Nuclear Magnetic Resonance Study of the Steric Effect in Dimethylphenols

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In their various physicochemical properties, six isomers of dimethylphenol (xylenol) were observed to be slightly different from each other[1-5]. These differences have been ascribed mainly to the difference in the steric effect of the methyl group on the formation of an intermolecular hydrogen bond. The present author observed obvious differences among the nuclear magnetic resonance spectra of dimethylphenols. The difference could be closely correlated with the position of the methyl groups in the benzene ring relative to the hydroxyl group.

Experimental

NMR measurements were carried out at 20°C with a Varian High Resolution NMR spectrometer operated at 56.4 Mc. The dimethylphenols measured were guaranteed grade reagents. The solvents used were carbon tetrachloride and acetone. These were purified with a Podobielniak fractional distillator. The values of the chemical shift were obtained referring to an external reference of water in a capillary, and the correction for bulk diamagnetic susceptibility was made. The solubility of dimethylphenols in carbon tetrachloride was poor except for 2,4-dimethylphenol. Therefore the measurements were made up to their saturated solutions at 20°C.

Results and Discussion

Figure 1 shows the chemical shift-concentration diagrams for dimethylphenols in carbon tetrachloride solution. The curves with the highest chemical shift are due to methyl protons, and the ones with lower chemical shift are due to benzene ring protons and hydroxyl proton (thick line). The resonance fields for the methyl protons and the ring protons decrease on dilution. This is a characteristic feature of aromatic systems and is ascribed to the effect of the ring current in the neighboring solute molecules. The detailed results and discussions for each proton group are described as follows.

Methyl Proton Resonance.—The methyl protons in 3,4- and 3,5-dimethylphenols give only one resonance line. This means that the difference between the screening constants for *m*- and *p*-Me protons is so small that it can not be observed. In contrast to this, the

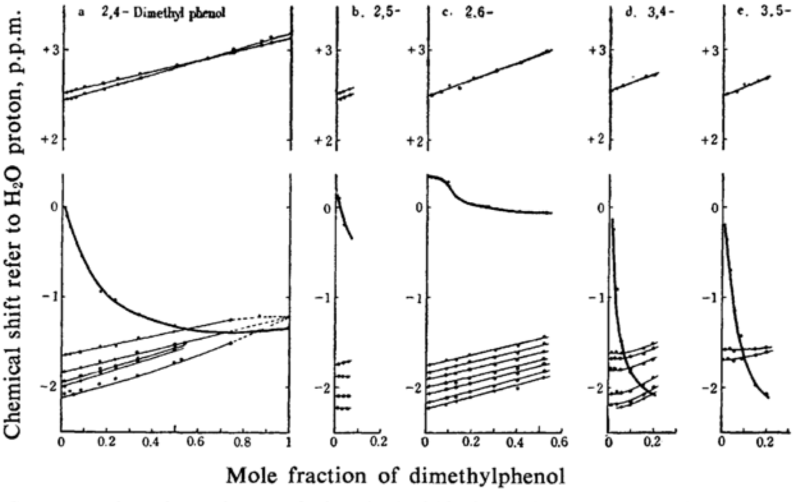

Fig. 1. Concentration dependence of chemical shift for CCl$_4$ solutions of dimethylphenols.

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1) W. C. Sears and L. J. Kitchem, *J. Am. Chem. Soc.*, **71**, 4110 (1949).

2) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, **1952**, 2310.

3) M. Neuilly, *Compt. rend.*, **238**, 781 (1954).

4) W. Suetaka and M. Sanesi, *Ann. chim.* (*Rome*), **46**, 1133 (1956).

5) D. Bono, *Bull. soc. chim. France*, **1956**, 1368; *Compt. rend.*, **242**, 375, 637 (1956).

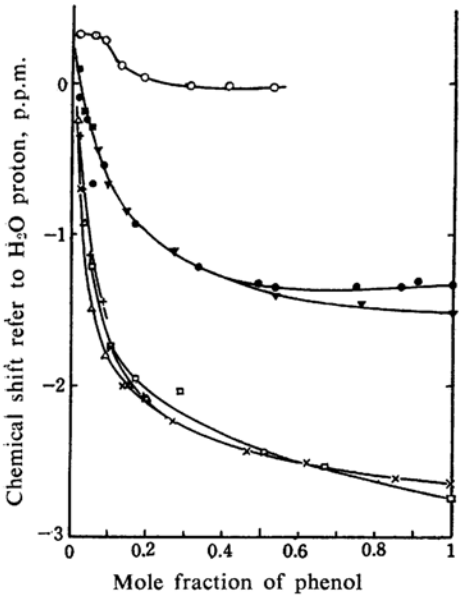

Fig. 2a. Concentration dependence of chemical shift of OH proton in various methyl phenols in CCl_4 solution.

—●— 2,4-Dimethylphenol
—■— 2,5- 〃
—○— 2,6- 〃
—△— 3,4- 〃
—+— 3,5- 〃
—▼— *o*-Cresol[a)]
—□— *m*- 〃 [a)]
—×— *p*- 〃 [a)]

a) I. Yamaguchi, unpublished work.

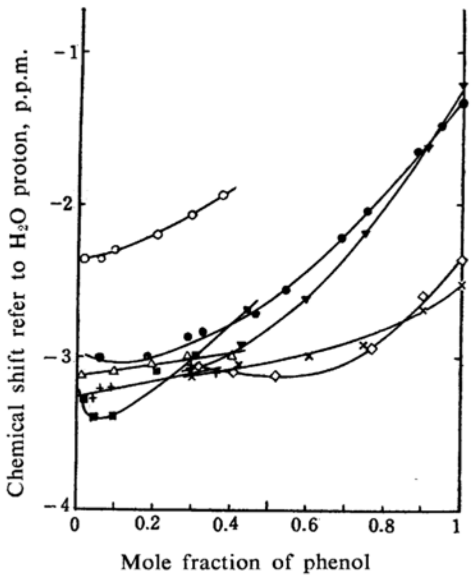

Fig. 2b. Concentration dependence of chemical shift of OH proton in various methylphenols in acetone solution.

—●— 2,4-Dimethylphenol
—■— 2,5- 〃
—○— 2,6- 〃
—△— 3,4- 〃
—+— 3,5- 〃
—▼— *o*-Cresol[b)]
—×— *p*- 〃 [b)]
—◇— Phenol[b)]

b) R. L. Batdort, Ph. D. Thesis, Univ. of Minnesota, 1955.

methyl protons in both 2,4- and 2,5-dimethylphenols give two resonance lines caused by the difference between the screening constants of the protons in 2(*o*)-Me group and that in 5(*m*)- or 4(*p*)-Me group. Furthermore, the two resonance curves for 2,4-dimethylphenol intersect each other at an intermediate concentration of carbon tetrachloride solution. Thus the concentration dependence of the resonance in 2(*o*)-Me protons is clearly different from that in 4(*p*)-Me protons. This suggests that the 2(*o*)-Me protons interact strongly with the OH group owing to the proximity of the two groups to each other.

Several effects are considered to induce the specific interaction between the groups. They might be the inductive and mesomeric effects of the OH group, effect of the electrostatic field[6)] originating from the bond moment of the OH group, or the effect of the dispersion force. The interaction caused by each effect should be greater with the *o*-Me protons than with the *m*- or *p*-Me protons. The magnitude of these effects would be affected by the change in the hydrogen bonding situations of the OH group. Therefore, the resonance line for the *o*-Me protons might be displaced by the change in the concentration of the solution in a way different from that for the *m*- or *p*-Me protons. However, it is unfortunately impossible to treat the resultant effect quantitatively. And at the present stage, we can not decide which curve should be assigned to *o*-Me protons.

Hydroxyl Proton Resonance.—Fig. 2 shows the concentration dependence of the chemical shift of the OH proton in dimethylphenols and cresols. Fig. 2a is of carbon tetrachloride solutions and Fig. 2b is of acetone solutions. Three types of the curves with distinctly different concentration dependence from one another are observed in the figures. The first group (a) at the highest field includes 2,6-dimethylphenol, the second (b) at the middle 2,4- and 2,5- dimethylphenols and *o*-cresol, and the third (c) at the lowest 3,4- and 3,5-dimethylphenols and *m*- and *p*-cresols. At the concetration of 1 mol. fraction (pure phenol), the values of the chemical shift are

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6) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

about (a) +0.1 p.p.m., (b) −1.3 p.p.m. and (c) −2.5 p.p.m. This classification clearly correlates with the location of the methyl groups in the molecule: The phenol in (a) has two methyl groups at both the ortho positions to the OH group, and those in (b) and (c) have one and no methyl group ortho to the OH respectively. The methyl groups at the meta and para positions do not take part in this classification. In carbon tetrachloride solutions, all of the curves approach about +0.3 p.p.m. at the concentration of infinite dilution (extrapolated). Therefore, it would be reasonable to consider that in a free single molecule the effect of the *o*-Me group on the screening constant of a non-hydrogen bonded OH proton is very small.

These results that the difference in the resonance field of the OH proton among the isomers may primarily be ascribed to the steric hindrance of the *o*-Me group to form the intermolecular hydrogen bond. The values of the chemical shift for pure phenols may correlate with the extent of the steric effect of the methyl group on the hydrogen bond formation.

A flat range was observed for 2, 6-dimethylphenol below the concentration of 0.05 mol. fractions. This implies the complete dissociation of the intermolecular hydrogen bond at the concentration range. This is an evidence that the two methyl groups at the 2(*o*)- and 6(*o*)-positions sterically inhibit the formation of the intermolecular hydrogen bond appreciably.

The concentration dependence of the chemical shift of the OH proton for the acetone solution is somewhat different from that for the carbon tetrachloride solution. For carbon tetrachloride solutions, the OH curve suggests a simple dissociation process of the intermolecular hydrogen bond on dilution. In contrast to this, for acetone solutions the curve shows a process to form a new hydrogen bond with acetone.

Ring Proton Resonance.—The dimethylphenol molecule has only three ring protons giving a rather simple spectrum. Therefore, the assignment of each spectral line to one of the protons can be made without any strict mathematical treatment of the spectrum. Fig. 3 shows the spectra for the ring protons in dimethylphenols in carbon tetrachloride and in acetone solutions with a concentration of about 0.1 mol. fractions. The position of the resonance field for each proton is indicated with a thick line with the figure of the location in the ring referring to the OH group.

The width of the ring proton resonance spectrum decreases generally with the increasing concentration as shown in Fig. 1. From detailed examinations of these spectra, it appears that the *o*- and *p*-proton resonance lines are at a higher field than that for the *m*-proton, and the slope of the curves for *o*- and *p*-protons is gentle compared with that for *m*-proton. Thus the curves for these protons approach each other as the concentration increases. This is the cause of the decrease of the width. The different concentration dependences of *o*- and *p*-protons from that of *m*-proton may be ascribed to the change in the magnitude of the mesomeric effect of the OH group on the ring protons with the change in the hydrogen bonding situation.

The differences between the ring proton spectra for carbon tetrachloride solution and that for acetone solution are observed as shown in Fig. 3. These arose from the different situations of the molecule in different mediums; one is a nearly free, non-hydrogen bonded molecule in carbon tetrachloride solution and another a hydrogen bonded molecule with the solvent in acetone solution. A noticeably different point is the displacement of the *o*-proton resonance lines to a lower field for 2, X-dimethylphenols (X=4 or 5) in acetone solution. It seems very probable that the displacement is caused by the formation of a hydrogen bond between the *o*-proton and the C=O group in an acetone molecule[7]: An

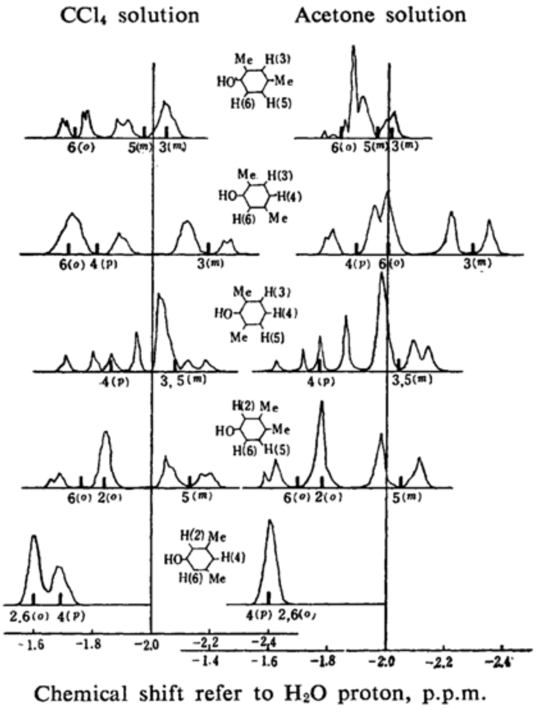

Fig. 3. Ring proton resonance spectra of dimethylphenols in CCl_4 and acetone solutions with concentration of about 0.1 mol. fraction.

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[7] T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, 32, 1218 (1960).

acetone molecule forms a strong hydrogen bond with the OH group. Therefore this O–H bond would be orientated inevitably to the side of the *o*-proton because of the steric hindrance of the *o*-Me group, and a weak hydrogen bond would be formed between the *o*-proton and the C=O group because of the proximity of these groups. Thus the decreased electron density in *o*-proton caused by the formation of the hydrogen bond would displace the resonance field of the *o*-proton to a lower field.

In 2, 6-dimethylphenol, two methyl groups would inhibit the formation of a hydrogen bond with any proton donor or acceptor. Therefore, merely a minute change is observed in the ring proton spectrum with the change is observed in the ring proton spectrum with the change in solvent and concentration. 3, X-dimethylphenols (X=4 or 5) also show minute changes in their ring proton spectra. These molecules have no *o*-Me group, and the OH group may be able to rotate freely about the C–O axis. Therefore, there is no specific steric effect on the *o*-protons. This would be a reason why the changes in solvent and concentration do not displace the *o*-proton resonance lines appreciably.

Summary

The nuclear magnetic resonance in dimethylphenols were observed. The dependences of the chemical shifts for the methyl, hydroxyl and ring protons on solvent and concentration were measured and several clear differences were observed among the spectra of the isomers. The phenols with one or two ortho methyl groups showed peculiar behaviors which may be ascribed to the interaction between the hydroxyl group and the ortho proton or ortho methyl protons. The evidence of the steric hindrance of the ortho methyl group to form an intermolecular hydrogen bond is also shown in the present measurements.

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