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Solvent Effects in the Proton Magnetic Resonance Spectra of Phenols

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Résumé.

On montre que les spectres de résonance magnétique nucléaire des cycles aromatiques des phénols sont influencés par la formation de complexes avec les accepteurs de protons. Dans le phénol associé, la distance entre la raie de l'ortho et du meta hydrogène est plus petite que dans le phénol monomère. La formation de complexe déplace la raie de l'ortho hydrogène vers les champs élevés, il lui correspond une diminution de l'influence de l'atome d'oxygène sur la distribution des charges dans le cycle du phénol.

Le déplacement chimique de la raie de résonance du proton du groupe OH a aussi été examiné. La formation de liaisons hydrogène avec les cétones, éthers, etc... déplace la raie vers les champs faibles, la complexation π avec des solvants aromatiques déplace par contre la raie vers les champs élevés, par rapport à la position de la raie du OH dans le phénol non associé.

Les spectres des accepteurs de protons sont aussi modifiés par la formation de complexes.

As it has been shown by several authors [1, 2], NMR-spectroscopy is a sensitive method of studying hydrogen bonds. The chemical shifts of the O-H resonance that accompany hydrogen bond formation in phenols have been investigated by Ch. Huggins, G. Pimentel, J. Shoolery [3] and by M. Saunders [4].

Contrary to the methods used by these people, who made their measurements only in CCl_4 -solutions, we examined the concentration dependent proton resonance shift of the O-H-group of phenol, p-chlorophenol and o-chlorophenol in a number of different solvents. The measured resonance shifts for phenol are shown in fig. 1. The chemical shifts were evaluated by reference to the resonance line of the para-proton.

There are obviously three groups of different solvents. This behaviour differs from that in other well-recognized hydrogen bonding systems e.g. in aliphatic alcohols [5, 6, 7], acetic acid [8], etc., and is typical for the phenols because of their acid character [9].

The solvents of the first group produce a chemical shift of the hydroxyl-proton to lower field. These solvents are all good proton acceptors forming strong hydrogen bonds with phenol which is a good proton donor. The negative shift is attributed to the intense hydrogen bond that reduces the magnetic shielding of the proton. No solvent of the second group can form associations with phenol. For these non-polar solvents the O-H-group

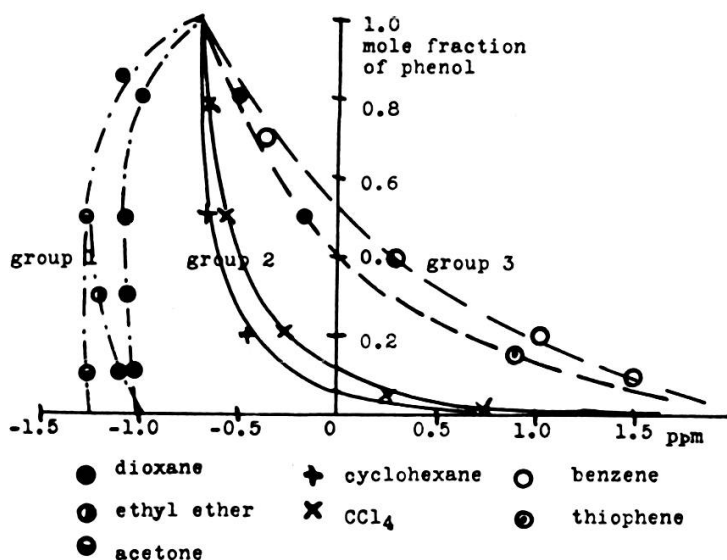


Fig. 1. O-H proton resonance of phenol in different solvents at a temperature of 23°.

shows the characteristic dilution-shift which corresponds to a dissociation of the intermolecular hydrogen bonds between the phenol molecules. M. Saunders has shown that in CCl_4 at a concentration of 0.01 mole fraction nearly all phenol is present as monomer.

The large shift of the hydroxyl-proton in the solvents of the third group suggests that here a hydrogen bond to the aromatic π -electrons of the solvent takes place. The infra-red measurements of L. Bellamy [10] display the same relationship. The π -cloud of the ring exhibits a diamagnetic shielding of the O-H proton and therefore its resonance line is shifted to higher field.

O-chlorophenol dissolved in the same substances shows a different behaviour than phenol and p-chlorophenol, see fig. 2.

For the first group the shift to lower field is much bigger in accordance with the fact that o-chlorophenol is a better proton donor than phenol. The solvents of the second and third group show the same properties. In

this case benzene acts as a solvent of the second group and is only able to break the intermolecular associations. This difference compared with phenol and p-chlorophenol comes from the presence of an intramolecular hydrogen bonding in o-chlorophenol that competes with the possibility of forming an intermolecular bond with the π -cloud.

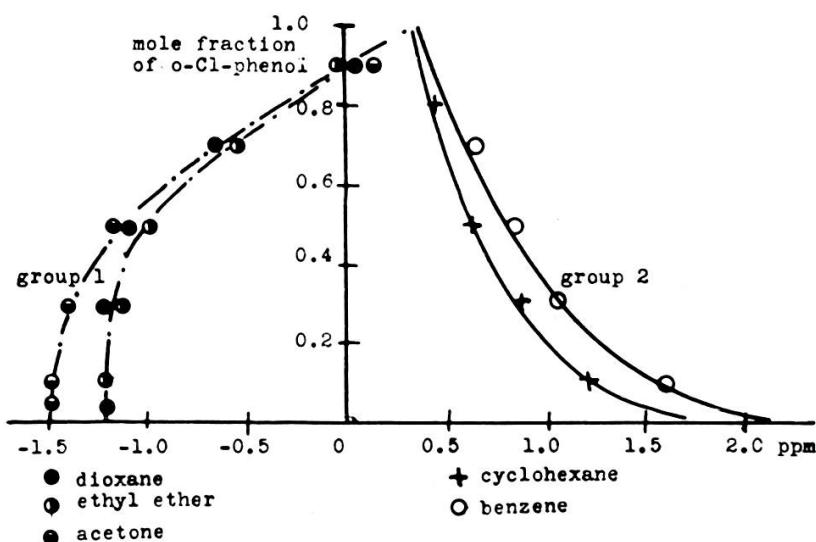


Fig. 2. O-H proton resonance of o-chlorophenol in different solvents.

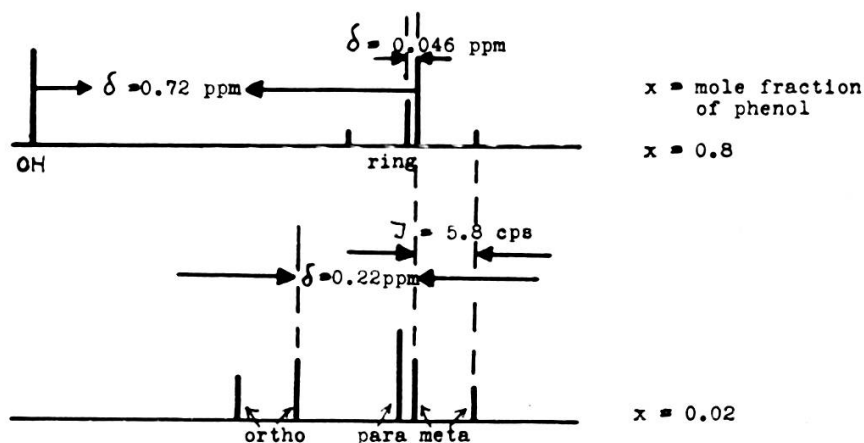


Fig. 3. Ring spectrum of phenol in the polymeric state and in the diluted state. Dissolved in carbon tetrachloride.

Investigations of the ring spectrum of phenols with a 56,4 Mc high resolution Varian spectrometer indicate a concentration dependent shift between the ortho- and meta-hydrogen proton resonance and there can be a rather big difference between the spectra of the pure and the diluted compound. At a concentration of 0,8 mole fraction of phenol in CCl_4 the

ortho- and the meta-lines lie close together (the para-line lies on the meta-line; because of the spin-spin coupling the ortho- and the meta-line are both split into a doublet). But in a solution where nearly all the phenol is present as monomer the distance between the ortho- and meta-line has increased, see fig. 3.

In the para-chlorophenol we have the same effect.

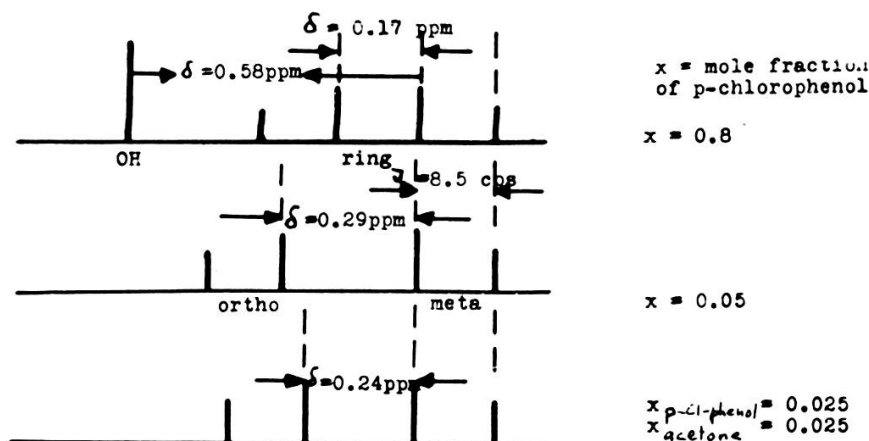


Fig.4. Ring spectrum of p-chlorophenol dissolved in carbon tetrachloride in the polymeric state, in the diluted state and with acetone.

If we attribute this shift to a break up of the hydrogen bonds, the distance between the resonances of the monomer should decrease again with an additional amount of a solvent of the first group such as acetone, or dioxane which participate in such bondings with phenols, see fig. 4.

Anisole which cannot form hydrogen bonds has at any concentration the same spectrum as phenol in the diluted state. So we can assume that this shift is an association effect due to hydrogen bond formation. There is a distinct shift between the meta- and ortho-lines of phenol or p-chlorophenol dissolved in acetone or ether etc., but it is not as large as in a solvent of the second group.

It seems that in the monomeric phase the difference between the shielding of the ortho- and the meta-hydrogen is much larger than in the associated phase, where the hydrogen bond formation weakens the influence of the oxygen atom on the ortho-protons, so that the ortho line lies at higher field in the polymeric state. In a benzene solution the shift between the ortho and meta hydrogen proton resonance is considerably larger than in the monomeric state. In this case the meta hydrogen seems also to be

influenced by the π -cloud. In a carbon tetrachloride solution with phenol concentration of 0.02 mole fraction the distance between the ortho and meta line of p-chlorophenol is 0.32 ppm while in a benzene solution of 0.05 the distance is 0.54 ppm.

Not only the proton donor shows this behaviour, also within the spectrum of the proton acceptor there is a shift, e.g. in tetrahydrofuran the distance between the two principal groups is bigger in a solution which contains phenol than in the pure state or in a solution with CCl_4 . Even in aliphatic alcohols such as ethylalcohol we have this effect. If a proton acceptor is present the distance between the CH_2 - and the CH_3 -resonances has increased, whereas in a solution with CCl_4 there is no remarkable shift.

In o-chlorophenol the shifts are less significant than in p-chlorophenol. There is hardly any difference between the shifts in the pure compound and a solution in a substance of the second or third group. A remarkable variation of the spectrum is visible in solutions with dioxane, acetone, ethyl ether, etc.

The influence of any association formed, especially on the ring spectra of aromatic compounds can be very significant.

An extended program of studies on these shifts due to hydrogen bond and to induced dipole interaction is in progress.

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