Intramolecular Hydrogen Bonds. XVII.[1] Intramolecular Hydrogen Bonding Involving the Mercapto Group as a Hydrogen Donor

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The SH stretching absorption spectra of some mercapto compounds in dilute carbon tetrachloride solutions and also in acetonitrile solutions have been measured at 20°C. Alkyl mercaptans show absorption bands which are suggestive of the rotational isomerism around the C–S bond. The spectral data indicate that benzyl mercaptan, ω-ethoxyalkyl mercaptans, and ethyl α- and β-mercaptoalkanoates form practically no intramolecular hydrogen bond between the SH group and the hydrogen-acceptor group. In thiosalicylic acid and its ethyl ester, the hydrogen-bonding to the carbonyl group is partially possible even in acetonitrile. On the other hand, the corresponding free carboxylic acids are not hydrogen-bonded between the S atom and the carboxyl group.

The mercapto group is well known[2,3] to form hydrogen bonds with oxygen, nitrogen, carbon, and sulfur atoms, and possibly with aromatic π-electrons as well, but it is apparently not capable of hydrogen bonding to such an extensive degree as occurs with the hydroxyl group. On the dilution of neat mercaptans with non-polar solvents, the stretching frequencies of the S–H bonds are only slightly shifted to the lower-frequency side and the chemical shifts of the proton magnetic resonance of the SH groups are extraordinarily small.

The literature contains scant information on the intramolecular hydrogen bonding involving the mercapto group. In ω-*N*,*N*-dialkylamino-alkyl mercaptans,[4] there is no evidence for the expected lowering of the SH-stretching frequency by hydrogen bonding. However, only a few thiols, such as ethyl β-mercapto-β-phenylacrylates,[5] *o*-amino- and *o*-hydroxy-thiophenols,[6] and ethyl thiosalicylate,[7] show relatively large spectral shifts of the bonded SH bands. More recently, Hirota and his co-workers[8] have suggested that, in *o*-substituted thiophenols, the hydrogen bonding may be indicated by an increased intensity of the SH stretching band and also by an increased downfield-shift of the SH proton resonance, even if no lowering of the SH stretching frequency is observed.

In previous papers,[9,10] it has been reported that α- and β-hydroxyalkanoic esters form an intramolecular hydrogen bond, predominantly between the hydroxyl and the ester-carbonyl groups. These results have prompted us to examine the corresponding mercapto compounds as well.

The present paper will deal with the intramolecular hydrogen bonding in benzyl mercaptan, ω-ethoxyalkyl mercaptans, ethyl α- and β-mercaptoalkanoates, and ethyl thiosalicylate, as studied by means of infrared spectroscopy. Furthermore, the SH spectra of alkyl mercaptans in dilute carbon tetrachloride solutions have also been measured, since there have been no detailed and systematic studies of them, although the SH frequencies of many thiols have been reported.[11]

Experimental

Samples. All the compounds examined were prepared in the usual manner except for commercially-available alkyl and benzyl mercaptans. The new *o*-mercaptobenzyl methyl ether was prepared form *o*-aminobenzyl methyl ether[12] by way of its diazonium salt. Their melting and/or boiling points were equal, or very close, to those previously reported, and their purity was established by gas chromatograms and/or NMR spectra. The unknown compounds had the analytical data shown in Table 1. Carbon tetrachloride and acetonitrile were fractionally distilled over phosphours pentoxide.

Infrared Measurement. This was carried out at *ca.* 20°C by the method previously described,[9] using a grating infrared spectrophotometer, Model DS-403G, of the Japan Spectroscopic Co. The concentrations used were 0.006 mol/*l* (SH spectra; cell-thickness: 5.0 cm) and 0.01 or 0.001 mol/*l* (CO spectra; cell-thickness: 1.1 or 10.0 mm), unless otherwise noted. The calculated spectral slit width was 1.5 cm^{-1} at the wave number of 1700 cm^{-1} and 0.8 cm^{-1} at 2600 cm^{-1}. Some of the unsymmetrical bands with relatively high intensities were graphically[9] divided into their components, particularly when the intensity ratios were desired.

Results and Discussion

Alkyl mercaptans. The spectra of some alkyl mercaptans in carbon tetrachloride are shown in Fig. 1, while the apparent spectral data are summarized in Table 2. The SH bands of *prim*- and *t*-alkyl mercaptans are practically symmetric, while those of *s*-alkyl mercaptans are unsymmetric; the shapes and the frequencies

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[1] Part XVI: N. Mori, M. Yoshifuji, Y. Asabe, and Y. Tsuzuki, This Bulletin, **44**, 1137 (1971).

[2] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco (1960), p. 201.

[3] S. H. Marcus and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3719 (1966) and the references cited therein.

[4] D. Plant, D. S. Tarbell, and C. Whiteman, *ibid.*, **77**, 1572 (1955).

[5] Z. Reyes and R. M. Silverstein, *ibid.*, **80**, 6367, 6373 (1958).

[6] J. G. David and H. E. Hallam, *Spectrochim. Acta*, **21**, 841 (1965).

[7] A. W. Wagner, H. J. Becher, and K. G. Kottenhahn, *Chem. Ber.*, **89**, 1708 (1956).

[8] A. Yamashita, T. Kobayashi, R. Hoshi, and M. Hirota, presented at the 23rd Annual Meeting of the *Chem. Soc.* of Japan (Tokyo, 1970), No. 14321.

[9] N. Mori, S. Omura, N. Kobayashi, and Y. Tsuzuki, This Bulletin, **38**, 2149 (1965).

[10] N. Mori, Y. Asano, and Y. Tsuzuki, *ibid.*, **41**, 1871 (1968).

[11] R. A. Spurr and H. F. Byers, *J. Phys. Chem.*, **62**, 425 (1958), and Ref. 16, p. 350.

[12] T. Thiele and O. Dimroth, *Ann.*, **305**, 110 (1899).

Table 1. The analytical data of unknown compounds

Compound	Bp °C/mmHg	Found		Calcd	
		C%	H%	C%	H%
$(CH_3)_2C(SEt)COOEt$	83/17	54.75	9.06	54.53	9.15
$(CH_3)_2C(SEt)COOH$	128/16	48.63	8.19	48.64	8.16
$CH_2(SEt)CH_2COOEt$	102/22	51.80	8.50	51.84	8.70
$CH_2(SEt)CH_2COOH$	134/12.5	44.57	7.43	44.77	7.52
o-$C_6H_4(SH)(CH_2OCH_3)$	88/ 5.5	62.43	6.44	62.32	6.54

of the bands vary with the type of the alkyl group (R). This variation can not be due to any molecular association, since thiols are generally already monomeric even in a concentration of 0.1 mol/*l* in the same solvent. By analogy with the case of the corresponding alkanols,[13] it is probably attributable to the rotational isomerism around the C–S bond.

Figure 3 shows three possible steric environments around the S–H group, which are projected along the C–S bond, where C denotes an alkyl group, and X, a hydrogen atom or an alkyl group, depending on the type of R. If the molecule takes a staggered conformation, but not an eclipsed one, the mercapto-hydrogen atom of methyl and *t*-butyl mercaptan always exists in the environment, I or III respectively, in any rotational position about the C–S bond to be favoured. Hence, the frequency-lowering by 14 cm^{-1} of *t*-butyl mercaptan can be attributed to the presence of the two methyl groups *skew* to the SH. The spectral pattern of isopropyl mercaptan changed with the temperature; the intensity of the stronger band-component relative to the shoulder decreases at a higher temperature. Therefore, the band consists of at least two band-components, which can probably be assigned to the SH species in the environments, I and II respectively. The practically symmetrical bands of ethyl and *n*-butyl mercaptan probably consist of two bands corresponding to the two environments, I and II, because there is a possibility that they exist in these environments and also because the half-band widths are relatively wide.

Table 2. The spectral data of alkyl, benzyl and ω-ethoxyalkyl mercaptans in CCl_4

Compound	ν_{SH}, cm^{-1}	ε	$\Delta\nu_{1/2}$, cm^{-1}
CH_3SH[a)]	2586	—	7
C_2H_5SH	2578	2.2	15
n-C_4H_9SH	2578	2.2	15
i-C_3H_7SH	2577 (2570)	3.0	20
s-C_4H_9SH	2577 (2570)	2.7	21
t-C_4H_9SH	2572	2.1	14
$C_6H_5CH_2SH$	2580	2.0	
$C_2H_5O(CH_2)_2SH$	2585	*ca.* 3	
$C_2H_5O(CH_2)_3SH$	2583	*ca.* 3	

a) The ε value was not determined, because the concetration was uncertain.

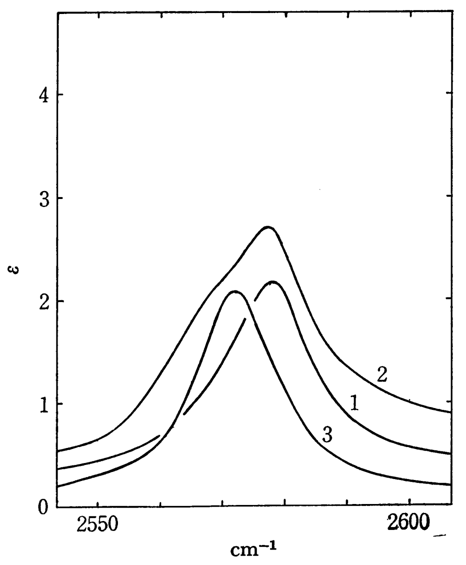

Fig. 1. The spectra of *n*-butyl (1), *s*-butyl (2), and *t*-butyl mercaptan (3).

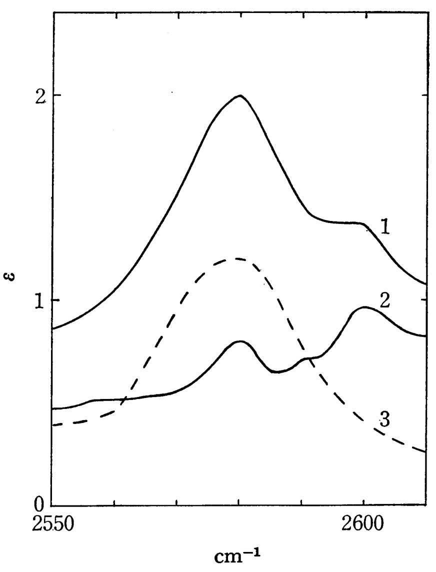

Fig. 2. The spectra of benzyl mercaptan (1) and benzyl methyl sulfide (2); (3) is the curve (2) subtrated from the curve (1).

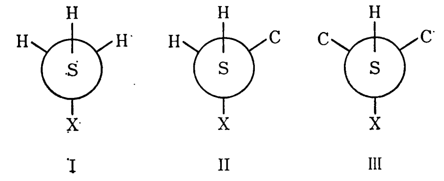

Fig. 3. Three steric environments around the SH group (X=H or C).

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[13] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

Benzyl mercaptan shows a complicated spectral pattern in the SH stretching region, but a simple unsymmetrical band can be obtained by subtracting the spectral curve of benzyl methyl thioether from it (Fig. 2); the peak frequency and intensity are very close to those of *prim*-alkyl mercaptans. It thus appears that the SH group is practically incapable of the interaction with the aromatic π-electrons which occurs with benzyl alcohols[14] and benzylamines.[15]

2- and 3-ethoxyalkyl mercaptans show, in carbon tetrachloride, single SH bands which are complicated by overlapping with other absorption bands on the higher-frequency side; the peak frequencies are rather close to that of methyl mercaptan, and the intensities are similar to those of alkyl mercaptans. Accordingly, the hydrogen bonding to the ethoxy group appears to be practically absent.

Furthermore, the SH frequencies of the above mercaptans are very close to those of thiophenols; hence, the electronic effects of substituents on them seem negligible. However, substituents have electronic effects on the intensities, as is indicated by the ε values of thiophenol and ethyl *p*-mercaptobenzoate (Table 5).

Ethyl α- and β-mercaptoalkanoates. Their SH spectra in carbon tetrachloride are shown in Fig. 4, while the apparent spectral data are summarized in Table 3. The bands of ethyl α-mercapto-acetate and -isobutyrate are almost symmetric, while ethyl α-mercaptopropionate shows an unsymmetric band. The frequencies and half-band widths are very close to those of the corresponding alkyl mercaptans; it thus appears that all the α-esters form no hydrogen bond. On the other hand, the high intensities, as compared with those of alkyl mercaptans, do not provide evidence for the hydrogen bond formation, because such an increase in intensity may also be caused by the electronic effects of the ethoxycarbonyl group. In order to clarify this point, the carbonyl data will be discussed further on the basis of a comparison with those of the corresponding *S*-ethylated compounds.

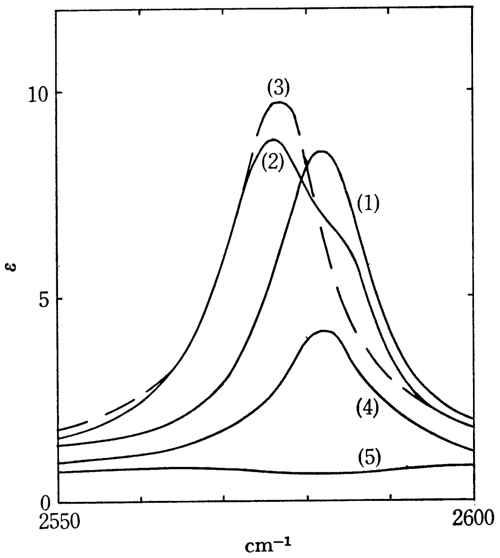


Fig. 4. The spectra of ethyl mercaptoacetate (1), α-mercaptopropionate (2), α-mercaptoisobutyrate (3), β-mercaptopropionate (4), and α-ethylthiopropionate (5).

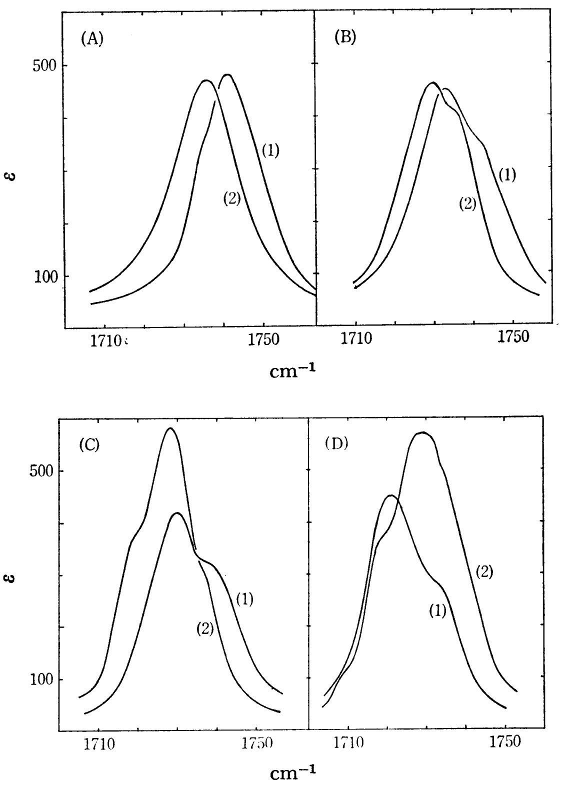
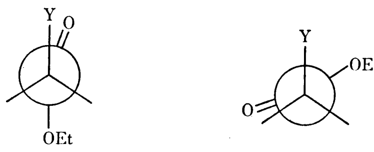


Fig. 5 (A)—(D). The CO spectra of ethyl mercaptoacetate (A) and its *S*-ethylated compound (B), α-ethylthiopropionate (C) and α-ethylthioisobutylate (D) in carbon tetrachloride (1) and acetonitrile (2).

Ethyl α-ethylthioalkanoates show, in carbon tetrachloride, two overlapped carbonyl bands with a spacing of about 10 cm,$^{-1}$ and the intensity of the higher-frequency band increases in acetonitrile relative to that of the lower-frequency band (Fig. 5A—5D). By analogy with the cases of α-halogeno-[16] and α-alkoxycarbonyl compounds,[10,17] as well as in view of the relatively high dipole moment of a C–S bond (*cf.* $\mu_{\text{C-S}}$: 1.2 D; $\mu_{\text{C-O}}$: 0.9 D; $\mu_{\text{C-Cl}}$: 1.7 D), this phenomenon can be suitably explained in terms of the rotational isomerism around the C_1–C_2 bond. Thus, the two bands can be assigned, in the usual manner, to the *cis* and *gauche* forms respectively:



cis-Form with a higher ν_{co} *gauche*-Form with a lower ν_{co}

On the other hand, ethyl α-mercaptoalkanoates show, in carbon tetrachloride, a strong band, with a weak shoulder centered at a position lower by about 6 cm^{-1} than the peak position, and the frequencies of

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[14] For example, M. Ōki, and H. Iwamura, *ibid.*, **32**, 955 (1959).

[15] M. Ōki and K. Mutai, *ibid.*, **33**, 784 (1960).

[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London (1958), p. 400.

[17] T. L. Brown, *J. Amer. Chem. Soc.*, **80**, 3513 (1958).

TABLE 3. THE APPARENT SPECTRAL DATA OF ETHYL α- AND β-MERCAPTOALKANOATES AND THEIR *S*-ETHYLATED COMPOUNDS[a]

Compound	in CCl_4						in CH_3CN		
	ν_{SH}, cm^{-1}	ε	$\Delta\nu_{1/2}$, cm^{-1}	ν_{CO}, cm^{-1}	ε	$\Delta\nu_{1/2}$, cm^{-1}	ν_{CO}, cm^{-1}	ε	$\Delta\nu_{1/2}$, cm^{-1}
$CH_2(SH)COOEt$	2582	8.5	15	1742 (1737)	450 (60)	17	1736	430	21
$CH_3CH(SH)COOEt$	2576 (2584)	8.8	21	1740 (1735)	450 (60)	17			
$(CH_3)_2C(SH)COOEt$	2577	9.7	16	1735 (1727)	450 (60)	20			
$CH_2(SH)CH_2COOEt$	2582	4.1	19	1738	600	16			
$CH_2(SEt)COOEt$				1743 1733	340 440	25	1736 1730	400 460	25
$CH_3CH(SEt)COOEt$				1739 1730	320 420	25	1728 1719	565 550	25
$(CH_3)_2C(SEt)COOEt$				1733 1721	280 500	20	1729 1719	660 360	25
$CH_2(SEt)CH_2COOEt$				1740	490	17			

a) The values in parentheses, obtained by band reflection, are approximate.

the two band-components are close to those of their *S*-ethylated compounds. In acetonitrile (Fig. 5A), ethyl mercaptoacetate shows a single, symmetric band at the same frequency as that of the *cis* form of the corresponding *S*-ethylated compound, suggesting that the ester exists exclusively in the *cis* form. Accordingly, the two bands which appear in carbon tetrachloride can probably be associated with the same rotational isomers, *cis* and *gauche*, as has been suggested in the case of ethyl α-ethylthioalkanoates. If this is true, it should be noticed, from the relative intensities of the bands, that the proportion of the *cis* form of ethyl α-mercaptoalkanoates in carbon tetrachloride is much higher than those which have hitherto been observed in α-halogeno- and α-alkoxy-carbonyl compounds (the intensities being taken as approximately indicative of the concentrations). The equilibrium between the *cis* and the *gauche* form is considered to be determined by two factors: (1) the electrostatically repulsive interaction between the C_α–Y and C=O dipoles (Y: an electronegative atom or group), which increases with the increasing polarity of the C–Y bond,[18] and (2) the sterically repulsive interaction between the Y and carbonyl-oxygen atoms[17,19] and between the Y and alkoxy-oxygen atoms,[18] both of which increase with the increasing bulkiness of Y. Since the dipole-dipole interaction should raise the double bond character of the carbonyl group and increase the stretching frequency of the C=O group, the fact that the spacing between the two carbonyl bands of ethyl ethylthioacetate (*ca.* 10 cm^{-1}) is lower than those of ethyl halogeno- and ethoxy-acetates (*ca.* 20 cm^{-1})[17] seems to indicate that the electrostatic interaction between the C–S and the C=O dipole is lower than those in the latter esters. From this, a higher proportion of the *cis* form may be expected in the former. On the other hand, the steric repulsion of Y exerting on the C=O group in the *cis* form and also exerting on the alkoxy group in the *gauche* form should be more highly operative in the ethylthioacetate than in the ethoxyacetate, because of the larger van der Waals radius of the sulfur atom.[20] Consequently, judging from the observation that the relative intensity (*cis* to *gauche*) of ethyl ethylthioacetate (*ca.* 0.8) is lower than the 1.94 of ethyl ethoxyacetate,[17] the steric repulsion between the Y and the carbonyl group must be much more important than the other electrostatic and steric repulsions. This is consistent with the conclusion by Brown[17] that the size, rather than the polarity, of Y in acetates is the determining factor.

In the case of ethyl mercaptoacetate, the mercapto group may be expected to be equal in size to, or smaller than, the ethylthio group.[21] If it is smaller, the steric repulsion between the Y and the carbonyl group should become lower, and the proportion of the *cis* form should be higher than that of the corresponding *S*-ethylated acetate. This expectation agrees with our observation that the *cis*-to-*gauche* ratio is *ca.* 8, but this ratio seems too high to be attributable to the decreased steric repulsion only, because no such high ratio has been observed even when the Y group has a bulkiness as small as the ethoxy group or the fluorine atom. In this connection, an attractive interaction between the SH and the carbonyl group may further be considered; it is not evident, however, whether this interaction is the usual hydrogen bonding or the electrostatic attraction, but it is probably the latter because no lowering of the SH and CO frequencies is observed. In this connection, it must be mentioned that ethyl glycolate

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[18] S. Mizushima, T. Shimanouchi, I. Ichishima, T. Miyazawa, I. Nakagawa, and T. Araki, *ibid.*, **78**, 2038 (1956).

[19] E. A. Mason and M. M. Kreevoy, *ibid.*, **77**, 5808 (1955); M. M. Kreevoy and E. A. Mason, *ibid.*, **79**, 4851 (1957).

[20] The van der Waals radius (*r*) of an atom (Y) is approximately equal to the C–Y bond distance: r=1.40 Å for O, 1.85 for S, and 1.35 for F; O–Y distance=1.43 Å (Y:O), 1.81 (S), and 1.38 (F); hence, the *r* value may be considered as a function of the steric interaction.

[21] In the cyclohexane system, the steric size of the SH group is close to, or somewhat lower than, that of the SCH_3 or SC_6H_5 group (*cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York (1965), p. 438).

exists exclusively in the *cis* form with the hydrogen bonding between the OH and CO group; thereby, both OH and CO frequencies are very much lowered.[9,10]

Ethyl β-mercaptopropionate may be internally unbonded, since both the frequency and the intensity of the SH band are comparable to those of *prim*-alkyl mercaptans, and the carbonyl data are very close to that of the corresponding *S*-ethylated compound.

α- and β-Ethylthioalkanoic Acids. The spectral data are summarized in Table 4. The α-acids show, in carbon tetrachloride, two split carbonyl bands in the monomer region (Fig. 6). Since only one OH band of the *cis*-carboxyl structure is observed, the band-splitting is not attributable to a hydrogen bond formation between the S atom and the *trans*-carboxyl group such as occurs in α-alkoxyalkanoic acids.[22] The reason for this is not clear at the present time, but at least two reasons can be considered: (1) the Fermi resonance or other absorptions and (2) the rotational isomerism, as has been suggested above in accounting for a similar phenomenon in the corresponding esters. A further study of this problem is in progress.

β-Ethylthiopropionic acid shows only single OH and CO bands in the monomer region, both corresponding to the *cis*-carboxyl structure. These findings agree with the conclusion, confirmed in ω-methylthioalkanols,[23] that the hydrogen-accepting ability of a sulfur atom is lower than that of an oxygen atom.

Thiosalicylic Acid and Related Compounds. In carbon tetrachloride, the free SH bands of aromatic thiols generally appear near 2585 cm^{-1} (*e.g.*, thiophenol, *o*-thiocresol, and ethyl *p*-mercaptobenzoate in Table 5), indicating that the steric and electronic effects on the SH frequency are not significantly operative. Ethyl *p*-mercaptobenzoate shows two bands in the SH region (Fig. 7); the higher-frequency band can be assigned to the SH group on the basis of a comparison with the spectrum of the corresponding *S*-methylated compound. Therefore, the band (ε=20; $\Delta\nu_{1/2}$=40 cm^{-1}) at 2560 cm^{-1} of *o*-mercaptobenzyl methyl ether can be assigned to the bonded SH group,[24] but this ether shows no free SH band. This fact is very interesting which differs from the case of *o*-hydroxybenzyl methyl ether in which a weak free OH band is observed apart from a strong bonded OH band.[25] The two split bands of ethyl thiosalicylate observed in the SH region (Fig. 8) can likewise be assigned to the SH species bonded to the ethoxy- and the carbonyl-oxygen atoms respectively; this assignment is consistent with the observation of two carbonyl bands which can be assigned to the free and bonded carbonyl groups (Fig. 9A).

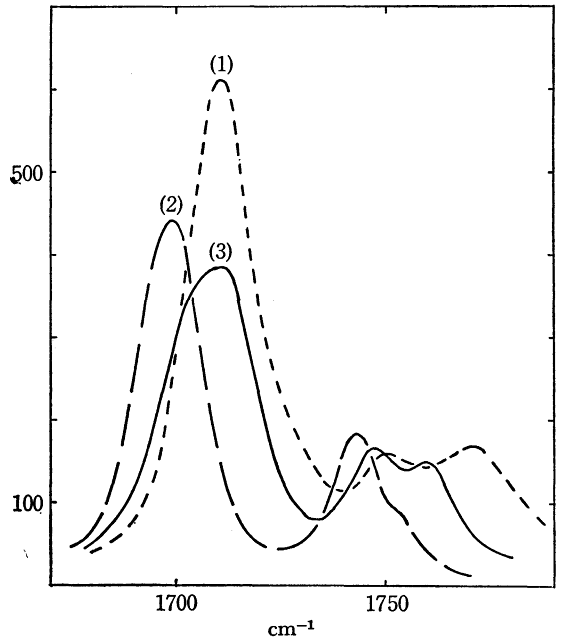

Fig. 6. The CO spectra of ethylthioacetic (1), α-ethylthiopropionic (2) and α-ethylthioisobutylic acid (3) in carbon tetrachloride.

Table 4. Apparent spectral data of α- and β-ethylthioalkanoic acids in CCl_4

Compound	Monomer				Dimer	
	ν_{OH}, cm^{-1}	ε	ν_{CO}, cm^{-1}	ε	ν_{CO}, cm^{-1}	ε
$CH_2(SEt)COOH$	3526	75	1771 1751	169 160	1711	610
$CH_3CH(SEt)COOH$	3528	55	1761 1747	147 164	1709	400
$(CH_3)_2C(SEt)COOH$	3529	56	1754 1743	85 183	1699	440
$CH_2(SEt)CH_2COOH$	3527	72	1762	200	1713	480

Thiosalicylic acid and its *S*-methylated compound show, in carbon tetrachloride, only single OH bands of the *cis*-carboxyl structure in the monomer region; hence, they form no hydrogen bond between the sulfur atom and the carboxyl group, although such a bonding occurs in *o*-alkoxybenzoic acids.[26] The two monomeric CO bands and the two SH bands of the former acid can probably be assigned much like those of its ester, because the spectral data of the two compounds are almost the same.

Ethyl *S*-methyl thiosalicylate shows, in carbon tetrachloride, two overlapped CO bands. In acetonitrile, the higher-frequency band is much weaker, with the frequency remaining almost unchanged, while the lower-frequency band shifts towards the lower-frequency side (Fig. 9B). This band-splitting is probably attributable to the Fermi resonance, but not to rotational isomerism or other absorptions, for the following reasons: (1) a band-splitting ascribed to the Fermi resonance is generally subject to a similar solvent effect,[27] while that ascribed to rotational isomerism

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[22] For example, M. Ōki and M. Hirota, This Bulletin, **33**, 119 (1960); **34**, 374 (1961).

[23] N. Mori, Y. Takahashi, and Y. Tsuzuki, *ibid.*, **40**, 2720 (1967).

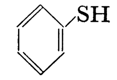
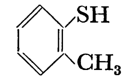
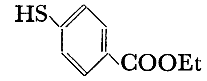
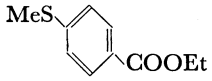
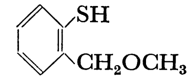
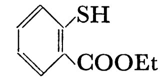
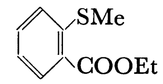
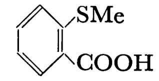
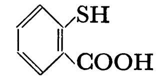
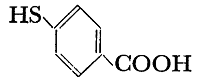
[24] The *S*-methyl ether of this compound shows no significant absorption near 2560cm^{-1}.

[25] N. Mori, unpublished data.

[26] For example, M. Ōki, and M. Hirota, *ibid.*, **34**, 378 (1961); **36**, 290 (1962), and Ref. 28.

[27] C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, N. Noack, R. J. D. Smith, and R. L. Jones, *Spectrochim. Acta*, **11**, 926 (1959); R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

TABLE 5. APPARENT SPECTRAL DATA OF THIOSALICYLIC ACID AND RELATED COMPOUNDS[a,b]

Compound	in CCl_4						in CH_3CN	
	ν_{SH}, cm^{-1}	ε	ν_{OH}, cm^{-1}		ν_{CO}, cm^{-1}	ε	ν_{CO}, cm^{-1}	ε
	2585	3						
	2585	3						
	2586	8			1719[c]	700	1720sh 1714	 710
					1719[c]	700	1720sh 1713	 800
	2560	20						
	2556 2523	8[e] 32			1720sh 1714 1698	 360 320	1720sh 1707 1699	 600 180[e]
					1722 1715	400 500	1720sh 1708	100[e] 620
			3531	(0.14)	1735 1691[d]	(0.11) (0.15)	1720sh 1718	 620
	2558 2530	(0.41) (0.34)	3528	(0.35)	1733 1717 1687[d]	(0.18) (0.21) (0.49)	1720 1702sh	520 200[e]
	2586				1742 1693[d]	(0.17) (0.44)		

a) The value in parentheses is an optical density instead of ε.
b) sh: shoulder.
c) Relatively broadened on the higher-frequency side.
d) Dimer absorption.
e) Obtained by band-reflection.[9]

shows a reverse trend of solvent effect,[28] and (2) even in the other *p*-substituted benzoates where rotational isomers are not expected, a similar band appears near 1720 cm^{-1}.

It is further interesting that, in acetonitrile, thiosalicylic acid and its ethyl ester show, apart from the band ascribed to the Fermi resonance, two carbonyl bands; the relative intensities of the lower-frequency bands are much lower than those in carbon tetrachloride. There are at least two possibilities for the band-splitting: (1) absorptions due to groups other than the carbonyl or due to rotational isomers, and (2) intramolecular hydrogen bonding. The first one can probably be rejected since the other aromatic compounds, even those *o*-substituted, show no splitting. The second possibility should thus be considered. The basicity of acetonitrile is so strong as to allow benzoic acid to be practically monomeric even in a concentration of 1 mol/*l*.[28] Further, it has now been found that acetonitrile is a base so strong that the aliphatic and aromatic carboxylic acids examined in the present work show negligible dimer absorptions at 0.01 mol/*l* in carbon

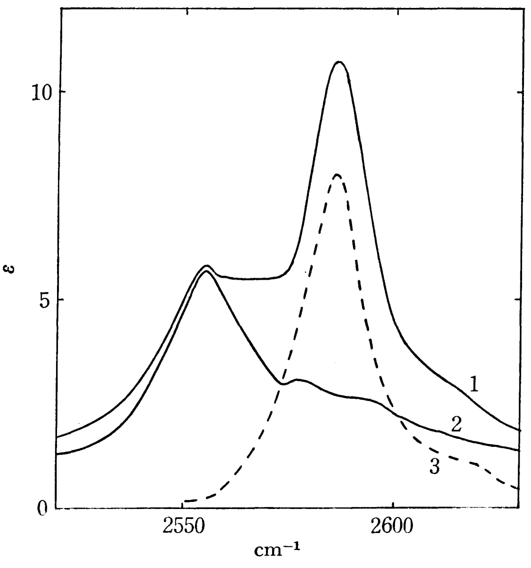


Fig. 7. The spectra of ethyl *p*-mercaptobenzoate (1) and its *S*-methylated compound (2); curve (3) is curve (2) subtrated from curve (1).

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[28] C. J. W. Brooks, G. Eglinton, and J. F. Morman, *J. Chem Soc.*, **1961**, 106.

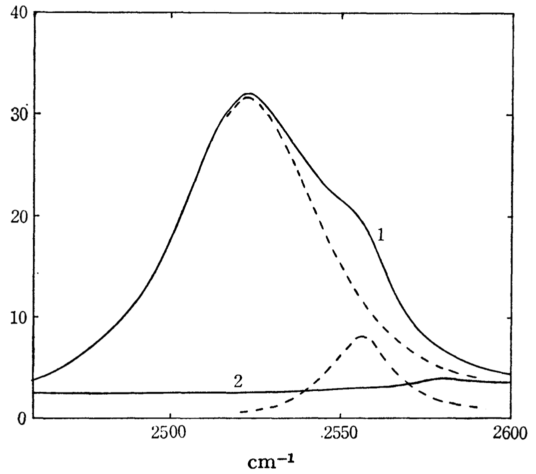

Fig. 8. The spectra of ethyl thiosalicylate (1) and its *S*-methylated compound (2); the dotted curves are the components graphically separated from curve (1).

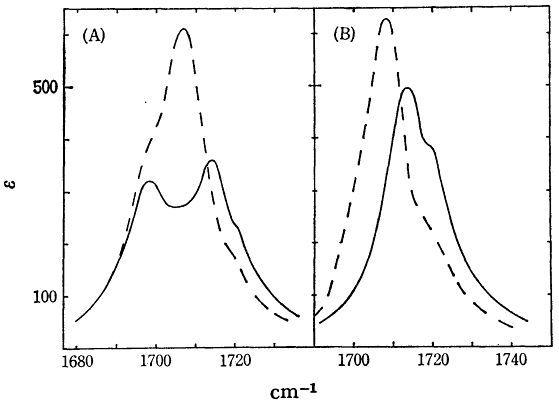

Fig. 9. The CO spectra of ethyl thiosalicylate (A) and its *S*-methyl compound (B) in CCl$_4$ (——) and CH$_3$CN (– – –).

tetrachloride containing 20% by volume of acetonitrile. Nevertheless, the intramolecular hydrogen bond between the OH and CO groups in salicylic acid and also in its methyl ester can not be broken at all in acetonitrile, while the dimer formation of the acid through intermolecular hydrogen bonding is practically completely prevented.[29] Accordingly, the intramolecular hydrogen bonding in thiosalicylic acid and its ester is probably possible to some extent even in acetonitrile; however, this is not expected at all because of the very poor hydrogen-donating property of the mercapto group.

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[29] N. Mori, unpublished results: for salicylic acid, $\nu_{CO}=1695$ (monomer) and 1662 cm^{-1} (dimer) in CCl$_4$ and 1682 cm^{-1} in CH$_3$CN; for the methyl ester, $\nu_{CO}=1680$ cm^{-1} in both solvents. On the other hand, ethyl glycolate is internally bonded in CCl$_4$, but not in CH$_3$CN.