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# The Intramolecular Hydrogen Bonding in *o*-Hydroxybenzyl Alcohol

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**Synopsis.** IR and PMR spectral investigations showed that *o*-hydroxybenzyl alcohol in a dilute solution in $CCl_4$ existed predominantly in two internally bonded forms, **A** and **B**, and probably also in **C**.

The infrared $\nu_{OH}$ data of *o*-hydroxybenzyl alcohol (**1**) in a dilute solution in $CCl_4$ have previously been reported,[1] but not discussed in detail in relation to the hydrogen bonding, probably because of its complicated system involving two hydroxyl groups and three hydrogen-accepting sites. This problem will be elucidated in this note.

In our infrared reinvestigation, **1** in a dilute $CCl_4$ solution obviously showed, in the $\nu_{OH}$ region, three bonded OH bands at 3620, 3605, and 3429 $cm^{-1}$; the first two overlapped one another, and there was no significant band due to a free aliphatic OH absorption. From a comparison with the data of the corresponding methyl ethers (**2** and **3**) listed in Table 1, the 3429 $cm^{-1}$ band can undoubtedly be assigned to the aromatic OH group bonded to the aliphatic OH-oxygen atom, and the 3605 $cm^{-1}$ band probably masks a free aromatic OH band which should appear near 3610 $cm^{-1}$. The $\varepsilon$ value of this masked band can be calculated to be *ca.* 24 by using the $\varepsilon$ values of the other aromatic OH bands ($=20.2\times 90.0/75.7$).

The 3620 and the 3605 $cm^{-1}$ bands must then be allocated to the aliphatic OH species bonded to two hydrogen-accepting sites, the aromatic OH-oxygen atom and the $\pi$-electrons; the weaker 3620 $cm^{-1}$ band can correspond to the $\pi$-bonded OH absorption of $\alpha$-unsubstituted benzyl acohols, which always appears near 3617 $cm^{-1}$, independently of the ring-substituent,[2] while the stronger 3605 $cm^{-1}$ band can be assigned to the O-bonded OH group. **4** shows only a single O-bonded OH band at 3608 $cm^{-1}$.

The above assignments are consistent with the OH-PMR data. The OH chemical shifts from TMS for *m*- or *p*-substituted benzyl alcohols at an infinite dilution in $CCl_4$ decrease with an increase in the sigma value of the substituent and with a decrease in the integrated-intensity ratio of the infrared $\pi$-bonded OH band,[3] as Fig. 1 shows; this indicates that the $\pi$-bonded OH-protons are subject to a diamagnetic anisotropy effect of the benzene ring and that this effect is dominant over a possible deshielding effect of the OH···$\pi$-bond. On the contrary, the OH-proton of **3** and **4** resonates at a lower field, and this down-field shift increases with an increase in the relative intensity of the infrared 3605 $cm^{-1}$ band. The PMR and IR data are consistent with one another if the 3605 $cm^{-1}$ band is due to the O-bonded OH group and if a deshielding effect of the hydrogen bond is

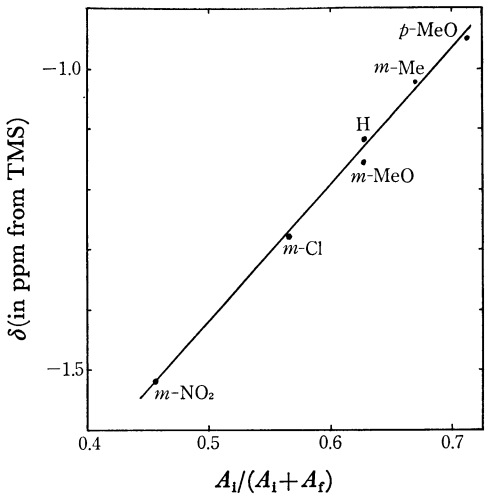
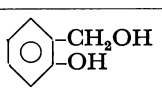
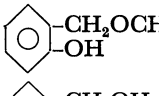
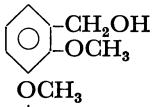
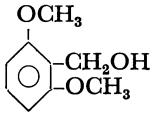


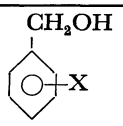

Fig. 1. Correlation between the OH-chemical shift ($\delta$) and the relative population of the $\pi$-bonded OH species ($A_1/(A_1+A_t)$).

Table 1. Apparent data of *o*-hydroxybenzyl alcohol and related compounds

| | Compound | $\nu_{OH}$ in $cm^{-1}$ ($\varepsilon$) of | | | |
|---|---|---|---|---|---|
| | | Free OH | $\pi$-bonded OH | O-bonded OH | |
| 1 |  | — | 3620(45.3)* | 3605(90.4) | 3429(75.7) |
| 2 |  | 3612(20.2) | — | — | 3395(90.0) |
| 3 |  | 3639(20.6)* | 3619(37.7)* | 3605(46.7) | — |
| 4 |  | — | — | 3608(76.5) | — |

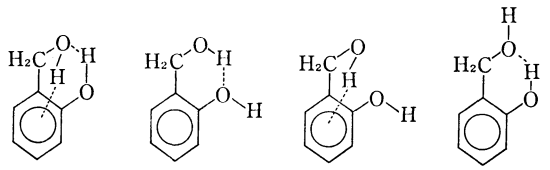
* Shoulder.

Table 2. Dilution shift for the OH-proton

|  | X | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *p*-$CH_3O$ | *m*-$CH_3$ | H | *m*-$CH_3O$ | *m*-Cl | *m*-$NO_2$ | *o*-$CH_3O$ | 2,6-di-$CH_3O$ |
| $\delta$ (in ppm from TMS) | −0.95 | −1.02 | −1.12 | −1.16 | −1.28 | −1.52 | −1.57 | −1.82 |

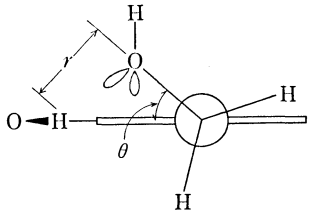
operative on the OH-proton; in this case, the proton is further subject to an anisotropy effect of the ring-current, which will be rather paramagnetic, because it must be located nearby on the plane of the benzene ring.

On the basis of the above findings and considerations, and, further, if the $\nu_{OH}$ of a free OH group is not decreased by the bonding of the O atom with another OH group,[5] the monomeric *o*-hydroxybenzyl alcohol in $CCl_4$ may exist predominantly in two internally bonded forms: **A**, in which the aromatic OH group is bonded to the oxygen atom of the $\pi$-bonded aliphatic OH group, and **B**, in which the aliphatic OH group is bonded to the free aromatic OH-oxygen atom, and probably also in **C**, in which the aromatic and the aliphatic OH group are free and $\pi$-bonded respectively, but not in **D**, in which the aromatic OH group is bonded to the free aliphatic OH-oxygen atom:



**A** **B** **C** **D**

In **A**, the aromatic OH group will lie substantially on the plane of the benzene ring, as was suggested in the case of 2,6-dialkylphenols,[8] and the C–O axis of the hydroxymethyl group will be staggered by $\theta$ around the ring plane and located at an O–H distance ($r$) which is not much longer than the O–H bond distance of 0.96 Å, in such a manner that one of the $sp^3$-orbitals occupied by the n-electrons of the oxygen atom is directed toward the aromatic O–H bond so as to overlap with the antibonding orbital of the latter, as is shown in the figure:



Such torsion of the C–O axis from the normal position[9] in relation to the ring plane must be caused by the hydrogen bonding with the aromatic OH group. A Büchi's Dreiding-model examination shows that, when $\theta$ is, *e.g.*, 30°, $r$ is equal to *ca.* 1.5 Å; in this case, the two OH groups will be able to be O- and $\pi$-bonded respectively, because (1) this O···H distance corresponds empirically to a spectral shift of *ca.* 100 $cm^{-1}$ of the bonded OH in aliphatic diols,[6] and to the much larger shift which can be expected for the bonded aromatic OH group in the figure, and (2) $\pi$-bonding is suggested in the quasi-equatorial form, with $\theta$ being somewhat larger than 30°, of 1-tetralols.[10]

## Experimental

All the alcohols are known and those except commercially available products were prepared by the usual methods; their purity was checked by their physical constants, PMR spectra and/or chromatograms.

The IR spectra were recorded at *ca.* 25 °C on a JASCO-DS-403G spectrometer (concentration: 0.003 mol/l or less in $CCl_4$: cell-thickness: 5.0 cm).

The PMR spectra were recorded on a JEOL-LNM-4H-100 spectrometer operating at 100 MHz; dilution experiments were carried out at concentrations down to 0.01 mol/l in $CCl_4$. The results are summarized in Tables 1 and 2.

### References

1) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1947**, 1260; M. M. Davies, *Trans. Faraday Soc.*, **36**, 1114 (1940); A. E. Martin, *Nature*, **166**, 474 (1950).

2) M. Ōki and H. Iwamura, This Bulletin, **32**, 955 (1959); and the value of $A_i/A_f$ described in this paper was converted into the ratio of $A_i/(A_i+A_f)$ in Fig. 1, where $A_i$ and $A_f$ denote the integrated intensities of the $\pi$-bonded and the free OH bands, respectively.

3) Such a notable substituent-dependence of $\delta$ is not observed in $\alpha,\alpha$-dimethylbenzyl alcohols.[4]

4) M. Oki and H. Iwamura, *ibid.*, **36**, 1 (1963).

5) This assumption is consistent with the available data of intramolecular OH···OH bondings, as was evidenced particularly in 1,4-diols with spectral shifts of *ca.* 150—190 $cm^{-1}$.[6,7]

6) L. P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2492 (1952).

7) L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, and L. E. Eberson, *ibid.*, **86**, 650 (1964).

8) K. U. Ingold, *Can. J. Chem.*, **38**, 1092 (1960); Z. Yoshida, N. Ishibe, and K. Shobatake, *Kogyo Kagaku Zasshi*, **68**, 808 (1965).

9) J. C. Evans, *Spectrochim. Acta*, **17**, 129 (1961).

10) H. Iwamura and K. Hanaya, This Bulletin, **43**, 3901 (1970); N. Mori, M. Yoshifuji, Y. Asabe, and Y. Tsuzuki, *ibid.*, **44**, 1137 (1971).