Vibrational Spectra and Molecular Conformations of Dialkyl Disulfides

Hiromu Sugeta, Akikatsu Go, and Tatsuo Miyazawa
Institute for Protein Research, Osaka University, Yamada-kami, Suita, Osaka 565

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The infrared and Raman spectra of several dialkyl disulfides were measured and their conformations were discussed in relation with the characteristic S–S and C–S stretching vibrations. The infrared spectra in the solid state and the temperature dependence of Raman spectra were measured for ethyl methyl disulfide and diethyl disulfide. For ethyl methyl disulfide, the *gauche-gauche* isomer was more stable than the *trans-gauche* isomer by about 0.9 kcal/mol while for diethyl disulfide the *gauche-gauche-gauche* isomer was more stable than the *trans-gauche-gauche* isomer by about 0.6 kcal/mol in the liquid state. Only the *gauche-gauche* form for ethyl methyl disulfide and only the *gauche-gauche-gauche* form for diethyl disulfide were observed in the solid state.

For vibrational analyses of Raman spectra of proteins, it is necessary to establish correlations between vibrational spectra and conformations of side-chain groups and related model molecules. The correlations between the S–S and C–S stretching frequencies and conformations of the disulfide group $\rangle$C–S–S–C$\langle$ were proposed in our previous communication.[1]

The stable conformation about the S–S bond of disulfide groups was established to be *gauche*, with the internal-rotation angle of nearly 90°. Accordingly, the molecular conformation of dialkyl disulfides was concerned with the internal rotation about the C–S and C–C bonds of the –C–C–S–S–C–C– group.

The infrared spectra of several dialkyl disulfides were studied early by Thompson and Trotter[2] and by Sheppard.[3] The vibrational assignments of dimethyl disulfide,[4] diethyl disulfide[5] and di-*n*-propyl disulfide[6] were made by Scott *et al.*, together with the collection of early data of infrared and Raman frequencies for their thermodynamic studies. Detailed investigations on dimethyl disulfide were made later by Hayashi[7] and by Frankiss.[8] The infrared and Raman spectra of di-*tert*-butyl disulfide were also measured by Scott *et al.*[9] in detail. The infrared and Raman spectra of a series of disulfides and diselenides were measured by Allum *et al.*[10] The normal vibrations of dimethyl disulfide, ethyl methyl disulfide and di-*tert*-butyl disulfide were treated by Scott and El-Sabban.[11]

In the present paper, the infrared and Raman spectra of several dialkyl disulfides are reported in some detail and molecular conformations of disulfides will be discussed, especially for ethyl methyl disulfide and diethyl disulfide.

Experimental

The dialkyl disulfides treated in the present study include dimethyl disulfide [CH_3SSCH_3], ethyl methyl disulfide [$CH_3CH_2SSCH_3$], diethyl disulfide [$CH_3CH_2SSCH_2CH_3$], diisobutyl disulfide [$(CH_3)_2CHCH_2SSCH_2CH(CH_3)_2$], diisopropyl disulfide [$(CH_3)_2CHSSCH(CH_3)_2$], di-*sec*-butyl disulfide [$CH_3CH_2CH(CH_3)SSCH(CH_3)CH_2CH_3$], methyl *tert*-butyl disulfide [$CH_3SSC(CH_3)_3$], di-*tert*-butyl disulfide [$(CH_3)_3CSSC(CH_3)_3$], and di-*tert*-amyl disulfide [$CH_3CH_2C(CH_3)_2SSC(CH_3)_2CH_2CH_3$].

Ethyl methyl disulfide was prepared from Bunte salt and ethyl mercaptan according to the method reported by Milligan and Swan.[12] Methyl *tert*-butyl disulfide was also prepared from Bunte salt and *tert*-butyl mercaptan, analogous to the method of Milligan and Swan[12] [bp 51 °C/20 Torr]. For other disulfides, commercial samples were used after distillation.

Infrared spectra in the liquid and solid states were measured with Hitachi EPI-G3 and EPI-L infrared spectrophotometers. Raman spectra in the liquid state were measured with a JEOL Raman spectrometer (Model JRS-02AS) with an argon-ion laser (488.0 or 514.5 nm).

Results and Discussion

S–S and C–S Stretching Vibrations. The Raman spectra in the region of the S–S and C–S stretching vibrations (750—500 cm^{-1}) of dialkyl disulfides are shown in Fig. 1. The characteristic S–S stretching frequencies of dialkyl disulfides are summarized in Table 1. S–S stretching vibrations of dialkyl disulfides give rise to strong Raman lines and weak infrared-absorption bands while C–S stretching vibrations give rise to strong Raman lines and fairly strong infrared-absorption bands. Accordingly, observations of Raman spectra as well as infrared spectra are important for identifications of S–S stretching vibrations.

As reported previously,[1] the S–S stretching frequencies of disulfide groups depend upon the molecular conformations about the C–S bonds. The frequencies of S–S stretching vibrations of the X–C–S–S–C–Y group are specified with the atoms X and Y which occupy the two *trans* sites with respect to the sulfur atoms; the S–S stretching vibrations lie at about 510 cm^{-1} for the conformation with two hydrogen atoms

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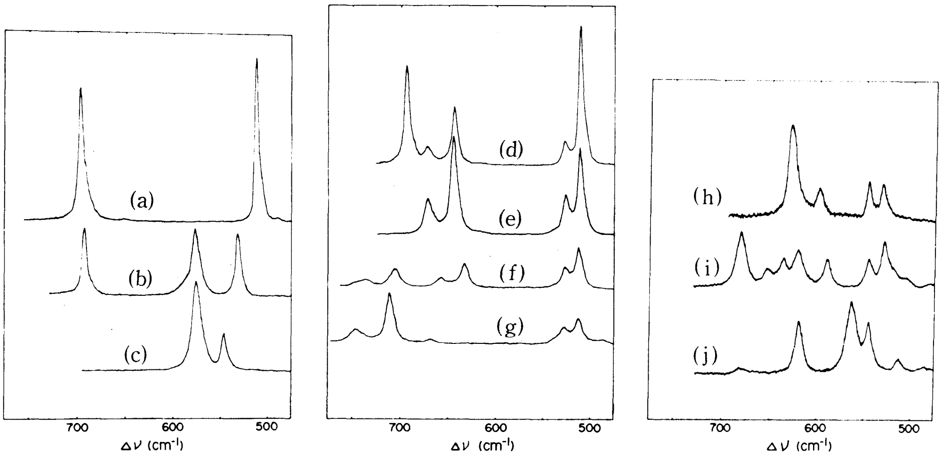

Fig. 1. The Raman spectra of dialkyl disulfides in the liquid state at room temperature.
(a): dimethyl disulfide, (b): methyl *tert*-butyl disulfide, (c): di-*tert*-butyl disulfide, (d): ethyl methyl disulfide, (e): diethyl disulfide, (f): di-*n*-propyl disulfide, (g): di-iso-butyl disulfide, (h): di-isopropyl disulfide, (i): di-*sec*-butyl disulfide, (j): di-*tert*-amyl disulfide. Excited with an argon-ion laser (488.0 nm).

TABLE 1. OBSERVED FREQUENCIES (cm^{-1}) OF S–S STRETCHING VIBRATIONS OF DIALKYL DISULFIDES[a)]

Molecule	ν(H, H)		ν(H, C)		ν(C, C)	
	Infrared	Raman	Infrared	Raman	Infrared	Raman
CH_3SSCH_3	509 m	508 vs	—	—	—	—
$CH_3SSC(CH_3)_3$	—	—	529 m	528 vs	—	—
$[-SC(CH_3)_3]_2$	—	—	—	—	545 vw	543 s
$CH_3SSCH_2CH_3$	510 w	509 vs	526 vw	524 m	—	—
$[-SCH_2CH_3]_2$	510 m	508 vs	525 w	523 s	—	—
$[-SCH_2CH_2CH_3]_2$	511 w	510 vs	524 w	523 s		
$[-SCH_2CH(CH_3)_2]_2$	513 w	512 s	527 w	525 m		
$[-SCH(CH_3)_2]_2$			528 w	527 s	543 w	542 s
$[-SCH(CH_3)CH_2CH_3]_2$			526 w	527 vs	542 vw	542 s
$[-SC(CH_3)_2CH_2CH_3]_2$	—	—	—	—	543 vw	543 s

a) Unexpected vibrations are marked with the — sign.

at both *trans* sites [ν(H,H)], at about 525 cm^{-1} for the conformation with a hydrogen atom at one *trans* site and a carbon atom at the other *trans* site [ν(H,C)], and at about 540 cm^{-1} for the conformation with two carbon atoms at both *trans* sites [ν(C,C)].

For dimethyl disulfide, methyl *tert*-butyl disulfide, and di-*tert*-butyl disulfide, no rotational isomers are expected other than the molecular conformation with the *gauche* S–S bond. In fact, for each of the three molecules, only one S–S stretching vibration was observed. On the other hand, for other disulfides with the possibility of rotational isomerism about the C–S bonds, two S–S stretching vibrations were in fact observed in the Raman scattering and infrared absorption. For di-*primary*-alkyl disulfides of the present study, two S–S stretching vibrations, ν(H,H) and ν(H,C), were observed in the liquid state (Table 1). This observation indicates that the *gauche-gauche-gauche* (GGG) and *trans-gauche-gauche* (TGG) isomers coexist for the $-C-CH_2-S-S-CH_2-C-$ group. For di-*n*-propyl disulfide and diisobutyl disulfide, two types (P_H and P_C) of C–S stretching vibrations were observed (see Ref. 1), indicating the coexistence of rotational isomers about the $>C-CH_2-$ bonds.

For di-*secondary*-alkyl disulfides [isopropyl or *sec*-butyl], two S–S stretching vibrations, ν(H,C) and ν(C,C), were observed (see Fig. 1 and Ref. 1), indicating the presence of rotational isomers about C–S bonds. For di-*sec*-butyl disulfide, two types of C–S stretching vibrations, S_{HH} and S_{CH}, were observed (see Ref. 1), indicating the coexistence of rotational isomers about the C–C bonds too.

For di-*tert*-amyl disulfide, rotational isomers about the C–S bonds are expected. However, for any isomer about the C–S bonds, the two *trans* sites are occupied by carbon atoms either of methyl groups or of methylene groups, and in fact only one S–S stretching vibration, ν(C,C), was observed in the Raman scattering. On the other hand, two types of C–S stretching vibrations, T_{HHH} and T_{CHH}, were observed for di-*tert*-amyl disulfide (see Ref. 1 and Fig. 1), indicating the coexistence of rotational isomers about the $-CH_2-C\lessdot$ bond.

Methyl tert-*Butyl Disulfide.* For methyl *tert*-butyl disulfide, no rotational isomers are expected other than the molecular conformation with the *gauche* S–S bond. Accordingly, the vibrational spectra of methyl *tert*-butyl disulfide were measured to confirm the characteristic vibrations of disulfide groups. The Raman spectrum of methyl *tert*-butyl disulfide in the liquid state is shown in Fig. 2. The infrared and Raman frequencies in the liquid state are given in Table 2, together with the vibrational assignments.

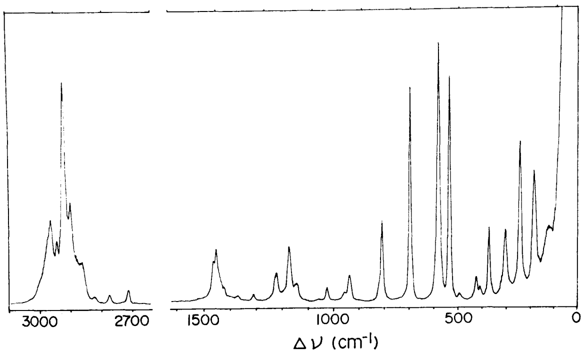

Fig. 2. The Raman spectrum of methyl *tert*-butyl disulfide in the liquid state at room temperature. Excited with an argon-ion laser (488.0 nm).

TABLE 2. OBSERVED FREQUENCIES (cm^{-1}), RELATIVE INTENSITIES,[a)] AND VIBRATIONAL ASSIGNMENTS OF METHYL *t*-BUTYL DISULFIDE IN THE LIQUID STATE

Infrared	Raman	Vibrational assignment
	116 w	S–S or C–S torsion
	176 s	C–S–S deform. of $(CH_3)_3C$–S–S
	236 s	C–S–S deform. of CH_3–S–S
299 vw	299 m	skeletal rock. of $(CH_3)_3C$–S
316 m	315 vw, sh	
365 w	366 m	sym. deform. of $(CH_3)_3C$–S
402 w	402 vw	asym. deform. of $(CH_3)_3C$–S
419 vw	419 w	
478		impurity
	490 vw	impurity ?
529 m	528 vs	S–S stretching [ν(H,C)]
573 m	575 vs	C–S stretch. [T_{HHH}] of $(CH_3)_3C$–S
689 m	691 vs	C–S stretch. of CH_3–S
802 w	805 m	C–C sym. stretch. of $(CH_3)_3C$–S
	815 vw, sh	
895	897	impurity
934 vw, sh	935 m	CH_3 rock. of $(CH_3)_3C$–S
953 s	955 vw	CH_3 rock. of CH_3–S
1020 s	1023 w	CH_3 rock. of $(CH_3)_3C$–S
1143 m	1143 w	
1168 vs	1169 m	methyl rock. and C–C asym. stretch. of $(CH_3)_3C$–S
1220 s	1221 m	
1307 s	1309 vw	CH_3 sym. deform. of CH_3–S
1363 vs	1365 vw	CH_3 sym. deform. of $(CH_3)_3C$–S
1391 m		
1416 m	1420 vw, sh	CH_3 asym. deform. of CH_3–S
1433 m		
	1447 m	CH_3 asym. deform. of $(CH_3)_3C$–S
1455 vs	1457 w	
1474 s		

a) vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, br: broad.

The vibrational assignments were readily made with reference to the vibrational spectra of dimethyl disulfide[7,8)] and di-*tert*-butyl disulfide,[9)] since the vibrational spectra of methyl *tert*-butyl disulfide were found to be practically the composite of those of dimethyl disulfide and di-*tert*-butyl disulfide. Three very strong Raman lines at 528, 575, and 691 cm^{-1} were assigned to the characteristic S–S stretching [ν(H,C)], CH_3–S stretching, and $C(CH_3)_3$–S stretching vibrations [T_{HHH}]. The vibrational frequencies higher than 800 cm^{-1} were assigned, as given in Table 2, to the vibrations of the CH_3–S and $(CH_3)_3C$–S groups. In the region lower than 450 cm^{-1}, skeletal deformation and torsional vibrations are expected. The vibrational frequencies in the region 420—300 cm^{-1} are assigned to the skeletal deformation vibrations of *tert*-butyl group as given in Table 2. The Raman lines at 236 and 176 cm^{-1} are assigned to the C–S–S bending vibrations of the CH_3–C–S–S and $(CH_3)_3C$–C–S–S group, respectively.

Ethyl Methyl Disulfide. Ethyl methyl disulfide is the simplest one of the dialkyl disulfides for which rotational isomers about C–S bonds are expected to coexist. The infrared spectra of ethyl methyl disulfide in the region 3500—500 cm^{-1} were previously reported by Allum *et al.*[10)]

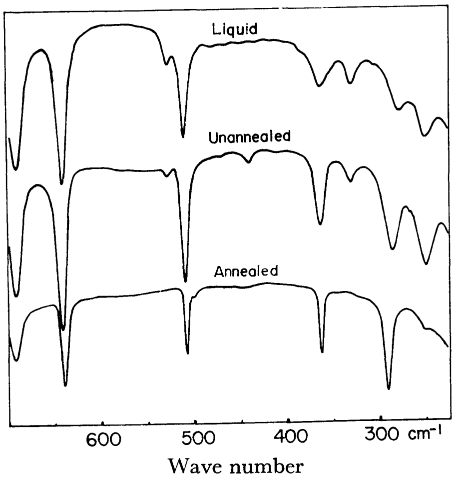

Fig. 3. The infrared spectra of the liquid (room temperature), unannealed solid (77 K), and annealed solid (77 K) of ethyl methyl disulfide.

TABLE 3. OBSERVED FREQUENCIES (cm^{-1}), RELATIVE INTENSITIES,[a)] AND VIBRATIONAL ASSIGNMENTS OF ETHYL METHYL DISULFIDE

Liquid		Annealed Solid	Assignments
Infrared	Raman	Infrared[b)]	
200 w	196 s		C–S–S deform.
248 w	246 s	—	C–S–S deform. (TG)
278 w	~280 vw, sh	290 m	C–S–S deform. (GG)
328 w	327 m	—	C–C–S deform. (TG)
361 w	362 w	362 m	C–C–S deform. (GG)
510 w	509 vs	500 vw, sh 508 m	S–S stretch. (GG)
526 vw	524 s	—	S–S stretch. (TG)
642 m	641 s	634 vw, sh 640 s	CH_2–S stretch. (GG)
667 vw	669 m	—	CH_2–S stretch. (TG)
692 m	692 vs	686 vw, sh 692 s	CH_3–S stretch. (GG) CH_3–S stretch. (TG)
761 s	759 w	758 vs	CH_2 rock. (GG)
781 m		—	CH_2 rock. (TG)

a) See the footnote a of Table 2.
b) The — sign indicates infrared bands which disappear on crystallization.

In the present study, the Raman spectra as well as infrared spectra were measured in the liquid state. The infrared spectra in the solid state (condensed from the vapor and then annealed) and the temperature dependence of the Raman intensities in the liquid state were also measured for detailed analyses of rotational isomerism. In Fig. 3, the infrared spectra in the region 700—200 cm^{-1} are shown for the liquid, unannealed solid and annealed solid. In Table 3, the observed vibrational frequencies in the region 800—200 cm^{-1} are given, together with the vibrational assignments. The infrared frequencies observed in the region higher than 500 cm^{-1} agree closely with the data reported previously by Allum *et al.*[10]

The infrared observation of two CH_2 rocking vibrations at 781 and 761 cm^{-1}, two C–S stretching vibrations at 667 and 642 cm^{-1}, two S–S stretching vibrations at 526 and 510 cm^{-1}, and five skeletal deformation vibrations below 400 cm^{-1} indicates the coexistence of the rotational isomers about the C–S bond in the liquid state. For the annealed solid, however, the infrared bands at 761, 642, and 510 cm^{-1} are still observed but the bands at 781, 667, and 526 cm^{-1} disappeared. Also the skeletal deformation vibrations at 328 and 248 cm^{-1} disappear on annealing.

For the molecule of ethyl methyl disulfide CH_3–CH_2–S–S–CH_3, there are two rotational isomers, *gauche-gauche* (GG or G′G′) and *trans-gauche* (TG or TG′). For the GG form, hydrogen atoms occupy the two *trans* sites with respect to the S–S bond and accordingly the S–S stretching vibration is expected to lie at about 510 cm^{-1} [ν(H,H)] whereas for the TG form, the two *trans* sites are occupied by one hydrogen atom and one carbon atom and the S–S stretching vibration is expected to lie at about 525 cm^{-1} [ν(H,C)]. Since on annealing the infrared band at 510 cm^{-1} remains but the band at 525 cm^{-1} disappears, it may be concluded that the TG and GG forms coexist in the liquid state but only the GG form persists in the solid state.

The energy difference between the TG and GG forms was studied by the measurement of the temperature dependence of the Raman spectra in the liquid state. Thus, over the temperature range +20—−65 °C, the relative intensities of Raman lines were measured for the pairs (TG and GG) at 669 and 641 cm^{-1}, 524 and 509 cm^{-1}, and 327 and 362 cm^{-1}. The GG isomer was found to be more stable than the TG isomer by 0.9±0.2 kcal/mol.

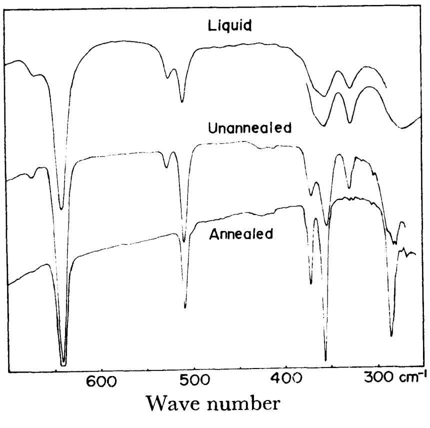

Fig. 4. The infrared spectra of the liquid (room temperature), unannealed solid (77 K), and annealed solid (77 K) of diethyl disulfide.

TABLE 4. OBSERVED FREQUENCIES (cm^{-1}), RELATIVE INTENSITIES,[a] AND VIBRATIONAL ASSIGNMENTS OF DIETHYL DISULFIDE

Liquid		Annealed Solid	Assignment[c]
Infrared	Raman	Infrared[b]	
	180 s		C–S–S deform.
200 w	200 m, sh		C–S–S deform.
	255 w, br		C–S–S deform. (TG$\underline{\text{G}}$)
275 w, br	287 w	285 m	C–S–S deform. (GGG)
	315 vw, sh		
329 w	327 m	—	C–C–S deform. ($\underline{\text{T}}$GG)
358 m	357 w	357 s	C–C–S deform. (GGG)
365 w, sh	366 w	362 m	C–C–S deform. (GGG)
510 m	508 vs	509 m	S–S stretch. (GGG)
525 w	523 s	—	S–S stretch. (TGG)
640 m	642 vs	641 s	C–S stretch. (GGG) C–S stretch. (TG$\underline{\text{G}}$)
667 vw	668 s	—	C–S stretch. ($\underline{\text{T}}$GG)
	735		impurity
762 s	760 w	760 vs	CH_2 rock. (GGG) CH_2 rock. (TG$\underline{\text{G}}$)
781 m	782 vw	—	CH_2 rock. ($\underline{\text{T}}$GG)

a) See the footnote a) of Table 2.
b) See the footnote b) of Table 3.
c) The underlined notations $\underline{\text{T}}$ and $\underline{\text{G}}$ indicate that the vibrational mode is largely localized on the side of the *trans* and *gauche* C–S bond, respectively.

Diethyl Disulfide. For the molecule of diethyl disulfide CH_3–CH_2–S–S–CH_2–CH_3, there are two C–S bonds about which rotational isomerism is expected. Possible rotational isomers are *gauche-gauche-gauche* (GGG or G′G′G′), *trans-gauche-gauche* (TGG or TG′G′), and *trans-gauche-trans* (TGT or TG′T).

Previous data of the infrared (>500 cm^{-1}) and Raman spectra were summarized by Scott *et al.*[5] In the present study, the infrared spectra (>200 cm^{-1}) were measured for the liquid, unannealed solid and annealed solid, and the Raman spectra of the liquid were measured at various temperatures. The infrared spectra (700—200 cm^{-1}) of the liquid, unannealed solid and annealed solid are shown in Fig. 4. In Table 4, the frequencies observed in the region 800—200 cm^{-1} are given, together with vibrational assignments. The vibrational frequencies in the region higher than 800 cm^{-1} agreed closely with previous data,[5] and accordingly are not included in Table 4.

On crystallization of the sample, the infrared band due to the S–S stretching vibration at 510 cm^{-1} [ν(H,H)] persists but the band at 525 cm^{-1} [ν(H,C)] disappears, similar to the case of ethyl methyl disulfide. Accordingly, it may be concluded that at least the GGG and TGG isomers coexist in the liquid state but only the GGG form persists in the crystalline state.

The infrared bands at 781 (CH_2 rock.), 667 (C–S stretch.), and 329 cm^{-1} (C–C–S deform.) disappear on crystallization and are assigned to the TGG form. These vibrations of the TGG form of diethyl disulfide closely correspond to those of the TG form of ethyl methyl disulfide, indicating that the vibrational modes are largely localized on the side of the *trans* C–S bond. For similar reasons, the infrared bands due to the CH_2 rocking, C–S stretching and C–C–S deformation vibrations largely localized on the side of the *gauche* C–S bond of the TGG form are possibly overlapped with the corresponding bands of the GGG form (762, 640, and 365 or 358 cm^{-1}) in the liquid state.

The energy difference between the TGG and GGG forms of diethyl disulfide was studied by the measurement of the temperature dependence of the Raman spectra in the liquid state. Over the temperature range +20—−68 °C, the relative intensity of the Raman lines at 523 (TGG) and 508 cm^{-1} (GGG) were measured. The GGG isomer was found to be more stable than the TGG isomer by 0.6±0.2 kcal/mol.