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Molecular Vibrations and Force Fields of Alkyl Sulfides. XII. Skeletal Conformations of Several Simple Aliphatic Sulfides

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Synopsis. A normal coordinate treatment of methyl propyl, methyl butyl, ethyl propyl, ethyl butyl, and dipropyl sulfides has been carried out. From the observed and calculated frequencies, the conformation about each of six C–C bonds—CSC–CC, CSC–CCC, CCSC–CC, CCSC–CCC, and CC–CSC–CC— was confirmed to be the T form in the annealed crystalline state.

It is very difficult to analyse completely the skeletal conformations for longer molecules. In the present study, we have determined the conformations about the C–C bonds adjacent to the C–S bonds for five sulfides: methyl propyl (CSCCC), methyl butyl (CSCCCC), ethyl propyl (CCSCCC), ethyl butyl (CCSCCCC), and dipropyl (CCCSCCC) sulfides.

A normal coordinate treatment has been carried out, using a modified Urey-Bradley force field. The molecular parameters, the potential terms—except the bending and repulsion constants, H(CCC) and F(CCC), and the bond-interaction term, p_C, between the adjacent C–C bonds— and the force constants used were all the same as those of the previous paper.[1] The additional constants were assumed to be H(CCC)=0.275 mdyn/Å, F(CCC)=0.335 mdyn/Å, and $p_C=-0.100$ mdyn/Å. For the longer sulfides, except for CSCCC, normal coordinates were treated here only in the cases of the typical forms.

The observed infrared and calculated frequencies of the C–S stretching and skeletal deformation regions are shown in Fig. 1.

CSCCC. The C–S stretching frequencies observed in the solid state are reproduced well by those calculated for the TT or GT form. The frequencies of the skeletal deformation bands appearing in the solid state are also explained well by these forms.

CSCCCC. The frequencies of the two solid-state bands observed in the C–S stretching region can be explained by the frequencies calculated for the TTT, GTT, TTG, or GTG form. From the data of the skeletal deformation region, however, we cannot obtain any clear and conclusive information on the skeletal

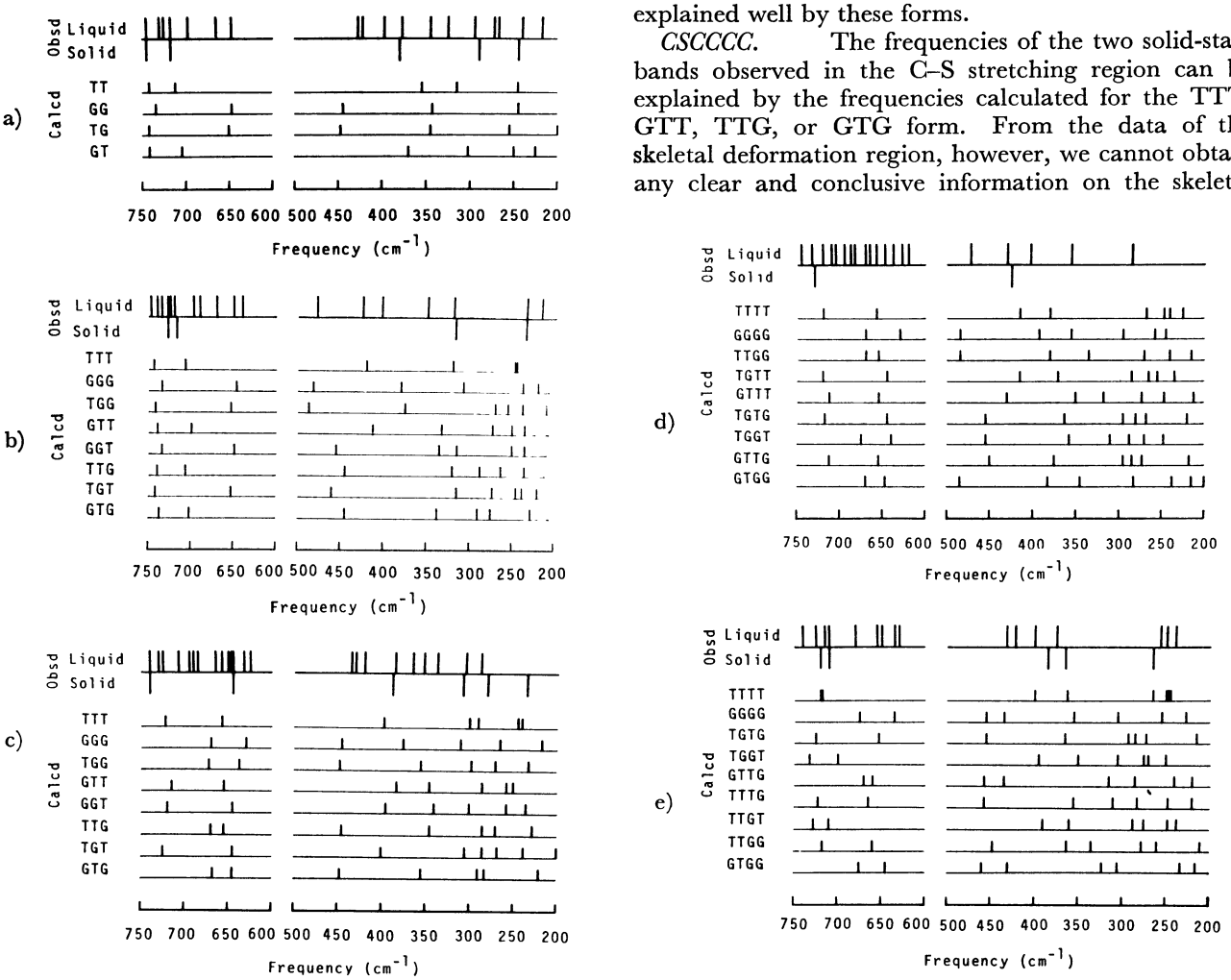


Fig. 1. Observed and calculated frequencies in the C–S stretching and skeletal deformation regions of a) CSCCC, b) CSCCCC, c) CCSCCC, d) CCSCCCC, and e) CCCSCCC.

forms.

CCSCCC. The observed frequencies in the C–S stretching region in the solid state are reproduced well by the frequencies calculated for the TTT, GTT, GGT, or TGT form. The frequencies of the four bands observed in the skeletal deformation region in the solid state can also be reproduced well by those calculated for one of these forms.

CCSCCCC. One each of the bands appeared in the C–S stretching and skeletal deformation regions in the solid-state spectra. The frequencies of these bands are reproduced well by the frequencies calculated for the TTTT, TGTT, GTTT, TGTG, or GTTG form.

CCCSCCC. Two and three bands appeared in the C–S stretching and skeletal deformation regions respectively in the solid-state spectra. The frequencies of these bands fit well to those calculated for the TTTT, TGGT, or TTGT form.

In this note, we are concerned with the skeletal conformations about the C–C bonds adjacent to the C–S bond, *i.e.*, CSC–CC, CSC–CCC, CCSC–CC, CCSC–CCC, and CC–CSC–CC. As we have mentioned above, the frequencies of the C–S stretching and skeletal deformation vibrations can be reasonably explained by the frequencies calculated only for the forms which have the *trans* conformation about the C–C bonds. We may, therefore, conclude that the stable forms in the crystalline state for these sulfides are as follows:

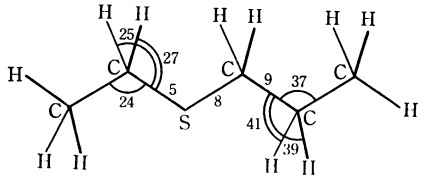
$$CSC_{\bar{T}}CC,\ CSC_{\bar{T}}CCC,\ CCSC_{\bar{T}}CC,\ CCSC_{\bar{T}}CCC,$$

$$\text{and } CC_{\bar{T}}CSC_{\bar{T}}CC.$$

Let us consider in some detail the relation between the C–S stretching frequency and the conformation about the C–C bond adjacent to the C–S bond. The frequencies and separations of two C–S stretching bands observed in the solid state are closely related to the conformation about this bond. The conformations about the other bonds do not much affect the C–S stretching frequencies. From the Jacobian matrix, the force constants which affect the C–S stretching frequencies with different conformations about these C–C bonds are, in general, H(CCC), H(CCH), H(SCC), F(SCH), Y_{C-C}, and p'. There are three questions which arise from these results: a) why do these force constants mainly affect the C–S stretching frequency?, b) why is the C–S stretching frequency affected by the conformation about the C–C bond adjacent to the C–S bond?, and c) why is the C–S stretching frequency not so much affected by the conformation about the C–S bond?

The ***F***-matrix elements themselves do not vary much with the different conformations. On the other hand, for some ***G***-matrix elements, different values appear with different conformations. Now let us consider the values of these elements, taking CCSCCC as an example. A part of the ***G***-elements now of interest are shown above, along with the coordinate numbering. In the off-diagonal elements, *e.g.*, R_8–R_{24}, R_8–R_{25}, R_8–R_{37}, and R_8–R_{41}, and also in the diagonal and off-diagonal elements in relation to the coordinates of C–S and C–C torsions, a different value appears with the T or G conformation about the C–C bond—R_9. These elements are directly related to the force constants, as has been mentioned above. Therefore, the main parts of the first two questions, a) and b), can be explained reasonably. The values of, for example, R_8–R_{24}, R_8–R_{25}, and R_8–R_{27} are much smaller than those of R_8–R_{37}, R_8–R_{41}, and R_8–R_{39}, since the atomic mass of the sulfur atom is much larger than that of carbon. This gives an answer to the c) question. As a result, it seems that most of the contribution to the C–S stretching frequency is due to the conformation about the 9—bond.

	TTT	GGG	
R_8–R_{24}	−1.7019	0.8509	($\times 10^{-2}$)
R_8–R_{25}	0.8509	−1.7019	
R_8–R_{27}	0.8509	0.8509	
R_8–R_{37}	−5.0970	2.5485	
R_8–R_{41}	2.5485	−5.0970	
R_8–R_{39}	2.5485	2.5485	
R_8–R_{52}	−0.0000	−0.0442	



52: torsion—9

The stable conformations in the solid state about the C–S bonds[1] for CS–CC and CC–S–CC and about the C–C bonds[2] for *n*-alkanes were established to be *trans*. Consequently, it can be expected that the stable conformations in the solid state for these sulfides are all of the *trans* form. However, we cannot decide exactly the whole conformation for these sulfides at present. Detailed treatments are now in progress; the results will be published elsewhere in the near future.

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References

1) M. Ohsaku, Y. Shiro, and H. Murata, This Bulletin, **46**, 1399 (1973).

2) For example: R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).