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^{1}H NMR SPECTRA AND INTERNAL ROTATION OF THE OH-GROUP IN 2,6-BIS-(DIETHYLAMINOMETHYL)-PHENOLS

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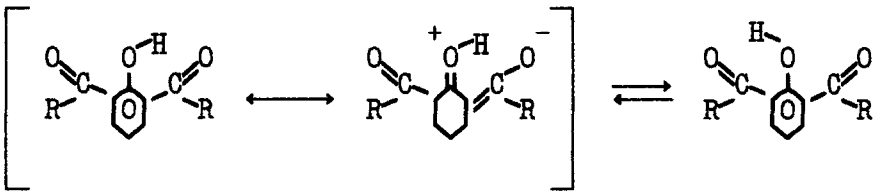
Abstract

^{1}H NMR spectra (200 MHz) of solutions containing various 4-X-2,6-bis-(diethylaminomethyl)-phenols (X= OCH_3, Cl, COOEt, NO_2) have been obtained in the temperature range 150 - 250 K. The signals of 3,5-aromatic protons as well as those of 2,6-CH_2-protons have been found to undergo doublet splitting due to slowing down internal rotation of the OH-group at 170 - 190 K. The frequency and activation energy values of the process have been determined by means of full line-shape analysis. The rotational barrier increases with strengthening of the intramolecular hydrogen bond, as indicated by the δ_{OH} chemical shift.

1. INTRODUCTION

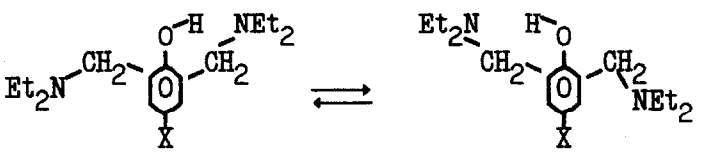
Internal rotation around a single C-O chemical bond in the molecules of phenols is known as a very fast process. The information about its frequences and rotational barrier values may be obtained from microwave spectra in gaseous phase

[1,2]. In the molecules of 2,6-disubstituted phenols with the substituents like NO_2, COR, COOR the rates of the rotation are low enough for the signals of non-equivalent nuclei in NMR spectra be observed separately at low temperature [3-5]. Two factors have been considered to be responsible for slowing down the process: 1) increase of the effective C-O bond order caused by a partial charge transfer to the substituent; 2) H-bonding between the groups which lowers the energy of the ground state and thus increases the energy level of the transitional state without H-bonding:



In the molecules studied earlier the two mechanisms affect the rotational barrier simultaneously, and it is difficult to separate them.

Di-substituted Mannich bases described in [6,7] seem to be suitable model substances for studies of H-bonding influence on the internal rotation process as no charge transfer takes place here. A strong H-bond has been found between the OH-group and the lone pair of the N-atom, with its spectral manifestations (δ_{OH}, ν_{OH}) depending on the substituent in the 4-position. (In some cases a partial intramolecular proton transfer has been detected [6].) In this paper the internal rotation in a range of 4-substituted 2,6-bis-(diethylaminomethyl)-phenols (X = OCH_3, Cl, COOEt , NO_2) is investigated by means of the dynamic ^1H NMR at low temperature (140 - 250 K):



The δ_{OH} chemical shift for the OH-proton is taken as an approximate measure of the H-bond energy [8].The absence of a considerable weight of the $O^{-}..HN^{+}$ ionic form with intramolecular proton transfer has been controlled by UV absorbtion spectra [6].

2. EXPERIMENTAL

2,6-disubstituted Mannich bases were synthesized as described earlier [7] and purified by molecular distillation at the room temperature. Deuterated solvents CD_2Cl_2 and C_2D_5Cl ("for NMR" grade) were purchased from "Isotope" (USSR). The technique of preparing samples for low temperature NMR using a vacuum line was reported in [8]. ^1H NMR spectra (200 MHz) were obtained using a AC-200Bruker instrument. The temperature was maintained and measured by a B-VT-1000 system with the accuracy $\pm$0.3 K. UV spectra were recorded on a UV-3100 Shimadzu spectrophotometer. Full line-shape analysis of the dynamic NMR spectra was performed using the procedure described in [9] in approximation of two collapsing singlets.

3. RESULTS AND DISCUSSION

Fig.1 shows the ^1H spectrum of 4-OCH_3-bis-(2,6-diethylaminomethyl)- phenol in a CD_2Cl_2 - C_2D_5Cl mixture at 163 K. The chemical shift of the OH-proton (δ_{OH}= 12.90 ppm) corresponds to a rather strong hydrogen bond.

The absence of any concentration dependence of the shift (in the range 10^{-4} - 10^{-3} M) proves the intramolecular character of this H-bond. The signals of 3,5-protons in the aromatic ring are observed separately, which indicates that the transformation of two equivalent forms at this temperature is a slow process in NMR time scale. It is to be noted, that the difference between the chemical shifts of 3,5-proton in this case is much larger (0.31 ppm), than for 2,6-dicar-

bonyl-phenols (0.05 ppm,[4]). This fact may be explained by a following speculation. The cis-conformation of the diethylaminomethyl- side chaine, not involved in H-bonding, would be unstable due to the interaction between the lone pairs of the nitrogen and oxygen atoms. Therefore, one of the two 3,5-aromatic protons must be situated in the field of the lone pair, the other being uninfluenced. The sygnals of two non-equivalent 2,6-CH_2-protons at 163 K are revealed separately, too. Heating leads to the collapse of the two doublets, corresponding to acceleration of the internal rotation (Fig.2).

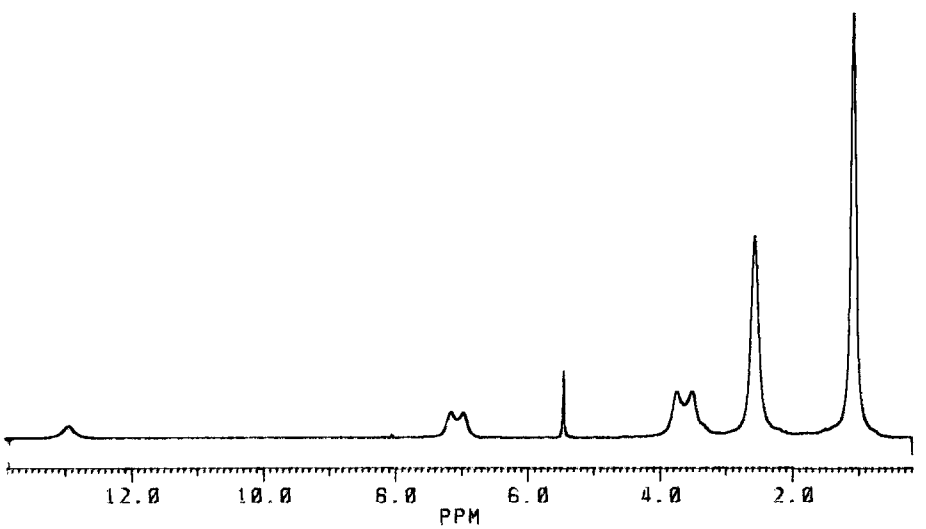


Figure 1. ^1H NMR spectrum of the solution, containing 5 10^{-4}M 4-OCH_3-bis-(diethylaminomethyl)-phenol in (CD_2Cl_2+C_2D_5Cl) at 163 K.

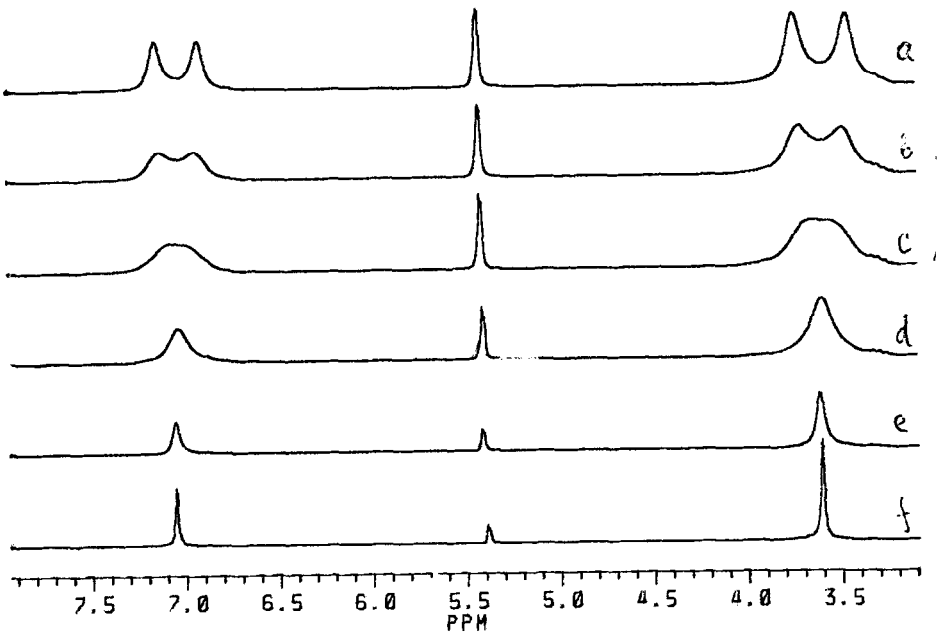


Figure 2. The spectrum of the solution (Fig.1) at 150 K (a); 163 K (b); 170 K (c); 178 K (d); 188 K (e); 198 K (f).

The spectra of the other 2,6-disubstituted Mannich bases appear similarly, the only difference being in the coalescence temperature of the signals. These spectra allow to evaluate the kinetic parameters of the process. As unresolved spin-spin coupling between the 3- and 5- aromatic protons must affect the shape of the corresponding signals and thus disturb the results, the lifetimes were calculated using the shape of the 2,6-CH_2- doublet. The T_2 values of the linewidths under the condition of the absense of any exchange process were obtained from the spectra of similar mono-2-substituted phenols. The data are presented in the table:

X	δ_{OH}(ppm)	$\tau^{-1}_{190\ K}(s^{-1})$	E_a(kcal/mole)
OCH_3	12.84	$7.5\ 10^3$	7.8
Cl	13.03	$1.2\ 10^3$	8.3
COOEt	14.23	$1.6\ 10^2$	9.7
NO_2	14.72	$3.2\ 10^1$	10.4

Rising of the δ_{OH} value in this range is caused mainly by strengthening of H-bond (though 4-substituent can give rise to some direct effect on δ_{OH}, which may hardly be measured). When compared with the rotational barrier for phenols without 2-substituents (3 - 4 kcal /mole, [1,2], the data obtained show, that the intramolecular H-bonding increases the activation energy of the internal rotation by the value of the H-bond energy (4 - 7 kcal /mole).

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