February, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 355—360 (1979) 355

CNDO/2 Parametrizations and the Applications to Some Organo-sulfur Molecules: $(CH_2SH)_2$, $(CH_2SCH_3)_2$, CH_3SCH_2SH, and $CH_3SCH_2SCH_3$[1]

Masaru OHSAKU,* Norihisa BINGO, Wataru SUGIKAWA, and Hiromu MURATA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

(Received July 31, 1978)

The CNDO/2 spd′ parametrizations of K_d, β_c, ζ_s, and β_s have been performed. Some of the valence and torsional angles of 1,2-ethanedithiol $(CH_2SH)_2$, 1,2-bis(methylthio)ethane $(CH_2SCH_3)_3$, methanethiol, ethanethiol, (methylthio)methanethiol CH_3SCH_2SH, and bis(methylthio)methane $CH_3SCH_2SCH_3$ have been optimized. In order to obtain further information on the rotational isomerism, CNDO/2 spd′ and sp calculations have been conducted for the molecules with variations in torsional angle.

Recently semi-empirical MO calculations have been widely applied and subsequently modified, *e.g.*, to the molecules including 2nd- and 3rd-row elements.[2,3] The authors have previously investigated the vibrational spectra of 1,2-ethanedithiol $(CH_2SH)_2$,[4] 1,2-bis(alkylthio)ethane $RSCH_2CH_2SR$ (R=Me, Et, *n*-Pr, and *n*-Bu),[5,6] bis(alkylthio)methane $RSCH_2SR$ (R=Me, Et, *n*-Pr, and *n*-Bu),[7–9] and (methylthio)methanethiol CH_3SCH_2SH.[10] With $(CH_2SH)_2$, electron diffraction[11] and EHMO[12] studies have been reported. The molecular structure of ethanethiol EtSH has appeared recently,[13–16] while for methanethiol MeSH and EtSH, the MINDO/3 calculations were performed;[17] however the MINDO/3 calculations do not always faithfully reproduce the experimental geometries. With oxygen analogs such as dimethoxymethane $CH_3OCH_2OCH_3$, the experimental structural analysis[18] and the theoretical conformational analyses by the semi-empirical and non-empirical methods have been attempted.[19]

In the present paper, to avoid the complexity of *ab initio* calculations, several of the CNDO/2 parameters have been reasonably optimized and the CNDO/2 method applied to examine the stable geometries of the molecules concerned. The CNDO/2 calculations have also been conducted on the oxygen analogs, 1,2-ethanediol $(CH_2OH)_2$, 1,2-dimethoxyethane $(CH_2OCH_3)_2$, and 1-methoxy-2-methylthioethane $CH_3OCH_2CH_2SCH_3$. The results of the CNDO/2 calculations will be compared with the observed values.

Optimization of Parameters

The Fock matrix[20] in the CNDO/2 method[21,22] can be expressed by

$$F_{\mu\mu} = -(1/2)(I_\mu+A_\mu) + [(P_{AA}-Z_A)-(1/2)(P_{\mu\mu}-1)]\gamma_{AA} + \sum_{B\neq A}(P_{BB}-Z_B)\gamma_{AB} \quad (\mu \text{ on A}),$$

$$F_{\mu\nu} = (1/2)KS_{\mu\nu}(\beta_A+\beta_B) - (1/2)P_{\mu\nu}\gamma_{AB} \quad (\mu \text{ on A}, \nu \text{ on B}),$$

where the notations are the same as those used by Pople *et al.*[21] The constant K of the off-diagonal core matrix element has been given by Pople *et al.*[21] as unity in relation to the first-row elements, and 0.75 in the 2nd-row elements. In this paper, hereafter K_d will replace K in relation to the 2nd-row elements. The constant β is the bonding parameter, and this will be estimated reasonably. The orbital exponent ζ is included in the radial distance r multiplied by a decaying exponential $\exp(-\zeta r)$.

SCF calculations using the parameters of Pople *et al.*[21] (POPLE) sometimes diverge for certain molecules having more than two 2nd-row elements. Moreover the POPLE method gives the organo-sulfur molecules rather larger dipole moments and higher energy barriers for internal rotation than observed. In order to overcome the first difficulty, the density matrix method,[23–25] and others have been used, but suffer from the disadvantage of requiring a lot of computation time. Consequently the value of the constant K_d has been varied. With reference to previous works,[26–28] K_d has been assumed to be 0.492 on the basis of the smoothness of the SCF using the molecular geometry of $(SiH_3)_2O$.[29] The ζ and β values have been optimized in relation to carbon and sulfur atoms. In the course of the parametrizations, the molecular geometry of T-EtSH,[13] and initial parameters reported[21] have been adopted. The optimizations have been made in the order:

i) β_c has been estimated using ζ_c as the Slater value to reproduce the observed r(C–C) of ethane.[30]

ii) ζ_s was then deduced using the revised β_c to fit the observed r(C–S) of T-EtSH.[13]

iii) β_s was optimized using the revised ζ_s to reproduce the observed ϕ(CSH) of T-EtSH.[13]

iv) Steps ii) and iii) were repeated until the two parameters, ζ_s and β_s, did not vary very much. In the present case, nine cycles were repeated. The parameters finally obtained are summarized in Table 1 together with those reported,[3,21] and the relation between ζ_s and β_s is shown in Fig. 1. The orbital exponents previously estimated by Clementi *et al.*[31] and Burns[32] are included. The ζ_s obtained here is larger than that

TABLE 1. CNDO/2 PARAMETERS, β IN eV

	Present work	Pople[a]	Höjer[b]
K_d	0.492	0.75	1.0
β_H	−9.	−9.	−7.00
β_C	−16.97	−21.	−15.00
β_S	−31.79	−18.15	−11.39
ζ_H	1.2	1.2	1.2
ζ_C	1.625	1.625	1.6083[c]
ζ_S	1.867	1.8167	2.1223[c]

a) From Ref. 21. b) From Ref. 3. c) Transferred from Ref. 31.

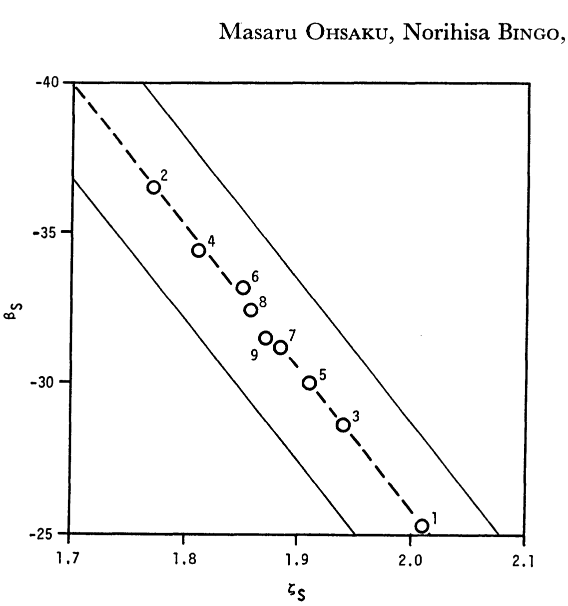

Fig. 1. Correlation plot of β_S vs. ζ_S.
Figures show the number of the repeated cycles.

used by Pople *et al.*[21] and smaller than that used by Clementi *et al.*[31] For β_S, a fairly small value was obtained. Hereafter, the method with the revised parameters will be employed as the MCNDO method. The method with K_d set at 0.492 and the others as the original ones[21] is named the KCNDO method. These methods have been applied to some of organo-sulfur molecules, and an attempt has been made to obtain information on the molecular conformations of these molecules.

Results and Discussion

Molecular geometries used were as follows: for $(CH_2SH)_2$— the geometry reported[11] except ϕ(CSH), for $(CH_2SCH_3)_2$, CH_3SCH_2SH, and $CH_3SCH_2SCH_3$, r(C–H)=1.09 Å, r(C–S)=1.82 Å, r(C–C)=1.54 Å, r(S–H)=1.335 Å. The angles around the carbon atom have been assumed as tetrahedral, and for MeSH[33] and EtSH[13,15] those observed. The dihedral angles were 180° and 60° for the T and G forms, respectively. The angles calculated and observed, and the stability of the molecules are summarized in Tables 2 and 3.

$(CH_2SH)_2$ and $(CH_2SCH_3)_2$. Using the molecular geometry reported above, optimizations were made on ϕ(CSH) of $(CH_2SH)_2$ and ϕ(CSC) of $(CH_2SCH_3)_2$. The calculated ϕ(CSH) are 95.5 and 96.5° for the MCNDO and POPLE methods respectively. The observed ϕ(CSH) has been reported as 90.5°[11] which is much smaller than those of the other thiols; MeSH: ϕ(CSH)=96.5°,[33] and T-EtSH: 96°13′.[13] With the ϕ(CSC) of

Table 2. Calculated and observed angles

Molecule		MCNDO	KCNDO	POPLE	sp	MINDO/3[d]	Obsd	Ref.
$(CH_2SH)_2$	ϕ(CSH)	95.5°		96.5°	101.9°		90.5°	11
$(CH_2SCH_3)_2$	ϕ(CSC)	115.5°						
MeSH	ϕ(CSH)	94.4°		94.5°	101.1°	111.9°	96.5°	33
T-EtSH	ϕ(CSH)	96.2°		97°	102.7°	105.1°	96°13′ 95.23°	13 14
G-EtSH	ϕ(CSH)	97.7°		98.5°	101.9°		96° 95.23°	15,16 14
	τ(C–S)	67°	64°	65°	<60°		61°45′ 58.75°	15,16 14
H_2S	ϕ(HSH)	92.7°		99°[a] 92.8°	99.5°	97°	92.06°	e)
H_2S_2	ϕ(SSH)	96.2°		95.7°	102.2°	102.9°	95° 91°21′	f) g)
n-PrSH	ϕ(CSH)	96.6°		97.2°	106.5°	96.4°		
CH_3SCH_2SH	ϕ(CSC)	113°[b]	107°[b]	113°[b]	103°			
	ϕ(CSH)	99°	<93.5°	99.5°	101.5°			
	τ(C–S)	75°	c)	76°	<40°			
$CH_3SCH_2SCH_3$	ϕ(CSC)	113°	107°	113°	103°			
	τ(C–S)	75°	77°	75°	63.5°			
MeOMe	ϕ(COC)						111°43′	43
$CH_3OCH_2OCH_3$	ϕ(COC)						114.2°	18
	τ(C–O)						66.3°	18
POM	ϕ(COC)						110°53′	45
	τ(C–O)						77°23′	45
MeSMe	ϕ(CSC)					115.4°	98°52′	44
PES	ϕ(CSC)						109.5°	34
PTM	ϕ(CSC)						106°52′	35
	τ(C–S)						65°59′	35

a) From Ref. 26. b) Assumed. c) Not performed. d) From Ref. 17. e) R. L. Cook, F. C. De Lucia, and P. Helminger, *J. Mol. Struct.*, **28**, 237 (1975). f) D. P. Stevenson and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 2872 (1938). g) G. Winnewisser, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, **49**, 3465 (1968). Geometries; $(CH_2SH)_2$: TGT, $(CH_2SCH_3)_2$: TGT, MeSH: from Ref. 33, EtSH: from Refs. 13 and 15, H_2S: e), H_2S_2: g) in G, *n*-PrSH: r(C–H)=1.09 Å, r(C–C)=1.54 Å, r(C–S)=1.82 Å, r(S–H)=1.335 Å, ϕ(CSH)=96.5°, angles around carbon atom=tetrahedral in TT, CH_3SCH_2SH: GT, $CH_3SCH_2SCH_3$: GG.

TABLE 3. STABILITY AS A FUNCTION OF INTERNAL ROTATION ANGLE

Molecule	Stability
$HOCH_2CH_2OH$	
Calcd	$\text{TTT}\underset{0.03}{>}\text{TGT}\underset{1.88}{>}\text{TGG}\underset{1.81}{>}\text{GGG}\underset{0.25}{>}\text{GTG}'\underset{0.01}{>}\text{GTG}$
Obsd[a)]	$-\underline{\text{G}}-$, $-\text{T}-$
$HSCH_2CH_2SH$	
Calcd MCNDO	$\text{TGT}\underset{0.18}{>}\text{TGG}\underset{3.03}{>}\text{GGG}\underset{14.9}{>}\text{TTT}\underset{0.31}{>}\text{GTG}\underset{0.20}{>}\text{GTG}'$
sp	$\text{TGT}\underset{0.32}{>}\text{TTT}\underset{1.17}{>}\text{TGG}\underset{1.30}{>}\text{GTG}\underset{0.01}{>}\text{GTG}'\underset{0.17}{>}\text{GGG}$
Obsd	$-\underline{\text{T}}-$, $-\text{G}-$[b)]
	$\underline{\text{TGT}}$, TGG, GTG′, TTT, GGG, GTG, one or more other rotamers[c)]
$CH_3OCH_2CH_2OCH_3$	
Calcd	$\text{TGT}\underset{0.05}{>}\text{TTT}\underset{2.83}{>}\text{TGG}\underset{2.78}{>}\text{GGG}\underset{0.06}{>}\text{GTG}'\underset{0.21}{>}\text{GTG}$
Obsd[d)]	$\underline{\text{TGT}}$, TTT, one or more other rotamers
$CH_3OCH_2CH_2SCH_3$	
Calcd MCNDO	$\text{GGT}\underset{2.01}{>}\text{TGG}\underset{6.24}{>}\text{TTG}\underset{0.91}{>}\text{GTT}\underset{0.87}{>}\text{GTG}\underset{0.27}{>}\text{TGT}\underset{6.26}{>}\text{GGG}\underset{1.23}{>}\text{TTT}\underset{3.68}{>}\text{GTG}'$
sp	$\text{TGT}\underset{0.25}{>}\text{TTT}\underset{1.55}{>}\text{TGG}\underset{0.25}{>}\text{TTG}\underset{1.00}{>}\text{GGT}\underset{0.35}{>}\text{GTT}\underset{1.40}{>}\text{GGG}\underset{0.44}{>}\text{GTG}'\underset{0.03}{>}\text{GTG}$
Obsd[e)]	$\underline{\text{TTG}}$, TGG, TGT, TTT, GTG or GTG′, GGT
$CH_3SCH_2CH_2SCH_3$	
Calcd MCNDO	$\text{TGG}\underset{9.73}{>}\text{GGG}\underset{1.51}{>}\text{TGT}\underset{0.58}{>}\text{GTG}\underset{9.28}{>}\text{TTT}\underset{2.37}{>}\text{GTG}'$
sp	$\text{TGT}=\text{TTT}\underset{2.20}{>}\text{TGG}\underset{1.71}{>}\text{GTG}'\underset{0.01}{>}\text{GTG}\underset{0.45}{>}\text{GGG}$
Obsd	$\underline{\text{GTG}'}$, GGG, one or more other rotamers[f)]
	$\underline{\text{TGT}}$, TTT, GTG′, GGG, one or more other rotamers[g)]
CH_3SCH_2SH	
Calcd MCNDO	$\text{GT}\underset{0.18}{>}\text{GG}\underset{0.97}{>}\text{GG}'\underset{18.8}{>}\text{TG}\underset{0.96}{>}\text{TT}$
sp	$\text{TT}\underset{0.99}{>}\text{GT}\underset{0.45}{>}\text{TG}\underset{1.61}{>}\text{GG}\underset{1.31}{>}\text{GG}'$
Obsd[h)]	$\underline{\text{GG}}$, GT, GG′, TG, TT
$CH_3SCH_2SCH_3$	
Calcd MCNDO	$\text{GG}\underset{18.7}{>}\text{TG}\underset{16.5}{>}\text{TT}\underset{229.}{>}\text{GG}'$
sp	$\text{TT}\underset{1.06}{>}\text{TG}\underset{1.73}{>}\text{GG}\underset{265.}{>}\text{GG}'$
Obsd[i,j)]	$\underline{\text{GG}}$, TG, TT

Small figures indicate the energy difference, in kcal/mol. —, stable form in the crystalline solid state. a) From Ref. 36. b) From Ref. 4a. c) From Ref. 4b. d) From Ref. 37. e) From Ref. 38. f) From Ref(s). 5 (and 38). g) From Ref. 6. h) From Ref. 10. i) From Ref. 7. j) From Ref. 8. Geometries; $(CH_2OH)_2$: from Ref. 12, $(CH_2OCH_3)_2$ and $CH_3OCH_2CH_2SCH_3$: $r(\text{C–O})=1.41$ Å, $\phi(\text{COC})=111°49'$, referred from M. Hayashi and K. Kuwada, Preprint of the 32nd National Meeting of the Chemical Society of Japan, Vol. 1, (1975) p. 121, and assumed $r(\text{C–H})=1.09$ Å, $r(\text{C–C})=1.54$ Å, $r(\text{C–S})=1.82$ Å, $\phi(\text{CSC})=99°$, angles around carbon atom=tetrahedral.

$(CH_2SCH_3)_2$, 115.5° was obtained which corresponds well to the 115.4° of MeSMe and 115.6° of MeSEt estimated by the MINDO/3 method.[17)] However, the calculated value 115.5° is somewhat larger than that observed for poly(ethylene sulfide) (PES) 109.5°[34)] and poly(thiomethylene) (PTM) 106°52′.[35)]

The calculations were conducted for each of six typical forms with $\phi(\text{CSH})=95.5°$ in $(CH_2SH)_2$ and $\phi(\text{CSC})=115.5°$ in $(CH_2SCH_3)_2$. The stability from the calculated energy is in the order, TGG>GGG>TGT>GTG>TTT>GTG′ for $(CH_2SCH_3)_2$. It had been previously concluded[6)] that the conformation about the C–C bond in the crystalline state is the G conformation. From the CNDO/2 calculations (KCNDO) assuming the four typical forms, TGT, GGG, TTT, and GTG′, the conclusion drawn is that the TGT form is the best form to explain the stable crystalline solid state.[6)] The main reason for the difference in stability between the present and previous calculations is due to the difference in geometry used. For $(CH_2SH)_2$ nearly the same order to that of $(CH_2SCH_3)_2$ was obtained. The sp calculations[22)] have also been conducted for these molecules. With $(CH_2SH)_2$, the CNDO/2 spd′ or sp calculation suggests that the most stable form is the TGT form. From this, it appears that the previous conclusion,[4a)] in which mainly the TTT and TGT molecular forms exist in the gaseous and liquid states and the TTT form alone persists in the solid state, is of doubtful validity. As a result, it may be concluded that the stable form in the crystalline solid state is the TGT form.

With $(CH_2SCH_3)_2$, if the observed spectra demonstrate[5,38] the mutual exclusion rule between the IR and Raman spectra, the actual molecular form in the crystalline solid state should be either the TTT or the GTG′ form. However, the CNDO/2 spd′ calculation does not support this conclusion, although the TTT form has been shown to be the fairly stable form from the sp calculation.

$(CH_2OH)_2$, $(CH_2OCH_3)_2$, and $CH_3OCH_2CH_2SCH_3$. The vibrational spectra, normal coordinate treatments, and conformational analyses of $(CH_2OH)_2$[36] and $(CH_2OCH_3)_2$[37] have been studied extensively. Recently, the vibrational spectra and rotational isomerism of $CH_3XCH_2CH_2YCH_3$ (X, Y=O or S) have been published.[38] The CNDO/2 calculations for these molecules have been conducted assuming the typical forms, the results of which are summarized in Table 3. The stability, determined with the aid of the CNDO/2 calculations for $(CH_2OCH_3)_2$ agree excellently with the observed, TGT>TTT>TGG>TTG,[38] although the present calculation was not performed on the TTG form. With $CH_3OCH_2CH_2SCH_3$, the observed frequencies[38] in the crystalline solid state can be well explained by the GGT form—the most stable form calculated from the MCNDO method—as well as by the TTG form, which was concluded as the stable form in the crystalline solid state.[38]

MeSH and EtSH. The relations between the bond order, bond lengths, and force constants have been reported by Coulson.[39,40] It has been previously shown that a linear relationship exists between the bond length r(X–H) and the X–H stretching frequency and the bond order matrix elements, $P_{1sH,n\mathrm{sX}}$ calculated by the POPLE method, where n is 2 or 3, and X is C, N, or Si.[41] The same is true in this case as shown in Fig. 2. These results, therefore, imply that most of the X–H stretching force constant K(X–H) can be explained in terms of the relation between the 1s AO of hydrogen and the ns AO of the X atom.

The angles ϕ(CSH), ϕ(HSH), and ϕ(SSH) of the molecules having the S–H bond are excellently reproduced, both by the POPLE and MCNDO methods (Table 2). The torsional angle is also fairly well reproduced. However, the sp calculations, in general, do not agree with the observed ones very well. With EtSH, the energy difference has been found and is summarized in Table 4. The experimental value obtained from the calorimetric data gives the stability G>T and the difference 0.3 kcal/mol,[42] and recent microwave data[14] the value 0.406 kcal/mol. The observed values are well explained by the calculations. The MCNDO method is refined a little in the energy difference.

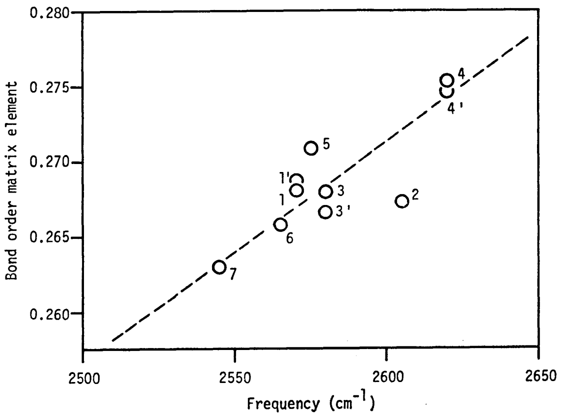

Fig. 2. Correlation plot of $P_{1sH,3sS}$ *vs.* ν_{SH}—POPLE. 1: $(CH_2SH)_2$, 2: MeSH, 3: EtSH, 4: H_2S, 5: H_2S_2, 6: *n*-PrSH, 7: CH_3SCH_2SH.

IR data (observed in the gaseous state except 7); 1: from Ref. 4a, 2: I. W. May and E. L. Pace, *Spectrochim. Acta, Part A*, **24**, 1605 (1968), 3: N. Sheppard, *J. Chem. Phys.*, **17**, 79 (1949), 4: J. W. Nibler and G. C. Pimentel, *J. Mol. Spectrosc.*, **26**, 294 (1968), 5: M. K. Wilson and R. M. Badger, *J. Chem. Phys.*, **17**, 1232 (1949), 6: M. Hayashi, Y. Shiro and H. Murata, *Bull. Chem. Soc. Jpn.*, **39**, 112 (1966), 7: from Ref. 10.

Geometries; 1: TGT, 1′: TTT, 2: from Ref. 33, 3: from Ref. 13 in T, 3′: from Ref. 15 in G, 4: e of Table 2 with r(S–H) = 1.3362 Å, 5: g of Table 2 in T, 6: see geometry listed in Table 2, 7: TT. $(CH_2SH)_2$: we have at first carried out the calculations using r(S–H) = 1.4 Å then we have obtained an extraordinarily low value of $P_{1sH,3sS}$: 0.2554. On the other hand the infrared frequency does not lie off the ordinary value. Therefore, we have assumed r(S–H) = 1.335 Å only in these calculations (bond order calculations).

Table 4. Energy difference (ΔE, kcal/mol), energy barrier height (V, kcal/mol), and dipole moment (D.M., Debye) of MeSH and EtSH

	MCNDO	KCNDO	POPLE	Obsd
ΔE, T-EtSH—G-EtSH	1.06	2.20	1.87	0.406[a] 0.3[b]
V-SH, MeSH	1.38	0.91	1.75	1.27[c]
V-Me, EtSH	9.42	6.84	14.25	3.260[d] 3.305[a] 3.75[b]
V-SH, EtSH	4.41	2.65	6.17	1.305[d] 1.258[a] 1.42[b]
D.M., MeSH	2.345	1.893	2.443	1.48[c]
T-EtSH	2.139	2.238	2.454	1.560[e] 1.58[a]
G-EtSH	2.223	2.248	2.512	1.61[a]

a) From Ref. 14. b) From Ref. 42. c) From Ref. 33. d) From Ref. 16. e) From Ref. 13. Geometries; MeSH: from Ref. 33, T-EtSH: from Ref. 13, G-EtSH: from Ref. 15, EtSH: from Ref. 13.

CH_3SCH_2SH and $CH_3SCH_2SCH_3$. The optimized angles are shown in Table 2 along with the observed values for dimethyl ether (MeOMe),[43] dimethyl sulfide (MeSMe),[44] $CH_3OCH_2OCH_3$,[18] poly(oxymethylene) (POM),[45] PES,[34] and PTM.[35] For the ϕ(CSC) of the molecules now of interest, it can be expected that the value is larger than that of MeSMe[44] and smaller than that of PTM.[35] The sp calculations reproduce the values as expected except for the τ(C–S) of CH_3SCH_2SH, but the spd′ calculations are somewhat too large. The CNDO/2 calculations were then performed with variations in the torsional angle. From the analyses of the vibrational spectra it has been concluded that for CH_3SCH_2SH only one form exists, the GG form in the crystalline solid state as compared with five

forms, GG, GT, TG, GG′, and TT, which coexist in the liquid and gaseous states.[10] With $CH_3SCH_2SCH_3$, the order of the stability has been reported as: GG>TG>TT≫GG′.[7,8] By the MCNDO method using the assumed geometry $\phi(CSC)=99°$ and $\phi(CSH)=96.5°$, the order for CH_3SCH_2SH has been established as: GT>GG>GG′>TG>TT, and for $CH_3SCH_2SCH_3$ as: GG>TG>TT≫GG′. With $CH_3SCH_2SCH_3$, the most stable form GG is well explained by the MCNDO method, the stable structure corresponding with that of the oxygen analog, $CH_3OCH_2OCH_3$.[18,19] With CH_3SCH_2SH, however, the most stable form has been calculated as GT by the MCNDO method, but this does not agree perfectly with the observed one.[10] In the course of the analyses of the IR spectra of this molecule, the most stable form expected was the GG or GT form. From the frequency shift of the S–H stretching vibration by D substitution it has been concluded that the most stable form is the GG. In the molecule CH_3SCH_2SH, the conformation about the bond CH_3SCH_2–SH is indeed very difficult to explain, since hydrogen is a very light and small atom. It may be concluded that the conformation about the bond CH_3S–CH_2SH is reproduced by the spd′ calculations. In the case of $CH_3SCH_2SCH_3$, it has been previously stated that the GG′ form is not the stable form even in the liquid state.[7,8] On the other hand the GG′ form has been taken into consideration for CH_3SCH_2SH.[10] These situations are well reproduced by the CNDO/2 method.

The sp calculations explain fairly well the geometries of CH_3SCH_2SH and $CH_3SCH_2SCH_3$ as reported above, but do not explain the stability. In the case of two sulfur atoms in a molecule, the interactions between the d-orbitals may play an important role in the conformational stability. Therefore, it is better to use the spd′ calculation for the molecules having more than two sulfur atoms in a molecule than the sp calculation.

The conclusions drawn are that the use of the POPLE and MCNDO parameters give fairly good $\phi(CSH)$ and internal rotation angles for simple aliphatic thiols. The present calculations also show that the molecular geometry reported for $(CH_2SH)_2$[11] appears ambiguous, in particular in $\phi(CSH)$ and $r(S–H)$. The energy barrier is better reproduced by the MCNDO method than by the POPLE one (Table 4). The dipole moment in general decreases in the order: POPLE>MCNDO>KCNDO and in these respects, the MCNDO method is better than the original CNDO/2 method. The angle $\phi(CSH)$ for RSH is better reproduced by the CNDO/2 spd′ method than by the MINDO/3 method.[17]

The CNDO/2 method now used, however, may not reproduce the energy difference itself between the rotational isomers which is very important in the analysis of rotational isomerism. Therefore in the CNDO/2 parameters there may be still some ambiguities, in particular relating to the 2nd-row elements. Generally, from the vibrational data and normal coordinate treatment, it is very difficult to determine which rotational isomer is more stable when the calculated frequencies of the rotational isomers are almost identical. In order to overcome this difficulty, the CNDO/2 method is helpful.

The authors wish to thank Prof. Akira Imamura of Shiga University of Medical Science for his kind advice. All calculations were performed at the Computing Center of Hiroshima University.

References

1) Presented in part at the 35th National Meeting of the Chemical Society of Japan, Sapporo, August 1976.

2) For example, the references cited in A. Veillard. *Chem. Phys. Lett.*, **33**, 15 (1975); Th. Weller, D. Klöpper, and H.-J. Köhler, *Chem. Phys. Lett.*, **36**, 475 (1975).

3) G. Höjer and S. Meza, *Acta Chem. Scand.*, **26**, 3723 (1972).

4) a) M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Jpn.*, **38**, 1734 (1965); b) M. Ohsaku and H. Murata, *J. Mol. Struct.*, in press.

5) M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Jpn.*, **39**, 118 (1966).

6) M. Ohsaku and H. Murata, *Spectrochim. Acta, Part A*, **34**, 869 (1978).

7) M. Ohsaku, Y. Shiro, and H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 113 (1972).

8) M. Ohsaku, *Bull. Chem. Soc. Jpn.*, **47**, 965 (1974).

9) M. Ohsaku, *Spectrochim. Acta, Part A*, **31**, 1271 (1975).

10) M. Ohsaku, Y. Shiro, and H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 3035 (1972).

11) I. Hargittai and Gy. Schultz, *J. Chem. Soc., Chem. Commun.*, **1972**, 323; Gy. Schultz and I. Hargittai, *Acta Chim. Acad. Sci. Hung.*, **75**, 381 (1973).

12) N. Hadjiliadis and T. Theophanides, *Chim. Chronika*, **2**, 37 (1973).

13) M. Hayashi, H. Imaishi, and K. Kuwada, *Bull. Chem. Soc. Jpn.*, **47**, 2382 (1974).

14) R. E. Schmidt and C. R. Quade, *J. Chem. Phys.*, **62**, 3864 (1975).

15) M. Hayashi, J. Nakagawa, and K. Kuwada, *Chem. Lett.*, **1975**, 1267.

16) J. Nakagawa, K. Kuwada, and M. Hayashi, *Bull. Chem. Soc. Jpn.*, **49**, 3420 (1976).

17) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1311 (1975).

18) E. E. Astrup, *Acta Chem. Scand.*, **25**, 1494 (1971).

19) a) I. Tvaroška and T. Bleha, *J. Mol. Struct.*, **24**, 249 (1975). b) D. G. Gorenstein and D. Kar, *J. Am. Chem. Soc.*, **99**, 672 (1977).

20) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

21) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); J. A. Pople and D. L. Beveridge, "Approximate Moleculer Orbital Theory," McGraw-Hill, New York, N. Y. (1970).

22) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

23) R. McWeeny, *Proc. R. Soc. London, Ser. A*, **235**, 496 (1956).

24) A. T. Amos, *Mol. Phys.*, **5**, 91 (1962).

25) A. Imamura and H. Fujita, *J. Chem. Phys.*, **61**, 115 (1974).

26) D. P. Santry, *J. Am. Chem. Soc.*, **90**, 3309 (1967).

27) J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

28) T. Morita, *Kagaku No Ryoiki*, **29**, 455 (1975).

29) A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, **17**, 2455 (1963).

30) D. E. Shaw, D. W. Lepard, and H. L. Welsh, *J. Chem. Phys.*, **42**, 3736 (1965).

31) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

32) G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964).

33) T. Kojima and T. Nishikawa, *J. Phys. Soc. Jpn.*, **12**, 680 (1957); T. Kojima, *J. Phys. Soc. Jpn.*, **15**, 1284 (1960).

34) Y. Takahashi, H. Tadokoro, and Y. Chatani, *J. Macromol. Sci., Part B*, **2**, 361 (1968); K. Tai and H. Tadokoro, *Macromolecules*, **7**, 507 (1974).

35) G. Carazzolo and G. Valle, *Makromol. Chem.*, **90**, 66 (1966).

36) H. Matsuura and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **40**, 85 (1967).

37) R. G. Snyder and G. Zerbi, *Spectrochim. Acta, Part A*, **23**, 391 (1967).

38) Y. Ogawa, M. Ohta, M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 650 (1977).

39) C. A. Coulson, *Proc. Soc. London, Ser. A*, **169**, 413 (1935).

40) For electronic population analysis: R. A. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, and 2343 (1955).

41) N. Bingo, M. Ohsaku, and H. Murata, *J. Sci. Hiroshima Univ.*, **A40**, 317 (1976).

42) D. Smith, J. P. Devlin, and D. W. Scott, *J. Mol. Spectrosc.*, **25**, 174 (1968).

43) U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).

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

45) H. Tadokoro, T. Yasumoto, S. Murahashi, and I. Nitta, *J. Polym. Sci.*, **44**, 266 (1960).