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1963

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Abstract

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INVESTIGATION OF THE HYDROGEN BOND BY THE N.M.R. METHOD

THE INFLUENCE OF STERIC HINDRANCE ON THE HYDROGEN BOND IN DI-ortho-ALKYLPHENOLS

(Presented by Academician V. N. Kondrat' ev, October 8, 1962)

Sterically hindered di-ortho-alkylphenols are widely used as inhibitors of free-radical reactions ([1]). One of the factors affecting the inhibiting activity of phenols is the degree of accessibility of the hydroxyl group. This steric factor may determine both the probability of abstraction of the hydrogen atom with formation of a phenoxyl radical and the stability of the latter. We investigated the influence of steric shielding of the OH group on the hydrogen bond of a series of di-ortho-alkyl-substituted phenols, using the method of high-resolution proton magnetic resonance (p.m.r.).

The measurements were carried out on a YaMR-US-2 spectrometer ([2]) at a frequency of 20.529 Mc/s. The chemical shifts of the p.m.r. signals τ ([3]) were measured relative to an internal standard, tetramethylsilane (TMS):

$$\tau = 10 - \frac{\Delta f}{20.529},$$

where Δf is the distance between the TMS signal and the line under investigation (in hertz). An increase in τ occurs when the signal is shifted into the region of a stronger magnetic field. The mean square error of measurement is ± 0.02. All measurements were carried out at room temperature, $20 \pm 2°$. The maximum concentration corresponded to a saturated solution, while the minimum was determined by the sensitivity of the spectrometer. In Figs. 1, 2, and 3 are shown, respectively, the dependences of the signals in the spectra of 2,6-xylenol, 2,6-diisopropylphenol, and ionol on the concentration in dry, alcohol-free CCl_4, ether, acetone, and triethylamine. The phenols studied were purified by distillation on a rectification column. The purity of the compounds was checked by plate chromatography. Owing to the use of an internal standard, the solvent effects (see, for example, ([4])) that cause a shift of the signal from the protons of the inert, nonpolar, and almost spherical TMS molecule are automatically taken into account. As is seen from Figs. 1, 2, and 3, the chemical shifts of the signals from the protons of the CH_3 groups and from the protons of the benzene ring remain practically unchanged, despite a change in the concentration of the compound with a magnetically anisotropic aromatic—

Fig. 1. Concentration dependences of the chemical shift τ of the proton signals of 2,6-xylenol for solvents: 1 —CCl_4, 2 —ether, 3 —acetone, 4 —triethylamine

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aromatic ring (4). In Figs. 1, 2, and 3 are shown the dependences of the positions of the signals from the methyl and ring protons only for dilution in CCl_4. Thus, it may be considered that the environment of the TMS molecules changes in the same way as the environment of the CH_3 groups and the hydrogen atoms of the benzene ring. Consequently, the change in the chemical shift of the proton signal from the OH group can be entirely attributed to the influence of intermolecular hydrogen bonding. Lowering the concentration of the substances studied in ether, acetone, and triethylamine causes a displacement of the OH signal toward a relatively weak field, whereas dilution in CCl_4 leads to a shift of the signal into a stronger field. This shows that the hydrogen bond formed by the hydrogen atom of the phenolic hydroxyl group with the donor atom of ether, acetone, or triethylamine is stronger than that between phenol molecules. The dependence upon dilution with triethylamine has a clearly expressed minimum at a ratio of 1 : 1, which corresponds to the formation of the maximum number of associates of the type

$$\overset{R}{}\quad \text{benzene ring} \quad —O \cdots HN^{+}(C_2H_5)_3$$

Fig. 2. Concentration dependences of the chemical shift τ of the proton signals of 2,6-diisopropylphenol. Notation as in Fig. 1.

The fact that dilution with acetone produces a more considerable shift of the OH signal toward weak field than dilution with ether is apparently connected with steric factors (the acetone molecule is more "suited" for penetration to the sterically shielded hydroxyl). This supposition is confirmed by the fact that, for unsubstituted phenol, the dilution curves with acetone and ether are located practically side by side (5).

Table 1

Shifts due to hydrogen bonding in infrared and NMR spectra

Compound	$\Delta\tau$	$\Delta\nu$, cm^{-1} (8)
Phenol	3.05	241
o-Cresol	2.04	172
2,6-Xylenol	0.72	120

Fig. 3

Figure 2: Fig. 3

Compound	$\Delta\tau$	$\Delta\nu$, cm^{-1} (^{8})
2,6-Diisopropylphenol	0.46	111
2,6-Di-*tert*-butylphenol	0.00	3

We shall consider the significance of the steric factor for self-association by comparing the dependence of the shift of the hydroxyl signal of a series of alkylphenols on concentration in CCl_4. In Fig. 4 are presented data for phenol (^{6}), *o*-cresol (^{7}), and the di-*ortho*-alkylphenols investigated in the present work. The role of steric shielding (the volume of the substituents in the *ortho* position) is manifested in the change in the initial chemical shift, in the character of the concentration dependence, and, above all, in the change in the magnitude of the displacement of the hydroxyl signal $\Delta\tau$ on going from the pure substance to zero concentration. The quantity $\Delta\tau$ may be taken as a characteristic of the strength of the hydrogen bond between molecules. In Table 1, with this quantity-

was compared with the frequency difference $\Delta\nu$ for the bands of the valence vibrations O—H corresponding to the free and bound states of the hydroxyl (^{8}). As the bulk of the ortho substituents increases, the band of the bound hydroxyl shifts toward higher frequencies, and the shift from the hydrogen bond $\Delta\tau$ decreases, which is evidently associated with an increase in the effective length of the hydrogen bond. The decrease in the strength of the hydrogen bond can explain the increase in inhibiting activity in the series 2,6-dimethyl-, 2,6-diisopropyl-, and 2,6-di-tert-butylphenol (^{9}) and the absence of further growth for the radicals C_6—C_8 (^{10}).

Fig. 3. Concentration dependences of the chemical shift τ of the proton signals of 2,6-di-tert-butyl-4-methylphenol (ionol). Designations are as in Fig. 1.

The concentration dependences of diorthoalkylphenols for solutions in CCl_4 are of interest because they have a horizontal portion in the region of low concentrations. As the bulk of the ortho substituents increases, “saturation” of the dependence occurs at higher concentrations, and for 2,6-di-tert-butylphenol and ionol (Figs. 3 and 4) the chemical shift of the hydroxyl does not depend at all on the concentration in CCl_4. Comparison of the experimental curves for 2,6-xylenol and 2,6-diisopropylphenol with theoretical curves obtained by the method of Saunders and Hyne (^{6}) indicates the predominance of tetrameric cyclic association. Dimeric formations, if they exist at all, are present in insignificant concentration.

Fig. 4

Figure 3: Fig. 4

Fig. 4. *I* –concentration dependences of the chemical shifts τ of the signals from the protons of the hydroxyl group of the following phenols: *a* –phenol (^{6}), *b* –*o*-cresol (^{7}), *v* –2,6-xylenol, *g* –2,6-diisopropylphenol, *d* –2,6-di-tert-butylphenol (^{11}). *II* –the same in the region of low concentrations.

Comparison of the values of the chemical shifts of the hydroxyl obtained by extrapolating the concentration curves for CCl_4 to zero concentration of phenols indicates a substantial influence of the substituents on the electron cloud of the O–H bond. For example, the chemical shift for ionol $\tau = 5.19$ appreciably exceeds the shift for 2,6-di-tert-butylphenol $\tau = 4.98$. Apparently, this circumstance is due to the influence of the inductive effect of the *p*-methyl group of ionol, which leads to an increase in the electron density at the hydroxyl proton and, consequently, to a shift of the ionol signal toward a stronger field.

One of the possible reasons for the change in the chemical shift of the OH signal upon introduction of alkyl groups into the *o*-positions may be the influence of the electric field of the dipole of the C–H bond (^{12}). Application of the equation

Buckingham' s (^{12}) shows that the indicated cause gives rise to a shift of 0.27 toward the weak field when a methyl group is introduced in place of hydrogen. This value agrees well with the difference in chemical shifts for phenol and 2,6-xylenol: $\Delta\tau = 0.21$.

The influence of substituents on the chemical shift of the OH group of phenols is currently being studied in greater detail.

The authors are grateful to T. Z. Shvartsman for participation in measuring the NMR spectra.

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Received
28 IX 1962

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