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CNDO/2 Calculations of MeSEt, MeS-*n*-Pr, MeS-*n*-Bu, $(Et)_2S$, EtS-*n*-Pr, EtS-*n*-Bu, and $(n\text{-Pr})_2S$[1]

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Synopsis. CNDO/2 sp calculations were carried out for MeSEt, MeS-*n*-Pr, MeS-*n*-Bu, $(Et)_2S$, EtS-*n*-Pr, EtS-*n*-Bu, and $(n\text{-Pr})_2S$. The stable conformations of these molecules were discussed.

Conformational analyses of MeSEt have been performed extensively on the basis of the vibrational spectra and a normal coordinate treatment[2-4] and on the basis of vapor-phase electron diffraction.[5] With the MeS-*n*-Pr,[6-8] MeS-*n*-Bu,[6,7,9] $(Et)_2S$,[2,9] EtS-*n*-Pr,[6,7,9] EtS-*n*-Bu,[6,7] and $(n\text{-Pr})_2S$[6,7] molecules the conformations have also been analysed by means of IR and Raman spectroscopy. However, the interpretations of the observed results were not always consistent with each other. In particular, the conformation about the C–S bond remains vague. In the present study, in order to obtain useful information on the skeletal conformation, especially about the C–S bond, we have investigated the conformational analyses of these molecules by the aid of the CNDO/2 method.[10]

The molecular geometry used is as follows: for MeSEt–referred to the data of elctron diffraction,[5] r(C–H)=1.117, r(C–S)=1.818, r(C–C)=1.526 Å, and ϕ(CSC)=103.9°; for the other molecules, r(C–H)=1.09, r(C–S)=1.81, r(C–C)=1.54 Å, and ϕ(CSC)=105°; while the other angles were assumed to be tetrahedral. The dihedral angles of these sulfides were taken to be 180 and 60° for the T and G conformations respectively, according to the energy minima of MeSEt, to be shown later. The observed data are summarized in Table 1.

Figure 1 shows that the T form is more stable than the G form in MeSEt. The results of the present calculations, therefore, are in good agreement with our observed results,[2] but they do not agree with the

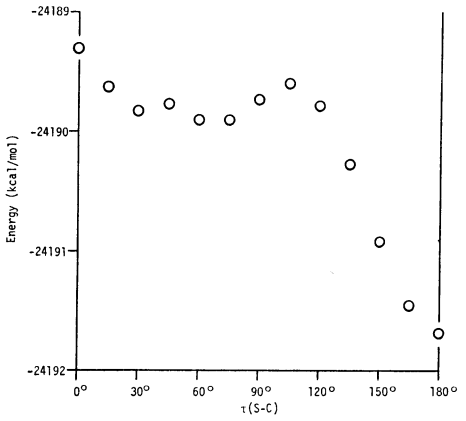

Fig. 1. Total energy as a function of the internal rotation angle in CS-CC.

TABLE 1. OBSERVED STABILITY/CONFORMATION AND ENTHALPY DIFFERENCES (cal/mol) OF DIALKYL SULFIDES

Molecule	Stability/Conformation[a]	Enthalpy differences	Ref
CS-CC	T*>G		2
	G*>T	30±50(gas), 140±50(liq)	4, 3
CS-C-CC (1)	around 1, T*		7
	GT*		8
CS-C-C-CC (1)	around 1, T*		7
	TTT*		9
CC-S-CC	TT*		2
	TT*>GG>TG	$\Delta H_{TT-TG}=460\pm100$(liq) $\Delta H_{GG-TG}=40\pm50$(liq)	9
CC-S-C-CC (1)	around 1, T*		7
	TTT*		9
CC-S-C-C-CC (1)	around 1, T*		7
CC-C-S-C-CC (1 1)	around 1, T*		7

a) With asterisk — the most stable form (conformation) in the crystalline solid state.

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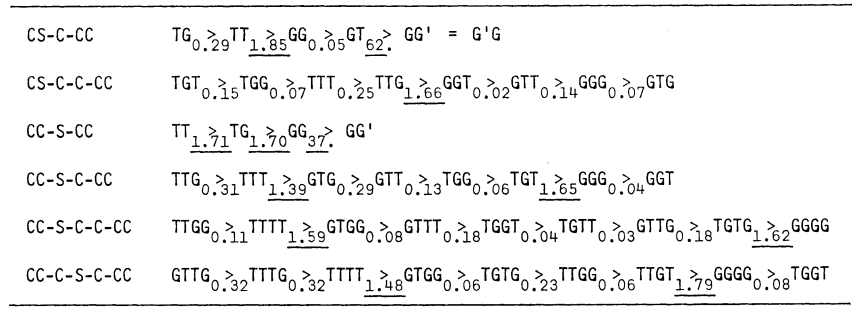

Fig. 2. Stability as a function of the internal rotation angle. Small figures indicate the energy difference, in kcal/mol, while those with underlines indicate fairly large differences.

latest observations[3,4] that the G form is more stable than the T form, although the energy difference observed between the two forms is very small.

Also, for the other longer methyl substituents, the sp calculations indicate that the forms which have the T conformation around the CS–R bond are more stable than those of the G conformation, as is summarized in Fig. 2. For example, for CS–C–C–CC, the TGT and TTT forms, for example, were estimated to be more stable than the other forms, *e.g.*, GGT and GGG. The calculations, therefore, explain reasonably well the experimental results.[6,7,9] With the ethyl substituents, the calculations indicate that the forms which have the TT conformation about the CC–S–R bonds are the most stable ones. For example, for CC–S–C–CC, the TTG and TTT forms can be expected from the calculations to be more stable than the other forms. The present results agree well with the observed ones.[6,7,9] Moreover, the calculations show that the TT form about the CCC–S–CCC bonds is the most stable of all. This agrees well with our previous inference, in which the molecule may all have the *trans* form in the crystalline solid state, judging from the IR spectra of the molecule.[6,7] As has been noted previously,[7] the stable conformation around the C–C bond adjacent to the C–S bond was the T form in the crystalline state, while the conformation around the C–S bond was fairly difficult to determine from only the vibrational spectra and the normal coordinate treatment. In the present case, therefore, the sp calculations and the treatment of the molecular vibrations play complementary roles.

Generally, the present method reproduces the energy-minimum conformations of the simple normal dialkyl sulfides fairly well. Therefore, this method is a helpful method of analysing the vibrational data of these molecules.

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