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MOLECULAR FORCE FIELD AND ROTATIONAL ISOMERISM OF ALKYL SELENIDES

Hiroatsu MATSUURA, Keiichi OHNO, and Hiromu MURATA
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Hiroshima 730

The molecular force field of alkyl selenides was determined from about 100 observed vibrational frequencies. The force field was applied to larger molecules of butyl methyl, ethyl propyl, and dipropyl selenides to study the rotational isomerism. The conformational stability of the selenides was compared with that of sulfides and ethers.

The rotational isomerism about the C–Se bond in alkyl selenides has been confirmed previously by the vibrational spectroscopic method,[1] and the conformations of the isomers of simple alkyl selenides such as ethyl methyl, methyl propyl, and diethyl selenides have been studied in relation to the C–Se stretching frequencies.[2] The results obtained in these studies encouraged us to determine a consistent set of force constants of alkyl selenides and to analyze on the basis of the normal-coordinate treatment the observed vibrational spectra more closely. The determination of the molecular force field, which has not been so far made systematically or in detail for selenides, is of importance for the discussion of nature of the Group VI elements in conjunction with the well-established force field of alkyl sulfides and ethers.[3] In this letter, we report on the molecular force field of the alkyl selenides and its applications to larger alkyl selenide molecules to determine the rotational isomers existing in various states of aggregation.

A consistent set of force constants of unbranched alkyl selenides in terms of the local symmetry coordinates was determined from about 100 independent observed frequencies of ethyl methyl, methyl propyl, and diethyl selenides.[1,2] The initial values of the force constants associated with the selenium part were estimated with reference to the corresponding force constants of sulfides and ethers.[3] The force constants of the alkyl part not directly associated with the selenium atom were transferred directly from paraffin molecules. Of the force constants of the selenium part, only nineteen important constants were refined by the method of least squares and the remaining less important constants were assumed to be the same as the corresponding constants of the sulfides. Only several cycles of the least-squares calculations sufficed to attain a satisfactory fit between the observed and calculated frequencies with the root-mean-square deviation of 5.9 cm^{-1} for about 140 frequencies. The structural parameters used were taken from the microwave result on dimethyl selenide.[4] In Table 1, some of the important force constants are listed together with those of ethers and sulfides.[3] The accuracies in these constants are good enough for us to discuss their numerical values in comparison with those of related molecules.

The C–Se stretching force constant has a value of 2.625 mdyn $Å^{-1}$, which is 0.33

mdyn Å^{-1} smaller than the value for the C–S stretching constant and is almost a half of the value for the C–O stretching constant. This trend is consistent with the bond lengths of 1.94, 1.82, and 1.41 Å, respectively, for the C–Se, C–S, and C–O bonds with increasing binding forces in this order. The value of the CSeC bending force constant for the CH_2SeCH_2 group, 1.264 mdyn Å, is smaller by 0.22 mdyn Å than that of the CSC bending constant but is larger by 0.05 mdyn Å than that of the COC bending constant. This apparently irregular variation in these values may be ascribable in part to the counterbalanced steric effect due to the increasing C–X bond lengths and the decreasing CXC valence angles in going from X=O to Se, but is perhaps related more essentially to the CXC valence bending forces. It is noted that the values of the CXC bending force constants for the terminal CH_3XCH_2 group are smaller than those of the corresponding constants for the CH_2XCH_2 group mentioned above by 3, 8, and 15 % for X=O, S, and Se, respectively, indicating that the restoring forces of the CXC bending in the terminal part are weaker than those in the inner part of the molecule, the difference being larger for heavier X atoms. The values of the deformation force constants of the methyl group CH_3–(X) and those of the methylene group (CH_2)–CH_2–(X) decrease systematically in going from X=O to Se as seen in Table 1.

The normal-coordinate analysis with the force constants thus obtained made it possible to examine closely the mode of the C–Se stretching vibrations previously assigned.[2] For methyl propyl selenide, the lower-frequency vibrations of 576 and 559 cm^{-1} (the gauche SeC–CC conformation) have some vibrational coupling with the SeCC deformation and the higher-frequency vibrations of 660 and 646 cm^{-1} (the trans SeC–CC conformation) have further coupling with the CCC deformation in addition to the SeCC deformation, making the C–Se stretching frequencies higher. The normal-coordinate treatment confirmed the previous vibrational assignments in other selenide molecules, giving conclusive evidences for the rotational isomerism of ethyl methyl, methyl propyl, and diethyl selenides.

The molecular force field determined for the simple selenides was subsequently applied to the longer molecules, butyl methyl, ethyl propyl, and dipropyl selenides,

Table 1. Diagonal force constants of ethers, sulfides, and selenides[a]

Skeletal		Methyl CH_3–(X)			
Stretching[b]			X = O–CH_2	S–CH_2	Se–CH_2
CH_2–O	5.037(22)	Sym. deformation[c]	0.679(13)	0.559(8)	0.527(3)
CH_2–S	2.959(57)	Deg. deformation[c]	0.550(10)	0.537(3)	0.530(2)
CH_2–Se	2.625(24)	Rocking[c]	0.875(16)	0.628(3)	0.561(3)
Bending (deformation)[c]		Methylene (CH_2)–CH_2–(X)			
CH_2–O–CH_2	1.217(11)		X = O	S	Se
CH_2–S–CH_2	1.481(22)	Scissors[c]	0.590(4)	0.551(5)	0.544(3)
CH_2–Se–CH_2	1.264(30)	Rocking[c]	0.820(31)	0.804(15)	0.749(5)
CH_2–CH_2–O	1.153(26)	Wagging[c]	0.764(11)	0.607(11)	0.582(3)
CH_2–CH_2–S	0.846(41)	Twisting[c]	0.699(16)	0.626(4)	0.586(4)
CH_2–CH_2–Se	0.901(49)				

a) Force constants of ethers and sulfides are taken from Ref. 3. Errors in the force constants, given in parentheses, apply to the last significant figure(s).
b) In units of mdyn Å^{-1}. c) In units of mdyn Å.

to study the rotational isomerism. The spectra of these molecules were recorded for the liquid and solid states as shown in Figs. 1 and 2 where the calculated frequencies for some important conformers are also given. The calculation for butyl methyl selenide $CH_3Se-CH_2-CH_2-CH_2CH_3$ demonstrates that the $Se-CH_2$ stretching frequencies are particularly sensitive to the conformations about the CSe–C–CC axes while the skeletal deformation frequencies to the conformations about the SeC–C–CC axes. The conformer existing in the solid state is clearly shown to be the GGT form with the gauche CSe–CC and SeC–CC axes and the trans CC–CC axis. The temperature dependence of the liquid-state spectra indicates that the GTT form (the gauche CSe–CC axis but the trans SeC–CC axis) is the most stable in the liquid state. The $Se-CH_2$ stretching frequencies of 662, 649, 581, and 563 cm^{-1} suggest the coexistence of at least four isomers in this state (the stronger 595 cm^{-1} band is assigned to the CH_3–Se stretching vibration for

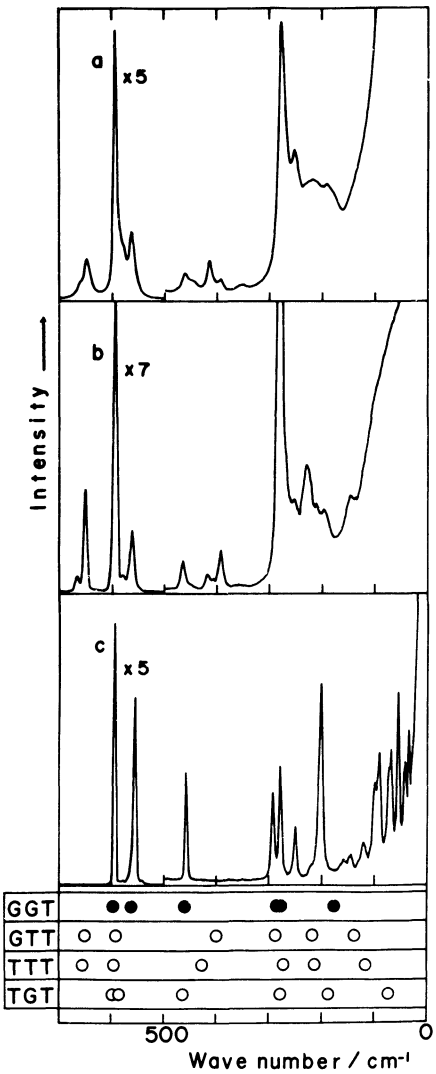

Fig. 1. Raman spectra and calculated frequencies of butyl methyl selenide. a: Liquid (room temp.), b: supercooled liquid (liq. nitrogen temp.), c: solid. The calculated frequencies given by filled circles indicate the vibrations in the solid state.

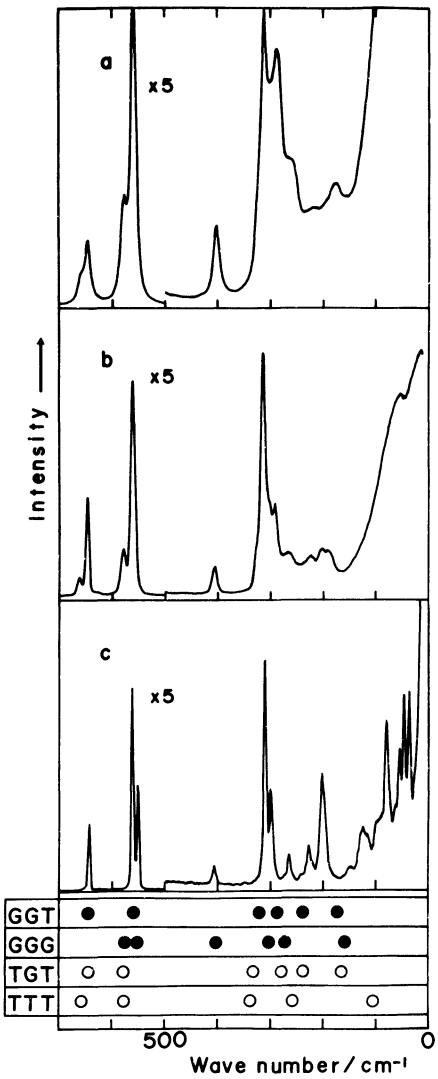

Fig. 2. Raman spectra and calculated frequencies of ethyl propyl selenide. a: Liquid (room temp.), b: supercooled liquid (liq. nitrogen temp.), c: solid. For filled circles, see caption of Fig. 1.

all conformers). Ethyl propyl selenide CH_3CH_2–Se–CH_2–CH_2CH_3 gives the Se–CH_2 stretching frequencies which are just a combination of the frequencies of diethyl and methyl propyl selenides. The solid-state spectrum is explained by the coexistence of the two forms, GGT and GGG. In the liquid state, the GGT and TGT forms are found to be more stable than others. For dipropyl selenide, the TGGT form persists in the solid state.

Table 2 gives the rotational isomers of butyl methyl and ethyl propyl selenides studied in this work and those of the corresponding sulfide and ether molecules for comparison. It should be remarked for these selenides as well as ethyl methyl, methyl propyl, and dipropyl selenides that the conformers existing in the solid state take the gauche conformation about the CSe–CC axis. Only diethyl selenide is a conformational exception and takes the TT form in the solid state. The corresponding ethers all crystallize with the trans CO–CC conformation, and the sulfides with the trans CS–CC conformation for some and with the gauche conformation for others. The most stable conformers of the selenides in the liquid state are similar to those of the sulfides, the gauche CX–CC axis (X=Se or S) being more stable than the trans, but differ from those of the ethers. The high stability of the gauche conformation about the CSe–CC axis is now evident from these experimental results and this conformation is probably more stabilized in the selenides than in the sulfides. The apparent inconsistency of the persisting conformer in the solid state with the most stable conformer in the liquid state is accounted for by the effect of more significant intermolecular interactions in crystal.

Table 2. Rotational isomers of butyl methyl selenide and ethyl propyl selenide and the corresponding sulfides and ethers

	CH_3X–CH_2–CH_2–CH_2CH_3		CH_3CH_2–X–CH_2–CH_2CH_3	
	Solid	Liquid[a)]	Solid	Liquid[a)]
X = Se	GGT	<u>GTT</u>, GGT and others	GGT, GGG	<u>GGT</u>, <u>TGT</u>, GGG and others
X = S[b)]	TTT	<u>GTT</u>, TTT, GGT, TGT and others	TTT	<u>GGT</u>, <u>TGT</u>, GTT, TTT, GGG and others
X = O[c)]	TTT	<u>TTT</u>, <u>TGT</u> and others	TTT	<u>TTT</u>, <u>TTG</u> and others

a) The conformers specifically indicated are more stable than others. The underlined ones are the most stable. b) M. Ohta, Y. Ogawa, H. Matsuura, I. Harada, and T. Shimanouchi, Bull. Chem. Soc. Jpn., <u>50</u>, 380 (1977). c) T. Shimanouchi, Y. Ogawa, M. Ohta, H. Matsuura, and I. Harada, Bull. Chem. Soc. Jpn., <u>49</u>, 2999 (1976).

References

1) K. Ohno, T. Hirokawa, S. Aono, and H. Murata, Chem. Lett., <u>1976</u>, 1221.
2) K. Ohno, T. Hirokawa, S. Aono, and H. Murata, Bull. Chem. Soc. Jpn., <u>50</u>, 305 (1977).
3) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, J. Phys. Chem. Ref. Data, to be published.
4) J. F. Beecher, J. Mol. Spectrosc., <u>4</u>, 414 (1966).

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