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Conformational Stabilization by Intramolecular OH···S and CH···O Interactions in 2-(Methylthio)ethanol. Matrix-Isolation Infrared Spectroscopy and ab Initio MO Calculations

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The conformational stability of 2-(methylthio)ethanol has been studied by matrix-isolation infrared spectroscopy and ab initio MO calculations. In an argon matrix, the conformer with gauche−gauche−gauche′ (GGg′) around the CS−C−C−OH bonds is the most stable and the G′Gg′ conformer is the second most stable. These and the TGg′ conformers are stabilized by intramolecular hydrogen bonding between the hydroxyl hydrogen atom and the sulfur atom. The relative strength of the hydrogen bonding in these conformers is in the order GGg′ > TGg′ > G′Gg′, as estimated from the nonbonded OH···S distance. In the G′Gg′ conformer, an additional intramolecular interaction between the methyl hydrogen atom and the hydroxyl oxygen atom is involved. The relative strength of this 1,5-CH···O interaction in the G′Gg′ conformer is the least among the three relevant conformers with G′G around the CS−C−COH bonds. The calculated results indicate that the geometry of this conformational form is considerably distorted so that it is simultaneously accessible to both of the interactions. This geometry is, however, not best suited for the respective interactions to be the most effective. The results for 2-(methylthio)ethanol have been compared with those for 2-methoxyethanol, in which the analogous intramolecular interactions are involved. The present study emphasizes the importance of the intramolecular interactions in the conformational stabilization of 2-(methylthio)ethanol and other relevant compounds.

Introduction

The conformation of molecules is determined by a number of factors including intramolecular and intermolecular interactions. One of those interactions responsible for the conformational stabilization is intramolecular hydrogen bonding. To elucidate the implications of intramolecular hydrogen bonding in the molecular conformation, many studies have been performed by vibrational spectroscopy on various relevant compounds, especially on those containing the OCH_2CH_2OH group.[1−9] For 1,2-ethanediol (ethylene glycol), $HOCH_2CH_2OH$, and 2-methoxyethanol (ME), $CH_3OCH_2CH_2OH$, the stable and less stable conformers have been identified by matrix-isolation infrared spectroscopy.[1−3,8] In an argon matrix at 11 K, the molecules of ME assume only the trans−gauche−gauche′ conformation, which is stabilized by an intramolecular hydrogen bond between the hydroxyl hydrogen atom and the ether oxygen atom.[8]

The conformation of the molecules in which an intramolecular hydrogen bond is formed between a hydroxyl hydrogen atom and a sulfur atom has been studied for several compounds that contain the SCH_2CH_2OH group. The previous microwave spectroscopic studies have shown that the molecules of 2-mercaptoethanol, $HSCH_2CH_2OH$,[10] and 2-(methylthio)ethanol (MTE), $CH_3SCH_2CH_2OH$,[11] in the gas phase adopt the conformation that is stabilized by the intramolecular OH···S hydrogen bond. In a previous theoretical study,[12] ab initio molecular orbital (MO) calculations have been performed on several conformers of the $CH_3XCH_2CH_2YH$ molecules, where X and Y are O or S, and the effect of the oxygen-by-sulfur substitution on the conformational stability and the relative strength of the intramolecular YH···X hydrogen bond have been discussed. There have been no close experimental studies, however, of the molecular conformation of MTE for understanding the effect of the intramolecular OH···S hydrogen bond on the conformation. In the molecule of MTE, another intramolecular interaction between one of the methyl hydrogen atoms and the hydroxyl oxygen atom, as mentioned below, may also be an important factor for the conformational stabilization.

Recent experimental[13,14] and theoretical[15] studies on 1,2-dimethoxyethane, $CH_3OCH_2CH_2OCH_3$, have shown that an intramolecular interaction between a hydrogen atom in the methyl group and the nonbonded oxygen atom plays an important role in determining the molecular conformation. This new type of interaction, termed 1,5-CH···O interaction, is anticipated to be relevant also to MTE. Thus, two types of intramolecular interactions, the OH···S hydrogen bonding and the 1,5-CH···O interaction, are involved in the conformational stabilization of the MTE molecule, and their cooperative effect may give rise to high stability of particular conformations.

For the purpose of gaining experimental evidence for the implications of these intramolecular interactions in the conformational stabilization, we have studied in the present work the molecular conformation of MTE by matrix-isolation infrared spectroscopy, supplemented by infrared and Raman spectroscopy in the condensed phases, and by ab initio MO calculations on all possible conformers of this compound. The results are discussed in comparison with the conformational stability of ME studied by matrix-isolation infrared spectroscopy and ab initio MO calculations.[8]

Experimental Section

MTE was commercially supplied by Sigma Chemical Co. The infrared spectra of MTE in an argon matrix were measured with a JEOL JIR-40X Fourier transform spectrophotometer equipped with a TGS detector. Mixed gas of Ar/MTE = 4000

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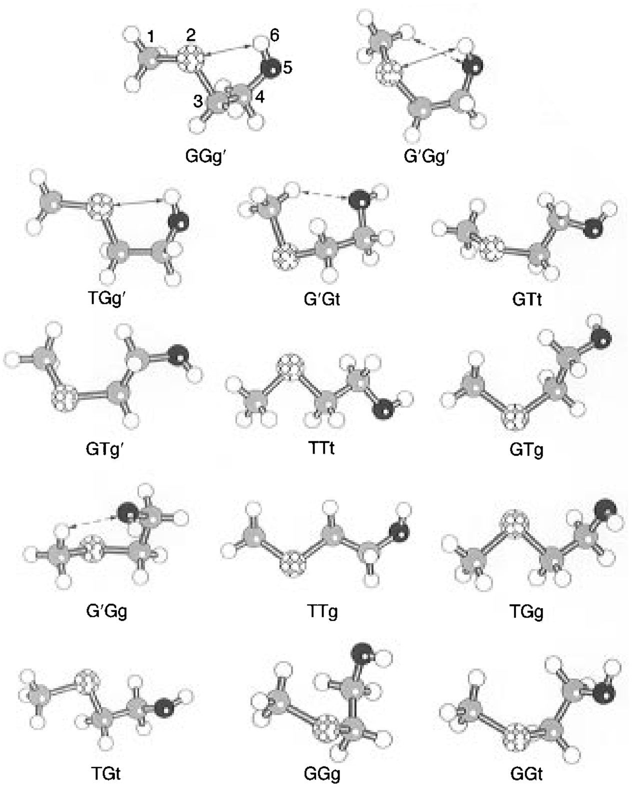

Figure 1. Optimized structures of 14 possible conformers of 2-(methylthio)ethanol. The solid arrows indicate the intramolecular OH···S hydrogen bonding, and the dashed arrows indicate the intramolecular 1,5-CH···O interaction.

was slowly sprayed onto a CsI plate cooled to 11 K by an Iwatani CryoMini D105 refrigerator. The spectra were obtained by coaddition of 100 scans at a resolution of 1 cm^{-1}. To study the spectral changes with increasing temperature, the deposited sample was annealed at different temperatures up to 41 K. The glassy state was obtained by spraying only the MTE gas onto a CsI plate at 11 K. The infrared spectra of liquid MTE were measured at room temperature with a Nicolet Impact 400 infrared spectrometer using a DTGS detector. The Raman spectra in the liquid state were measured with a JEOL JRS-400D spectrophotometer equipped with a Hamamatsu R649 photomultiplier. The 514.5 nm line of an NEC GLG3200 argon ion laser was used for Raman excitation.

Calculations

Ab initio MO calculations of the energies and the optimized structural parameters were performed on all of the 14 possible conformers of MTE, shown in Figure 1, by the restricted Hartree−Fock (RHF) method using the 6-31G and 6-31G** basis sets and on the most stable four conformers by the second-order Møller−Plesset (MP2) perturbation theory using the 6-31G* basis set. The MO calculations were carried out by using the GAUSSIAN 92 program[16] at the Computer Center of the Institute for Molecular Science, Okazaki, and the GAUSSIAN 94 program[17] at the Information Processing Center of Hiroshima University.

TABLE 1: Relative Energies of 14 Possible Conformers of 2-(Methylthio)ethanol Calculated at Different Levels

	relative energy[a]/kcal mol^{-1}			
conformer	RHF/6-31G	RHF/6-31G**	MP2/6-31G*	interactions involved[b]
GGg′	0.00	0.00	0.00	OH···S
G′Gg′	0.14	0.53	0.37	OH···S, CH···O
TGg′	0.42	0.69	1.05	OH···S
G′Gt	0.31	1.15	1.76	CH···O
GTt	1.09	1.35		
GTg′	1.35	1.39		
TTt	1.32	1.63		
GTg	1.78	1.68		
G′Gg	1.53	1.73		CH···O
TTg	1.88	1.80		
TGg	3.03	2.35		
TGt	2.81	2.56		
GGg	2.49	2.59		
GGt	2.99	2.90		

[a] Relative energy with respect to the energy for the GGg′ conformer. [b] OH···S, intramolecular OH···S hydrogen bonding; CH···O, intramolecular 1,5-CH···O interaction.

Normal coordinate analysis was carried out with the NCTB program[18] at the Computer Center of the University of Tokyo on the 14 conformers of MTE on the basis of the ab initio MO calculations by the RHF method using the 6-31G basis set with the transferred scale factors[8] that conform to the scaled quantum mechanical method.[19] The force constants in the Cartesian coordinate space obtained by the ab initio MO calculations were transformed into the group coordinate force constants.[20,21] The normal coordinate analysis based on the MP2 calculations with the 6-31G* basis set was also performed on the most stable four conformers of MTE by utilizing a uniform scale factor of 0.95.

Results and Discussion

Energies of Conformers. The relative energies of the conformers of MTE calculated at the RHF/6-31G, RHF/6-31G**, and MP2/6-31G* levels are given in Table 1, where the intramolecular interactions involved are indicated for the relevant conformers. The correlation diagram of the energies for the conformational states between MTE and ME is shown in Figure 2. The molecular conformation is designated by using the generic symbols[22] T or t for trans, G or g for gauche$^{\pm}$, and G′ or g′ for gauche$^{\mp}$; the lower-case symbols apply to the conformation around the CC−OH bond.

The most stable three conformers of MTE, namely, GGg′, G′Gg′, and TGg′, are obviously stabilized by the intramolecular hydrogen bond between the hydroxyl hydrogen atom and the sulfur atom, and the energy differences between these conformers are less than 1.0 kcal mol^{-1}. These results show that the intramolecular OH···S hydrogen bond is a dominant factor for the conformational stabilization of the MTE molecule.

The correlation diagram of the energies calculated at the RHF/6-31G** level indicates that the relative energies for all of the conformers of MTE lie within 3 kcal mol^{-1}, but those for the conformers of ME range over more than 5 kcal mol^{-1}.[8] These calculated results show that this difference in the conformational stability between MTE and ME is associated primarily with the different intrinsic conformational preference of the CS−CC and CO−CC bonds; the gauche conformation is more stable than the trans conformation for the CS−CC bond by less than 0.5 kcal mol^{-1}, whereas the trans conformation is more stable than the gauche conformation for the CO−CC bond by more than 1.5 kcal mol^{-1}. The effect of the intramolecular interactions involved in MTE on the molecular conformation will be discussed later in some detail.

Matrix-Isolation Infrared Spectra and Molecular Conformation. Figure 3 shows the infrared spectra of MTE in an argon matrix with Ar/MTE = 4000 at various temperatures during the heating process. The spectra were analyzed on the basis of the normal coordinate analysis. For examining the molecular conformation of MTE, the C−S stretching vibrations are of great use, since their wavenumbers are sensitive to the

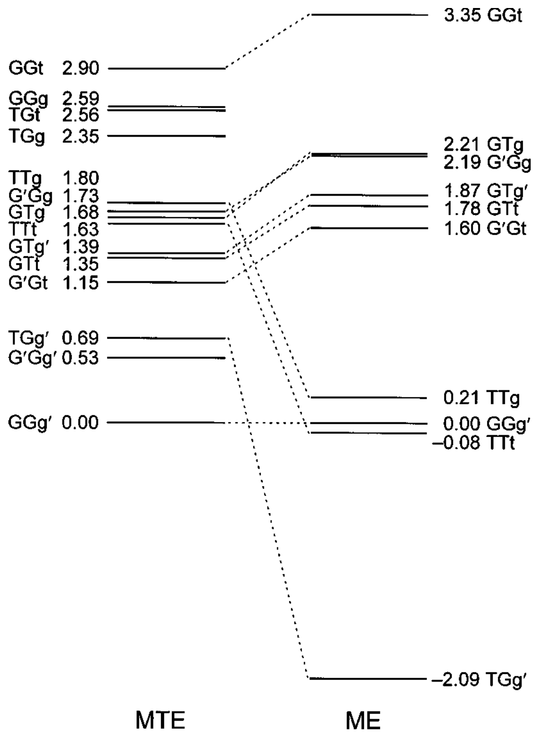

Figure 2. Correlation diagram of the energies for the conformational states between 2-(methylthio)ethanol (MTE) and 2-methoxyethanol (ME). The relative energies calculated at the RHF/6-31G** level are shown in units of kcal mol^{-1} with respect to the energy for the GGg′ conformer. The energies for 2-methoxyethanol are taken from ref 8; for the G′Gg′, TGg, TGt, and GGg conformers, minimum energy geometry was not attained.

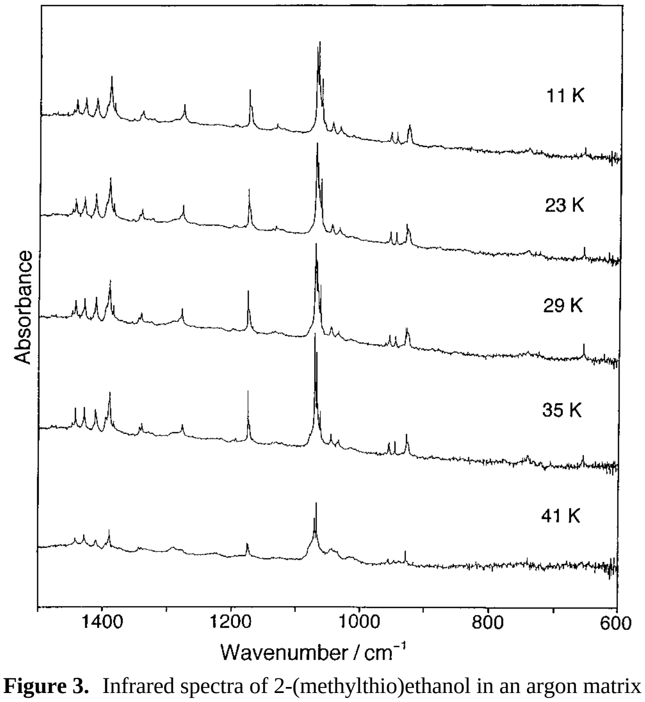

Figure 3. Infrared spectra of 2-(methylthio)ethanol in an argon matrix with Ar/MTE = 4000. The sample was deposited at 11 K and annealed at 23, 29, 35, and 41 K.

conformation in the vicinity of the C−S bond.[23] In the 600 −800 cm^{-1} region of the matrix-isolation spectra at 11 K, only one well-defined band is observed at 656 cm^{-1}. On the basis of the established correlation between the C−S stretching wavenumbers and the conformation,[23] this band is assigned to the S−C(H_2) stretching vibration of the gauche−gauche and gauche′−gauche conformations around CS−C−CO bonds. This matrix-isolation band corresponds to the Raman band at 655 cm^{-1} observed for liquid MTE, which is assigned decisively to the above conformations, as will be described later. This observation of the matrix-isolation spectra implies that the conformers existing in the matrix are GG*x* and/or G′G*x*, where *x* denotes either t, g, or g′.

In the spectral region of the O−H stretching vibrations, two bands are observed at 3537 and 3549 cm^{-1} in the argon matrix. These bands are associated with the intramolecularly hydrogen-bonded O−H stretching vibrations, and their wavenumbers are in excellent agreement with the calculated wavenumbers by the MP2 method, 3537 and 3552 cm^{-1} for the GGg′ and G′Gg′ conformers, respectively. The matrix-isolation spectra exhibit no bands that may be assigned to the free O−H stretching vibrations.

The results of the normal coordinate analysis further show that all of the bands observed in the argon matrix at 11 K are assigned consistently to the two conformers GGg′ and G′Gg′ but are not assignable to any others. The calculated wavenumbers and vibrational assignments for these conformers, together with the observed wavenumbers, are given in Tables 2 and 3. The discriminated assignments of the observed bands to the GGg′ and G′Gg′ conformers are consistent with the observed intensity behavior with increasing temperature. It may be remarked that most of the matrix-isolation bands associated with the GGg′ conformer are observed in doublet, while those associated with the G′Gg′ conformer are observed in singlet. The origin of the doublet for the GGg′ conformer is, however, not clear from the present analysis. The spectral evidence for the predominant existence of the GGg′ and G′Gg′ conformers in the matrix-isolated state agrees with the theoretical prediction from the calculated energies (Table 1).

On heating the matrix sample up to 29 K, the bands due to the G′Gg′ conformer, such as a prominent band at 1064 cm^{-1}, decrease in intensity, while the bands due to the GGg′ conformer persist in the matrix (Figure 3). This spectral observation indicates that the GGg′ conformer is the most stable in the argon matrix, since the annealing process induces a transformation of less stable conformers trapped in the matrix at lower temperatures into the most stable conformer. These experimental results are again in agreement with the calculated energies.

In a previous microwave spectroscopic study of MTE,[11] only the GGg′ conformer has been identified in the gas phase.[24] The present study has confirmed the existence of the second most stable conformer of G′Gg′ in the argon matrix. Both of the GGg′ and G′Gg′ conformers are stabilized by the intramolecular OH···S hydrogen bond, and the latter conformer is additionally stabilized by the 1,5-CH···O interaction, although this form assumes a sterically unfavorable G′G conformation in the $CH_3S-CH_2-CH_2O$ group. The implications of the intramolecular interactions in the conformational stabilization will be discussed later.

At temperatures higher than about 40 K, all of the persisting bands become significantly weaker, and broad features grow instead in the spectra, which are ascribed to the aggregates of the molecules produced by the loosening of the matrix lattice in the heating process. Since some of the broad bands are not assignable to either of the GGg′ and G′Gg′ conformers, it is obvious that the molecular aggregation accompanies the conformational changes. The previous study on ME[8] has shown that the conformation around the CO−C−COH bonds being trans−gauche is maintained on the molecular aggregation. For MTE, on the other hand, the molecules can adopt various possible conformations around the CS−C−COH bonds on the aggregation, since the energies of most of the conformers lie within 2 kcal mol^{-1} (Table 1 and Figure 2).

TABLE 2: Observed and Calculated Wavenumbers[a] and Vibrational Assignments for the GGg′ Conformer of 2-(Methylthio)ethanol

	ν_{calc}/cm^{-1}		
$\nu_{obs}{}^{b}$/cm^{-1}	MP2/ 6-31G*[c]	RHF/ 6-31G[d]	vibrational assignment[e]
3537 m	3537	3616	O−H stretch (100)
1482 vw	1496	1471	C_bH_2 scissor (100)
1443 m	1471	1441	CH_3 asym deform (91)
1430 m	1454	1435	CH_3 asym deform (89)
1412 m	1433	1417	C_aH_2 scissor (96)
1395 w, 1390 s	1387	1369	C_bH_2 wag (71), C−O−H bend (21)
1345 w, 1341 w	1369	1344	C−O−H bend (33), C_bH_2 wag (23)
1332 vw	1348	1326	CH_3 sym deform (100)
1278 m	1299	1279	C_aH_2 wag (71), C_bH_2 twist (16)
1195 vw	1201	1190	C_aH_2 twist (57), C−C stretch (10)
1177 s, 1174 m	1162	1151	C_bH_2 twist (54), C−O−H bend (18)
1072 s, 1069 s	1070	1081	C−O stretch (52), C−C stretch (36)
1047 w	1055	1062	CH_3 rock (25), C_aH_2 rock (20)
958 w, 957 w	979	986	CH_3 rock (89)
948 w	961	976	CH_3 rock (46), C_bH_2 rock (26)
929 m, 927 m	929	945	C−C stretch (26), C_bH_2 rock (21)
	820	837	C_aH_2 rock (53), C−O stretch (19)
	734	726	CH_3−S stretch (90), C−S stretch (14)
656 w	659	645	C−S stretch (80), CH_3−S stretch (18)
	469	472	C−C−O bend (62), C−C−S bend (21)
	420	338	C−O torsion (98)
	323	304	C−S−C bend (37), C−C−S bend (26)
	222	210	C−S−C bend (63), C−C−S bend (30)
	181	135	C−C torsion (56), CH_3−S torsion (27)
	141	111	CH_3−S torsion (68), C−C torsion (32)
	68	56	S−C torsion (110), C−O torsion (18)

[a] The CH_3 and CH_2 stretching vibrations are omitted from the table. [b] Observed wavenumbers for an argon matrix. Approximate relative intensities: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [c] All wavenumbers have been scaled by a uniform factor of 0.95. [d] Wavenumbers have been scaled by the scaled quantum mechanical method (see text). [e] Vibrational assignment for $CH_3SC_aH_2C_bH_2OH$ is given in terms of the group coordinates; sym, symmetric; asym, asymmetric. Potential energy distributions (%) evaluated from the RHF/6-31G calculations are shown in parentheses.

TABLE 3: Observed and Calculated Wavenumbers[a] and Vibrational Assignments for the G′Gg′ Conformer of 2-(Methylthio)ethanol

	ν_{calc}/cm^{-1}		
$\nu_{obs}{}^{b}$/cm^{-1}	MP2/ 6-31G*[c]	RHF/ 6-31G[d]	vibrational assignment[e]
3549 w	3552	3628	O−H stretch (100)
	1486	1465	C_bH_2 scissor (100)
1448 w	1482	1448	CH_3 asym deform (95)
1433 sh	1455	1434	CH_3 asym deform (95)
1415 w	1438	1421	C_aH_2 scissor (95)
1386 w	1381	1364	C_bH_2 wag (96)
1355 vw	1363	1355	C−O−H bend (52), C_bH_2 twist (23)
1324 vw	1358	1325	CH_3 sym deform (100)
1282 sh	1299	1280	C_aH_2 wag (65), C_bH_2 twist (17)
1200 vw	1208	1201	C_aH_2 twist (41), C_aH_2 wag (19)
1170 vw	1160	1146	C_bH_2 twist (40), C_aH_2 twist (27)
1064 s	1063	1073	C−O stretch (55), C−C stretch (34)
1035 w	1041	1052	CH_3 rock (32), C_aH_2 rock (18)
963 vw	986	994	CH_3 rock (91)
	970	979	CH_3 rock (46), C_bH_2 rock (26)
932 m	927	945	C−O stretch (24), C−C stretch (24)
	812	834	C_aH_2 rock (53), C−O stretch (17)
	729	720	CH_3−S stretch (91), C−S stretch (14)
656 w	674	660	C−S stretch (75), CH_3−S stretch (17)
	463	470	C−C−O bend (62), C_aH_2 rock (21)
	438	319	C−O torsion (107)
	292	271	C−S−C bend (42), C−C−S bend (33)
	243	239	C−S−C bend (52), C−C−S bend (35)
	174	130	CH_3−S torsion (98)
	139	110	C−C torsion (95), C−O torsion (10)
	104	66	S−C torsion (175), C−O torsion (26)

[a−e] See footnotes *a*−*e*, respectively, of Table 2.

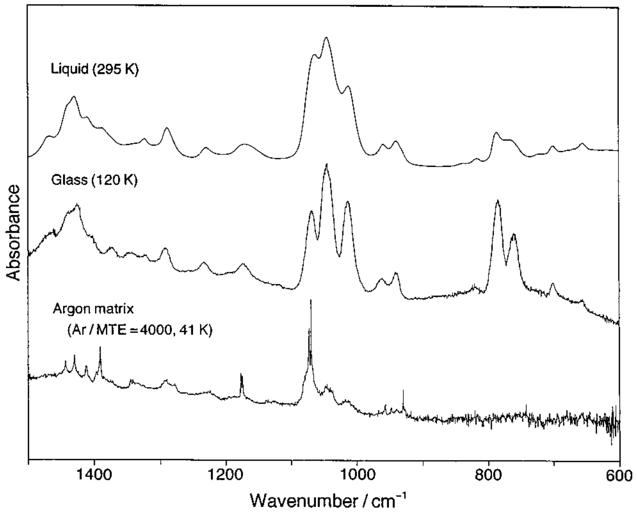

Figure 4. Infrared spectra of 2-(methylthio)ethanol in the liquid state at 295 K, the glassy state at 120 K, and the aggregated state in an argon matrix with Ar/MTE = 4000 at 41 K.

Infrared and Raman Spectra in the Condensed Phases. The infrared spectra of MTE in the liquid and glassy states are shown in Figure 4, where the matrix-isolation infrared spectrum at 41 K is shown for comparison. The spectra of the liquid and glassy states are significantly different from the spectra of the isolated and aggregated states in the argon matrix. In the liquid state, additional bands, not observed in the argon matrix at low temperatures, are noted at 1045, 1011, 786, 766, and 700 cm^{-1}. The appearance of these bands suggests the coexistence of various conformers in these condensed phases.

The Raman spectrum in the 600−800 cm^{-1} region of MTE in the liquid state is shown in Figure 5, where the C−S stretching bands are observed. Since the C−S stretching wavenumbers are sensitive to the conformation,[23] these bands provide important information about the skeletal conformation of the MTE molecule. The wavenumbers and conformational assignments of the C−S stretching bands for liquid MTE are given in Table 4. The strong band at 701 cm^{-1} is assigned to the gauche−trans conformation around the CS−C−COH bonds and the weaker bands at 676 and 771 cm^{-1} are assigned to the trans−gauche and trans−trans conformations, respectively. These Raman spectral observations indicate that there exist a number of conformers, GG*x*, G′G*x*, TG*x*, GT*x*, and TT*x*, in the liquid state. The orientation of the hydroxyl group is not clear in the condensed phases because of the complicated intermolecular hydrogen bonding in these phases.

Intramolecular OH···S and CH···O Interactions and Structural Parameters. In the conformational stabilization of

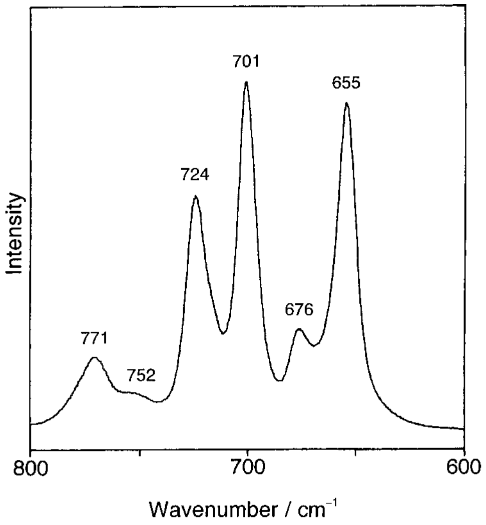

Figure 5. Raman spectrum of 2-(methylthio)ethanol in the liquid state at 295 K.

TABLE 4: Observed and Calculated Wavenumbers of the C−S Stretching Vibrations for 2-(Methylthio)ethanol

$\nu_{obs}{}^{b}$/ cm^{-1}	$\nu_{calc}{}^{a}$/cm^{-1}									
	GGg′	G′Gg′	TGg′	G′Gt	GTt	GTg′	TTt	GTg	G′Gg	TTg
771 w							776			780
752 vw					771	778		778		
724 m	726	720	730	725					725	
715 sh							719			719
701 s					700	699		700		
676 w			662							
655 s	645	660		658					650	

[a] Calculated at the RHF/6-31G level. [b] Observed wavenumbers in the Raman spectrum in the liquid state. For approximate relative intensities, see footnote *b* of Table 2.

the MTE molecule, two types of intramolecular interactions are involved; one is the OH···S hydrogen bonding and the other is the 1,5-CH···O interaction. These interactions are discussed below in relation to the energies and the structural parameters for the relevant conformers. The optimized structural parameters for the 14 conformers of MTE calculated at the RHF/6-31G** level are given in Table 5. Numbering of atoms for the MTE molecule is shown in Figure 1, where the intramolecular interactions in question are indicated by arrows.

The ab initio MO calculations of the energies show that the OH···S hydrogen bonding stabilizes to a great extent the *X*Gg′ conformers, where *X* is either T, G, or G′. The matrix-isolation infrared spectra of MTE have in fact evidenced the theoretical prediction that the GGg′ conformer is the most stable and the G′Gg′ conformer is the second most stable. The relative strength of the intramolecular OH···S hydrogen bonding can be estimated from the nonbonded OH···S distance. Of the three relevant conformers GGg′, G′Gg′, and TGg′, the first conformer has the shortest OH···S distance and the second conformer has the longest distance. These OH···S distances imply that the strength of the intramolecular hydrogen bonding in these conformers is in the order GGg′ > TGg′ > G′Gg′. In accordance with this decreasing trend of the strength of the hydrogen bonding, the O−H bond length in these conformers decreases in the same order. The results in Table 5 indicate that the length of the O−H bond is increased on the formation of the intramolecular hydrogen bond by roughly 0.002 Å.

It appeared difficult at first to understand the high stability of the G′Gg′ conformer, for which the methyl group and the hydroxyl group come close to each other. This peculiar conformational property is explained by the significant 1,5-CH···O interaction, which has been well-established to be an important factor to stabilize the gauche′−gauche conformation of the $CH_3O-CH_2-CH_2OCH_3$ structure of 1,2-dimethoxyethane.[13,14] It is remarked that the optimized geometry of the G′Gg′ conformer of MTE is considerably distorted so that the C−S−C−C torsion angle, −96.6°, is deviated greatly from the normal gauche$^-$ angle of −60°. This geometry is elucidated as a consequence of being a compromise configuration which is simultaneously accessible to both the OH···S hydrogen bonding and the 1,5-CH···O interaction. Without being distorted, the methyl hydrogen atom and the hydroxyl hydrogen atom would be heavily hindered by each other. It is clear that this distorted geometry is not best suited for the respective interactions to be the most effective. This is the reason why the hydrogen bonding in the G′Gg′ conformer is not so strong as in GGg′ or TGg′, for which no such complication is involved.

For ME, intramolecular OH···O hydrogen bonding, which is analogous to the OH···S hydrogen bonding in MTE, stabilizes the TGg′ and GGg′ conformers, but the G′Gg′ conformer failed to be appropriately optimized in the ab initio MO calculation.[8,25] The optimization of the G′Gg′ conformation actually resulted in the conversion into the TGg′ conformation with an increased C−O−C−C torsion angle, being consistent with the result that the trans conformation around the CO−CC bond is significantly more stable than the gauche conformation.

The intramolecular 1,5-CH···O interaction is important for the stabilization of the G′Gg′ conformer of MTE, as described above, and other conformers in which the gauche′−gauche conformation of the $CH_3S-CH_2-CH_2OH$ structure is involved, namely, the G′Gt and G′Gg conformers. The relative strength of this interaction can be estimated from the relevant nonbonded CH···O distance. According to the results in Table 5, this distance is the shortest for G′Gt and is the longest for G′Gg′ among the three conformers. This implies that the strength of the 1,5-CH···O interaction is in the order G′Gt > G′Gg > G′Gg′. In conformity with this decreasing trend, the length of the methyl C−H bond associated with this interaction increases in the same order. It is remarked that the length of the C−H bond decreases when it is involved in the CH···O interaction, while the length of the O−H bond increases when it is involved in the hydrogen bonding. The present finding that the relative strength of the 1,5-CH···O interaction is the least for G′Gg′ among the three G′G*x* conformers is again consistent with the distorted geometry of this conformation, which is not best suited for this interaction to be the most effective. In the G′Gg′ conformer, the two intramolecular interactions involved, namely, the OH···S hydrogen bonding and the 1,5-CH···O interaction, are competing in the conformational stabilization of this form, leading to the heavy geometrical constraint and accordingly to the diminished effect of the respective interactions.

In a previous study,[12] Gil et al. have discussed on the basis of the ab initio MO calculations the conformational stability of the $CH_3XCH_2CH_2YH$ molecules, where X and Y are O or S. They focused on the effect of the intramolecular YH···X hydrogen bonding on the conformation in a series of analogous compounds. The present study has clarified the importance of the intramolecular 1,5-CH···O interaction as well as the hydrogen bonding in the conformational stabilization of the MTE molecule. This interaction should also be important for other $CH_3XCH_2CH_2YH$ compounds, but the previous authors did not consider in their calculations the conformational forms in which this interaction is involved.[12,26] In another work,[27] the previous authors have discussed a different type of intramolecular CH···O interaction relevant to the alkoxyl part of the $CH_3(CH_2)_{n-1}OCH_2CH_2OH$ molecules, where $n \geq 3$. This

TABLE 5: Optimized Structural Parameters for 14 Conformers of 2-(Methylthio)ethanol Calculated at the RHF/6-31G Level**

structural parameters[a]	GGg′ [b]	G′Gg′ [b,c]	TGg′ [b]	G′Gt[c]	GTt	GTg′	TTt
Bond Lengths/Å							
C_1-H	1.0820	1.0808[d]	1.0821	1.0785[d]	1.0820	1.0818	1.0821
	1.0822	1.0824	1.0825	1.0827	1.0823	1.0823	1.0828
	1.0829	1.0825	1.0825	1.0830	1.0829	1.0828	1.0828
C_1-S_2	1.8109	1.8134	1.8084	1.8115	1.8109	1.8110	1.8081
S_2-C_3	1.8195	1.8227	1.8215	1.8159	1.8138	1.8145	1.8162
C_3-C_4	1.5247	1.5246	1.5252	1.5176	1.5192	1.5250	1.5189
C_4-O_5	1.3942	1.3978	1.3957	1.4020	1.4025	1.4012	1.4019
O_5-H_6	0.9447	0.9438	0.9442	0.9424	0.9427	0.9430	0.9427
Bond Angles/deg							
$C_1-S_2-C_3$	101.56	101.27	100.93	102.52	101.65	101.60	99.90
$S_2-C_3-C_4$	114.25	113.61	110.49	115.68	114.03	114.21	110.43
$C_3-C_4-O_5$	112.57	113.02	112.73	109.17	107.08	111.41	106.99
$C_4-O_5-H_6$	109.17	108.77	109.59	109.93	109.98	109.90	109.82
Torsion Angles/deg							
$C_1-S_2-C_3-C_4$	76.96	−96.58	−159.57	−81.18	79.03	76.94	180.00
$S_2-C_3-C_4-O_5$	62.31	58.09	69.59	69.31	−179.72	−178.16	180.00
$C_3-C_4-O_5-H_6$	−58.96	−74.51	−60.70	−174.14	−177.80	−70.97	180.00
Nonbonded Interatomic Distances/Å							
$C_1H\cdots O_5$		2.7899		2.5507			
$O_5H_6\cdots S_2$	2.7770	2.8642	2.8066				

structural parameters[a]	GTg	G′Gg[c]	TTg	TGg	TGt	GGg	GGt
Bond Lengths/Å							
C_1-H	1.0819	1.0787[d]	1.0821	1.0823	1.0824	1.0814	1.0825
	1.0823	1.0826	1.0827	1.0833	1.0832	1.0823	1.0828
	1.0832	1.0837	1.0829	1.0833	1.0834	1.0833	1.0834
C_1-S_2	1.8109	1.8113	1.8083	1.8085	1.8084	1.8083	1.8096
S_2-C_3	1.8144	1.8151	1.8161	1.8170	1.8183	1.8152	1.8158
C_3-C_4	1.5249	1.5240	1.5253	1.5241	1.5173	1.5283	1.5192
C_4-O_5	1.4012	1.4012	1.4002	1.3966	1.3989	1.3943	1.3976
O_5-H_6	0.9429	0.9431	0.9429	0.9433	0.9423	0.9432	0.9421
Bond Angles/deg							
$C_1-S_2-C_3$	101.74	102.78	100.07	99.58	99.60	102.03	101.00
$S_2-C_3-C_4$	114.28	116.05	110.49	111.58	111.62	116.49	115.54
$C_3-C_4-O_5$	111.38	113.55	111.29	113.62	108.85	114.76	108.54
$C_4-O_5-H_6$	110.03	109.79	109.88	110.21	110.09	110.48	110.22
Torsion Angles/deg							
$C_1-S_2-C_3-C_4$	77.79	−75.43	−178.40	169.80	167.36	52.61	80.18
$S_2-C_3-C_4-O_5$	176.69	68.44	−181.42	56.72	64.92	46.98	69.62
$C_3-C_4-O_5-H_6$	70.78	70.56	72.10	57.36	189.19	44.56	−169.53
Nonbonded Interatomic Distances/Å							
$C_1H\cdots O_5$		2.5740					
$O_5H_6\cdots S_2$							

[a] For numbering of atoms, see Figure 1. [b] Conformer in which the intramolecular OH···S hydrogen bonding is involved. [c] Conformer in which the intramolecular 1,5-CH···O interaction is involved. [d] C−H bond associated with the intramolecular 1,5-CH···O interaction.

interaction has been found to be important for the stabilization of the gauche conformation around the CC−CO bond.[27]

The conformation of a particular part of the MTE molecule is correlated with the structural parameters as shown in Table 5. The *X*Gg′ conformers, which are capable of forming the intramolecular OH···S hydrogen bond, have a longer O−H bond than the normal O−H bond as described before. In accordance with the increased O−H bond length in these conformers, the S−C(H_2) bond length is increased and the C−O−H angle is decreased as compared with those for other conformers. The methyl C−H bond in the G′G*x* conformers, which is associated with the 1,5-CH···O interaction, is shorter than other C−H bonds in the methyl group as mentioned above. It is noted that the C−C bond is longer for the conformers with the gauche CC−OH bond, but it is shorter for those with the trans bond. For the conformers with the trans CS−CC bond, the C−S−C and S−C−C angles are smaller than those with the gauche bond.

Conclusions

Matrix-isolation infrared spectroscopy has clarified that the most stable conformer of MTE is GGg′ and the second most stable conformer is G′Gg′, in agreement with the energies calculated by the ab initio MO method. These conformers and the TGg′ conformer, which is the third most stable according to the calculation, are stabilized by the intramolecular hydrogen bonding between the hydroxyl hydrogen atom and the sulfur atom. For the G′Gg′ conformer, in which an additional intramolecular interaction between the methyl hydrogen atom and the hydroxyl oxygen atom is involved, the two interactions are competing in the conformational stabilization of this form, leading to the heavy geometrical constraint and accordingly to the diminished effect of the respective interactions. For ME, on the other hand, the G′Gg′ conformation is unstable owing to strong preference of the trans conformation around the CO−CC bond. The present study emphasizes the importance of the intramolecular interactions in the conformational stabilization of MTE and other relevant compounds.

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References and Notes

(1) Frei, H.; Ha, T.-K.; Meyer, R.; Günthard, Hs. H. *Chem. Phys.* **1977**, *25*, 271−298.

(2) Takeuchi, H.; Tasumi, M. *Chem. Phys.* **1983**, *77*, 21−34.

(3) Park, G. G.; Tasumi, M. *J. Phys. Chem.* **1991**, *95*, 2757−2762.

(4) Iwamoto, R. *Spectrochim. Acta, Part A* **1971**, *27*, 2385−2399.

(5) Singelenberg, F. A. J.; van der Maas, J. H. *J. Mol. Struct.* **1991**, *243*, 111−122.

(6) Singelenberg, F. A. J.; Lutz, E. T. G.; van der Maas, J. H.; Jalsovszky, G. *J. Mol. Struct.* **1991**, *245*, 173−182.

(7) Singelenberg, F. A. J.; van der Maas, J. H.; Kroon-Batenburg, L. M. J. *J. Mol. Struct.* **1991**, *245*, 183−194.

(8) Yoshida, H.; Takikawa, K.; Ohno, K.; Matsuura, H. *J. Mol. Struct.* **1993**, *299*, 141−147.

(9) Yoshida, H.; Takikawa, K.; Kaneko, I.; Matsuura, H. *J. Mol. Struct.* (*THEOCHEM*) **1994**, *311*, 205−210.

(10) Sung, E.-M.; Harmony, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 5603−5608.

(11) Marstockk, K.-M.; Møllendal, H.; Uggerud, E. *Acta Chem. Scand.* **1989**, *43*, 26−31.

(12) Gil, F. P. S. C.; Amorim da Costa, A. M.; Teixeira-Dias, J. J. C. *J. Phys. Chem.* **1995**, *99*, 16586−16589.

(13) Yoshida, H.; Kaneko, I.; Matsuura, H.; Ogawa, Y.; Tasumi, M. *Chem. Phys. Lett.* **1992**, *196*, 601−606.

(14) Yoshida, H.; Tanaka, T.; Matsuura, H. *Chem. Lett.* **1996**, 637−638.

(15) Tsuzuki, S.; Uchimaru, T.; Tanabe, K.; Hirano, T. *J. Phys. Chem.* **1993**, *97*, 1346−1350.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*, Revision F.3; Gaussian Inc.: Pittsburgh, PA, 1992.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision D.3; Gaussian Inc.: Pittsburgh, PA, 1995.

(18) Shimanouchi, T. *Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules*; The University of Tokyo, 1968.

(19) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037−7047.

(20) Matsuura, H.; Tasumi, M. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1983; pp 69−143.

(21) Yoshida, H.; Tasumi, M. *J. Chem. Phys.* **1988**, *89*, 2803−2809.

(22) Shimanouchi, T.; Ogawa, Y.; Ohta, M.; Matsuura, H.; Harada, I. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2999−3008.

(23) Nogami, N.; Sugeta, H.; Miyazawa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2417−2420.

(24) This conformation was denoted as GGg in the original paper,[11] but it should be designated properly as GGg′ in accord with the geometrical structure actually determined.

(25) The RHF/6-31G** calculations on the G′Gg′ and GGg conformers of ME, which had not been treated in the previous study,[8] were performed in the present work for comparison with the results for the corresponding conformers of MTE.

(26) Gil, F. P. S. C.; Fausto, R.; Amorim da Costa, A. M.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 689−695.

(27) Gil, F. P. S. C.; Amorim da Costa, A. M.; Teixeira-Dias, J. J. C. *J. Phys. Chem.* **1995**, *99*, 8066−8070.