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Intramolecular Hydrogen Bonding of *ortho*-Substituted Benzenethiols

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From the infrared, NMR, and dipole moment measurements on several substituted benzenethiols, the intramolecular hydrogen bonding in *o*-halo, *o*-methoxy, *o*-nitro, and *o*-carbomethoxybenzenethiols is verified. Five-membered S–H···X hydrogen bonds cause remarkable enhancements of their S–H stretching absorptions without considerable frequency shifts. The favorable *s-cis* conformations in these thiols are also proved by comparing their experimental dipole moments with theoretical values. By far stronger hydrogen bond is observed in *o*-carbomethoxybenzenethiols which can form six-membered chelate ring by the intramolecular hydrogen bonding.

Several investigations on the hydrogen bonding of thiols have been reported and the hydrogen donating properties of the sulfhydryl groups have been discussed.[1–9] From these investigations, it is assumed that the hydrogen donating power of the S–H group is rather weak and that thiols behave as softer acids than alcohols and phenols in case of hydrogen bond formation. The existence of such weak hydrogen bonds can be best investigated by NMR spectroscopy. Thus the S–H···S intermolecular hydrogen bond in ethyl mercaptan[2] and the S–H···O intramolecular hydrogen bond[10] have been verified by this method. The present authors also reported on the PMR spectra of *o*-methoxy- and 2,6-dimethoxy-benzenethiols, and concluded the existence of the intramolecular hydrogen bonds by the comparison with the behaviors of the corresponding phenols.[11]

In order to establish the extent and the limit of the existence of the S–H···X intramolecular hydrogen bonds and to compare their relative strengths for various hydrogen acceptors, the PMR, IR, and dipole moments of several *ortho*-substituted benzenethiols were determined and the existence of the intramolecular hydrogen bonds were concluded in benzenethiols carrying alkoxy-, halogeno-, nitro-, alkoxycarbonyl-substituents at the *ortho*-positions.

Experimental

Materials. *p*-Toluenethiol, *p*-methoxybenzenethiol, *o*-toluenethiol, 2-bromo-4-methylbenzenethiol, *o*-iodobenzenethiol, *o*-methoxybenzenethiol, and 2,6-dimethoxybenzenethiol were prepared according to the method reported by Sutar.[12] *o*-Nitrobenzenethiol was obtained by the reduction of 2,2′-dinitrodiphenyl disulfide.[13] All of these thiols were known compounds and were purified by repeated recrystallization or fractional distillation until their physical constants agree with those reported in literatures.[12–16]

All solvents used were commercially available spectro-grade ones or were purified by the usual methods. The solvents were dried over appropriate desiccants and re-distilled when necessary.

Spectral and Dielectric Measurements. Infrared spectra in the S–H stretching region were measured with a Perkin-Elmer 112G infrared spectrophotometer. The measurements were carried out on a dilute solution of the thiol in carbon tetrachloride or chloroform employing a quartz cell of 2 cm in path length.

Proton magnetic resonance spectra were determined with a JEOL JNM-C60H spectrometer. The spectra were obtained over a wide range of concentrations (0.1 to 100% of solute) in carbon tetrachloride and chloroform-*d* to ascertain the existance of the intramolecular hydrogen bonds.

Dielectric constants of the benzene or carbon tetrachloride solution of the thiols were determined at 25°C, except the case of temperature dependence measurement, using a heterodyne apparatus. The dipole moment values were calculated by employing the method of Halverstadt and Kumler[17] from the dielectric constants of the solutions at varying concentrations. The molar refraction was calculated from the bond refraction values in the literature.[18]

Results and Discussion

Infrared S–H stretching absorptions and chemical shifts of the S–H protons at infinite dilution are given in Table 1. The thiols No. 1 to 4 are those without intramolecular hydrogen bonds, and intermolecular hydrogen bonding is also excluded by the measurement

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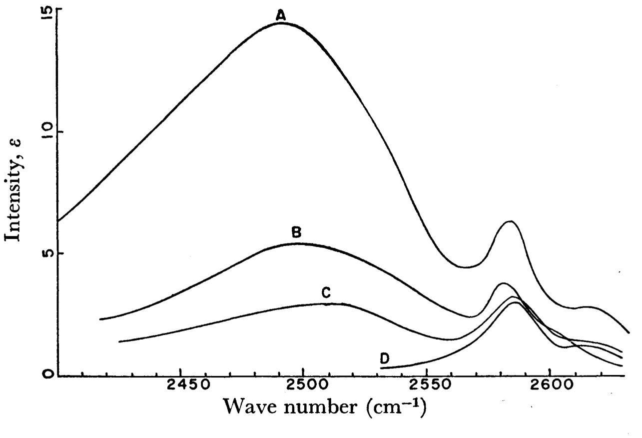
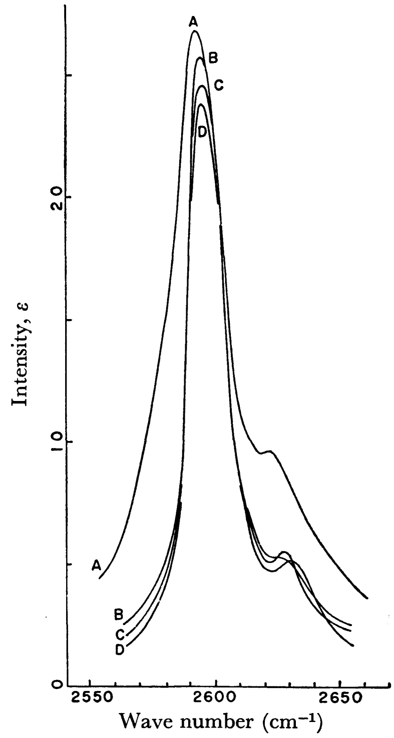
TABLE 1. INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA OF VARIOUS BENZENETHIOLS

Substituent	No. of compd.	Carbon tetrachloride solution				Chloroform solution			
		S–H stretching band			PMR spectra	S–H stretching band			PMR spectra
		ν(cm^{-1})	ε(l/mol·cm)	A(10^2l/mol·cm^2)	δ_{SH}(ppm from TMS)	ν(cm^{-1})	ε(l/mol·cm)	A(10^2l/mol·cm)^2	δ_{SH}(ppm from TMS)
4-CH_3	(1)	2588	3.2	2.58	3.17	2586	6.9	5.23	3.36
4-CH_3O	(2)	2583	3.4	3.44	3.14	—	—	—	3.33
2-CH_3	(3)	2582	2.1	2.13	3.06	—	—	—	3.23
2-Cl	(4)	2587	14.2	6.76	3.82	2586	17.9	9.07	3.90
2-Br-4-CH_3	(5)	2579	17.1	7.99	3.80	2584	16.4	10.7	3.92
2-I	(6)	2560	14.4	6.74	4.02	2558	12.2	7.51	—
2-CH_3O	(7)	2593	18.9	10.3	3.66	2592	17.3	12.5	3.79
2,6-$(CH_3O)_2$	(8)	2595	24.5	13.8	3.75	2592	28.4	16.5	4.00
2,6-Br_2-4-CH_3	(9)	2572	36.0	13.0	4.77	2569	32.4	15.9	4.72
2-NO_2	(10)	2598	27.4	15.9	4.05	2601	8.60	7.59	
2-$COOCH_3$	(11)	2534	33.3	65.1	5.26	2546	15.9	49.5	4.75

in extremely dilute solution of inert solvents. Their S–H absorption have rather low intensities ($\varepsilon_{max}=3$ in CCl_4) and not affected considerably by the introduction of *ortho* and *para* substituents, if the *ortho* substituents are incapable of forming intramolecular hydrogen bonds. On the other hand, the introduction of the hydrogen accepting substituents at the *ortho* position causes a remarkable increase in intensity as shown in Table 1. The absolute values of the integrated intensity is larger in chloroform than in carbon tetrachloride, while the intensity enhancement is more predominant in latter solvent. In contrast to the remarkable increase in intensity, the S–H absorption frequencies are not affected by the introduction of the hydrogen accepting substituents except the case of *o*-carbomethoxybenzenethiol. The introduction of a methyl group forming no intramolecular hydrogen bond to the *ortho*-position does not strengthen the S–H intensity, and the steric effect caused by the *ortho*-substituent might not be responsible for the intensity enhancement. The possibility of the electronic effect (mesomeric effect) is excluded by the fact that the intensity of the S–H absorption is little affected by the methoxy substituent in *p*-methoxybenzenethiol. In analogy with the substituent effect on the ν_{O-H} intensities of substituted phenols,[19] the electron donating character of the methoxy group at the *ortho*- or *para*-position is expected to decrease the intensity of S–H absorption. Thus the observed increase in intensity cannot be explained by the electronic effect.



a



b

Fig. 1. The S–H stretching absorptions of *p*-toluenethiol (1a) and 2,6-dimethoxybenzenethiol (1b) in carbon tetrachloride–dimethyl sulfoxide mixtures.
A: 5.24 wt% DMSO in CCl_4, B: 1.36 wt% DMSO in CCl_4, C: 0.686 wt% DMSO in CCl_4, D: 100 wt% CCl_4.

In conclusion, the enhancement of the intensity might be attributed to the intramolecular hydrogen bond formation. Such an evidence was obtained by the investigation on the intermolecular interaction of the thiols with some solvents having proton accepting ability. The ν_{SH} intensities of *p*-toluenethiol (1) and 2,6-dimethoxybenzenethiol (8) are recorded in several sol-

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[19] G. A. Stone and H. W. Thompson, *Spectrochim. Acta*, **10**, 16 (1957).

TABLE 2. S–H STRETCHING BAND INTENSITIES AND HALF WIDTHS OF THE TWO TYPICAL BENZENETHIOLS

Thiol		Solvent			
		CCl_4	$CHCl_3$	$(CH_3)_2CO$	DMSO (8%) in CCl_4
p-$CH_3C_6H_4SH$	ε(*l*/mol·cm)	3.2	6.9	30.0	14.6
	$\Delta\nu_{1/2}$ (cm^{-1})	51.4	48.3	76.5	*ca.* 110
2,6-$(CH_3O)_2$-C_6H_3SH	ε(*l*/mol·cm)	34.5	28.4	29.0	26.7
	$\Delta\nu_{1/2}$ (cm^{-1})	35.8	37.0	42.5	29.0

vents and listed in Table 2. The thiols selected in Table 2. are the typicals of the intermolecular and intramolecular hydrogen bonded ones, respectively. Of the usual benzenethiols without *ortho*-hydrogen acceptor (1), the S–H absorption band tend to be more intense and broader when measured in hydrogen accepting solvents. (See also Fig. 1) However, the S–H absorption of 2,6-dimethoxybenzenethiol (8) is not remarkably affected by such solvents. In this compound, the S–H group is shielded by the two methoxy groups, and the solvent molecules are hardly accessible to the S–H group. Hence, the intermolecular hydrogen bonding might not disturb the intramolecular hydrogen bond of the latter thiol to a considerable extent. The increase in intensity is quite general with the intramolecularly hydrogen-bonded compounds carrying O–H and N–H groups.[20] Some experiments also showed that the S–H groups participating in the hydrogen bonds have stronger S–H absorptions.[21]

In the case of rather weak hydrogen bond, both the hydrogen bonded and the free X–H absorption bands must be observed. However, only one absorption band assigned to the S–H stretching vibration can be observed in most cases, though some weak bands whose origins are uncertain appear in the spectra of some thiols. The spectra in Fig. 2 show that the ν_{S-H} bands are intensified remarkably by the introduction of the additional hydrogen accepting substituent to the 6-positions of the 2-methoxy- and 2-bromobenzenethiols. This means that the hydrogen bonded form is increased by the introduction of the second substituent, and the existence of free *s-trans* form (II) is expected in the benzenethiol carrying one hydrogen accepting substituent at the *ortho* position. Because of the absence of the remarkable hydrogen bond shift, weaker S–H absorptions of the free species might be masked by the stronger S–H absorptions of the intramolecularly hydrogen bonded species. The S–H stretching spectrum of *o*-carbomethoxybenzenethiol in Fig. 3 shows the appearance of an additional band of low intensity in normal S–H stretching region, which can be assigned to the free S–H stretching vibration.

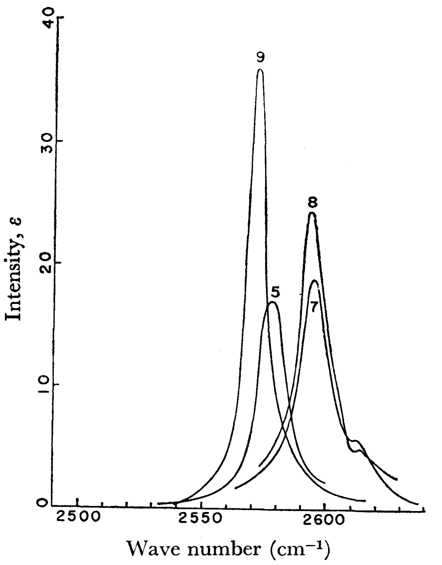

Fig. 2. The S–H stretching absorptions of 2-X- and 2,6-di-X-benzenethiols in carbon tetrachloride.

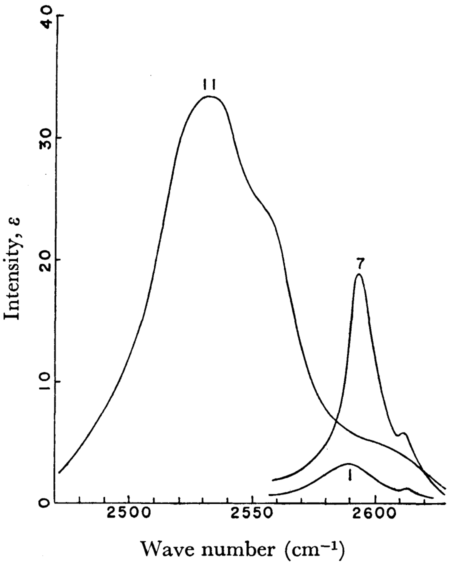

Fig. 3. The S–H stretching absorptions of the typical benzenethiols with five-membered and six-membered hydrogen bonded chelates (in carbon tetrachloride).

The PMR chemical shifts of the S–H protons in very dilute solutions are also given in Table 1. As reported previously by the present authors,[11] the PMR spectra are useful in the discussion of the hydrogen bonding of thiols and the chemical shifts of S–H protons at infinite dilution displace to considerably lower fields when the thiols exist as the intramolecularly hydrogen bonded forms. Thus, the usual thiols ((1) to (3) in Table 1) have δ_{SH} values ranging 3.0 to 3.3 ppm in carbon tetrachloride and 3.2 to 3.4 ppm in chloroform-*d*, while the thiols carrying *ortho* hydrogen accepting substituents have δ_{SH} values ranging 3.6 to 5.3 ppm and 3.7 to 4.8 ppm, respectively, in the above solvents. The ν_{S-H} intensity *vs.* δ_{SH} plot is illustrated in Fig. 4, and a fairly good linear relation is observed even though no correction for the magnetic anisotropy effect by the substituents are taken into accounts.

Additional evidence for the intramolecular hydrogen

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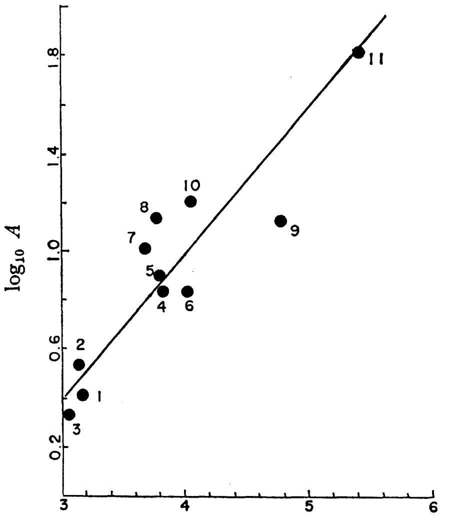
[20] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., San Francisco (1960) p. 167.

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



Chemical shift, δ (ppm)

Fig. 4. Integrated intensity (A_{SH}) *vs*. SH chemical shift (δ_{SH}) plot.

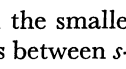
TABLE 3. DIPOLE MOMENTS OF VARIOUS BENZENETHIOLS

Substituent	No. of compound	Dipole moment (D) Theoretical *s-cis*	Theoretical *s-trans*	Experimental	Abundance (%) *s-cis*	*s-trans*
a) Benzene solution at 25°C						
None	(12)	—	—	1.21[a)]	—	—
4-CH_3	(1)	—	—	1.51[a)]	—	—
2-CH_3	(3)	1.35	0.81	0.90	13±10	87±10
2-Cl	(4)	1.72	2.73	1.91	85±5	15±5
2-Br-4-CH_3	(5)	2.08	2.96	2.25	84±6	16±6
2-CH_3O	(7)	—	—	2.25	—	—
2-NO_2	(10)	3.90	5.14	4.24	76±4	24±4
b) Carbon tetrachloride solution at 25°C						
2-Cl	(4)	1.72	2.73	1.78	95±5	5±5
2-Br-4-CH_3	(5)	2.08	2.96	2.05	97±6	3±6

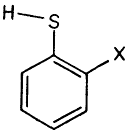
a) Calculated dipole moments of benzenethiol and *p*-toluenethiol are 1.19D and 1.50D, respectively. These are obtained from the group moments employed in this investigation.

TABLE 4. THE GROUP DIPOLE MOMENT VALUES

Group (X)	μ_{C-X}	θ
SH	1.19	44°
CH_3	0.4	180°
Cl	1.58	0°
Br	1.54	0°
OCH_3	1.28	108°
NO_2	4.01	0°

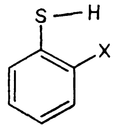


bonding in benzenethiols with *ortho*-substituents of hydrogen accepting ability is supplied by the dipole moment data given in Table 3. The theoretical dipole moment for each conformation is calculated from the group moments in Table 4.[22)] When *o*-halo- and *o*-nitrobenzenethiols form intramolecular hydrogen bond, the *s-cis* conformation (I) of these thiols should exist more favorably than the corresponding *s-trans* conformation. To obtain the ratios of *s-cis* and *s-trans* conformations, the experimental dipole moment values of the thiols are assumed to be expressed as the resultants of the mean squares of the theoretical dipole moments of the two conformers, and the following equation is employed,



s-trans

(II)

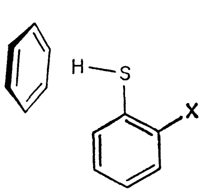


s-cis

(I)

$$\mu^2 = \frac{\mu_t^2 N_t + \mu_c^2 N_c}{N_t + N_c}$$

where μ_t and μ_c, N_t and N_c are the theoretical dipole moments and the numbers of the molecules of *s-trans* and *s-cis* conformers, respectively. Thus the experimental dipole moment 0.90 D of *o*-toluenethiol (3) in benzene solution at 25°C gives the result that 87% of the molecules take *trans* conformation and the rest of them have *cis* conformation. This means that *cis* conformation is unfavorable, and might be due to the steric hindrance between the methyl and sulydrylfh hydrogen atoms. On the other hand, the observed dipole moments of *o*-chloro-, 2-bromo-4-methyl-, and *o*-nitrobenzenethiols are closer to the theoretical values for *s-cis* conformations. When dissolved in benzene, 85%, 84%, and 76% of them, respectively, exist as *cis* conformations, and the proportions of *cis* conformers increase further when dissolved in carbon tetrachloride. The conclusions on the conformations obtained from the dipole moment measurements again supports the existence of intramolecular hydrogen bonding. Increased population of *s-trans* conformers in benzene solutions is explained by the stabilization caused by the S–H···π intermolecular interaction with the solvent molecules, as illustrated by (III).



(III)

The dipole moment of *o*-methoxybenzenethiol does not agree with the favorable *s-cis* conformation. This may arise from the smaller difference of the theoretical dipole moments between *s-cis* and *s-trans* conformers and from the ambiguity of the direction of methoxy group moment caused by the rotation around the C–O bond.

In conclusion, the intramolecular S–H···X hydrogen bonds exist in some *ortho*-substituted benzenethiols forming both five-membered and six-membered chelate rings. Similar to the corresponding phenols, benzenethiols with *o*-methoxy-, *o*-chloro-, *o*-bromo-, *o*-iodo-, *o*-

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22) a) L. E. Sutton, "Determination of Organic Structures by Physical Methods," ed. by E. A. Braude and F. C. Nachod, Academic Press Inc., N. Y. (1955) p. 373. b) T. Shimozawa, "Interpretation of Dielectric Constant," Kyoritsu Shuppan Co., Tokyo (1967) p. 55.

nitro-, and *o*-methoxycarbonyl-substituents form intramolecular S–H···X hydrogen bonds, and it would be foreseen that the benzenethiols with *o*-acyl, *o*-formyl, and other hydrogen accepting substituents also form the intramolecular hydrogen bonds.

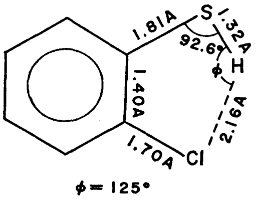

Fig. 5. Geometry of the planar *s-cis* conformation of *o*-chlorobenzenethiol (4).

Table 5. Molecular geometries of some *o*-substituted benzenethiols

Substituent	*d* (H···X) Å	(∠S–H···X)
2-Cl	2.16	125°
2-Br	2.20	130°
2-I	2.25	135°
2-OCH_3	2.16	117°
2-NO_2	1.15	140°
2-$COOCH_3$	1.35	151°

Then, some discussions will be given on the stereochemistry of the intramolecular hydrogen bond of this type. The H···X distances *d* and S–H–X angles were calculated by assuming the geometry in Fig. 5 for the *cis* conformers and the results were listed in Table 5. The main factors determining the strength of the intramolecular hydrogen bond are i) the kinds of the hydrogen donating and accepting groups, ii) the linearity of the hydrogen bond, and iii) the distance between the donor and the acceptor atoms. In the discussion on the stereochemistry, the latter two factors play important roles. The hydrogen bond becomes stronger when the hydrogen atom comes closer to the accepting atom and when the S–H···X arrangement is nearer to the linear one. In these points of view, the six-membered chelation is stronger than the five-membered one, which is in agreement with the above results. The most suitable S–H···X distance values are rarely found in the previous investigations. However, the O–H···X distances are reported by many authors[24] and the O–H···Cl and the O–H···O distances in hydrogen bonded molecules are 3.1 to 3.2 Å and 2.5 to 2.8 Å, respectively. The H···X distances are then 1.5 to 1.8 Å and 2.1 to 2.2 Å. The calculated X···H distances in Table 5 are mostly within these ranges, but the H···O distance in *o*-nitrobenzenethiol[10] is rather too short, and the repulsive force between the atoms may cause the deviation from the planar six-membered ring. This could be a reason why the intramolecular hydrogen bond in (10) is weaker than expected.

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23) Bond lengths and bond angles employed were taken from a) "Kagaku Benran," Fundamental Volume II, ed. by Chem.Soc. Japan, Maruzen Book Co., Tokyo (1966) p. 1209 and b) "Kagaku Benran," ed. by Chem. Soc. Japan, Maruzen Book Co., Tokyo (1958) p. 966.

24) p. 255 of Ref. 20.