Proton Magnetic Resonanace Spectra of p-Cresol

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Schaefer and Schneider⁽¹⁾ investigated the ring proton resonance spectra of the *p*-substituted toluene derivatives and obtained many fruitful results concerning the interaction between ring protons and solvent molecules. The present author previously reported an NMR study of several hydrogen-bonded systems⁽²⁻⁵⁾. In these reports, explanations of the NMR behavior of the ring protons were made when the protons are affected by a change in the hydrogen-bonding situation in the molecule. In the present work, the NMR spectra of *p*-cresol, which gives rather a simple spectrum for the ring protons, were measured in various solutions and the NMR behaviors of methyl, hydroxyl and ring protons were interpreted in terms of hydrogen bond formation.

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

2) I. Yamaguchi, This Bulletin, 34, 353 (1961).

3) I. Yamaguchi, ibid., 34, 744 (1961).

4) I. Yamaguchi, ibid., 34, 451 (1961).

5) I. Yamaguchi, to be published.

Experimental

The NMR measurements were made with a Varian NMR spectrometer at a resonance frequency of 56.4 Mc./sec. and at a temperature of 20°C. Chemical shifts of methyl, hydroxyl and ring protons from an external reference of water proton were determined by the side band technique and the susceptibility corrections were applied. *p*-Cresol was a guaranteed grade reagent and was purified by distillation. The solvents used were benzene, chloroform, carbon tetrachloride, dioxane, acetone and pyridine. These were purified with a Podobielniak distillator. Solutions with concentrations between 0.02 and 1 mol. fractions were prepared for each solvent.

Results and Discussion

Figure 1 shows the concentration dependence of the chemical shifts of the methyl, hydroxyl and ring protons in carbon tetrachloride solutions. The hydroxyl proton resonance curves show characteristic behavior of each solution as shown in Fig. 2. On the other hand, the methyl and ring proton resonance curves show slight dependence on the solvent. Generally, the resonance fields of the methyl and ring protons decrease on dilution. The greater part of the causes of this inclination can be ascribed to the diamagnetic anisotropy effect of aromatic rings in the solution[6]. The resonance in the ring protons shows an interesting concentration dependence: Pure cresol liquid gives a single line spectrum while it gives a spectrum with a structure in dilute solution, arising from the proton pairs being chemically different from each other.

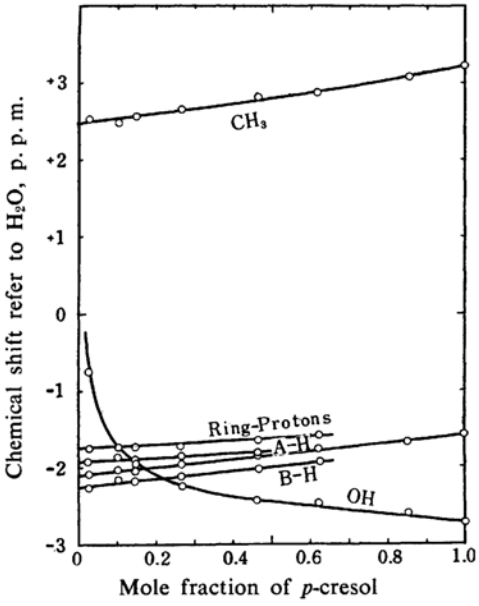

Fig. 1. Concentration dependence of chemical shift for *p*-cresol in CCl_4 solution.

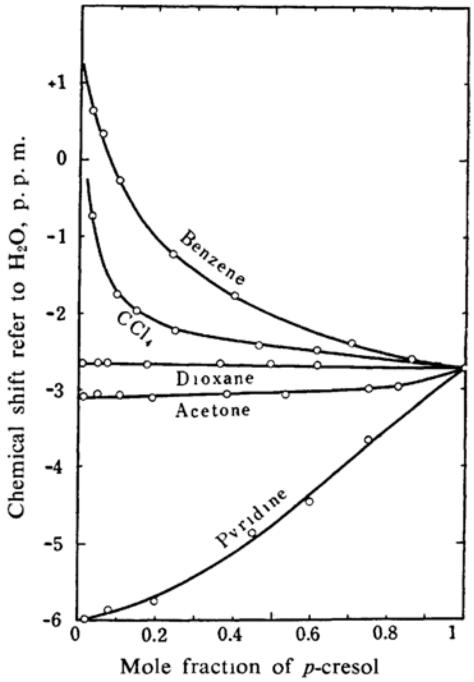

Fig. 2. Concentration dependence of OH proton chemical shift for *p*-cresol in various solutions.

Methyl Proton. — The chemical shift of the methyl protons for benzene and pyridine solutions is apparently independent of the concentration because the net content of aromatic rings in the solutions is almost invariable. Those for the other solutions show the concentration dependence which is characteristic of the anisotropic effect of benzene rings of the solute in these solvents. The dilution shifts are almost the same as those for ring protons in benzene[6]* for the same solutions. The slope of the curve for the acetone solution is smaller than the others and this finding is parallel to the case of the ring protons in benzene. There seemed to be no notable effect of the hydrogen bonding on the methyl proton resonance.

Hydroxyl Proton. — Pure *p*-cresol gives a hydroxyl proton resonance line at slightly lower field than that in pure phenol[7]. This may be caused by the strengthening of the hydrogen bond by the hyperconjugation effect of the *p*-methyl group, although the hydrogen bond energies for the two compounds are comparable

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[6] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

* The curves appeared in Ref. 6 were corrected for the susceptibility of the solutions.

[7] R. L. Batdorf, Ph. D. Thesis, Univ. of Minnesota, 1955.

to each other[8]. The solvent and concentration dependences of the hydroxyl proton resonance are shown in Fig. 2. The curves for benzene, chloroform and carbon tetrachloride solutions show the dissociation process of the hydrogen bond between the solute molecules on dilution. The curves for dioxane, acetone and pyridine solutions suggest new hydrogen bond forms between the solute and the solvents on dilution.

The curves for the carbon tetrachloride solution are as similar as those for phenol in carbon tetrachloride solution[9], exhibiting a representative NMR behavior of the dissociation process of a hydrogen bond system. The curve for the concentration above the concentration of about 0.3 mol. fraction is considered to correspond to the dissociation process of polymer species. In the range below about 0.05 mol. fraction the dissociation of dimer molecules is considered to be dominant. The resonance field for the benzene solution increases simply on dilution. This behavior of the curve is caused by several factors; the dissociation of the associated molecules, the ring current effect of benzene and the hydrogen bond formation with the π-electron system of the solvent molecule. The last may cause the rapid increase of the resonance field on dilution.

In dioxane and acetone solutions, the solute is considered to form a new hydrogen bond with the solvent molecules on dilution while the associated *p*-cresol molecules dissociate. The new hydrogen bonds are probably weaker ones than the intermolecular hydrogen bond of *p*-cresol. This is because the resonances at the infinite dilution are due to a more shielded proton than that in the intermolecular hydrogen bond of *p*-cresol. Pyridine, a strong proton acceptor, appeared to form a strong hydrogen bond with *p*-cresol as suggested by the curve. Pyridine seems to destroy the hydrogen-bonded association or chelation[2] of a compound by its strong proton accepting power.

Ring Proton.—The ring proton resonance in solutions appears at a slightly higher field than those for benzene in respectively the same solvents. This is due to the electron-releasing substituents of methyl and hydroxyl groups in *p*-cresol. *p*-Cresol liquid gives a single resonance line for the ring protons while diluted *p*-cresol with any solvent gives a spectrum with a characteristic structure of the A_2B_2 system[10] as shown in Fig. 1. The slope of the concentration-dependence curves for ring protons is due mainly to the anisotropic effect of the aromatic rings in the solutions. The slope of the curves for B-protons (ortho to methyl group) in chloroform, carbon tetrachloride, dioxane and acetone solutions are slightly gentler than those for benzene in respectively the same solutions[6]. This easier characteristic of the slope may be ascribed to the bulkier molecular size of *p*-cresol compared to that of benzene[11]. Therefore the B-protons can plausibly be assumed to be scarcely affected by the varying situations of the hydrogen bonding but to some effect proper to the proton in an aromatic ring. The slope for A-protons (ortho to hydroxyl group) is much easier than that for the B-protons.

If the effect of the ring current is removed for simplicity's sake from considerations of NMR behavior of the ring protons, the B-proton resonance is nearly independent of the concentration of the solutions, while the A-proton resonance is displaced to a higher field on dilution. The cause of this inclination for the A-protons may be ascribed to some changes in the following effects affected by the hydrogen bond formation; (i) the inductive and mesomeric effects of the hydroxyl group, (ii) the electrostatic field which originated from the hydroxyl bond moment, (iii) effect of magnetic anisotropy of the solvent molecule in the proximity of A-proton, (iv) preferential hydrogen bond formation between A-proton and solvent molecule, and (v) dispersion effect of solvent molecule on the A-proton. The effects (i) and (ii) have their origin in the molecule itself while (iii), (iv) and (v) come from the interaction with the solvent. Since the behavior for the A-proton is common to all solutions, the effects (iii) and (iv) are ruled out. It is difficult to consider a preferential dispersion effect on the A-proton, and the effect (v) is also ruled out. On hydrogen bond formation, the length and the polarization of the O–H bond may increase[12] and hence the electrostatic field at the A-protons originating from the bond moment may be altered. This electric field might cause the displacement of the A-proton resonance. However, the direction of the displacement is to a higher field with increasing bond moment. Therefore, the contribution of the effect (ii) should be small. For this reason, the effect (i) is considered to be dominant to cause the displacement of the resonance in A-proton. With the effect (i), this inclination for the A-protons

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[8] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", Freeman, San Francisco (1960), Appendix B.

[9] C. M. Huggins, G. C. Pimentet and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

[10] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957); R. E. Richards and T. P. Schaefer, *J. Mol. Spectroscopy*, **2**, 1280 (1958).

[11] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance, "McGraw-Hill, New York (1959), p. 426.

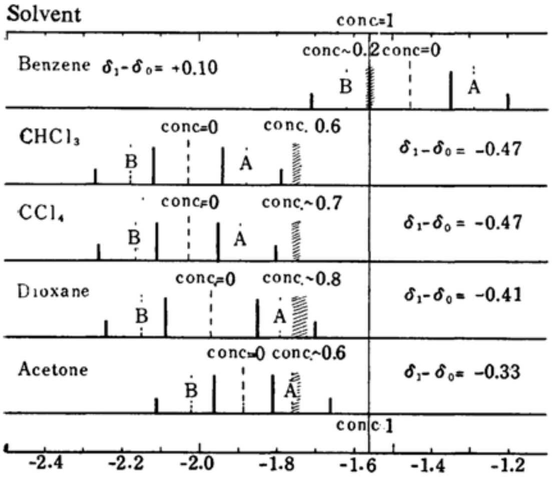
[12] See for example: A. Burawoy, "Hydrogen Bondnig", Ed. by D. Hadzi, Pergamon Press, New York (1959), p. 259.

TABLE I. CHEMICAL SHIFTS, DILUTION SHIFT, COUPLING CONSTANT AND COALESCENT CONCENTRATION OF RING PROTON SPECTRUM IN *p*-CRESOL

Solvent	δ_{ring} (p. p. m.)		Dilution shift (p. p. m.) $\delta_1-\delta_0$	δ_{AB} (c./sec.)	J_{AB} (c./sec.)	Coalesc. conc. (mol. fraction)
	conc. = 1	conc. = 0				
Benzene	−1.56	−1.46	+0.10	18.6	8.5	~0.2
$CHCl_3$	〃	−2.03	−0.47	16.6	〃	~0.6
CCl_4	〃	−2.03	−0.47	15.3	〃	~0.7
Dioxane	〃	−1.97	−0.41	20.3	〃	~0.8
Acetone	〃	−1.89	−0.33	14.7	〃	~0.6

may be interpreted as follows: On formation of a strong intermolecular hydrogen bond between *p*-cresol molecules, the electron density on the oxygen atom should increase. This dense distribution of the negative charge is supplied from the ring, especially from the ortho-positions by inductive and mesomeric mechanisms. Thus the chemical shift of the A-proton is displaced to a lower field in the concentrated range. This qualitative explanation is plausible for the systems of hydroxyl hydrogen bond so far investigated by the present author[2,3].

Table I gives the chemical shift of the ring proton systems (δ_{ring}) at the concentrations of zero and 1 mol. fractions, the dilution shift ($\delta_1-\delta_0$), the relative chemical shift and the spin coupling constant between A and B protons at infinite dilution, and the concentration where the lines of the spectrum coalesce. Figure 3 shows the position of the spectra of the ring protons schematically for the solutions investigated. The spectrum for benzene solution is displaced to a considerably high field compared to those for the other solutions. This is due to the anisotropic effect of benzene. The B-proton resonance at the infinite dilution for chloroform, carbon tetrachloride and dioxane solutions occur at about the same field in relation to one another, whereas the A-proton resonance for them occurs at fields different from one another. This fact also supports the inactiveness of the B-protons against the change in the environments. The B-proton resonance for acetone solution is the only exception: The resonance occurs at a slightly higher field than for the other solutions mentioned above. The same is observed for the ring protons of benzene in acetone solution[6]. Therefore, the preferential hydrogen bond interaction of an acetone molecule with the B-proton as suggested by Schneider and Schaefer[1] is denied in this case. This discrepancy may partly be attributed to the large dielectric constant of acetone[1].



Chemical shift refer to H_2O

Fig. 3. Ring proton spectra for *p*-cresol in various solutions.

In Fig. 3, the field where the resonance lines coalesce to a single line is indicated by a shaded range. It is surprising that the fields are almost the same for all solutions (about −1.74 p.p.m.) except benzene solution although the concentrations are different from one another. The coincidence of the field may have some meaning concerning the structure of the solutions or may rather be an accident. However, in this work, this phenomenon could not be well interpreted with the anisotropic effect of the aromatic rings in the solutions at the coalescent concentration. The single coalesced line in the concentrated range may suggest that only the same species of associated polymers as in pure *p*-cresol exists in this range. In benzene solution, the coalescence occurs at an exceptionally low concentration. This may be ascribed to the poor ability of the benzene molecule to disrupt the hydrogen bonds due to the geometrical similarity of the flat molecular shape of benzene and *p*-cresol.

It may be noted that the resonance fields of the methyl protons at the coalescent concentration for the four solutions are approximately +2.95 p. p. m., and this value is also nearly independent of the solvent. Accompanying the ring proton resonance data, this fact may also supply some information about the structure of the solutions.

Summary

The proton magnetic resonance spectra of *p*-cresol in several solutions were measured. The concentration dependence of the resonance in methyl protons suggests no remarkable effect of the hydrogen bonding on methyl protons. The resonance in the hydroxyl proton shows characteristic concentration dependences which are ascribed to the dissociation of the associated molecule in benzene, chloroform and carbon tetrachloride solutions and to the formation of new hydrogen bonds with solvent in acetone, dioxane and pyridine solutions. The ring proton resonance spectrum is a single line in concentrated range whereas it is an A_2B_2 type spectrum in dilute range. The splitting of the spectrum in dilute solutions is ascribed to the change in the screening of the proton ortho to the hydroxyl group affected by the change in the intermolecular hydrogen-bonding situation. The shielding of the proton ortho to the methyl group appeared to be unaffected by the same change.

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