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PROTON MAGNETIC RESONANCE SPECTRA AND THE INTRAMOLECULAR HYDROGEN BONDING OF *o*-ALKOXY-PHENOLS AND -BENZENETHIOLS

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Abstract—The PMR spectra of several methoxy substituted benzenethiols and related phenols have been examined in various solvents over a wide range of concentrations. The positions of the sulfhydryl proton resonance signals (δ_{SH}) of *o*-methoxybenzenethiol and 2,6-dimethoxybenzenethiol in inert solvents, and the δ_{SH} values of the thiols carrying *o*-OMe groups are less affected by the interaction with the solvents than those without *o*-OMe groups. The significant differences in the behaviour of chemical shifts of these compounds have been best interpreted by the intramolecular S—H···O H-bonding. Additional evidence for the intramolecular H-bonding in *o*-OMe substituted benzenethiols have been obtained from the IR spectroscopic data.

STUDIES on NMR spectra of thiols have been reported by several authors,[1-9,15,16] but the existence of the S—H···X H-bonding had not been confirmed before the recent investigations by Copley[10] because the SH group is affected slightly by the H-bond formation. His studies showed that arylmercaptans forms an S—H···N or S—H···O intermolecular H-bond with the nitrogen- or oxygen-containing solvent as hydrogen acceptor.

Formation of such weak H-bonds, particularly if intramolecular, is observed by nuclear magnetic measurements, so that great progress in this field has been made within recent years. It was confirmed first by Fórsen[2] that an intermolecular H-bond of the S—H···S type exists in ethylmercaptan in the liquid state.

As to the intramolecular H-bond of thiols, Wagner *et al.* concluded the existence of the S—H···O intramolecular H-bond in thiosalicylic acid and its esters by means of IR spectroscopy.[13] However, the intramolecular H-bonding of thiols has not been extensively studied.[15] It is well known that the 5-membered rings formed by O—H···X intramolecular H-bonds are present in phenols carrying *ortho* substituents (X) of proton accepting ability (X = OMe, halogen and others);[17,18] therefore the presence of intramolecular H-bonds analogous to those in phenols is expected in properly substituted benzenethiols.

In order to investigate the formation of intermolecular and intramolecular H-bonds in *ortho* substituted benzenethiols, PMR spectra of several OMe substituted benzenethiols and related compounds were determined in various solvents over a wide range of concentration. IR spectra of these compounds were also measured and the results compared with those from PMR spectra.

RESULTS AND DISCUSSION

The PMR spectra of benzenethiols and phenols investigated are given in Table 1. As shown, the positions of the sulfhydryl proton resonance signals δ_{SH} of *o*-methoxybenzenethiol and 2,6-dimethoxybenzenethiol are located at lower fields than in *p*-methoxybenzenethiol, and the δ_{SH} values of the thiols increase in the order: *p*-methoxybenzenethiol < *o*-methoxybenzenethiol < 2,6-dimethoxybenzenethiol. The δ_{SH} values are less affected by the interaction with the solvents than the δ_{OH} of the corresponding phenols, though the two series of compounds behave similarly when the solvents are altered.

The chemical shifts of sulfhydryl proton of benzenethiols in various solvents (Table 1) are plotted against a solvent polarity parameter $(\varepsilon - 1)/(2\varepsilon + 2{\cdot}5)$, where ε is the dielectric constant of the solvent, and it is proposed as a measure of the polarity of the solvent by Onsager.[20] But no good linear relations were observed and the deviation from the line is particularly significant with the phenol series. As to the thiols, the deviation of the δ_{SH} values from the line is considerably large in DMSO, which is a very polar solvent and is regarded as strong proton acceptor, as well as in aromatic solvents. The deviation might be caused by specific solvent-solute interaction.

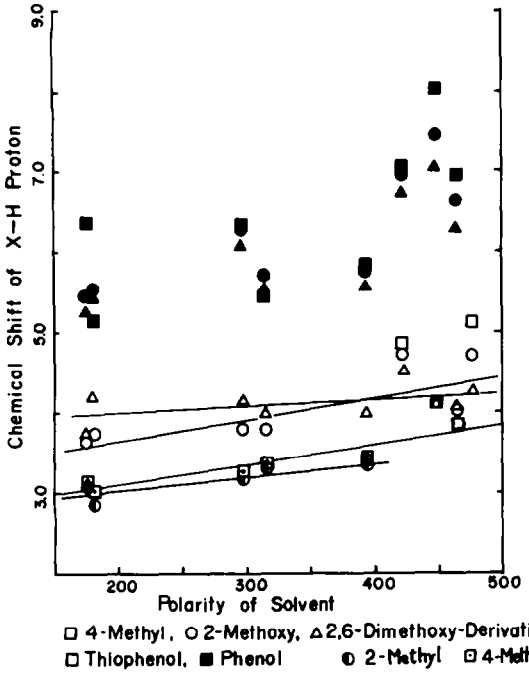


FIG. 1 The plots of NMR chemical shifts of the hydroxyl or sulphhydryl protons versus Onsager's parameter.

The solvent shift of the O—H stretching absorption of methanol ($\Delta\nu$), which has been used as a criterion for the hydrogen accepting power and sometimes referred as "hydrogen bond shift", was chosen as another parameter for the property of solvent. The H-bond shift is defined as the difference between the ν_{OH} frequency in the reference solvent (CCl_4 in this investigation) and that in the designated solvent.

TABLE 1. THE PMR SPECTRA OF BENZENETHIOLS AND THE CORRESPONDING PHENOLS IN VARIOUS SOLVENTS

(a) The chemical shifts of the sulfhydryl protons in benzenethiols

Solvents	δ_{SH} (p.p.m. from TMS)				
	p-MeO	*p*-Me	*o*-MeO	*o*-Me	2,6-$(MeO)_2$
Carbon Tetrachloride	3·14	3·17	3·66	3·06	3·75
Chloroform-d	3·33	3·36	3·79	3·23	4·00
Methylene Chloride	3·40	3·42	3·40	3·34	4·01
Acetonitrile		3·83	3·94		4·08
Acetone-d_6	4·02	4·10	4·07	4·02	4·07
Dimethyl Sulfoxide-d_6		5·11	4·71		4·25
Benzene	3·02	3·04	3·74	2·85	4·20
Anisole	3·25	3·28	3·80	3·15	4·14
Toluene		2·99	3·68		4·09
Xylene		3·20	3·66		4·04
Mesitylene		3·18	3·62		3·97
Pyridine		4·88	4·70		4·52
Pure Substance	3·42	3·27	3·85	3·22	4·06

(b) Other proton in benzenethiols

Solvents	δ_{OCH_3}			δ_{ArH}					$\delta_{Ar\cdot CH_3}$	
	p-MeO	*o*-MeO	2,6-$(MeO)_2$	*p*-MeO	*p*-Me	*o*-MeO	*o*-Me	2,6-$(MeO)_2$	*p*-Me	*o*-Me
Carbon Tetrachloride	3·72	3·83	3·81	6·90	7·03	6·86	6·96	6·46	2·27	2·26
Chloroform-d	3·73	3·85	3·85	6·97	7·08	6·89	7·06	6·57	2·76	2·27
Methylene Chloride	3·73	3·85	3·84	6·97	7·06	6·90	7·05	6·60	2·25	2·27
Acetonitrile		3·82	3·83		7·08	6·95		6·67	2·74	
Acetone-d_6	3·73	3·82	3·83	7·01	7·08	6·95	7·08	6·67	2·92	2·25
Dimethyl Sulfoxide-d_6		3·79	3·80		7·08	6·97		6·71	3·40	
Benzene	3·17	3·20	3·28	6·73	6·85	6·79	6·79	6·38	1·17	2·03
Anisole	3·40	3·43	3·45	6·79	6·85	6·79	7·05	6·83	2·03	2·12
Toluene		3·23	3·28							
Xylene		3·25	3·35							
Mesitylene		3·31	3·37							
Pyridine		3·65	3·68		7·24	7·23		7·24	2·17	

(c) The OH protons in phenols

δ_{OH} (p.p.m. from TMS)			δ_{OBH_3}	
p-Me	*o*-MeO	2,6-$(MeO)_2$	*o*-MeO	2,6-$(MeO)_2$
5·83	5·47	5·27	3·80	3·79
5·44	5·66	5·51	3·83	3·85
5·84	5·76	5·58	3·83	3·81
6·97	6·60	6·29	3·82	3·78
8·02	7·43	7·05	3·80	3·77
9·05	8·85	8·21	3·70	3·68
5·17	5·53	5·45	3·11	3·33
6·12	6·27	6·09	3·36	3·48
7·05	6·93	6·76	3·72	3·77
7·56	6·67	5·91	3·44	3·72

Thus the solvent shift is expressed by the equation: $\Delta\nu \equiv \nu_{OH}(CCl_4) - \nu_{OH}(\text{solvent})$. Here the monomeric ν_{OH} frequencies of methanol in dilute solution are used to calculate the shift values. In the present investigation, having been unable to find a proper set of the $\Delta\nu$ values of the solvents used for the PMR measurement, we determined them by the IR spectral measurement. The δ_{SH} values of the thiols, as well as the δ_{OH} values of the corresponding phenols, were plotted against the $\Delta\nu$ values and shown in Fig. 2. As the $\Delta\nu$ is a parameter evaluating the overall effect of the solvent polarity

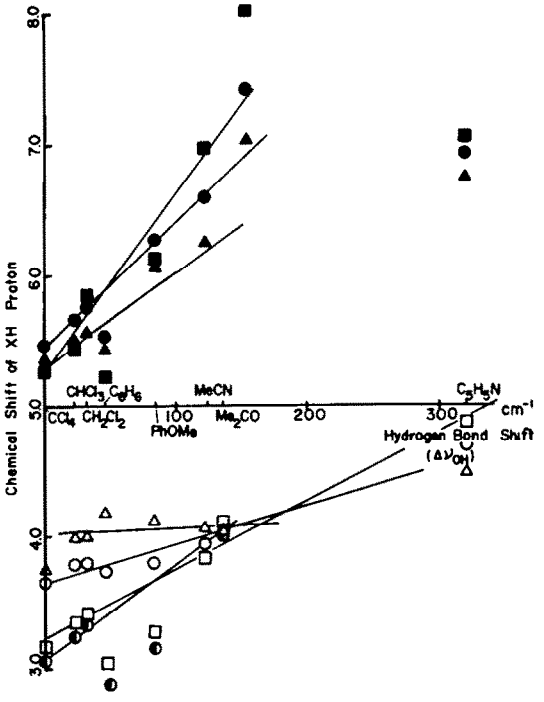
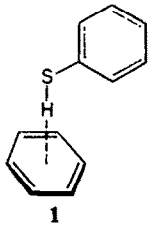


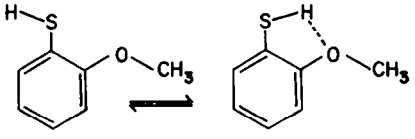
FIG. 2 The plots of NMR chemical shifts of XH protons δ_{XH} versus hydrogen bond shifts $\Delta\nu_{OH}$ for various solvents.

and the association through intermolecular H-bonding, a better linear relation is expected, and in practice the deviation from the line is much less marked except with proton-accepting aromatic solvents. The abnormal δ_{SH} values in the aromatic solvents is due to the specific S—H$\cdots\pi$ interaction between the aromatic π-electrons and the sulfhydryl hydrogen. In the interacted state, the sulfhydryl hydrogen is located at a position just above the aromatic nucleus of the solvent molecule as illustrated by (**1**) and the shift of the δ_{SH} value to a higher field is effected by the anisotropy of the aromatic ring.



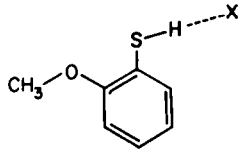
1

The signals of the sulfhydryl hydrogen of *o*-OMe substituted benzenethiols appear at considerably lower fields than those of the benzenethiols without *o*-OMe group in non-polar solvents incapable of forming H-bonds, and the deviation from the plot of δ_{SH} *vs* $\Delta\nu$ or the solvent polarity parameter $(\varepsilon - 1)/(2\varepsilon + 2{\cdot}5)$ is not so significant for 2,6-dimethoxy- or *o*-methoxy-benzenethiol as for the unsubstituted one. The intramolecular S—H···O H-bonds are present in both 2,6-dimethoxybenzenethiol and *o*-methoxybenzenethiol, and the intramolecular H-bonded *cis*-conformation (**2a**) of *o*-methoxybenzenethiol is assumed to be more favorable than the free conformation (**2b**). These two conformations are in equilibrium and, in solvents of hydrogen accepting ability, the intramolecular H-bond in the *cis* conformation is replaced by the intermolecular H-bond with solvents, in which the *trans* conformation (3) is more favorable. Thus the intermolecularly H-bonded *trans* conformation (3) becomes predominant as the hydrogen accepting ability of the solvent increases and this causes a shift of the sulfhydryl proton signal toward lower field.



2
free

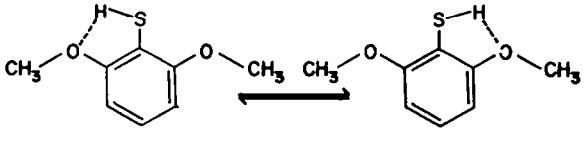
2b
hydrogen-bonded



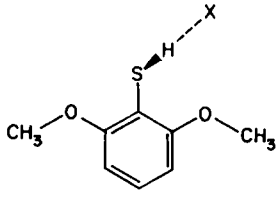
X= C=O, S=O, N etc

3

But the low field shift of the δ_{SH} and the tangent of the line are the least in 2,6-dimethoxybenzenethiol in which the non-planar conformation is enforced to associate with the solvent molecule and the most in the benzenethiols without *o*-OMe group. The above mentioned facts are interpreted as follows. 2,6-Dimethoxybenzenethiol remains in the planar intramolecular H-bonded conformation in most solvents except those of very strong proton accepting ability, so the δ_{SH} is nearly independent of the nature of the solvent unless it is strongly basic. *o*-Methoxybenzenethiol, which exists as an equilibrium mixture of the intramolecularly H-bonded *cis*- and associated *trans*-conformations, are affected more than 2,6-dimethoxybenzenethiol but less than benzenethiols which have no *o*-OMe groups and exist entirely as associated forms with the solvents.



4
both conformations are intramolecularly hydrogen-bonded



4a
non-planar

To reject the possibility of the steric crowding to hinder the intermolecular H-bonding with solvents, the behavior of the δ_{SH} of *o*-toluenethiol was compared with those of *o*-methoxybenzenethiol and *ortho* unsubstituted benzenethiols. If the δ_{SH} values of *o*-methoxybenzenethiol are less sensitive to the solvent effect, due to the steric hindrance of the *o*-OMe group to association with solvents, then the δ_{SH} of *o*-toluenethiol should behave similarly to *o*-methoxybenzenethiol, since the Me group is bulkier than the OMe group and a steric effect of the same order as the *o*-OMe derivative is expected to occur. But the solvent effect on the δ_{SH} of *o*-toluenethiol is similar to that of *p*-methoxybenzenethiol and *p*-toluenethiol, and no steric effect on the solvent-solute association is evident. So the nature of the solvent effect is best explained by the intramolecular H-bonding.

Additional evidence for the intramolecular H-bonding in *o*-OMe substituted benzenethiols are obtained from the IR spectroscopic data. Thus the S–H stretching absorptions of several benzenethiols were measured in carbon tetrachloride, chloroform and acetone, and shown in Fig. 3. As exemplified by the spectrum of *p*-toluenethiol in carbon tetrachloride, the S–H stretching bands of free thiols are weak in intensity, but the intensity of the S–H stretching band increases considerably with the formation of the H-bond. This infers that the S–H bond is elongated and polarized by the H-bond formation and that the transition moment of the stretching vibrational transition (proportional to $(d\mu/dr)$) increases as a result. The ν_{SH} absorptions of *o*-methoxybenzenethiol and 2,6-dimethoxybenzenethiol are much stronger than that of *p*-toluenethiol even in carbon tetrachloride which is additional evidence of the presence of the intramolecular H-bonds in these compounds. Details of the IR spectra of substituted benzenethiols will be reported elsewhere.

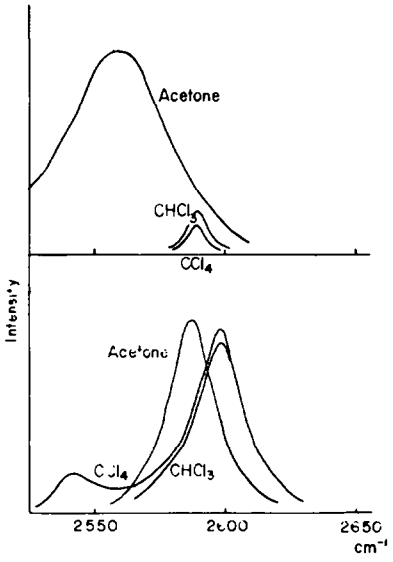


FIG. 3 The S–H stretching bands of benzenethiols at concentrations about 5 wt % in three solvents.

The concentration dependence of the δ_{SH} of several benzenethiols were shown in Fig. 4. On the whole, the chemical shift of the S–H group moves to higher field on dilution with carbon tetrachloride and to lower field on dilution with acetone. The δ_{SH} values change slightly by the dilution when the concentration of the solution is below 5%, and the solutions of the benzenethiols investigated (Table 1) are so prepared that their concentrations are below this concentration. The δ_{SH} of *o*- and *p*-toluenethiols are affected only to a small extent by the dilution with carbon tetrachloride, and this can be interpreted that the self-association of benzenethiols is weak and does not alter the state of the S—H bond. On the other hand, the intermolecular H-bonding between the sulfhydryl and the OMe groups may occur in *p*-methoxybenzenethiol at high concentrations, resulting in more marked low field shifts with increase in concentrations.

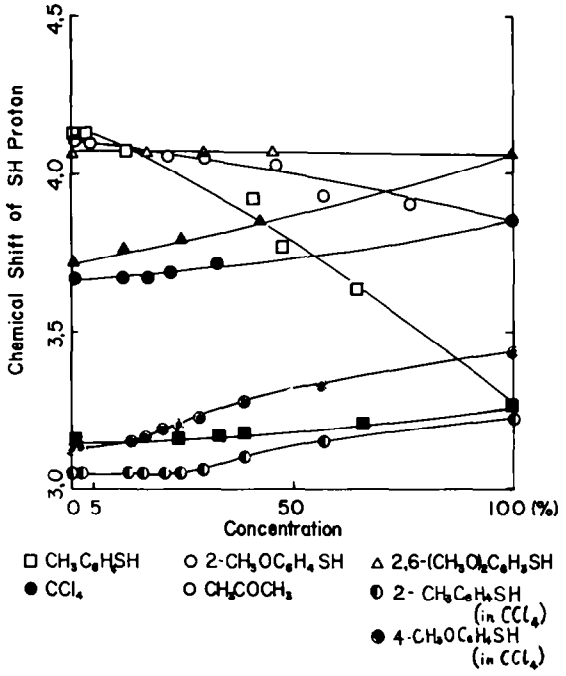


FIG. 4 Dilution chemical shifts for the S–H protons of the benzenethiols in two solvents.

EXPERIMENTAL

Benzenethiols employed (*p*-toluenethiol, *p*-methoxybenzenethiol, *o*-methoxybenzenethiol, *o*-toluenethiol and 2,6-dimethoxybenzenethiol) were prepared according to Sutar[19] and purified by recrystallization or fractional distillation. All solvents used were commercially available spectro-grade or were purified by the usual methods. The solvents were dried over appropriate desiccants and re-distilled when necessary.

NMR spectra were obtained with a JEOL JMN C-60H spectrometer in a soln of a concentration of approximately 5% of various solvents. Further dilution does not affect the spectra remarkably. The concentration dependence of the chemical shifts of some thiols were measured in CCl_4 and acetone solns over the concentrations ranging from 0·1 to 100 wt % of the solutes. In solid samples at ordinary temp, the spectrum was measured at an elevated temp. The spectra at very low concentrations were obtained with a JRA-1 spectrum accumulator.

The IR spectra in 4000–650 cm^{-1} region were obtained by a Hitachi EPI spectrophotometer. High resolution spectra in the S–H stretching region were observed with a Perkin Elmer Model 112G IR spectrophotometer.

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