Steric Effects of ortho-Groups on Hydrogen Bond Formation in Phenol Derivatives as Studied by Nuclear Magnetic Resonance

By Ichiro YAMAGUCHI

(Received December 20, 1960)

In the previous report¹⁾, the author pointed out that the chemical shift of the OH proton depends greatly on the relative position of the methyl groups to the OH group in dimethyl phenol isomers, and this was attributed to the steric effects of the methyl group on the formation of intermolecular hydrogen bond. The present report shows a dependence of the OH proton chemical shift on the size of the ortho-group.

The compounds investigated are 2, 6-dichlorophenol, 2, 6-dimethyl phenol and 2, 6-di-*t*-butyl-*p*-cresol. The chemical shifts of the OH proton in various solutions were determined by the side band technique refering to water as an external standard. The correction for the bulk diamagnetic susceptibility was not applicable except to the values extrapolated to infinite dilution because reliable data of the susceptibility for these compounds were not available.

In Figs. 1a and 1b, the OH resonance shifts (in p.p.m.) are plotted against the concentration of the solutions (in mole fraction). The curves for various solutions are comparatively separated in a wide range of the magnetic field from one another for 2, 6-dichlorophenol and 2, 6-dimethyl phenol, but not for 2, 6-di-*t*-butyl-*p*-cresol. This suggests that the size of the ortho-group would be a factor which affects the ability of the formation of an intermolecular hydrogen bond of a phenol. This effect was qualitatively pointed out by Batdorf with his NMR measurements²⁾.

As a measure of the extent of the ability of the hydrogen bond formation, the difference between the chemical shift at infinite dilution (extrapolated and then corrected for bulk diamagnetic susceptibility of the solvents) for carbon tetrachloride solution and that for acetone solution is taken. In Fig. 2, the values of the difference, Δ, are plotted against the size of the ortho-groups, for instance the Van der Waals radii. The data for phenol²·³⁾ are also plotted.

In Fig. 2, the followings are observed: First, the Δ value is larger as the radius is smaller. Secondly, the Δ value for 2, 6-dichlorophenol is found above the line connecting the points for phenol and dimethyl phenol. This discrepancy may be due to weak intramolecular hydrogen bond between OH and Cl groups. Linear extrapolation of the

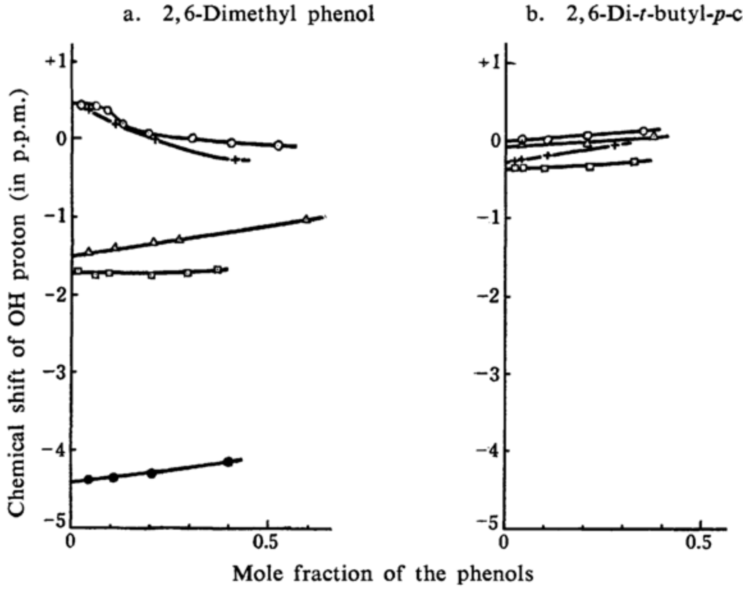
a. 2,6-Dimethyl phenol   b. 2,6-Di-*t*-butyl-*p*-cresol

Fig. 1. OH proton resonance shift refer to H_2O proton (susceptibility correction is not applied.).
Solvent: -○- CCl_4 -+- $CHCl_3$ -△- Ether -□- Acetone -●- Pyridine

---

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

2) R. L. Batdorf, Ph. D. thesis, Univ. of Minnesota, 1955.

3) C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

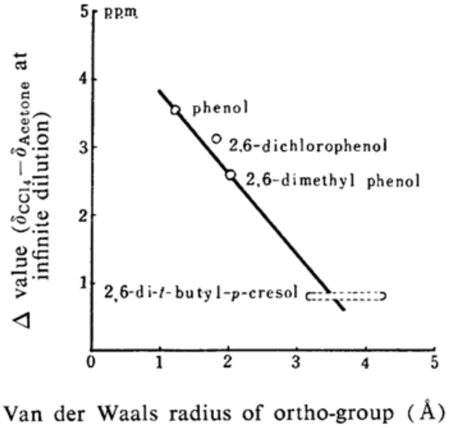

Fig. 2. Dependence of the ability of hydrogen bond formation of phenols on the size of ortho-group.

line connecting two points for 2, 6-di-alkyl phenols (alkyl=H and CH_3) to the Δ value of 0.8 gives a value approximately 3.5 Å as the Van der Waals radius corresponding to the size of the *t*-butyl group. This value seems to be reasonable for this group. Therefore it may be concluded that the ability of the formation of an intermolecular hydrogen bond in phenol derivatives is a linear function of the size of the ortho-group.

Radiation Applications Division
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken