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A Theoretical Analysis of Rotational Isomerism; CNDO/2 Calculations of *i*-PrSMe, *i*-PrSEt, *i*-Pr-S-*n*-Pr, and (i-Pr)$_2$S[1)]

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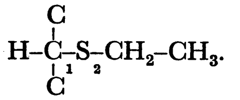
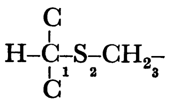
Synopsis. CNDO/2 calculations of *i*-PrSMe, *i*-PrSEt, *i*-Pr-S-*n*-Pr, and (i-Pr)$_2$S gave the stable conformations of these molecules and the optimized angles of ϕ(CSC) of the first three molecules considered.

Conformational analyses of *i*-PrSMe, *i*-PrSEt, *i*-Pr-S-*n*-Pr, and (i-Pr)$_2$S have been performed extensively on the basis of vibrational spectra and normal coordinate treatment.[2-4)] However, for these molecules no theoretical conformational analysis has yet been performed. In the present study in order to test the previous experimental results, the present authors investigated the conformational analyses of these molecules by the CNDO/2 method.[5)]

The molecular parameters used for the computations are as follows: r(C–H)$=1.09$ Å, r(C–S)$=1.81$ Å, r(C–C)$=1.54$ Å—ϕ(CSC)$=99°$ or the optimized values for *i*-PrSMe, *i*-PrSEt, *i*-Pr-S-*n*-Pr, and ϕ(CSC)$=99$, 104, or 109° for (i-Pr)$_2$S—and the other angles were assumed to be tetrahedral. The dihedral angles were 180 and 60° for the *trans* (T) and *gauche* (G) forms, respectively.

With *i*-PrSMe, a local minimum appeared at a rotational angle of *ca.* 60 °. That is, the calculations show that the G (C_1) form is more stable than the T (C_s) form. The present result agrees well with the observed.[2)]

For *i*-PrSEt, the stability was assumed to be in the order: GT>GG>TT.[4)] In this molecule, conformations are taken into consideration around bonds 1 and 2,  $\mathrm{H{-}\underset{C}{\overset{C}{C}}\underset{1}{-}S\underset{2}{-}CH_2{-}CH_3}$. The CNDO/2 calculations indicate the stability: GT>TT>GG>TG. The most stable form, GT, is well reproduced by the calculations. However, the stabilities for the TT and GG forms are in reverse order of those observed.[4)] For the IR study, the most unstable form, TG, is excluded from consideration, since the repulsions between methyl groups in the ethyl and isopropyl groups may be too great.[4)] This is explained qualitatively by the present calculations.

For *i*-Pr-S-*n*-Pr, conformations were taken into consideration around bonds 1, 2, and 3,  $\mathrm{H{-}\underset{C}{\overset{C}{C}}\underset{1}{-}S\underset{2}{-}CH_2\underset{3}{-}CH_2{-}CH_3}$, and from the calculations it was found that the forms which have the T conformation about bond 2 are more stable than those of the G conformation. This agrees well with the experimental result that GTT is the most stable form,[4)] although the present calculations show that the energy minimum form is GTG. As has been noted previously,[6)] the conformation around the

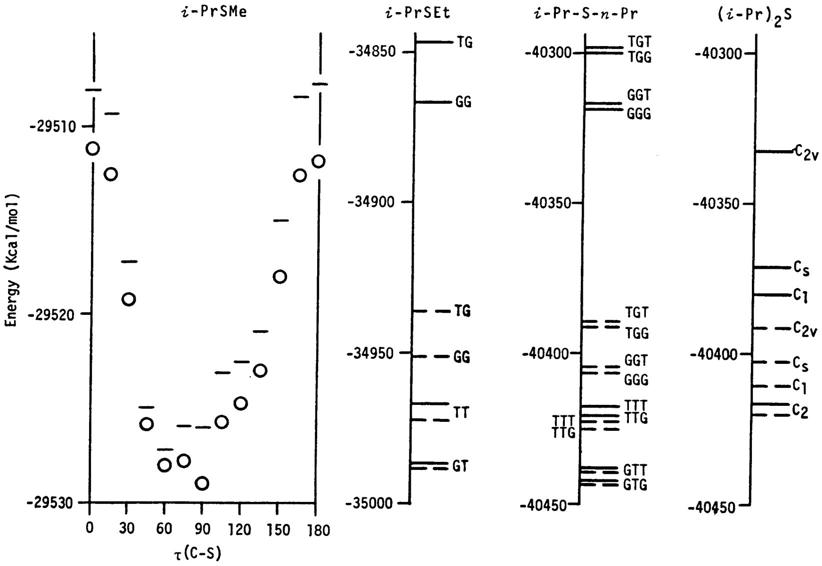


Fig. 1. Total energy as a function of internal rotation angle—original parameters.[5)]
i-PrSMe: — ϕ(CSC)$=99°$, ○ ϕ(CSC)$=105°$.
i-PrSEt: — ϕ(CSC)$=99°$, -- ϕ(CSC)$=105.6°$.
i-Pr-S-*n*-Pr: — ϕ(CSC)$=99°$, -- ϕ(CSC)$=105.9°$.
(i-Pr)$_2$S: ϕ(CSC)$=99°$; $C_2=-40413$, $C_1=-40303$, $C_s=-40295$, $C_{2v}=-40183$ (kcal/mol), — ϕ(CSC)$=104°$, -- ϕ(CSC)$=109°$.

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C–S bond is very difficult to determine from only the vibrational spectra and the normal coordinate treatment. Therefore, the CNDO/2 method is available to determine the conformation around the C–S bond for these molecules.

Four conformations can be assumed for $(i\text{-Pr})_2S$: C_2, C_s, C_1, and C_{2v}. It appears that the conformational energy is due mainly to the interactions between methyl groups of the isopropyl groups on both sides. In connection with these interactions, the stability can be predicted to be in the order: $C_2>C_s>C_1>C_{2v}$. The vibrational spectra confirm this order.[4] The CNDO/2 calculations give the result, $C_2>C_1>C_s>C_{2v}$, and the stability between the C_1 and C_s forms is reversed. However, the most stable and unstable forms are well reproduced by the calculations.

The CSC angle was then optimized without changing the other structural parameters assuming the G, GT, and GTT forms for *i*-PrSMe, *i*-PrSEt, and *i*-Pr–S–*n*-Pr, respectively. The angles obtained are 105, 105.6, and 105.9° for *i*-PrSMe, *i*-PrSEt, and *i*-Pr–S–*n*-Pr, respectively. The angles become larger with increasing weight of the normal alkyl group. These angles are rather large in comparison with the 98°52′ of MeSMe[7] and rather close to the 103.9° for MeSEt.[8] Therefore, these angles appear to be reasonably optimized. The results of the calculations using the optimized angles are also considered. The tendency is nearly the same as in the case of $\phi(\text{CSC})=99°$. For $(i\text{-Pr})_2S$, the optimization of angle $\phi(\text{CSC})$ was not carried out. The total energy decreases with increasing angle from 99° to 109°. Therefore, it is predicted that the angle is larger in this molecule than in other molecules treated.

All of the calculations were also carried out using $K_d=0.492$ instead of 0.75 and others original values,[5] where K_d is the constant of the off-diagonal core matrix elements in relation to third-row elements. As a result, the order of the stability scarcely varied from the case of $K_d=0.75$, but the energy difference between the rotational isomers was slightly refined, *e.g.*, the energy difference between the T and G forms of *i*-PrSMe is postulated to be *ca.* 1—1.5 kcal/mol from the IR study.[2]

Recently, the appropriateness of CNDO/2 studies of molecular conformations has been discussed for some molecules involving third-row elements.[9,10] Generally, the CNDO/2 calculation gives larger energy differences between the rotational isomers than observation. However, this method reproduces energy minimum conformations and some angles fairly well. The CNDO/2 calculation, therefore, is useful as one of the methods of analyzing experimental results, such as the normal coordinate treatment.

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References

1) Presented in part at the 34th Annual Meeting of the Chemical Society of Japan, Hiratsuka, April, 1976.

2) M. Ohsaku, Y. Shiro, and H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 3480 (1972).

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

4) M. Ohsaku, H. Murata, and Y. Shiro, *Spectrochim. Acta*, to be published.

5) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y. (1970).

6) M. Ohsaku, *Bull. Chem. Soc. Jpn.*, **48**, 1037 (1975).

7) L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961).

8) K. Oyanagi, T. Fukuyama, and K. Kuchitsu, Preprints of the 32nd Annual Meeting of the Chemical Society of Japan, Vol. 1, (1975), p. 112.

9) A. Veillard, *Chem. Phys. Lett.*, **33**, 15 (1975).

10) Th. Weller, D. Klöpper, and H. -J. Köhler, *Chem. Phys. Lett.*, **36**, 475 (1975).