Molecular Vibrations and Force Fields of Alkyl Sulfides. II. Infrared Spectra of $CH_3S(CH_2S)_nCH_3$ ($n=0-3$)

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Infrared spectra recorded in the liquid and solid states of dimethyl sulfide, CH_3SCH_3, bis(methylthio)methane, $CH_3SCH_2SCH_3$, bis(methylthiomethyl) sulfide, $CH_3SCH_2SCH_2SCH_3$, and bis[(methylthio)methylthio]methane, $CH_3SCH_2SCH_2SCH_2SCH_3$, are reported. For the $CH_3SCH_2SCH_3$ species, the gaseous spectra were also recorded. For these molecules, the observed bands were assigned to the fundamental modes of the vibrations with reference to those of reported analogous-structure molecules. The existence of the rotational isomers of the last three compounds was postulated. The regularity of the wave number of the fundamentals obtained and the intensity change in some of the bands for this series of compounds were discussed. The frequency shift in the liquid-solid phase transition was also described for a few bands.

The vibrational analysis of dimethyl sulfide, CH_3SCH_3, has been reported elsewhere.[1-4] For bis(methylthio)methane, $CH_3SCH_2SCH_3$, and bis(methylthiomethyl) sulfide, $CH_3SCH_2SCH_2SCH_3$, Welti and Whittaker[5] have reported an infrared treatment. Complete assignments, however, were not made. For bis[(methylthio)methylthio]methane, $CH_3SCH_2SCH_2SCH_2SCH_3$, we have not found any vibrational treatment reported up to 1970. In the first paper of this series,[4] we determined the molecular force fields of dimethyl sulfide. However, we could not obtain complete experimental results with the low-resolution instrument we used. Therefore, we recorded the spectra of dimethyl sulfide a new. On the molecular series of $CH_3S(CH_2S)_nCH_3$ ($n=0$—3), some correlations may exist between those vibrational spectra and the degree of n. Rotational isomerism is also expected in the molecular species of $n=1$—3. From this point of view, we have investigated the infrared spectra of this series: $CH_3S(CH_2S)_nCH_3$ ($n=0$—3). This paper will treat the vibrational interpretation of polythiomethylene.

Experimental

Materials. The dimethyl sulfide was commercially obtained (Tokyo Kasei Co., Tokyo) and distilled in a vacuum over phosphorus pentoxide before use. The other materials used in the infrared recording were prepared according to the method reported by Fehér and Vogelbruch.[6]

Bis(methylthio)methane
found bp 149—150°C/760 mmHg, 44°C/14 mmHg; purity (above 99%)
lit.[5-6] bp 148—150°C/760 mmHg, 45°C/14 mmHg

Bis(methylthiomethyl) Sulfide
found bp 106°C/5 mmHg; purity (above 98%)
lit.[5-6] bp 100—103°C/3.5 mmHg, 113°C/13 mmHg

Bis[(methylthio)methylthio]methane
found bp ~135°C/1—2 mmHg, mp 17.0°C; purity (above 90%)
lit.[6] bp 117.5°C/0.7 mmHg, mp 17.2°C

The purity of all the samples was estimated by means of gas chromatography. The infrared spectra were measured in the liquid and solid states in the range of 4000—200 cm^{-1} with a Perkin-Elmer Model 621 Spectrophotometer equipped with KBr and CsI cells. The liquid spectra of dimethyl sulfide were recorded at a temperature slightly above its melting point. The other materials were recorded at room temperature (*ca.* 22°C). For the $CH_3S(CH_2S)_nCH_3$ ($n=1$—3) series the infrared spectra in CS_2 and CH_3NO_2 solutions were also recorded (1400—600 cm^{-1}). The solid spectra were obtained with a conventional cell which was cooled by liquid nitrogen. The spectrum of the solid film was recorded before and after annealing near the melting point. The gaseous spectra of $CH_3SCH_2SCH_3$ were also investigated in the 850—600 cm^{-1} region at temperatures of 26—129°C. The wave numbers thus obtained were calibrated by the use of bands of indene and polystyrene. The frequency of the obtained spectra has measured with an estimated accuracy of ± 1 cm^{-1} at 2000—400 cm^{-1} and with an accuracy of ± 2 cm^{-1} at 4000—2000 cm^{-1}; the accuracy of the 400—200 cm^{-1} region may be within 5 cm^{-1}. The $\sim$ sign in Tables 2—4 shows that the wave number of its band was poorly estimated.

Vibrational Assignment

The assignments of the observed bands were made on the basis of those of dimethyl sulfide,[1-4] monochloromethyl methyl sulfide,[7] (methylthio)methanethiol,[8] polymethylene disulfide,[9] and 1,3,5-trithiane.[10]

Dimethyl Sulfide. The assignments are summarized in Table 1. The annealed spectra are more finely resolved than the liquid spectra. We compared the spectra of liquid and solid states, and found that a new band, which was not observed in the liquid spectra, appeared in the C–H stretching, CH_3 degenerate deformation, and CH_3 rocking regions, in the solid state.

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3) J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).
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5) D. Welti and D. Whittaker, *J. Chem. Soc.*, **1962**, 4372.
6) F. Fehér and K. Vogelbruch, *Chem. Ber.*, **91**, 996 (1958).
7) M. Hayashi, *Nippon Kagaku Zasshi*, **80**, 1073 (1959).
8) M. Ohsaku, Y. Shiro, and H. Murata, unpublished work.
9) M. Hayashi, Y. Shiro, and H. Murata, This Bulletin, **39**, 1857 (1966).
10) M. Ohsaku and H. Murata, *J. Sci. Hiroshima Univ.*, A-II, **33**, 179 (1969).

Table 1. Infrared frequencies (cm^{-1}) and assignments of dimethyl sulfide[a)]

Liquid	Solid		Assignment
	Unannealed	Annealed	
	2986 sh, vw	2986 w	C–H str (A_2)
2982 m	2979 m	2979 m	C–H str
2965 s	2965 s	2965 s	C–H str
2915 s	2915 vs	2917 vs	C–H str
2901 sh, m	2901 sh, m	2903 sh, m	C–H str
2855 m, br	2858 m, br	2860 m, br	$2\times CH_3$ deg or C–H str
2830 m	2830 m	2830 s	C–H str or $2\times CH_3$ deg
1451 sh, w	1448 m	1448 s	CH_3 deg def
1429 vs	1432 sh, m	1432 m	CH_3 deg def
	1427 sh, w	1428 w	CH_3 deg def (A_2)
1421 sh, s	1421 vs	1421 vs	CH_3 deg def
1329 vvw	1331 m	1331 m	CH_3 sym def
1307 m	1305 m	1303 m	CH_3 sym def
1038 s	1039 vs	1039 vs	CH_3 rock
984 s	985 vs	985 vs	CH_3 rock
	951 vw	952 w	CH_3 rock (A_2)
909 w	910 w	910 w	CH_3 rock
742 vw	743 w	744 w	C–S str
691 m	692 s	693 s	C–S str
275 vw	275 vw	275 vw	skel def

s, strong, m, medium, w, weak, v, very, sh, shoulder, br, broad.

a) Above 3000 cm^{-1} and 2800—1500 cm^{-1} regions are omitted.

Dimethyl sulfide has a C_{2v} symmetry. However, if the site symmetry of C_{2v} does not remain in the solid state, the forbidden bands may appear. Moreover, one each of C–H stretching, CH_3 degenerate deformation, CH_3 rocking, and torsional vibrations belong to the A_2 species. In the spectral region we treated, the former three bands are expected. This sufficiently coincident with the observed result that only three bands belonging to the A_2 vibrations appeared in the solid state, in addition to the bands in the liquid state. The obtained wave numbers closely agreed with the calculated wave number of the previous normal coordinate treatment.[4)] Thus, these observations lead to the findings that the site symmetry of the dimethyl sulfide molecule changes to C_2 or C_s in the solid state and that the new bands can be assigned to the A_2 mode. In the spectra obtained in the solid state, unannealed or annealed, seven bands were observed in the 2900 cm^{-1} region. Among these bands the overtone bands of the CH_3 degenerate deformation vibrations may be confused; they are hardly distinguishable from each other. In the annealed spectra around 1400 cm^{-1}, we obtained four bands, at 1448, 1432, 1428, and 1421 cm^{-1}. Among these bands, the band at 1428 cm^{-1} is assigned to the CH_3 degenerate deformation vibration of the A_2 species. In the region around 1300 cm^{-1}, two bands were obtained finely in the solid film. In our previous paper,[4)] we considered that these CH_3 symmetrical deformation bands overlapped each other with a low resolution of the spectrometer. For the CH_3 rocking region, we obtained three bands in the liquid, and four bands in the solid, film. The band at 952 cm^{-1} appeared only in the solid film. This band corresponds well to the band (960—950 cm^{-1}) obtained from the Pd and Pt complex of dimethyl sulfide.[11)] As for the weak band obtained at 909 cm^{-1} (liquid), we previously identified it as an impurity band. Scott and El-Sabban treated[12)] the normal coordinate treatment and identified it as the sum-combination of the A_2 torsional and B_1 C–S stretching vibrations. Allkins and Hendra treated[3)] the vibrational spectra of CH_3XCH_3 spectral series (X=S, Se, and Te) and identified it as the fundamental. If the band around 900 cm^{-1} of CH_3SCH_3 is the sum-combination, the sum-combination for CH_3SeCH_3 and CH_3TeCH_3 would not be observed in this region. However, in the expected region, the corresponding band due to the fundamental was reported.[3)] Thus, the band around 900 cm^{-1} is not to be considered as a sum-combination, but can be assigned to a rocking fundamental. For the C–S stretching region, a couple of the bands were obtained, at 744 and 693 cm^{-1}, in the annealed state. Below 400 cm^{-1} the skeletal deformation bands can be expected. The weak band at 275 cm^{-1} may be assigned to the skeletal deformation vibration.

Bis(methylthio)methane. The obtained infrared data of bis(methylthio)methane are summarized in Table 2. The annealed spectra are well resolved in the C–H stretching, CH_3 degenerate deformation, and CH_3 rocking regions. The bands around 2950 cm^{-1} may due to the C–H stretching vibrations. In this region the overtone bands of the CH_3 degenerate deformation fundamentals may be present. As for the CH_3 degenerate deformation, the bands obtained around 1430 cm^{-1} may be assigned. For the region 1400—1100 cm^{-1}, the CH_2 bending, CH_3 symmetrical deformation, CH_2 wagging, and the CH_2 twisting vibrations are expected. The medium band obtained at 1387 cm^{-1} and the very strong band at 1203 cm^{-1} in the liquid spectra separate into two components upon crystallization. This splitting may be attributed to the crystal field effect or to the imperfection annealing. Around 960 cm^{-1} two bands appeared in the liquid state and three bands in the crystalline state. The liquid-solid phase transition shift of this region is fairly large. The bands obtained in this region may be due to the CH_3 rocking vibrations. A rather puzzling feature of the spectra is the infrared band of a weak intensity at 874 cm^{-1}. It seems too high for a CH_2 rocking fundamental and too low for a CH_3 rocking fundamental; we can not explain reasonably. For the C–S stretching region, 760—600 cm^{-1}, we observed seven bands, including three shoulder bands, in the liquid state. This molecule has four C–S stretching vibrational freedom for one conformation. Actually, in the solid state, four bands appeared. For the skeletal deformation region, 400—200 cm^{-1}, we obtained nine very weak and fairly broad bands in the liquid state.

11) J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, **24A**, 1305 (1968).

12) D. W. Scott and M. Z. El-Sabban, *J. Mol. Spectrosc.*, **30**, 317 (1969).

Table 2. Infrared frequencies (cm^{-1}) and assignments of bis(methylthio)methane[a)]

Liquid	CS_2 soln	CH_3NO_2 soln	Solid		Assignment
			Unannealed	Annealed	
2985 sh, m			2985 sh, m	2985 sh, w	C–H str
				2977 sh, w	C–H str
2975 s			2971 m	2969 m	C–H str
2955 sh, w			2955 sh, w	2958 m	C–H str
2914 vs			2914 s	2910 s	C–H str
				2881 w	C–H str
2857 m			2856 w	2851 w	C–H str or 2 × CH_3 deg
2832 m			2825 w	2821 w	C–H str or 2 × CH_3 deg
1441 sh, vw			1441 sh, w	1441 sh, w	CH_3 deg def
1435 vs			1435 s	1436 s	CH_3 deg def
			1422 sh, w	1421 sh, w	CH_3 deg def
1423 vs			1418 s	1417 s	CH_3 deg def
1387 m	1385 m		1390 sh, w 1382 m	1391 m 1385 sh, w	CH_2 bend
1327 sh, vw	1327 sh, vw		—	1325 vw	
1318 m	1318 m		1316 w	1311 m	CH_3 sym def
			1306 sh, vw	—	CH_3 sym def
1203 vs	1205 vs	1207 vs	1205 s	1218 m 1210 s	CH_2 wag
1163 sh, vw	1164 sh, vvw		—	—	
1155 w	1153 w		1161 m	1166 m	CH_2 twist
1124 vw	1123 vw		—	—	
986 s	985 s	988 s	988 s	995 vs	CH_3 rock
959 s	958 s	961 s	959 s	960 m 952 s	CH_3 rock
(874 w)	(874 w)		(876 w)	(874 vw)	?
824 sh, w	825 sh, w	825 sh, vw	—	—	
806 s	806 s	807 m	807 m	808 s	CH_2 rock
758 sh, m	757 sh, m	760 sh, m	—	—	
746 vs	746 vs	748 vs	747 vs	747 vs	C–S str
724 w	724 w	724 w	726 w	725 w	C–S str
705 sh, vw	705 sh, vw	706 sh, w	—	—	
694 vs	694 vs		694 vs	693 vs	C–S str
669 sh, vw	669 sh, vw		—	—	
649 w	649 w		651 w	653 w	C–S str
~360 sh, vvw			—	—	
~350 sh, vvw			—	—	
340 vw, br			339 vw	341 vw	skel def
321 sh, vvw			314 w	314 w	
303 vvw, br			305 sh, vw	305 sh, vw	
~270 sh, vvw			~270 vvw	—	
~265 vvw, br			~260 vvw	—	
~235 vvw, br			~235 vvw	~235 vvw	skel def
216 vvw, br			~220 vvw	~220 vvw	

s, strong, m, medium, w, weak, v, very, sh, shoulder, br, broad.
The sign, —, shows the band which disappears in the solid state.
a) Above 3000 cm^{-1} and 2800—1500 cm^{-1} regions are omitted.

Bis(methylthiomethyl) Sulfide. The obtained spectra of an annealed film of bis(methylthiomethyl) sulfide were well resolved. The infrared data we obtained are summarized in Table 3. The molecule has two methylene groups and six C–S bonds. The obtained spectra of bis(methylthiomethyl) sulfide are more complicated than those of bis(methylthio)methane. However, the spectral features in the 3000—1300 cm^{-1} region are similar to those of bis(methylthio)methane. The bands which appeared around the 1200 and 1150 cm^{-1} regions are to be assigned to the CH_2 wagging and twisting vibrations respectively. As for the CH_3 rocking region, two bands appeared in the liquid state. In the crystalline state, three sharp bands were obtained, at 969, 961, and 955 cm^{-1}. To the CH_2 rocking vibrations, two bands at 844 and 780 cm^{-1} in the solid state are assigned. The bands around 700 cm^{-1} may due to the C–S stretching vibrations. In this region, seven bands, including three shoulder bands, appeared in the liquid state. In the crystalline film, five bands of them are retained, their intensities changed. In the region 400—200 cm^{-1}, the skeletal deformation vibrations

Table 3. Infrared frequencies (cm^{-1}) and assignments of bis(methylthiomethyl) sulfide[a)]

Liquid	CS_2 soln	CH_3NO_2 soln	Solid		Assignment
			Unannealed	Annealed	
2985 sh, w			2983 sh, w	2981 w	C–H str
2973 m			2970 m	2973 m	C–H str
2963 sh, w			2957 sh, w	2954 w	C–H str
2915 vs			2914 s	2914 s	C–H str
2854 w			2853 w	2853 w	C–H str or 2 × CH_3 deg
2830 w			2825 w	2815 w	C–H str or 2 × CH_3 deg
1441 sh, w			1439 sh, w	1439 sh, s	CH_3 deg def
1435 s			1435 s	1434 s	CH_3 deg def
1423 s			1422 sh, w	1416 sh, m	CH_3 deg def
1420 sh, w			1419 s	1410 s	CH_3 deg def
1395 w			—	—	CH_2 bend
1379 s	1379 s		1378 s	1381 m 1372 s	CH_2 bend
1327 sh, vw			—	—	CH_3 sym def
1317 w	1316 m		1314 w 1307 sh, vw	1312 w 1306 vw	CH_3 sym def
1218 w	1216 m	1221 m	1220 w	1219 m	CH_2 wag
1193 vs	1190vs	1195 vs	1191 s	1193 s	CH_2 wag
1165 sh, w	1163 sh, w		1171 w	1167 w	CH_2 twist
1132 w	1131 m	1134 m	1135 m	1133 m	CH_2 twist
1119 sh, vw	1120 sh, vw		—	—	
974 s	974 s	975 s	978 s	969 s	CH_3 rock
961 s	959 s	961 s	961 m	961 s 955 m	CH_3 rock
855 sh, vw			—	—	
841 w	841 w	841 w	844 w	844 m	CH_2 rock
834 w	832 w	832 w	—	—	
820 sh, vw			—	—	
778 s	779 s	778 s	778 s	780 m	CH_2 rock
754 sh, w	753 sh, w	754 sh, w	—	—	
742 vs	741 vs	742 vs	743 vs	746 s 736 s	C–S str C–S str
712 m	711 m	712 s	714 s	711 w	C–S str
700 s	698 s	699 s	699 vs	695 vs	C–S str
690 sh, vw			—	—	
661 w	660 w		661 m	657 s	C–S str
645 sh, vw	645 sh, vw		647 vw	—	
365 sh, vw			—	—	
350 vvw			355 vvw	—	
~340 sh, vvw			—	—	
331 vw			331 vw	339 vw	skel def
315 sh, vvw			—	318 vw	
305 sh, vvw			305 vvvw	—	
277 vvw			~275 vvw	275 vvw	skel def ?
259 sh, vvw			~260 vvw	—	
254 sh, vvw			—	—	
244 w			250 vw	247 w	skel def

s, strong, m, medium, w, weak, v, very, sh, shoulder, br, braod.
The sign, —, shows the band which disappears in the solid state.
a) Above 3000 cm^{-1} and 2800—1500 cm^{-1} regions are omitted.

would appear. We obtained ten bands in the liquid state.

Bis[(methylthio)methylthio]methane. The infrared data of bis[(methylthio)methylthio]methane we obtained are summarized in Table 4. In this molecule, there are two methyl and three methylene groups, and eight C–S bonds. The infrared spectra of bis[(methylthio)methylthio]methane we obtained are similar to those of bis(methylthiomethyl) sulfide without any CH_2 deformation region. The spectra in the C–H stretching region are not well resolved. The spectra in the CH_3 degenerate deformation region are, however, well resolved in the solid state. The spectral features of this region are similar to those in the same region of dimethyl sulfide. The bands around 1200 cm^{-1} and 1150 cm^{-1} can be assigned to the CH_2 wagging and

Table 4. Infrared frequencies (cm^{-1}) and assignments of bis[(methylthio)methylthio]methane[a)]

Liquid	CS_2 soln	CH_3NO_2 soln	Solid		Assignment
			Unannealed	Annealed	
2984 sh, m			2985 sh, vw	2985 sh, vw	C–H str
2967 m			2965 m	2965 m	C–H str
2912 vs			2907 m	2906 m	C–H str
2854 w			2854 vw	2854 vw	C–H str or 2×CH_3 deg
2826 w			2824 vw	2824 vw	C–H str or 2×CH_3 deg
			1444 sh, m	1446 m	CH_3 deg def
1438 sh, s			1438 sh, m	1441 sh, m	CH_3 deg def
1434 s			1430 s	1431 vs	CH_3 deg def
1422 s			1418 m	1418 m	CH_3 deg def
1401 sh, w			—	—	
1394 sh, m			1378 m	1379 s	CH_2 bend
1378 s	1377 s		1369 vs	1369 vs	CH_2 bend
			1354 sh, vw	1355 w	CH_2 bend
1316 w	1316 w	1318 w	1329 vw	1332 w	CH_3 sym def
			1310 vw	1311 vw	CH_3 sym def
1223 sh, w	1222 sh, w	1223 sh, w	1220 w	1220 w	CH_2 wag
1205 sh, w	1205 sh, w	1205 sh, w	—	—	
1199 sh, s	1198 sh, s		1204 m	1204 m	CH_2 wag
1188 vs	1186 vs	1191 vs	1182 m	1182 m	CH_2 wag
1171 sh, w	1171 sh, w	1168 sh, w	1172 sh, w	1173 sh, w	CH_2 twist
1145 w	1144 w	1147 w	1152 w	1153 w	CH_2 twist
1125 w	1124 w	1123 w	1126 w	1126 w	CH_2 twist
971 s	971 s	973 s	973 vs	974 vs	CH_3 rock
960 sh, s	958 s	961 sh, s	957 sh, w	957 sh, w	CH_3 rock
858 w	859 w	860 w	864 s	866 s	CH_2 rock
820 w	819 w	819 w	811 w	811 w	CH_2 rock
785 w	785 w	786 w	—	—	
763 s	763 s	764 s	759 m	760 m	CH_2 rock
740 vs	740 vs	740 vs	742 s	742 s	C–S str
731 sh, s	728 s	729 sh, s	729 s	729 s	C–S str
712 sh, vw	712 sh, w		—	—	
700 vs	699 vs	698 vs	699 vs	701 vs	C–S str
687 sh, w	687 sh, w		—	—	
663 w	663 w		663 s	665 s	C–S str
651 sh, vw	650 sh, vw		652 w	654 w	C–S str
~640 sh, vw	~640 sh, vw		—	—	
360 sh, vvw			—	—	
338 vvw, br			326 w, br	331 w, br	skel def
305 vvw, br			—	—	
272 sh, vvw			274 w	275 w	skel def
265 vw			266 sh, w	269 sh, w	
235 vvw, br			~240 vvvw	235 vvvw	
217 vvw, br			~220 vvw	~220 vvvvw	

s, strong, m, medium, w, weak, v, very, sh, shoulder, br, broad.
The sign, —, shows the band which disappears in the solid state.
a) Above 3000 cm^{-1} and 2800—1500 cm^{-1} regions are omitted.

twisting vibrations respectively. The bands obtained around 970 cm^{-1} may be due to the rocking vibrations of the terminal CH_3 groups. The strong shoulder band of the liquid state at 960 cm^{-1} decreases in its intensity in the solid state. Three bands of the CH_2 rocking vibrations are expected for this molecule. Actually, four bands appeared in the liquid state, at 858, 820, 785, and at 763 cm^{-1}, and in the annealed film, three bands appeared, at 866, 811 and at 760 cm^{-1}. The C–S stretching vibrations are obtained around 700 cm^{-1}. We obtained eight bands in the liquid state (740, 731, 712, 700, 687, 663, 651, and 640 cm^{-1}) and five bands in the crystalline state (742, 729, 701, 665, and 654 cm^{-1}). In the region 400—200 cm^{-1}, seven bands appeared in the liquid state.

Discussion

The existence of the rotational isomer of the series of the compounds discussed above may be investigated by means of studying the spectra in the region of the CH_2 rocking, C–S stretching, and the skeletal deformation

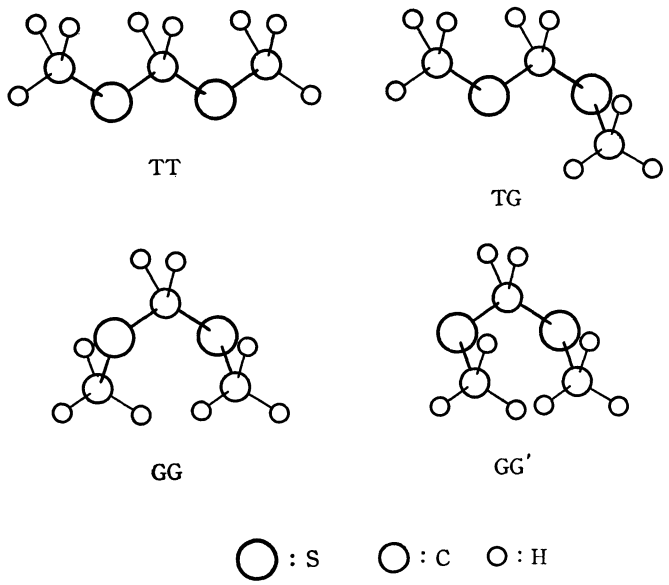


Fig. 1. Structures and conformations of bis(methylthio)methane.
T=*Trans*, G=*Gauche*.

vibrations. Among these vibrations, the ones which were sufficiently covered in the spectral range we treated are the CH_2 rocking and C–S stretching vibrations. On bis(methylthio)methane, one CH_2 rocking and four C–S stretching bands can be expected. Actually, two CH_2 rocking and seven C–S stretching bands appeared in the liquid-state spectra. In bis(methylthiomethyl) sulfide, two CH_2 rocking and six C–S stretching bands can be expected. We obtained five CH_2 rocking and eight C–S stretching bands in the liquid spectra. In the case of bis[(methylthio)methylthio]methane, treatment is above only with difficulty. In this molecule, three CH_2 rocking and eight C–S stretching vibrations can be expected; we observed four CH_2 rocking and eight C–S stretching bands in the liquid state.

On bis(methylthio)methane, four conformations (TT, TG, GG, and GG') may be supposed on theoretical, as is shown in Fig. 1. We revealed the existence of the rotational isomers by means of a comparison between the spectra of the liquid and solid states, since some bands of the liquid spectra disappeared in the solid state. Moreover, in order to confirm the existence of the rotational isomers, we attempted to investigate the temperature dependence of the band intensity of the gaseous state in the 850—600 cm^{-1} region on $CH_3SCH_2SCH_3$. The wave numbers of the gaseous bands we obtained are summarized in Table 5, together with the corresponding wave numbers of the liquid and solid spectra. From the gaseous envelopes obtained at different temperatures, we found that the intensity change was not large enough to determine the energy differences between and/or among the rotational isomers. Therefore, in order to observe the wave number change due to the rotational angles, we have made a normal coordiante treatment of $CH_3SCH_2SCH_3$ with four conformations: TT, TG, GG, and GG', using the Urey-Bradley force field. The details of the normal coordinate treatment will be reported in a separate paper.[13]

Table 5. Infrared frequencies of the gaseous bands with their corresponding liquid and solid bands, and assignments of bis(methylthio)methane (850—600 cm^{-1})

Solid	Liquid	Gaseous	Assignment
808	806	812 sh, w 805 w 798 sh, w	CH_2 rock
—	758	762 sh, w 759 m	C–S str
747	746	753 m 747 m 740 sh, m	C–S str
725	724	720 vvw	C–S str
—	705	705 w	C–S str
693	694	698 w 691 w 687 sh, w	C–S str
—	669	669 vw	C–S str
653	649	647 vvw	C–S str

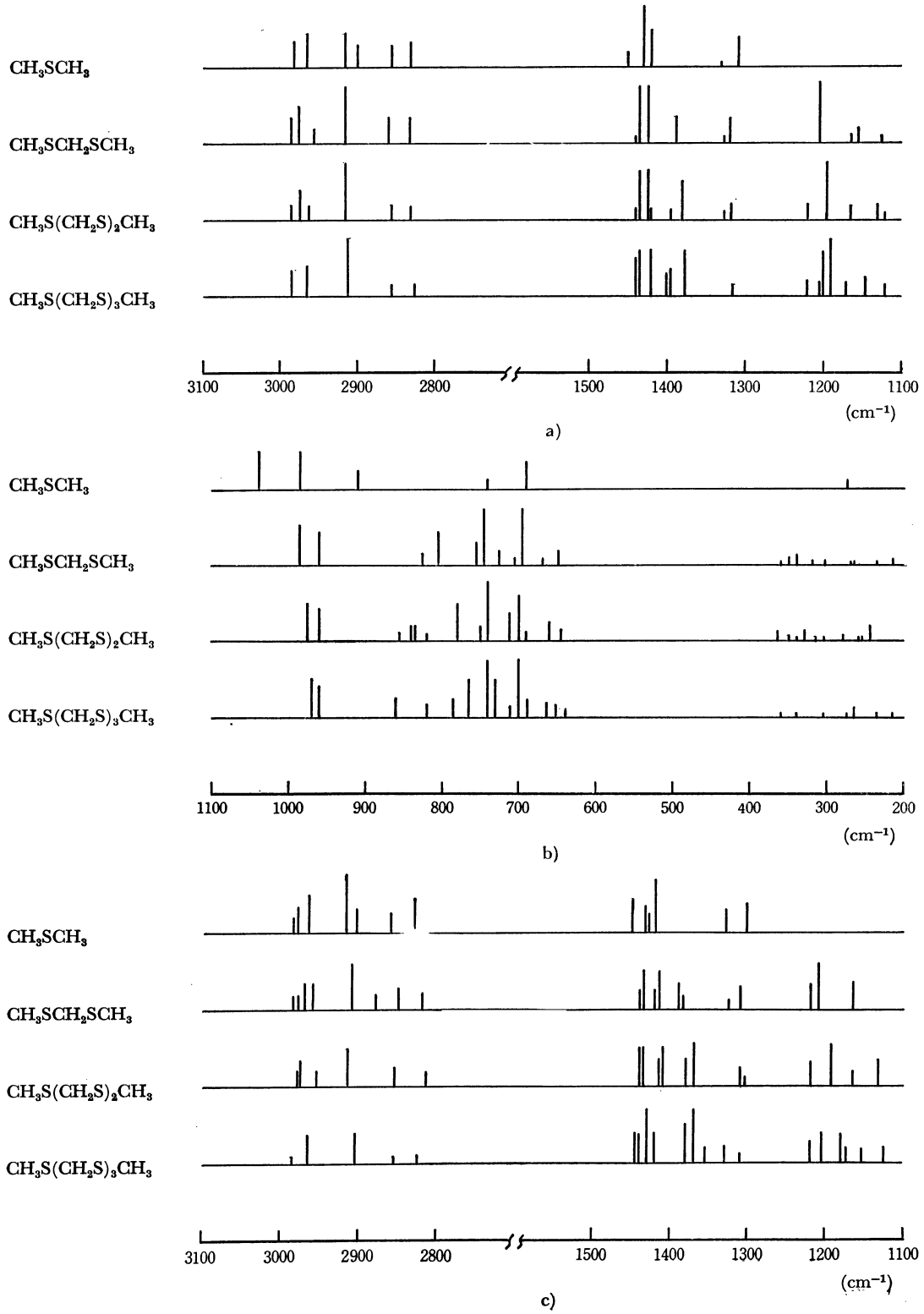
Table 6. Observed and calculated frequencies (cm^{-1}) of bis(methylthio)methane in the C–S stretching region

Obsd	Calcd			
	TT	TG	GG	GG'
758[a)]	756	757		753
746	741		750	
724		732	739	730
705[a)]	709	702		
694			689	693
669[a)]	660			
649		643	625	627

a) Not appeared in the solid state.

13) M. Ohsaku, Y. Shiro, and H. Murata, to be published.

The computed wave numbers of the C–S stretching vibrations are listed in Table 6. As is shown in Table 6, the calculated wave number changes with the skeletal conformations. The bands which disappeared in the solid state may be identified as fundamentals. Among the four conformations, the GG′ form might have a higher energy than the other forms. Therefore, three conformations remain: TT, TG, and GG. We, at present, can not venture to decide how many conformations (two or three) may exist in the liquid or gaseous state with stability. However, from only these data, we can not deny that these three conformations coexist in either the liquid or gaseous state. In the solid state, this molecule may have one conformation. In the case of bis(methylthiomethyl) sulfide and bis-[(methylthio)methylthio]methane, a large number of conformations can be expected. The situation is difficult in studying the longer molecules. The difficulty



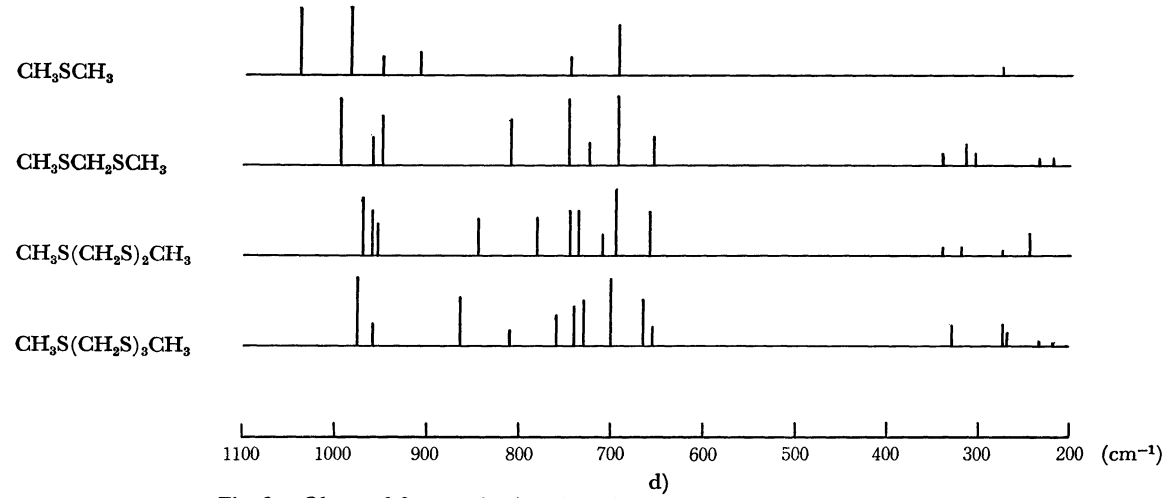


Fig. 2. Observed frequencies (cm^{-1}) and relative intensities of $CH_3S(CH_2S)_nCH_3$ (n=0—3).
a) 3000—1100 cm^{-1} (Liquid) b) 1100—200 cm^{-1} (Liquid)
c) 3000—1100 cm^{-1} (Annealed) d) 1100—200 cm^{-1} (Annealed)

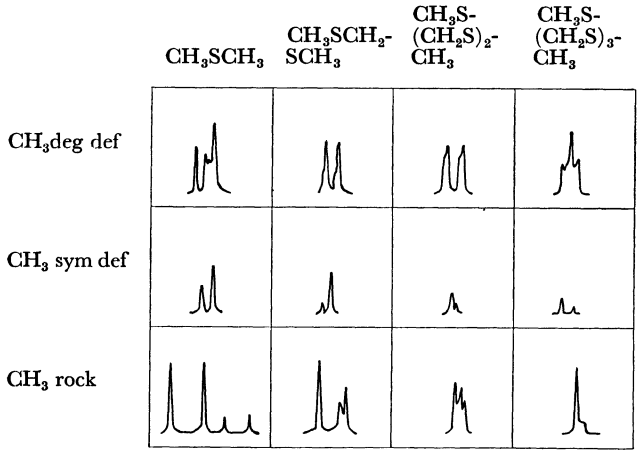


Fig. 3. Infrared band shapes of terminal CH_3 groups (Annealed): $CH_3S(CH_2S)_nCH_3$ (n=0—3).

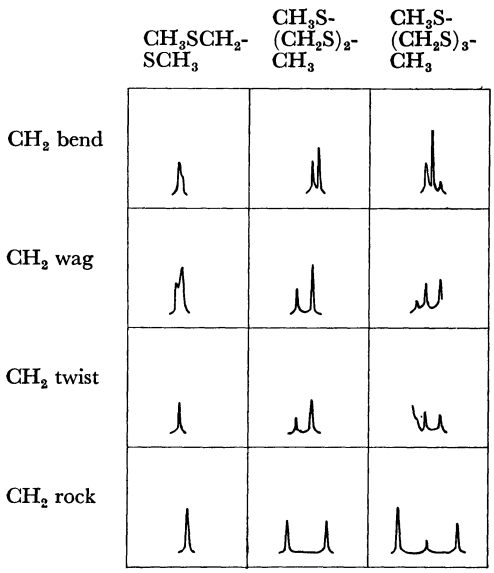


Fig. 4. Infrared band shapes of internal CH_2 groups (Annealed): $CH_3S(CH_2S)_nCH_3$ (n=1—3).

in the recognition of the rotational isomer will be reported separately in connection with the normal coordinate treatment of this series of compounds.

The observed frequencies for the spectral series studied, $CH_3S(CH_2S)_nCH_3$ (n=0—3), are graphically summarized in Fig. 2. Figures 3 and 4 show the band shapes thus obtained in relation to the CH_3 and CH_2 groups (annealed). Tables 7 and 8 show the infrared frequencies of the terminal CH_3 groups and the internal CH_2 groups obtained in the crystalline state. The C–H stretching region shows no definite tendency in either the liquid or solid state. The frequency of the CH_3 degenerate deformation and the CH_3 symmetrical deformation bands obtained in the liquid state changes little from dimethyl sulfide to bis[(methylthio)methylthio]methane. However, the frequency obtained in the annealed state shows a little irregularity. The spacing of two CH_3 symmetrical deformation bands also shows a little irregularity. The CH_2 bending, wagging, and the twisting vibrations constantly shifted to a lower frequency region with increase in the molecular chain length. The frequency difference among CH_3 rocking bands becomes small hyperbolically with an increase in the chain length. This shows that the intramolecular interaction of methyl groups between the two ends rapidly decreases with an increase in the chain length. We observed the CH_2 rocking vibrations in the wider range around 800 cm^{-1}. It is interesting that, in the annealed spectra, the central band at 811 cm^{-1} of bis-[(methylthio)methylthio]methane has nearly the same frequency of that of bis(methylthio)methane (808 cm^{-1}), and that the spacings between their bands and their side bands are nearly the same width on both sides (55 and 51 cm^{-1}). For the C–S stretching region, the bands obtained are gradually complicated with an increase in the molecular chain. However, a couple of more intense bands appeared at nearly the same wave number in any case; that is, in the liquid spectra the intense bands were 742 and 691 cm^{-1}, 746 and 694 cm^{-1}, 742 and 700 cm^{-1}, and 740 and 700 cm^{-1} for dimethyl sulfide, bis(methylthio)methane, bis-(methylthiomethyl) sulfide, and for bis[(methylthio)-

Table 7. Infrared frequencies (cm^{-1}) of terminal CH_3 groups (annealed): CH_3S-$(CH_2S)_nCH_3$ (n=0—3)

	n=0	n=1	n=2	n=3
CH_3 deg def	1448 (16) 1432 (4) 1428 (7) 1421	1441 (5) 1436 (15) 1421 (4) 1417	1439 (5) 1434 (18) 1416 (6) 1410	1446 (5) 1441 (10) 1431 (13) 1418
CH_3 sym def	1331 (28) 1303	1325 (14) 1311	1312 (6) 1306	1332 (21) 1311
CH_3 rock	1039 (54) 985 (33) 952 (42) 910	995 (35) 960 (8) 952	969 (8) 961 (6) 955	974 (17) 957

Figures in parentheses show the difference between adjacent bands.

Table 8. Infrared frequencies (cm^{-1}) of internal CH_2 groups (annealed): $CH_3S(CH_2S)_nCH_3$ (n=1—3)

	n=1	n=2	n=3
CH_2 bend	1391 1385	1381 (9) 1372	1379 (10) 1369 (14) 1355
CH_2 wag	1218 1210	1219 (26) 1193	1220 (16) 1204 (22) 1182
CH_2 twist	1166	1167 (34) 1133	1173 (20) 1153 (27) 1126
CH_2 rock	808	844 (64) 780	866 (55) 811 (51) 760

Figures in parentheses show the difference between adjacent bands.

methylthio]methane respectively.

The intensities of various fundamentals are of interest. That is, the intensities of fundamentals arising from CH_3 groups, *i.e.*, the CH_3 degenerate deformation, CH_3 symmetrical deformation, and the CH_3 rocking fundamentals, decrease, while on the other hand, the intensities of the fundamentals arising from CH_2 groups, *i.e.*, the CH_2 bending, CH_2 wagging, CH_2 twisting, and the CH_2 rocking fundamentals, increase with an increase in the chain length.

The relations of the obtained wave numbers will be discussed in detail by the aid of the normal coordinate treatment analysis. The results of the normal coordinate treatment of the molecules described in this paper will be reported separately.[13]

Conclusion

The infrared spectra of the $CH_3S(CH_2S)_nCH_3$ (n=0—3) series obtained in the liquid and solid states have been assigned. For the last three molecules, the rotational isomer can be expected. On the $CH_3SCH_2SCH_3$ molecular species, the existence of more than two conformations was confirmed in the liquid or gaseous states by two procedures: a) a comparison between the liquid and solid spectra, and b) a normal coordinate treatment. Moreover, in the solid state, the species $CH_3SCH_2SCH_3$ would be one conformation. We tried to ascertain the temperature dependence of the gaseous envelopes. However, the differences by which to determine the energy difference based on the rotational isomer were not obtained. It seems that some regularities stay in the fundamentals of this series thus obtained: $CH_3S(CH_2S)_nCH_3$ (n=0—3).

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