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Ab Initio Self-consistent Field MO Calculations of Ethanethiol and Ethanol

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Ab initio self-consistent field MO calculations were performed on EtSH and EtOH, and the optimized geometries were obtained by the use of the STO-3G and STO-3G* basis sets. It was found that *ab initio* MO calculations reproduced the observed geometries of these molecules sufficiently well. The variation in the observed bond angle, α(CCX) (X=S and O), from the *trans* to the *gauche* rotamers, which was observed by means of microwave spectroscopy, was very reasonably reproduced from the results of these calculations. The total energy calculated gives a reasonable explanation of the stability between the rotational isomers.

Ethanethiol is well known as one of the simplest molecules to exhibit *trans-gauche* isomerism around the CC–SH bond. Ethanol is its oxygen analog. However, up to the present time, there have appeared no reports which have successfully determined independently the molecular structures of the *trans* and *gauche* forms of ethanol; this has been because of the very large spectral splitting due to the internal rotation of the OH group. A very large number of experimental works in the geometrical mode have been published during the last decade: For EtSH, *e.g.*, by microwave[1–4) and far-IR[5,6) spectroscopies, and for EtOH, by microwave studies.[7,8) Among these publications, the main interests of spectroscopists have been on the experimental result that the bond angle α(CCS) of EtSH widens sharply from the *trans* form (T-form) to the *gauche* form (G-form).[3,4) The same trend is also seen in the structurally analogous molecules, *e.g.*, ethyl methyl sulfide.[9,10) A part of these experimental results has already been explained by *ab initio* calculations.[11) Theoretical works on the basis of the LCAO SCF molecular orbital calculations had also been performed with various methods; that is, semiempirical calculations on EtSH[12–14) and *ab initio* calculations on EtOH[15,16) and related molecules[17–19) have been carried out. However, as far as we know, no *ab initio* conformational study of ethanethiol has been published; although an *ab initio* calculation was performed on MeSH very early in the *ab initio* age.[20) Some other thiols have also been treated by semiempirical and *ab initio* MO procedures.[13,21)

In the present article, the geometry of EtSH was optimized by means of the *ab initio* energy-gradient method, and the difference in α(CCS) between *trans* and *gauche* forms was explained in terms of the through-space interaction. Similar calculations were performed on EtOH for comparison.

Method of Calculations

Calculations were performed by the use of the Gaussian 80 program package.[22) Geometry optimization was made by the gradient method,[23) which is included in the Gaussian 80 package. The basis sets used were STO-3G and STO-3G*. The 3-21G basis was also partly used for EtSH, and the 4-31G* basis, was for EtOH.

First, in order to confirm the observed geometrical parameters of EtSH, a full geometrical optimization was performed by the use of the STO-3G and STO-3G* basis sets.

For further analysis, in order to save computer cpu time, only the α(CCS) angle was then optimized, while the other geometries were transferred from the observed *trans* ones and were fixed during the optimization;[2) that is, in the calculations for the T- and G- forms, the geometry of the observed *trans* form was commonly used.

Nonbonded atomic interactions which correspond to the through-space interaction were then quantitatively analyzed by means of the following procedure. The SCF equation can be expressed as in Eq. (1);[24)

$$\mathrm{FC} = \mathrm{SCE}. \tag{1}$$

Elements of Fock matrix and overlap integrals were written as in Eqs. (2) and (3) respectively:

$$\mathrm{F}_{rs} = \mathrm{I}_{rs} + \sum_{t=1}^{m}\sum_{u=1}^{m}\mathrm{P}_{tu}[(\mathrm{rs}|\mathrm{tu}) - (1/2)(\mathrm{rt}|\mathrm{su})] \tag{2}$$

$$\mathrm{S}_{rs} = \int \mathrm{x}_r(1)\mathrm{x}_s(1)\mathrm{d}\tau, \tag{3}$$

where I_{rs}, P_{tu}, and (rs|tu) or (rt|su) indicate the one-electron integral, the density matrix, and the two-electron integral respectively. When the Fock matrix elements, F_{rs}, and the overlap integral, S_{rs}, between certain atomic orbitals, *e.g.*, r and s, are set equal to zero, the SCF equation, in which the interaction between those pairs is not taken into account, can be obtained as in Eq. (4);

$$\mathrm{F'C'} = \mathrm{S'C'E'}. \tag{4}$$

When all of the interactions between the AOs which belong to, *e.g.*, the A atom and those belonging to the B atom are cut off, the interaction between the A and B atoms can be considered to be dropped. The difference in the total energy obtained between Eqs. (1) and (4) shows the interaction energy between the certain atomic pair, A and B, in question. Using these equations, the interaction energy between nonbonded atoms (the through-space interaction) can be obtained quantitatively. For this purpose, a part of the Gaussian 80 program package was modified, and during these calculations the geometry was fixed. It should be mentioned that a more sophisticated procedure of analysis might be possible by using the localized orbitals as the basis sets in Eq. (2). The programming for this purpose is not so easy. In the present paper, therefore, the rough procedure presented above was employed for the analysis as a first approximation.

Results and Discussion

Ethanethiol. The optimized geometries are shown in Tables 1-a and -b.

There is an excellent agreement between the theoretically calculated and the observed geometries, and it can be seen that there is no remarkable difference between the geometries obtained by the STO-3G and STO-3G* basis sets. However, the STO-3G* basis set, which has a polarization function on the sulfur atom, gives a geometry different from that obtained by the use of STO-3G. As for the bond lengths, the r(C–H) and r(C–C) values do not depend greatly on the difference in the basis set. However, r(C–S) and r(S–H) vary with the change of the set. That is, the STO-3G basis set gives

TABLE 1-a. STO-3G AND STO-3G* OPTIMIZED STRUCTURAL PARAMETERS[a] OF EtSH FOR THE *trans* CONFORMATION, COMPARED WITH THE MICROWAVE-SPECTROSCOPY DATA

Group	Parameters[b]	Experiment		Theory	
		Set A[c]	Set B[d,e]	STO-3G*	STO-3G
CH_3C	r(CH_s)	1.095	1.093	1.086	1.086
	r(CH_a)	1.092		1.086	1.086
	α(CCH_s)	109.67	109.70	110.28	110.26
	α(CCH_a)	110.58		110.86	110.90
	α(H_sCH_a)	108.88	(109.23)	108.24	108.27
	α(H_aCH_a)	108.12		108.34	108.34
CCH_2S	r(CH)	1.090	1.088	1.091	1.089
	r(CC)	1.529	1.530	1.546	1.541
	α(CCS)	108.57	(108.55)	110.24	110.76
	α(HCH)	108.90	(107.23)	107.09	107.11
	α(HCC)	110.23	109.57	108.78	108.99
	α(HCS)	109.43	110.92	110.92	110.35
CSH	r(SH)	1.322	1.328	1.320	1.331
	r(SC)	1.820	1.829	1.790	1.806
	α(HSC)	96.22	95.23	94.95	95.26

a) Bond lengths are in A; angles, in degrees. b) See also Fig. 1. c) From Ref. 2. d) From Ref. 4. e)Figures in parentheses are those derived from the proposed parameters.

TABLE 1-b. STO-3G AND STO-3G* OPTIMIZED STRUCTURAL PARAMETERS[a] OF EtSH FOR THE *Gauche* CONFORMATION, COMPARED WITH THE MICROWAVE-SPECTROSCOPY DATA

Group	Parameters[b]	Experiment		Theory	
		Set A[c]	Set B[d,e]	STO-3G*	STO-3G
CH_3C	r(CH_s)			1.087	1.087
	r(CH^1_a)	1.091	1.093	1.086	1.086
	r(CH^2_a)			1.085	1.086
	α(CCH_s)	110.50		109.54	109.41
	α(CCH^1_a)	110.62	109.70	111.20	110.14
	α(CCH^2_a)			110.23	109.83
	α($H_sCH^1_a$)	109.03		107.87	108.06
	α($H_sCH^2_a$)		(109.23)	108.90	108.74
	α($H^1_aCH^2_a$)	106.92		111.64	110.44
CCH_2S	r(CH^1)	1.089	1.088	1.090	1.087
	r(CH^2)			1.091	1.088
	r(CC)	1.528	1.530	1.548	1.545
	α(CCS)	113.62	(113.27)	113.49	113.30
	α(H^1CH^2)	106.58	(107.32)	109.04	109.39
	α(H^1CC)	110.70	109.57	109.87	109.88
	α(H^2CC)	111.32		109.31	109.31
	α(H^1CS)	104.88	(106.12)	104.72	106.33
	α(H^2CS)	109.27	(110.80)	110.48	108.67
CSH	r(SH)	1.336	1.328	1.320	1.330
	r(SC)	1.814	1.829	1.792	1.808
	α(HSC)	96	95.23	94.98	95.36
Dihedral angle	τ(CCSH)	61.75	(60)	62.80	61.87

a) Bond lengths are in A; angles, in degrees. b) See also Fig. 1 c) From Ref. 3. d) From Ref. 4. e) Figures in parentheses are those derived from the proposed parameters.

longer bond lengths of r(C–S) and r(S–H) than those of the STO-3G*. A similar tendency was found in ethyl methyl sulfide;[11] *i.e.*, the bond length, r(C–S), calculated by the use of the STO-3G* set is *ca.* 0.015 A shorter than that obtained by the use of the STO-3G set. With these bond angles, we cannot see any clear differences between the geometries calculated by the STO-3G and STO-3G* sets except for the ones including the sulfur atom. The STO-3G basis reproduced poorly the α(CCS) of the protonated species $EtSH_2^+$. It is well known that the d-functions on the sulfur atom are also necessary to produce a proper geometry in the ionized sulfur compounds.[25] Therefore, most of the calculations to be discussed hereafter were those based on the STO-3G*.

We then optimized the α(CCS) angle of EtSH using the observed geometrical parameters[2] in order to save computer cpu time and simplify the problem. The geometry of the *gauche* form was transferred from the *trans* form except for the dihedral angle about the CC–SH bond; 60° was used for this angle. The results of the optimization are 109.10° and 113.50°, obtained by means of the STO-3G* basis set for the *trans* and *gauche* forms respectively. There is a very good agreement with the experimental values:

108°34′ (*trans*) and 113°37′ (*gauche*),[2,3]

108°33′ (*trans*) and 113°16′ (*gauche*).[4]

With ethyl methyl sulfide, the same tendency of the α(CCS) angle has previously been found in experimentation between the *trans* and *gauche* forms[9,10] and this has been reproduced by calculations.[11] The difference in the total energy ($E_{trans}-E_{gauche}$) between the *trans* and *gauche* forms obtained is 369 cal/mol, (1 cal = 4.184 J) a value obtained by using the STO-3G* basis set under the optimized α(CCS), while that observed is 406±43 cal/mol.[4] Between the observed and calculated values, an excellent agreement is obtained.

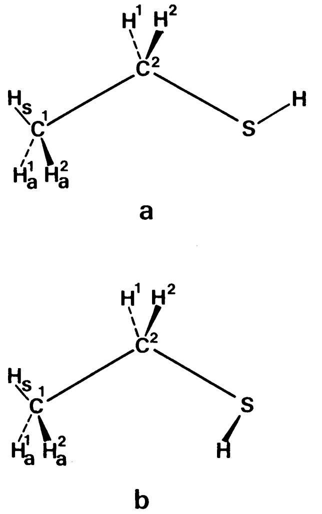

Fig. 1. Schematic structure and atom numberings for the *trans* and *gauche* isomers of EtSH. In the case of EtOH, S atom is substituted by O atom.
a) *Trans* form, b) *Gauche* form.

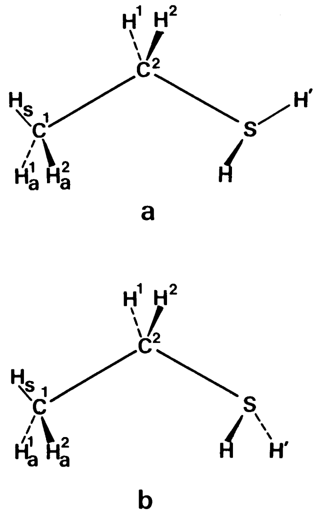

Fig. 2. Two possibilities of a proton addition onto a lone-pair orbital on a sulfur atom. Newly added proton is indicated as H′. In the case of EtOH, S atom is substituted by O atom.
a) *Gauche*-1 form, b) *Gauche*-2 form.

In order to analyze the effect of the lone pairs on the sulfur atom or of some other interactions on the variation of the α(CCS) angle, some model calculations were performed on the $EtSH_2^+$ species, in which a proton is attached to a lone pair orbital of the sulfur atom in the EtSH molecule. Here, in the case of the *trans* form, there is only one possibile way to attach a proton onto one of the lone pair orbitals, as one can easily understand from Fig. 1. However in the case of the *gauche* form, there are two possibilities, as is shown in Fig. 2, and these two forms can be distinguished from each other. These two forms are named *gauche*-1 and *gauche*-2 in the present article. By calculating the total energies for these structures, we can estimate the effect of the lone pair orbitals on the sulfur atom or of some other interactions which govern the geometry.

In order to evaluate the result for $EtSH_2^+$, a negative ionic species, EtS^-, was also calculated. The calculated bond populations between methyl carbon and thiol hydrogen are listed in Table 2, together with the optimized α(CCS) values for EtSH, $EtSH_2^+$, and EtS^-. By examining the variation in the bond population between the $C_1 \cdots H(SH)$ shown in this table, the population was found to change little from the EtSH to the $EtSH_2^+$ species in the case of the *trans* form. The value of the *gauche*-1 form varies considerably from the EtSH to the $EtSH_2^+$ species, but it varies little in

TABLE 2. BOND POPULATION AND α(CCS) OF EtSH, $EtSH_2^+$, AND EtS^- (STO-3G*)

I) Bond population $C^1(Me) \cdots H(SH)$

	EtSH	$EtSH_2^+$	EtS^-
Trans	0.000600	0.000591	
Gauche-1[a)]	−0.001343	−0.000186	
Gauche-2	−0.001343	−0.001137	

II) α(CCS)[b)]

	EtSH	$EtSH_2^+$	EtS^-
Trans	109.10	105.65	111.24
Gauche-1[a)]	113.50	104.26	111.24
Gauche-2	113.50	113.53	111.24

a) See also Fig. 2. b) Unit: degree

Table 3. Total energy and energy difference of EtSH with or without interaction between certain bonds(STO-3G*)[a)]

Cut	*Trans*(a)[c)]	*Trans*(b)[c)]	*Gauche*(b)	*Gauche*(a)
Normal	−295880.659	−295880.025	−295881.028	−295880.336
$C^1\cdots H$[b)]	−295875.670	−295875.516	−295907.161	−295916.480
	−4.989	−4.509	26.133	36.144
$H_a^2\cdots H$	−295880.680	−295880.077	−295886.736	−295891.125
	0.021	0.052	5.708	10.789

a) Unit: kcal/mol b) See also Fig. 1. c) In (a), the α(CCS) angle used was 109.10°, and in (b), that used was 113.50°.

Table 4. Structural parameters[a)] of EtOH used for computations

Group	Parameters[b)]	Values[c)]
CH_3C	$r(CH_s)$	1.088
	$r(CH_a)$	1.091
	$\alpha(CCH_s)$	110.5
	$\alpha(CCH_a)$	110.1
	$\alpha(H_sCH_a)$	108.8
	$\alpha(H_aCH_a)$	108.4
CCH_2O	r(CH)	1.098
	r(CC)	1.512
	α(CCO)	Optimized
	α(HCH)	108.0
	α(HCC)	110.7
COH	r(OH)	0.971
	r(OC)	1.431
	α(HOC)	105.4

a) Bond lengths are in A; angles, in degrees. b) Notations used are the same as those used for the sulfur analog. c) From Ref. 8.

Table 5. Bond population and α(CCO) of EtOH, $EtOH_2^+$ and EtO^- (STO-3G)

I) Bond population C^1(Me)$\cdots$H(OH)

	EtOH	$EtOH_2^+$	EtO^-
Trans	0.002796	0.001915	
Gauche-1[a)]	−0.002963	−0.001214	
Gauche-2	−0.002963	−0.001017	

II) α(CCO)[b)]

	EtOH	$EtOH_2^+$	EtO^-
Trans	108.52	111.59	111.03
Gauche-1[a)]	113.42	110.19	111.03
Gauche-2	113.42	115.78	111.03

a) See also Fig. 2. b) Unit: degree

the case of the *gauche*-2. Here in this table, the positive figure indicates the attractive interaction, while the negative one, the repulsive one. In the case of the *gauche*-1 form, whose geometrical situation after protonation is very analogous to the *trans* form of $EtSH_2^+$, the quantity of the variation is the largest of all. In the case of the T-form, the interaction between the nonbonded pair $C_1\cdots H$(SH) is attractive. On the other hand, in the case of the G-form, the interaction between them is repulsive. As a result, it can be understood, that in the case of the *gauche*-1 form, the repulsive interaction could be weakened by the addition of a proton to the sulfur atom. This is reflected in the variation in the α(CCS) angle, 113.50° → 104.27°, as will be discussed in the following section.

Let us now discuss the variation in the α(CCS) bond angle. The α(CCS) angle of the T-form narrows about four degrees from the EtSH to the $EtSH_2^+$ species. That of the *gauche*-1, though, decreases dramatically upon the proton addition and stays around nearly the same value as the *trans* form. However, in the case of the *gauche*-2 form, it does not vary any more on the variation from the EtSH to the $EtSH_2^+$ species. This implies that one of the lone pair orbitals, the one which lies on the C–C–S plane, plays an important role in governing the α(CCS) angle of the EtSH. This is one of the most important findings of the present article. It is also very interesting that the angle α(CCS) of the EtS^- species becomes nearly the average value of the *trans* and *gauche* forms.

In order to analyze the interaction between the nonbonded atomic pairs, we have carried out SCF calculations by cutting off the Fock matrix elements, F_{rs}, and, at the same time, the overlap integrals, S_{rs}, between certain atomic pairs according to the procedure described above. The calculations were performed with two geometrical sets, the optimized ones at the T- and G-forms. The pairs contributing greatly to governing the energy are summarized in Table 3.

By cutting off the interactions between the $C_1\cdots H$(SH) pair, the *trans* form raises the energy, while the *gauche* form lowers it. The positive value of the energy difference shows that the cut interaction in question is repulsive, while negative value is attactive.

Here, two types of interactions were taken into consideration: a) $C_1\cdots H$(SH) and b) $H_a^2\cdots H$(SH), because in these pairs the difference in the bond population between the *trans* and *gauche* forms is the largest of all.

From Table 3, it is found, for the *trans* form, that the total energy including the $C_1\cdots H$ interaction is lower than that without this interaction; that is, the $C_1\cdots H$ interaction stabilizes the molecule in the *trans* form. Upon a variation in α(CCS), the interaction energy is larger in the case of a smaller α(CCS) angle. This implies that a smaller α(CCS) angle is more favorable than a larger one in the *trans* case. On the other hand, in the case of the *gauche* form, the state without this interaction is more stable than the state with it. When this interaction is included, the repulsive force becomes smaller in a wider α(CCS) angle than in a narrower angle. As a result, the *gauche* form has a wider angle of α(CCS) than that of the T-form.

With the $H_a^2\cdots H$ interaction, in the case of the *trans* form, the magnitude of the interaction energy is rela-

TABLE 6. TOTAL ENERGY AND ENERGY DIFFRENCE OF EtOH WITH OR WITHOUT INTERACTION BETWEEN CERTAIN BONDS (STO-3G)$^{a)}$

Cut	*Trans*(a)$^{c)}$	*Trans*(b)$^{c)}$	*Gauche*(b)	*Gauche*(a)
Normal	−95464.947	−95463.916	−95464.712	−95463.750
$C^1...H^{b)}$	−95448.521	−95448.853	−95530.287	−95550.590
	−16.426	−15.063	65.575	86.840
$H^2_a...H$	−95465.243	−95464.300	−95470.786	−95475.864
	0.296	0.384	6.074	12.114

a) Unit: kcal/mol b) See also Fig. 1. c) In (a), the α(CCO) angle used was 108.52°, and in (b), that used was 113.42°.

tively small, and it does not depend greatly on the α(CCS) angle. However, in the case of the *gauche* form, it seems that a wider α(CCS) is more favorable.

The calculated results indicate a reasonable explanation of the observed geometry. As a result, it can be concluded that, in addition to the lone pair orbital, such nonbonded interactions as those between C_1··· H(SH) and between H^2_a···H(SH) are also responsible for the determination of the α(CCS) angle. This is another interesting finding of the present work.

Ethanol. In order to confirm the result obtained for EtSH, the present analysis was extended to test the oxygen analog, EtOH. With this molecule, the geometry optimization by using the 4-21G set had already been performed by Schäfer *et al.*[15,16] Therefore in the present article, the α(CCO) angle alone was optimized for the analysis. The geometry used for the calculation is summarized in Table 4. Geometrical parameters were commonly both used for the *trans* and *gauche* forms except for the dihedral angle τ(CC–OH), whose value, 60.0°, was used for the G-form. The STO-3G set was used for the computations, while the 4-31G* set was partly used for the sake of comparison. The total energy of the T-form obtained is smaller than that of the G-form : $E_{gauche} - E_{trans} = ca.$ 0.2 kcal/mol. This agrees well with the previous calculations.[15,16] The bond population and α(CCO) are shown in Table 5. The angle of α(CCO) obtained for the *gauche* form is wider by *ca.* 5 degrees than that for the *trans* form, although the geometrical parameters for the *gauche* form has not yet been experimentally determined. The bond population decreases in the *trans* form from EtOH to $EtOH_2^+$, while it increases in the *gauche*-1 and *gauche*-2 forms. In the case of EtSH, the population of the *trans* form varies very slightly. However, in the case of EtOH, it changes remarkably. The tendency of the population in the G-form of EtOH is also different from that of EtSH. That is, in the case of EtSH, the populations of *gauche*-1 and *gauche*-2 are considerably different from each other. However, in EtOH, the bond populations of the *gauche*-1 and *gauche*-2 forms show nearly the same trend.

Now let us discuss the variation in the α(CCO) angle. The angle of the *trans* form widens by *ca.* three degrees from the parent to the protonated species. An inverse tendency has already been seen in the sulfur analog. In the case of the G-form, the angle decreases in the *gauche*-1 and increases in the *gauche*-2 for $EtOH_2^+$, in comparison with EtOH. The same tendency was also seen in EtSH. In EtO^-, the angle of α(CCO) obtained is nearly the average of those of the *trans* and *gauche* forms.

TABLE 7. DIPOLE MOMENT (Debye)

I) EtSH

	Obsd		Calcd		
			STO-3G*	STO-3G	3-21G
Trans	1.56$^{a)}$	1.58$^{c)}$	0.472	1.016	2.043
Gauche	1.77$^{b)}$	1.61$^{c)}$	0.472	1.038	2.150

a) From Ref. 2. b) From Ref. 3. c) From Ref. 4.

II) EtOH

	Obsd	Calcd	
		STO-3G	4-31G*
Trans	1.441$^{d)}$	1.442	1.857
Gauche		1.533	1.955

d) From Ref. 27.

The change in the total energy by cutting off a certain Fock element and the overlap integral is given in Table 6. The tendency obtained on EtOH is, in general, analogous to that of EtSH. An examination of the absolute value shows that the interaction energy between H^2_a···H(OH) in EtOH is nearly the same as in EtSH. However, in the case of C_1···H(OH), the variations in the interaction energy in EtOH are much larger than those in EtSH. This means that the interaction between C_1 and H(OH) in EtOH is much stronger than the corresponding one in EtSH. This type of interaction may stabilize the *trans* form more, and may destabilize the *gauche* form more in EtOH than in EtSH.

Dipole Moments. It is very difficult to obtain an agreement between the experimental and calculated values in the dipole moments. We have summarized in Table 7 the observed and calculated dipole moments of EtSH. An examination of the observed moments[2–4] shows that the value of the *gauche* form is a bit larger than the *trans* one. From the estimation of the dielectric constant, however, a rather smaller value (1.39 Debye) was proposed.[26] The tendency between the *gauche* and *trans* forms is also seen in the calculations by using the STO-3G and 3-21G basis sets. The absolute values did not, however, perfectly reproduce the observed values when any of these basis sets was used. The STO-3G* basis set reproduces a fairly smaller value than those of the observed. On the other hand, the 3-21G reproduces values a bit larger. The value of the STO-3G lies between those calculated by STO-3G* and 3-21G.

The dipole moment of EtOH has been reported,[27] and the present STO-3G basis set reproduces the observed values well.

Conclusions

The relative conformational stability of EtSH and EtOH was very well reproduced by *ab initio* MO calculations. The interesting changes in α(CCX) (X=S or O) with the variation in the rotational isomers could also be explained by the present analysis. That is, the main factors governing the α(CCX) angle (X=S or O) are: (a) one of the lone pair orbitals on the sulfur or oxygen atom, (b) the interaction between the non-bonded $C_1\cdots H(XH)$ (X=S or O), and (c) that between $H^2_a\cdots H(XH)$ (X=S or O).

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