Hydrogen bonding in phenols. X*
The nuclear magnetic resonance data of hydrogen bonds of 2-hydroxydiphenylmethane, 2-hydroxydiphenyl ether, sulfide, and selenide

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On the basis of temperature measurements intramolecular and intermolecular hydrogen bonds of 2-hydroxydiphenylmethane, 2-hydroxydiphenyl ether, sulfide, and selenide in $CDCl_3$ solution have been studied. o-Cresol, guaiacol, 2-hydroxythioanisole, and 2-hydroxyselenoanisole have been used as model compounds. From the temperature dependence of the chemical shifts of OH protons a possibility to resolve various types of hydrogen bonds in the compounds studied has been discussed.

На основе температурных измерений изучались внутримолекулярные и межмолекулярные водородные связи 2-гидроксидифенилметана, 2-гидроксидифенилоксида, 2-гидроксидифенилсульфида и 2-гидроксидифенилселенида в ~0,2 М растворе $CDCl_3$. В качестве модельных соединений использовали о-крезол, гваякол, 2-гидрокситиоанизол и 2-гидроксиселеноанизол. Обсуждается возможность различать отдельные типы водородных связей в изучаемых соединениях на основе полученных зависимостей химических сдвигов OH протонов от температуры.

It is known that the chemical shift of the proton involved in hydrogen bonding is observed at lower fields than that of the free proton. However, in some cases, namely if proton-acceptor group is aromatic, chemical shifts of OH protons involved in hydrogen bonding are observed at higher fields [1, 2]. Besides this the chemical shifts are influenced by an anisotropy and an orientation of the proton-acceptor group. While the chemical shifts of protons involved in the intermolecular hydrogen bonding strongly depend on temperature and concentration, those involved in intramolecular hydrogen bonding are only little influenced, and even by strong hydrogen bonds the change of chemical shifts is not measurable.

In this work, chemical shifts of the OH protons of eight o-substituted phenols recorded at various temperatures are interpreted.

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Experimental

Phenols investigated were prepared according to the literature: 2-hydroxydiphenyl-methane (*II*) [3] (b.p. 171—173°C/1733 Pa, 32% yield); 2-hydroxydiphenyl ether (*IV*) [4] (m.p. 103.5—105°C, 53% yield); 2-hydroxydiphenyl sulfide (*VI*) [5] (b.p. 140—141°C//400 Pa, 25% yield); 2-hydroxydiphenyl selenide (*VIII*) [6] (b.p. 130—131°C/66.6 Pa, 63% yield); 2-hydroxyselenoanisole (*VII*) [7] (b.p. 53—54°C/133.3 Pa, 35% yield), and 2-hydroxythioanisole (*V*) [8] (b.p. 104—105°C/2932.6 Pa, 65% yield). Compounds were purified by crystallization and chromatographically.

The n.m.r. spectra were recorded with a Tesla BS 487 A instrument (80 MHz) with TMS as internal standard. Measurements were carried out for 0.19 → 0.12 M solutions in CDCl$_3$ at several temperatures (−70°C → +60°C ± 1°C) with accuracy ±0.05 p.p.m.

Results and discussion

One should expect the lowest and the highest chemical shifts of protons with selene and oxygen compounds, respectively. However, from the n.m.r. spectral data of the compounds studied (Table 1) it is evident that the chemical shifts of proton are influenced by the nature of the atoms (O, S, Se) involved in hydrogen bonding as well as by the geometry of the carbon group attached to these atoms. Actually, the highest chemical shifts of protons are observed with sulfides pointing out that the OH proton is most strongly bonded on sulfur atom and therefore it is the least shielded. This is in agreement with the fact that the smallest influence of temperature over the range from −70°C to +30°C on the chemical shift of the OH proton is observed with compound *V* (6.92 → 6.62 δ) and with compound *VI* (6.70 → → 6.50 δ).

The temperature dependence of the chemical shifts of the OH protons of o-cresol and 2-hydroxydiphenylmethane in the mentioned temperature range can be seen in Fig. 1. With o-cresol, as it appears from the temperature dependence of the chemical shift of the OH protons (Fig. 1) only one type of intermolecular association can exist which could be explained by a linear association through the OH   O bond. With increasing temperature the chemical shift gradually decreases and approaches the value δ(p.p.m.) = 4.50 which belongs to the signal of the OH proton of o-cresol at infinite dilution *i.e.* without intermolecular hydrogen bonding. The shape of the curve of 2-hydroxydiphenylmethane suggests that at given concentration over the temperature range used this system can form also another type of hydrogen bond (inflex at −10°C) besides a linear intermolecular hydrogen bond of the OH   O type.

If we observe the shape of the curve of 2-hydroxydiphenylmethane starting from +60°C to lower temperatures we can see that this curve is parallel to −10°C with the curve of o-cresol. From this it can be assumed that in this range the changes are similar to those in o-cresol *i.e.* it forms the OH   O intermolecular hydrogen bond. The inflex at −10°C is rather unexpected while with decreasing temperature one could expect another intermolecular association through the OH   O bond (the course of the curve denoted by dotted line) or through another type of hydrogen bond which should mean a further deshielding of the OH protons and the course of the curve should be steeper. In our case another type of association can exist in which a part of protons is paramagnetically shielded. Over the whole temperature

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Table 1

The temperature dependence of the chemical shift (δ) of OH protons of compounds of the type
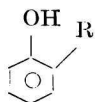
Com-pound	R	Temperature, °C																	
		−70	−60	−50	−40	−35	−30	−25	−20	−15	−10	0	10	20	24	30	40	50	60
I	CH$_3$		5.85		5.41						4.96			4.72	4.71			4.58	
II	CH$_2$Ph	5.57		5.25			5.00		4.95		4.92	4.80	4.73		4.66	4.63		4.56	
III	OCH$_3$		⁻.90		5.82				5.75				5.65		5.61	5.60			
IV	OPh	6.02		5.88			5.79				5.72		5.64		5.59	5.56		5.50	5.47
V	SCH$_3$		6.92		6.85				6.78		6.74		6.69		6.63	6.62		6.55	
VI	SPh	6.70		6.65		6.62		6.60		6.59		6.56	6.53		6.50	6.50	6.48		
VII	SeCH$_3$	6.81		6.75			6.68				6.61		6.54		6.50	6.48			6.40
VIII	SePh	6.75		6.59			6.55				6.50		6.45		6.40	6.40		6.36	6.34

range the average values of chemical shifts of the OH protons of 2-hydroxydiphenyl-methanes are also influenced by the intramolecular hydrogen bond of the OH · π type. As chemical shifts over the whole temperature range are shifted to higher fields as compared with the values of o-cresol, one could assume that besides the deshielding of proton due to hydrogen bond the shielding effect of the aromatic nucleus plays also a definite role.
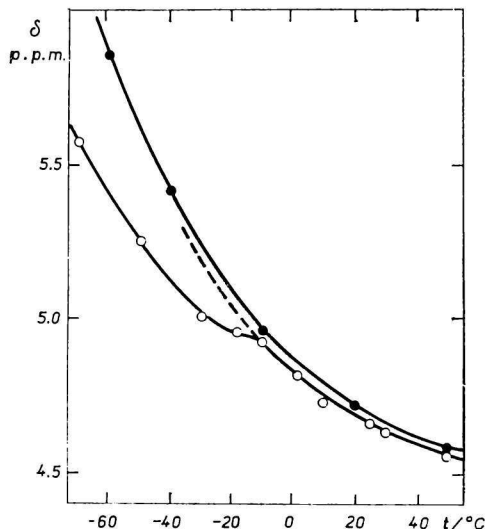

Fig. 1. The temperature dependence of the chemical shift of OH protons of o-cresol (●) and 2-hydroxydiphenyl-methane (○).
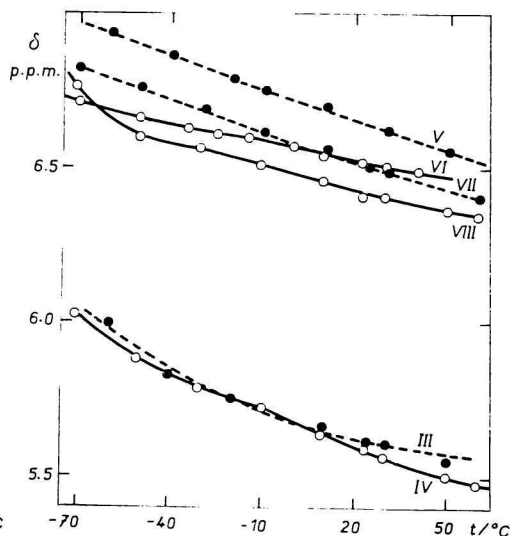
Fig. 2. The temperature dependence of the chemical shift of OH protons of compounds III—VIII.

In Fig. 2 the curves illustrate the temperature change of chemical shifts of the OH proton of guaiacol and 2-hydroxydiphenyl ether, 2-hydroxythioanisole and 2-hydroxydiphenyl sulfide, 2-hydroxyselenoanisole and 2-hydroxydiphenyl selenide.

The possibility of forming intermolecular associations through hydrogen bonds with these compounds is larger than that with the above-mentioned. This fact is also reflected in the shape of the appropriate curves. Assigning of individual inflexes to certain associated forms is problematic without further detailed investigation. The difference in δ(p.p.m.) values in the case of compounds containing various bridge atoms (O, S, Se) is given by different energy of the OH O, OH · S, and OH Se interaction. With respect to the complexity of interpretation of the results obtained with the compounds studied it is not possible to correlate chemical shifts of the OH protons and their relative changes, respectively, with wavenumber shifts of the stretching vibrations of OH bonds.

References

1. Emsley, J. W., Feeney, J., and Sutcliffe, L. H., *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. *1*. Pergamon Press, Oxford, 1966.
2. Vinogradov, S. N. and Linnel, R. H., *Hydrogen Bonding*. Van Nostrand — Reinhold New York, 1971.
3. Wheatley, W. B., Cheney, L. C., and Binkley, S. B., *J. Amer. Chem. Soc. 71*, 64 (1949).
4. Ungnade, H. E., *J. Amer. Chem. Soc. 63*, 2091 (1941).
5. Hilbert, G. E. and Johnson, T. B., *J. Amer. Chem. Soc. 51*, 1526 (1929).
6. Keimatsu, S., Yokota, K., and Suzuki, H., *J. Pharm. Soc. Jap. 52*, 961 (1932); *Chem. Abstr. 27*, 2434^5 (1933).
7. Keimatsu, S., Yokota, K., and Satoda, I., *J. Pharm. Soc. Jap. 53*, 993 (1933); *Chem. Abstr. 29*, 7301 (1935).
8. Holmes, E. L., Ingold, Ch. K., and Ingold, E. H., *J. Chem. Soc. 1926*, 1687.

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