)
1112 VW	1107 M	1116 VW	1114 M	CH_2(Br) twist (GT 1126, GG 1118, TG 1117)
1036 W	1035 W	1045 M	1043 W	CC stretch (TT 1020, TG 1014, GT 1009, GG 1000)
989 VW	989 W	998 W	999 M	CH_3 ip-rock (GG 970, GT 969, TG 967, TT 965)
975 VW	972 W,sh	970 VW	969 M	CH_3 op-rock (TT 960, GT 958, GG 958, TG 958)
960 VW	959 M			(S)CH_2 rock (TT 947)
911 VW	908 W	920 VW 913 W	914 W	CH_2(Br) rock (GT 931, GG 917), (S)CH_2 rock (TG 928)
896 VW	891 VW,sh			CH_2(Br) rock (TG 866)
828 VW	827 W			(S)CH_2 rock (GG 850)
752 S	751 W,sh	750 S	751 W	SC(H_2) stretch (GT 759, TT 751)
739 M,sh	738 W	741 M	738 W	CH_2(Br) rock (TT 748), (S)CH_2 rock (GT 737)
725 W	723 VW,sh			C(H_3)S stretch (TT 727, TG 726)
718 W				C(H_3)S stretch (GG 723)
697 VS	691 W	695 VS 683 VW	695 W	C(H_3)S stretch (GT 698)
675 VW,sh				SC(H_2) stretch (TG 665)
655 W	651 VW			SC(H_2) stretch (GG 653)
613 VS	607 S	601 VS	600 S 595 S	CBr stretch (GT 630, TT 625)
		585 W	579 VW	^{13}CBr stretch ? (GT)
565 M				CBr stretch (TG 556)
555 W,sh	557 W			CBr stretch (GG 553)
401 VW				SCC deform (TG 405)
392 VW	389 VW			SCC deform (GG 363)
313 W	313 VW	320 W	320 VW	CSC bend (TT 329, GG 321, GT 318)
228 S		242 M		CCBr deform (TG 246, GT 216), SCC deform (TT 235)
215 M,sh				CSC bend (TG 214)
207 S		207 S		SCC deform (GT 200)

TABLE 2. Continued

Observed frequency (cm^{-1})[a]				Assignment[b]
Liquid		Crystalline solid		
Raman	Infrared[c]	Raman	Infrared[c]	
		177 VW		Torsions and lattice vibrations
		136 W		
		122 M		
		117 M,sh		
≈100 sh		109 M		
		84 VW		
		61 M		
		45 S		
		37 VS		
		32 S		
		25 S		

a) See a) of Table 1. b) All the calculated frequencies for the individual rotational isomers are given in parentheses except for those of the CH stretching and torsional vibrations and the lowest skeletal deformation frequencies for the TT form (125 cm^{-1}, CCBr deform) and for the GG form (89 cm^{-1}, CCBr deform) which are not included in the table. c) See c) of Table 1.

and 650—660 cm^{-1}, respectively.[10,11] These frequency-conformation correlations show that the 763 cm^{-1} band of 2-chloroethyl methyl sulfide corresponds definitely to the C–S stretching of $P_{C'}$, and therefore is assigned to the C–S stretching of P_{Cl}. Thus, the (S)C–C(Cl) axis in this molecule is determined to be in the *trans* conformation and the molecular conformation is either TT or GT. No observation of the C–Cl stretching band of P_H also suports this conformation. The band at 703 cm^{-1} (710 cm^{-1} in the liquid state) is assigned to the C–Cl stretching of the P_S conformation with reference to the P_C frequency of 720—730 cm^{-1}. The remaining band at 680 cm^{-1} is then assigned to the CH_3–S stretching vibration. All of these vibrational assignments are confirmed by the normal coordinate calculations as shown in Table 1.

The conformation about the (C)S–C(C) axis is found to be in *gauche* in the solid state by examining the skeletal deformation vibrations as mentioned below. The Raman bands are observed in this state at 333, 274, and 228 cm^{-1} between 500 and 180 cm^{-1} (the corresponding frequencies in the liquid state are 332, 265, and 223 cm^{-1}). On the other hand, the normal coordinate calculations give the frequencies of 335 and 288 cm^{-1} in the same range for the TT form and 337, 257, and 204 cm^{-1} for the GT form. The number of the observed bands and their frequencies are explained only by the GT form. The Raman band at 282 cm^{-1}, which is observed in the liquid state but disappears on solidification, is in fact assigned to the TT form.

Close examinations of the observed Raman and infrared spectra, incorporated with the results of the normal coordinate calculations (Table 1), indicate that the TG, GG, and TT forms coexist in the liquid state in addition to the GT form. The frequencies of the observed bands which are assigned only to a single molecular form are 863, 663, and 422 cm^{-1} (TG form), 845, 632, and 412 cm^{-1} (GG form), and 282 cm^{-1} (TT form). The existence of the GG′ form is not certain but this conformation is quite unlikely to exist as suggested from the expected large steric repulsions.

The liquid-state Raman spectra were measured at higher and lower temperatures in order to study the relative conformational stabilities among the existing rotational isomers (Fig. 2). Although most of the individual Raman bands are more or less overlapped by other bands, it is evidently shown that the bands due to the GT form increase at lower temperature as compared with the bands due to the other forms. The GT form is thus found to be the most stable in the liquid state. The relative conformational stability for the other forms is not definitive from the present spectral measurements.

2-Bromoethyl Methyl Sulfide. The S–CH_2 and C–Br stretching frequencies are useful in determining the conformation about the (S)C–C(Br) axis, similarly to the case of 2-chloroethyl methyl sulfide for which the S–CH_2 and C–Cl stretching frequencies have been used.

In the crystalline solid state, the distinct bands are observed at 750, 741, 695, and 601 cm^{-1} in the range between 800 and 500 cm^{-1}. The 601 cm^{-1} band (613 cm^{-1} in the liquid state) is assigned to the C–Br stretching vibration of the P_S conformation, since the C–Br stretching frequencies for the P_C and P_H conformations of alkyl bromides are 635—645 and 555—565 cm^{-1}, respectively,[12] and the corresponding frequency for the P_S conformation is expected to be lower than the P_C frequency on account of a heavier atom of sulfur. The P_H frequencies of the C–Br stretching vibration is observed, in fact, at 565 and 557 cm^{-1} in the liquid state. Thus, the (S)C–C(Br) axis is determined to be in the *trans* conformation and the molecular conformation in the solid state is either TT or GT. The 741 cm^{-1} band, which is the least strong of the four Raman bands and corresponds to the 745 cm^{-1} band of the chloride, is assigned to the CH_2 rocking vibration. The band at 750 cm^{-1} is associated with the S–CH_2 vibration of the P_{Br} conformation in accord with the P_C frequency of 745—760 cm^{-1}, and the band at 695 cm^{-1} is assigned to the CH_3–S stretching vibration. It is noted that the

Table 3. Rotational isomers of 2-halogenoethyl methyl sulfides

	$CH_3SCH_2CH_2Cl$	$CH_3SCH_2CH_2Br$
Liquid[a]	GT, TG, GG, TT	GT, TG, GG, TT
Crystalline solid	GT	GT

a) For both 2-chloro- and 2-bromoethyl methyl sulfides, the GT form is the most stable in the liquid state.

C–Br stretching Raman band is stronger than the C–S stretching Raman band. For the chloride, a similar observation is also made that the C–Cl stretching vibration gives rise to a stronger Raman intensity than the C–S stretching vibration.

In the solid-state spectra, the bands are observed at 320, 242, and 207 cm^{-1} in the region between 500 and 180 cm^{-1}.[13] The TT form gives two calculated frequencies of 329 and 235 cm^{-1} in this region and the GT form three calculated frequencies of 318, 216, and 200 cm^{-1}. The comparison of the observed and calculated frequencies readily leads to the conclusion that the molecular conformation in the solid state is the GT form. Thus, the normal coordinate calculation is shown to be important in determining the conformation about the (C)S–C(C) axis in both cases of the chloride and the bromide.

In the liquid-state spectrum, there appear several bands which are not found in the solid-state spectrum. These are reasonably assigned to the rotational isomers other than the GT form on the basis of the spectral analyses and the results of the normal coordinate calculations. Of the bands observed only in the liquid state, the following bands are associated exclusively with a single rotational isomer: 960 cm^{-1} (TT form), 896, 675, 565, 401, and 218 cm^{-1} (TG form), and 828, 718, 655, 555, and 392 cm^{-1} (GG form). The GT, TG, GG, and TT forms are thus found to coexist in the liquid state, but the GG′ form is again unlikely to exist. If the GG′ form existed, the Raman spectrum would exhibit a band around 270 cm^{-1}, since the normal coordinate calculation on this form gives this frequency for a quasi-totally symmetrical deformation of the molecular skeleton.

The Raman spectra in the liquid state at higher and lower temperatures (Fig. 4) show the relative intensities of the bands assigned to the GT form are stronger at lower temperature than those assigned to the other forms. Accordingly the GT form is the most stable in the liquid state similarly to the case of the chloride.

Discussion

The rotational isomerism of 2-chloroethyl methyl sulfide has been studied by Hayashi[14] and the molecular form in the solid state has been reported to be either GT or TT.

In the present study, the following results on the rotational isomerism have been obtained for 2-chloro- and 2-bromoethyl methyl sulfides in common. (1) The molecular form in the crystalline solid state is the GT form. (2) The GT, TG, GG, and TT forms coexist in the liquid state, the GT form being the most stable.

For both 2-chloro- and 2-bromoethyl methyl sulfides, the GT form is the most stable in the liquid state, the (C)S–C(C) and (S)C–C(X) axes being in the *gauche* and *trans* conformations, respectively. The previous studies on unbranched alkyl sulfides indicated that the *gauche* conformation about the (C)S–C(C) axis is slightly more stable than the *trans* conformation[3–5,15,16] and for ethyl methyl sulfide the enthalpy difference between the *trans* and *gauche* conformation was shown to be $\Delta H_{T-G}=140\pm50$ cal mol^{-1} in the liquid state.[15] Accordingly, the conformational stability of the (C)S–C(C) part in the halogeno sulfides is in line with that for other sulfides.

The most stable isomer of the halogeno sulfide molecules takes the *trans* conformation about the (S)C–C(X) axis. For unbranched alkyl halides, the *gauche* (C)C–C(X) axis was found to be slightly more stable than the *trans* axis.[1] The conformational stability of the (O)C–C(X) axis in halogeno ethers was also studied and the *gauche* conformation was found to be more stable than the *trans* conformation.[17] Accordingly, the stability of the (S)C–C(X) axis is different from that of the (C)C–C(X) or (O)C–C(X) axis.

The Raman spectrum of 2-bromoethyl methyl sulfide in the liquid state (Fig. 3) shows that the C–Br stretching band at 613 cm^{-1} due to the *trans* (S)C–C(Br) conformation is much stronger than the corresponding bands at 565 and 555 cm^{-1} due to the *gauche* conformation.[18] For 2-bromoethyl methyl ether, however, the C–Br stretching Raman band of the *trans* (O)C–C(Br) conformation at 668 cm^{-1} is weaker than that of the *gauche* conformation at 571 cm^{-1} (Fig. 4 of Ref. 17) in contrast with the case of 2-bromoethyl methyl sulfide. This spectral difference for the two molecules suggests the difference of the conformational stability of the (S)C–C(Br) and (O)C–C(Br) axes as mentioned above, on the assumption that the ratio of the Raman intensity, per molecule, of the *trans* conformation to that of the *gauche* conformation does not change for these molecules. The validity of this assumption may be diagnosed in part by examining the coupling of these C–Br stretching vibrations with other vibrations. The calculated potential-energy distributions indicate that the bands assigned to the C–Br stretching have contributions from other vibrations less than 20% in any case of 2-bromoethyl methyl sulfide and 2-bromoethyl methyl ether. Accordingly, the assumption can be approximately valid for discussing the relative conformational stability.

For 1-bromobutane, the C–Br stretching Raman band of the *trans* (C)C–C(Br) conformation is weaker than the corresponding band of the *gauche* conformation (Fig. 11 of Ref. 1), similarly to the case of 2-bromoethyl methyl ether, but the intensity ratio of the *trans* to *gauche* band is larger than that of 2-bromoethyl methyl ether. Hence, the *gauche* conformation of the (O)C–C(Br) axis is shown to be more stabilized than the *gauche* conformation of the (C)C–C(Br) axis on the assumption of the constant Raman intensity ratio. The spectral observations on the above-mentioned molecules give a suggestion that a sulfur atom lowers, as compared with a carbon atom, the energy of the *trans* conformation but an oxygen atom lowers the energy of the *gauche* confor-

mation of the (A)C–C(X) axis, where A is S or O and X is a halogen atom.

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