Vibrational Spectra and Rotational Isomerism of Isopropyl Methyl Selenide and Diisopropyl Selenide

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The infrared and Raman spectra of isopropyl methyl selenide and diisopropyl selenide were measured for the liquid and solid states. The fundamental vibrations were assigned and the rotational isomerism was studied on the basis of the spectral observations and the normal coordinate treatment. For isopropyl methyl selenide, the C_1 and C_s forms coexisted in the liquid state and the enthalpy difference between them was obtained as $\Delta H(C_1-C_s)=-0.52\pm0.05$ kcal mol^{-1}. For diisopropyl selenide, it was presumed that only the C_2 form persisted in the solid state while the C_2, C_s, and C_1 forms coexisted in the liquid state, the C_2 form being the most stable.

The vibrational spectra of unbranched dialkyl ethers and sulfides have been studied extensively in relation to the rotational isomerism.[1] Recently, we have reported the existence of the rotational isomers about the C–Se axis[2] and the correlations of the C–Se stretching wave numbers to the molecular conformations.[3] Among the most simple molecules with the C–Y (Y= O, S, and Se) internal rotation axis, the T form is more stable than the G form for ethyl methyl ether,[4] but the reverse is true for ethyl methyl sulfide[5] and selenide.[2,6] Therefore, we have taken an interest in studying these molecules, in which the hydrogen of the methylene group is replaced by a methyl group, in order to obtain information on the stability of the molecular conformations. The studies for isopropyl methyl ether[7] and sulfide[8] have already been reported. In this paper, we will deal in detail with the molecular vibrations and rotational isomerism of isopropyl methyl selenide and diisopropyl selenide by treating their normal coordinates.

Experimental

The samples were prepared by the treatment of alkylhalides with selenium[9] and were purified by fractional distillation. The purities of the samples were checked by means of NMR and gas chromatography.

The Raman spectra in the region below 4000 cm^{-1} were recorded on a JEOL spectrophotometer (Model JRS 400D) with a Coherent Radiation CR-2 argon-ion laser. The Raman spectra were measured for the liquid state at various temperatures and for the solid state at liquid nitrogen temperature. For the determination of the enthalpy difference between isomers, the integrated intensities of the Raman lines were measured in the liquid state; each experiment was repeated several times after attaining a constant temperature. The infrared spectra in the 300—4000 cm^{-1} region were recorded on a Perkin-Elmer spectrophotometer (Model 621). The solid state was obtained by depositing vapor of the sample onto a CsI window cooled with liquid nitrogen and annealing it repeatedly.

Results and Discussion

Normal Coordinate Treatment. For isopropyl methyl selenide, the existence of the rotational isomers has already been reported[2] and the molecular forms have been determined from the calculation of the skeletal vibrations.[3] Thus, the normal vibrations were calculated in order to obtain a reasonable set of the force constants for the branched dialkyl selenide and information on the molecular forms and the vibrational assignment of diisopropyl selenide. The Urey-Bradley force field was used in the calculation. The structural parameters used were the same as those reported previously.[3] The force constants were initially transferred from those of isopropyltrichlorosilane[10] and dimethyl selenide[11] and some of them were adjusted by the least-squares method to reproduce better the observed wave numbers of isopropyl methyl selenide. The force constants obtained were then transferred to those of diisopropyl selenide. The accuracy of the calculation was good enough for analyzing the observed spectra. The observed and calculated wave numbers are given in Tables 1 and 2, together with the assignment based on the predominant potential energy distributions. The force constants used are listed in Table 3.

Vibrational Assignment. Figures 1—4 show the infrared and Raman spectra of isopropyl methyl selenide and diisopropyl selenide in the region below 1500 cm^{-1}. The observed wave numbers above 800 cm^{-1} resemble very closely those of the corresponding sulfides. In the region below 800 cm^{-1}, only the C–Se stretching, skeletal deformation, and torsional vibrations are expected. Therefore, the fundamental vibrations are easily assigned by comparing the spectra with those of the sulfides and the relative intensities between the infrared bands and the Raman lines. Table 4 lists the isopropyl group vibrations of the selenides, together with those of the corresponding ethers[7] and sulfides.[8] It is noteworthy that the wave numbers of the isopropyl group vibrations of isopropyl methyl selenide are nearly

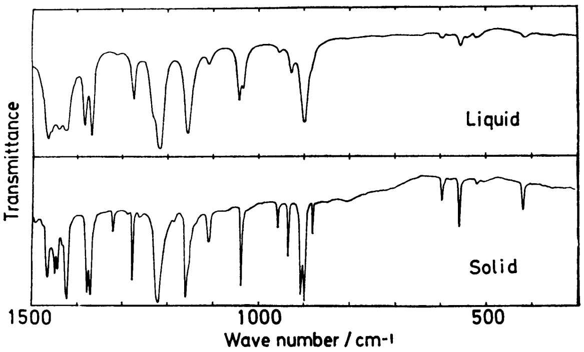

Fig. 1. Infrared spectra of isopropyl methyl selenide in the liquid and solid states in the 300—1500 cm^{-1} region.

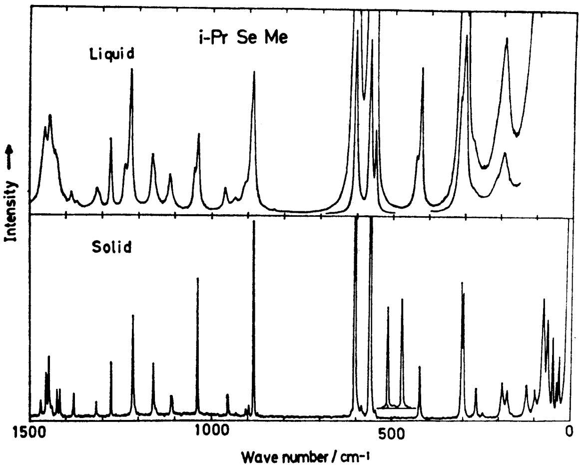

Fig. 2. Raman spectra of isopropyl methyl selenide in the liquid and solid states in the region below 1500 cm^{-1}.

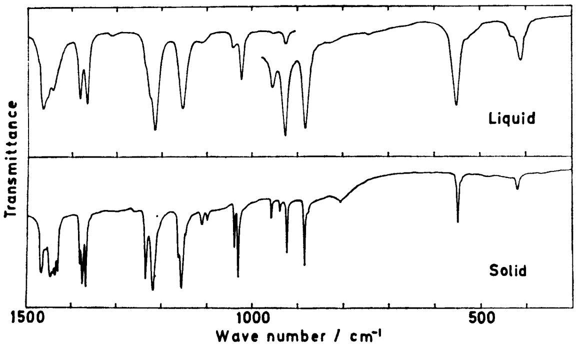

Fig. 3. Infrared spectra of diisopropyl selenide in the liquid and solid states in the 300—1500 cm^{-1} region.

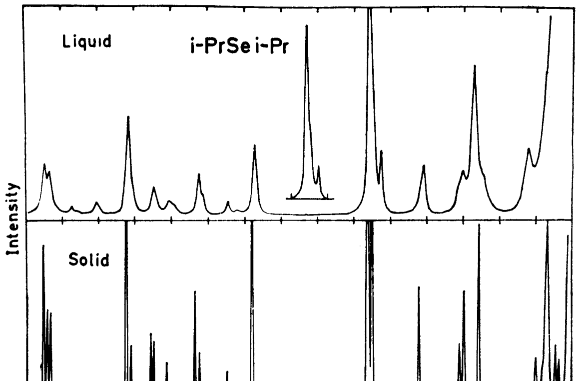

Fig. 4. Raman spectra of diisopropyl selenide in the liquid and solid states in the region below 1500 cm^{-1}.

the same as those of diisopropyl selenide and those of the sulfides.

Rotational Isomers. Isopropyl methyl selenide has one C–Se axis and has two possible rotational isomers, with the C_1 or C_s symmetry (the C_1 and C_s forms). Useful information on the rotational isomers has been obtained from the C–Se stretching vibrations. For isopropyl methyl selenide, the very intense Raman lines at 557 and 597 cm^{-1} in the solid state were assigned to the C–Se stretching vibrations of one isomer. The Raman line at 539 cm^{-1} in the liquid state was assigned to the C–Se stretching vibration of the other isomer. It has been reported[2] from the calculation of the skeletal vibrations that the Raman lines at 557 and 597 cm^{-1} can be assigned to the CH–Se and CH_3–Se stretching vibrations, respectively, of the C_1 form and the Raman lines at 539 and 597 cm^{-1} to those of the C_s form. This conclusion is also confirmed from the present normal coordinate treatment.

Diisopropyl selenide has two C–Se axes and has four possible isomers with the C_{2v}, C_2, C_s, or C_1 symmetry (the C_{2v}, C_2, C_s, and C_1 forms). All the fundamental vibrations for these molecular forms are infrared and Raman active, except for the vibrations of the A_2 species of the C_{2v} symmetry which are infrared inactive. For diisopropyl selenide, information of the rotational isomers is obtained only from the C–Se stretching and skeletal deformation vibrations. The comparison of the observed wave numbers with the calculated ones indicates that the Raman lines at 555 and 529 cm^{-1} are to be assigned to the CH–Se stretching vibration of the C_2 and C_s forms and the C_1 and C_{2v} forms, respectively. In the solid state, the former line persists but the latter disappears. However, the molecular form persisting in the solid state cannot be determined from the calculation, because the C_2 and C_s forms have nearly the same calculated wave numbers, as in the case of diisopropyl sulfide.[12] For diisopropyl selenide, the magnitude of the H···H nonbonded repulsion between the methyl groups is in the order: the C_{2v} form$>$the C_1 form$\gtrsim$the C_s form$>$the C_2 form. On the assumption that the stability of the molecular forms is mainly due to the nonbonded repulsion, it is expected that only the C_2 form persists in the solid state and that the C_2, C_s, and C_1 forms coexist in the liquid state. However, the existence of the C_{2v} form is unlikely, because the GG′ form, with the large H···H nonbonded repulsion between the methyl groups, has not been reported to exist for diethyl ether,[1] diethyl sulfide,[1] or diethyl selenide.[6]

Enthalpy Difference between Isomers. The enthalpy difference can be determined from the intensity ratios of the Raman lines belonging to different isomers. The relative intensities of the Raman lines assigned to the CH–Se stretching vibration were measured in the liquid

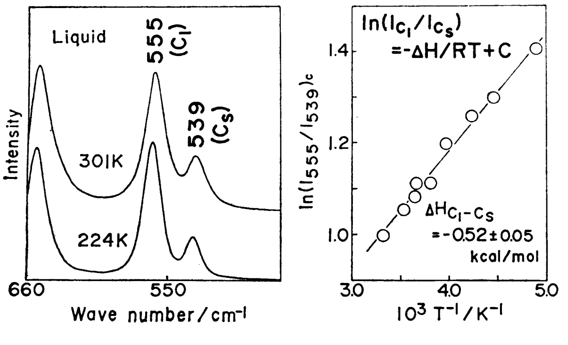

Fig. 5. Observed Raman spectra in the 510—600 cm^{-1} region and a plot of $\ln(I_{555}/I_{539})_c$ *vs.* $1/T$.

TABLE 1. OBSERVED AND CALCULATED WAVE NUMBERS OF ISOPROPYL METHYL SELENIDE (cm^{-1})[a)]

Liquid			Solid		Calcd[b)]		Assignment[c)]
IR	Raman		IR	Raman	C_s	C_1	
1465s			1465m	1473vw	1451A′	1452	$\delta_a CCH_3$
1457s	1455w	dp		1458w	1449A″	1450	
			1449m	1450w	1449A′	1449	
1440s	1441w	dp	1444m	1442vw	1449A″	1449	
			1433w	1430vw	1425A′	1425	$\delta_a SeCH_3$
1425s	1426vw, sh	dp	1423s	1420vw	1424A″	1424	
1382s	1382vw		1378s	1382vw	1379A′	1380	$\delta_s CCH_3$
1366s	1367vvw		1370s		1379A″	1380	
1310vvw	1311vw		1320w	1319vw		1297	δCH o.p., $r_s CCH_3$
	1304vw, sh				1296A″		
1274m	1275m	p	1278s	1279w	1277A′	1276	$\delta_s SeCH_3$
1230s, sh	1233w	p			1224A′		δ CH i.p., $r_s CCH_3$
1217vs	1219s	p	1221vs	1218m		1224	
1154s	1156vw		1159s	1162w	1137A′	1136	$r_a CCH_3$, ν_sC–C
1108w	1108vw	dp	1109w	1111vw	1098A″	1101	ν_aC–C, $r_a CCH_3$
1040m	1040vw	p	1037s	1040s		1035	$r_s CCH_3$, δ CH i.p.
1031m	1031w	p			1036A′		
952vw	953vw	dp	956w	953vw	973A″	973	$r_a CCH_3$, ν_aC–C
925w	925vw		933m	932vw	922A″	924	$r_s CCH_3$, δCH o. p.
			904s	904vw	897A′	895	$r_s SeCH_3$
897s	894vw, sh		895vs	895w	893A″	893	$r_a SeCH_3$
884w, sh	876m		878w	881vvs	878A′	877	ν_sC–C, $r_a CCH_3$
594vw	596vvvs	p	594w	597vvvs	599A′	595	νCH_3–Se
				580vw			
552w	555vvvs	p	555m	557vvvs		554	νCH–Se
538vw	539vvs	p			550A′		
	421w	p	416w	417m		411	$\nu_s C_2CSe$
409vw	410s	p			419A′		$\delta_s C_2CSe$, $\delta_a C_2CSe$
	301vs, sh	p		(302s		300	$\delta_a C_2CSe$
				(298s			
	292vs	p			288A′		$\delta_a C_2CSe$
					287A″		$\delta_a C_2CSe$
	265w, sh			261vw		267	$\delta_a C_2CSe$, $\delta_s C_2CSe$
				242vvw			
	198w, sh			187vw	203A′	204	$\tau_s CCH_3$
					202A″	201	$\tau_a CCH_3$
	178m	dp		175vw	167A′	178	δCSeC
				120vw	159A″	159	$\tau SeCH_3$
				97vw			τCHSe and lattice vibrations
				74s	75A″	75	
				63m			
				48m			
				37vw			
				30w			

a) Wave numbers above 1500 cm^{-1} are not included and infrared spectra below 300 cm^{-1} are not recorded. s: Strong, m: medium, w: weak, v: very, sh: shoulder, b: broad, p: polarized, and dp: depolarized. b) A′, A″: A′ and A″ species in the C_s symmetry. c) ν: stretching, s: scissoring, w: wagging, t: twisting, r: rocking, δ: deformation, τ: torsion, i.p.: in-plane mode, o.p.: out-of-plane mode, a: asymmetric mode, and s: symmetric mode.

state at different temperatures. For isopropyl methyl selenide, Fig. 5 gives the intensity ratio of the Raman line at 555 cm^{-1} (the C_1 form) to that at 539 cm^{-1} (the C_s form). From the slope of the straight line of $\ln(I_{555}/I_{539})_C$ *vs.* $1/T$, the enthalpy difference $\Delta H(C_1-C_s)$ was obtained as -0.52 ± 0.05 kcal mol^{-1}.

For diisopropyl selenide, the relative intensity of the Raman line at 555 cm^{-1} belonging to the C_2 and/or C_s forms increases with decreasing temperature, as compared with that of the Raman line at 529 cm^{-1} belonging to the C_1 form. Therefore, for these compounds the molecular form with more C_1 conformations of the isopropyl parts is more stable than the others.

Stability of Molecular Conformation. For isopropyl methyl selenide, the C_1 form is found to be more stable than the C_s form by 0.52 ± 0.05 kcal mol^{-1} in the liquid

Table 2. Observed and calculated wave numbers of diisopropyl selenide (cm^{-1})[a)]

Liquid			Solid		Calcd[b)]				Assignment[c)]
IR	Raman		IR	Raman	C$_2$	C$_s$	C$_1$	C$_{2v}$	
1466s			1468s	1477vw					
1456s, sh	1457w	dp	1458m	1459vs	1451A,B	1451A′,A″	1451	1451A$_1$,B$_1$	δ_aCCH$_3$
			1447s	1450m					
1443s	1442w	dp	1443s	1441m	1449A,B	1449A′,A″	1449	1449A$_1$,B$_1$ A$_2$,B$_2$	δ_aCCH$_3$
			1437s						
			1431s						
1382s	1383vw	p	1382s	1384vw	1379A,B	1379A′,A″	1379	1379A$_1$,B$_1$ A$_2$,B$_2$	δ_sCCH$_3$
			1376vs						
1366s	1368vvw		1368vs	1369vvw					
1313vw, b	1314vw	dp		1314w	1299A	1300A′	1298	1298A$_2$	δCH o.p., r_sCCH$_3$
	1307vvw, sh			1307vvw	1297B	1295A″	1296	1294B$_2$	
1224s, sh	1226m	p	1235vs	1231vs	1224A	1224A′	1225	1225A$_1$	δCH i.p., r_sCCH$_3$
1214vs	1218w, sh	p	1219vs	1218m	1224B	1224A″	1223	1224B$_1$	
			1163m	1164m	1137A	1137A′	1139	1139A$_1$	r_aCCH$_3$, ν_sC–C
1153s	1156vw		1156vs	1156m	1136B	1136A″	1135	1136B$_1$	
			1147w						
1121vw, b	1114vw	dp		1120w	1106A				ν_aC–C, r_aCCH$_3$
	1109vw, sh		1111vw			1104A′	1101	1100B$_2$	
	1100vw, sh		1100vw	1097vw	1097B	1098A″	1098	1096A$_2$	
1041vw			1039m	1043s	1036A	1037A′	1038	1038B$_1$	r_sCCH$_3$, δCH i.p.
	1033w	p	1030vs	1031w	1035B			1035A$_1$	
1023m	1022vw	p				1033A″	1034		
954vw	952vw	dp	958w	952w	975A	974A′	973	973B$_2$	r_aCCH$_3$, ν_aC–C
			939vw		972B	973A″	973	972A$_2$	
925vw	928vvw		923s	927vw	925A	926A′	924	923A$_2$	r_sCCH$_3$, δCH o.p.
					923B	922A″	922	921B$_2$	
881vw	879m		885s	882vvs	877A	877A′	879	881A$_1$	ν_sC–C, r_aCCH$_3$
			877vw, sh	874vw	876B	876A″	876	876B$_1$	
	564vvs	p		563vvs	560B	558A″	568	570B$_1$	ν_aCH–Se
549vw	555s,sh	p	548m	552vvs	553A	554A′			ν_sCH–Se
	529m	p					545	543A$_1$	
424vw	422vw, sh	p	418vw	423s	414A	415A′	422	430A$_1$	δC$_2$CSe
410vw	413w	p			408B	407A″	407	407B$_1$	
	315w, sh			313m	307A	316A′	318	304A$_1$	
	305w			300s	299B	299A″		302B$_2$	
	275s	p					289		
				268vvw	274B	260A″	264	272A$_2$	
	252w, sh	p		258vs	243A	246A′	254	252B$_1$	
				247vvw	203A	203A″	202	203A$_2$	τCCH$_3$
				219vvw	202A	202A′	202	202A$_1$	
					201B	202A′	201	202B$_2$	
					199B	200A″	200	199B$_1$	
	125w	dp		139vw	116A	118A′	111	104A$_1$	δCSeC
				99w					τCHSe and lattice vibrations
				80w, sh					
				69vs	59A	56A″	63	69A$_2$	
				45w	55B	56A′	50	46B$_2$	
				36w					

a), b), c) See a), b), and c) of Tabel 1.

state. For isopropyl methyl sulfide, which is one of the (CH$_3$)$_2$CHYCH$_3$-type molecules (Y=O, S, and Se), the C$_1$ form is also more stable than the C$_s$ form by 1—1.5[8a)] and 0.19±0.03 kcal mol^{-1} [8b)] in the liquid state. However, for isopropyl methyl ether the C$_1$ form has predominantly existed in the liquid state.[7)] On the other hand, in the CH$_3$CH$_2$YCH$_3$-type molecules (Y=O, S, and Se), the T form has been more stable than the G form by 1.1—1.5 kcal mol^{-1} in the gaseous and liquid states for ethyl methyl ether,[4)] but the reverse is true for ethyl methyl sulfide (ΔH(T−G)=−0.03±0.05 kcal mol^{-1} in the gaseous state[5a)] and −0.14±0.05 kcal mol^{-1} in the liquid state[5b)]) and ethyl methyl selenide (ΔH(T−G)=−0.28±0.05 kcal mol^{-1} in the

TABLE 3. FORCE CONSTANTS FOR BRANCHED DIALKYL SELENIDES[a)]

Force constant	Value	Force constant	Value
K(C–H),CCH$_3$	4.198	F(C·C·C)	0.355
K(C–H),CH	4.100	F(C·C·Se)	0.290
K(C–H),SeCH$_3$	4.379	F(C·Se·C)	0.060
K(C–C)	2.144	κ(CCH$_3$)	0.024
K(C–Se)	1.356	κ(CH)	−0.053
H(H–C–H),CCH$_3$	0.370	κ(SeCH$_3$)	0.029
H(H–C–H),SeCH$_3$	0.355	Y(C–CH$_3$)	0.076
H(C–C–H),CCH$_3$	0.194	Y(Se–CH$_3$)	0.047
H(C–C–H),CH	0.177	Y(Se–CH)	0.095
H(Se–C–H),CH	0.044	p(C–H),CCH$_3$	−0.122
H(Se–C–H),SeCH$_3$	0.035	p(C–H),SeCH$_3$	−0.094
H(C–C–C)	0.358	p(C–Se)	−0.075
H(C–C–Se)	0.208	n(CCH$_3$)	0.021
H(C–Se–C)	0.219	n(SeCH$_3$)	0.014
F(H·C·H)	0.200	t(CCH$_3$,CCH)	0.122
F(C·C·H)	0.540	g(CCH$_3$,CCH)	−0.029
F(Se·C·H)	0.617		

a) The Urey-Bradley force field; the units of the force constants are in mdyn/Å for stretching, K; bending, H; repulsion, F; bond interaction, p; and in mdyn·Å for intramolecular tension, k; torsion, Y; angle interaction between the CCH and HCH angles of methyl group, n; *trans* coupling, t; *gauche* coupling, g.

liquid state[6)]).

The above results indicate that for isopropyl methyl sulfide and selenide the C_1 form with fewer methyl-methyl *gauche*-dispositions is more stable than the C_s form with more methyl-methyl *gauche*-dispositions, although for ethyl methyl sulfide and selenide the conformation with the methyl-methyl *gauche*-disposition (the G form) is more stable than the other (the T form). This inconsistency suggests the following. The H···H nonbonded repulsion between the methyl groups may affect the stability of the molecular forms and so the dihedral angles for the *gauche* $CH_3CH_2YCH_3$-type molecules (Y=O, S, and Se) and the C_1 form of the $(CH_3)_2CHYCH_3$-type molecules would be slightly larger than the 60° of the original *gauche* position. The C_s form of the $(CH_3)_2CHYCH_3$-type molecules (Y=O, S, and Se) inevitably has the dihedral angle of 60°. Therefore, the C_1 form may be more stable than the C_s form because of the H···H nonbonded repulsion. For ethyl methyl ether and isopropyl methyl ether with the shorter C–O bond length, the stability of the molecular forms can be interpreted in terms of the larger H···H nonbonded repulsion between the methyl groups.

Recently, Oyanagi and Kuchitsu[13)] have reported from an electron diffraction study that the G form of ethyl methyl ether has the dihedral angle of 84±6°, far away from the original *gauche* position, and that the G form of ethyl methyl sulfide has an angle of 66±9°. For the *gauche* $CH_3CH_2YCH_3$-type molecules (Y=O, S, and Se), the nearest H···H nonbonded distances between the methyl groups were calculated by using the structural parameters determined by the electron diffraction study, where the values of ethyl methyl selenide were assumed to be the same as those of ethyl methyl sulfide, except for the C–Se bond of 1.943 Å and the CSeC valence angle of 96° 11′. The dihedral angle ϕ used in the calculation was taken as 60°, the original *gauche* position, and the values determined by the electron diffraction study. The H···H distance calculated is 1.74 Å (ϕ=60°) and 2.09 Å (ϕ=85°) for ethyl methyl ether, 1.95 Å (ϕ=60°) and 2.03 Å (ϕ=66°) for ethyl methyl sulfide, and 2.09 Å (ϕ=60°) and 2.17 Å (ϕ=66°) for ethyl methyl selenide. Therefore, the H···H nonbonded repulsion may rapidly decrease with increasing values of the dihedral angle under a potential such as the Lennard-Jones type. On the other hand, trithia[5]heterohelicene has been shown to have a spiral configuration because of the steric repulsion between the terminal atoms by the X-ray study.[14)] The nearest H···H nonbonded distance of the terminal rings has been reported to be 2.15 Å. It should be noted that the nearest H···H nonbonded distance is in the range of about 2.03 to 2.15 Å for ethyl methyl ether with the dihedral angle of 85°, ethyl methyl sulfide with the dihedral angle of 66°, and trithia[5]heterohelicene.

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TABLE 4. OBSERVED WAVE NUMBERS OF ISOPROPYL GROUP VIBRATIONS[a)]

Description	Ethers[b)]			Sulfides[c)]			Selenides[d)]		
	i-PrOMe	(i-Pr)$_2$O		i-PrSMe	(i-Pr)$_2$S		i-PrSeMe	(i-Pr)$_2$Se	
CH$_3$ symmetric deformation	1381	1379		1383	1382		1382	1383	
	1372	1365		1366	1367		1367	1368	
CH out-of-plane bending	1345	1337	1326	1312	1312	1301	1311	1314	1307
CH in-plane bending	1338	1326	1313	1244	1251	1239	1219	1226	1218
CH$_3$ rocking and C–C stretching	1214	1169	1162	1159	1158	1152	1156	1156	
	1136	1127	1100	1113	1113	1096	1108	1114	1100
	1115	1018	994	1064	1064	1045	1040	1043	1033
	938	938	932	952	952		953	952	
	921	919	908	927	927		925	928	
	799	852	798	884	882		876	879	

a) The vibrations of the C–H stretchings and the CH$_3$ asymmetric deformations are not included. b) Infrared wave numbers in the solid state. From Ref. 7. c) Infrared wave numbers belonging to the C_1 form in the liquid state. From Ref. 8. d) Raman wave numbers belonging to the C_1 form in the liquid state.

References

1) T. Shimanouchi, Y. Ogawa, M. Ohta, H. Matsuura, and I. Harada, *Bull. Chem. Soc. Jpn.*, **49**, 2999 (1976); M. Ohta, Y. Ogawa, H. Matsuura, I. Harada, and T. Shimanouchi, *ibid.*, **50**, 380 (1977).

2) K. Ohno, T. Hirokawa, S. Aono, and H. Murata, *Chem. Lett.*, **1976**, 1221.

3) K. Ohno, T. Hirokawa, S. Aono, and H. Murata, *Bull. Chem. Soc. Jpn.*, **50**, 305 (1977).

4) T. Kitagawa, K. Kusaki, and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **46**, 3685 (1973).

5) a) M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 111 (1977); b) N. Nogami, H. Sugeta, and T. Miyazawa, *ibid.*, **48**, 3573 (1975).

6) H. Matsuura, K. Ohno, and H. Murata, to be published.

7) A. D. H. Clague and A. Danti, *Spectrochim. Acta, Part A*, **24**, 439 (1968); R. G. Snyder and G. Zerbi, *ibid.*, **23**, 391 (1967).

8) a) M. Ohsaku, Y. Shiro, and H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 3480 (1972); b) M. Sakakibara, I. Harada, H. Matsuura, and T. Shimanouchi, *J. Mol. Struct.*, **49**, 29 (1978).

9) T. Hashimoto, M. Sugita, H. Kitano, and K. Fukui, *Nippon Kagaku Zasshi*, **88**, 991 (1967); F. Challenger and M. L. Brid, *J. Chem. Soc.*, **1942**, 570.

10) K. Ohno, K. Taga, I. Yoshida, and H. Murata, to be published.

11) Y. Shiro, M. Ohsaku, M. Hayashi, and H. Murata, *Bull. Chem. Soc. Jpn.*, **43**, 619 (1970).

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

13) K. Oyanagi and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **51**, 2237; 2243 (1978).

14) M. Imano, Y. Saito, K. Yamada, and H. Kawamo, Molecular Structure Symposium, October 1978, Hiroshima, Japan.