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NMR STUDY OF THE HYDROGEN BONDING OF STERICALLY
HINDERED PHENOLS WITH ALICYCLIC ETHERS AND PYRIDINE

Key Words: hydrogen-bond chemical shift, enthalpy change, hindered phenols,
alicyclic ethers, pyridine

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INTRODUCTION

In a preliminary report¹ it was shown that the hydrogen-bond chemical shift, Δ_{AB} , correlates with the change in enthalpy, ΔH , in the interaction of chloroform with a series of closely related oxygen and nitrogen bases. In this communication, we report the hydrogen bonding parameters for the interaction in cyclohexane medium between 2,4,6-tri-*t*-butylphenol and tetrahydrofuran, tetrahydropyran and pyridine, and between 2,6-di-1-adamantyl-4-*t*-butylphenol and pyridine. There is correlation between the Δ_{AB} and ΔH for the same proton donor (2,4,6-tri-*t*-butylphenol) and the closely related alicyclic bases, and for the same base (pyridine) and the two closely related sterically hindered phenols. The temperature dependence of the Δ_{AB} in these systems is also reported.

EXPERIMENTAL

The procedures for the purification of the materials used, the preparation of the acid base solutions in cyclohexane for the chemical shift measurements, the NMR spectrometer used, and the evaluation of the hydrogen bonding parameters, K , Δ_{AB} , ΔH and ΔS , have been described

previously.² The synthesis of 2,6-di-1-adamantyl-4-*t*-butylphenol has been described.³ The Δ_{AB} is the difference between the chemical shift of the phenolic proton in the acid base dimer AB and the chemical shift of the free phenolic proton in cyclohexane solution at the same temperature.

RESULTS AND DISCUSSION

The highly hindered phenols are not expected to self-associate in dilute cyclohexane solution, but the bases which can form hydrogen bonds of appreciable strength with them are limited to cyclic ones such as alicyclic ethers and pyridine whose particular geometry can permit the electron donor site to gain access to the hydroxyl proton. The *ortho* adamantyl groups offer more steric hindrance to the approach of a proton donor than do the *t*-butyl groups, as the alicyclic ethers show smaller extent of interaction with the di-*ortho*-adamantyl-substituted phenol. The Table shows the parameters obtained for the various hydrogen bonding systems.

The Δ_{AB} and ΔH values for the interaction of 2,4,6-tri-*t*-butylphenol with tetrahydrofuran are significantly different from those for the interaction with tetrahydropyran, the difference no doubt reflects the differences in the basicity of the oxygen donors and the steric hindrance effect of the alicyclic chains in the association. However, there is remarkable agreement in the ratios of Δ_{AB} to ΔH in these two interactions, indicating that the Δ_{AB} correlates with the ΔH for minor structural changes in the base.

In the case of pyridine interacting with the two substituted phenols, the Δ_{AB} and ΔH values are significantly different as a result of the

TABLE 1
Hydrogen Bonding Parameters obtained in Cyclohexane Medium*

Phenol	Base	$\frac{K}{M^{-1}}$ 34°C	$\frac{\Delta_{AB}}{\Delta_{AB}}$ (ppm)	$\Delta_{AB} = f(t)$ (ppm, $t^{\circ}\text{C}$)	ΔH (kJ/ mol)	ΔS (J K $^{-1}$ mol $^{-1}$)	$\Delta_{AB}/ \Delta H $ (ppm kJ $^{-1}$ mol) (34°C)
2,4,6-tri-t-Bu	Tetrahydrofuran	0.35	1.14	1.21 - 0.0025t	18.0	67	0.0633
2,4,6-tri-t-Bu	Tetrahydropyran	0.36	1.02	1.13 - 0.0031t	15.5	59	0.0658
2,4,6-tri-t-Bu	Pyridine	0.65	2.93	3.29 - 0.011t	16.9	59	0.173
2,6-di-l-Ad- 4-t-Bu	Pyridine	0.46	2.28	2.55 - 0.0079t	14.2	53	0.160

* Uncertainties: $K \pm 0.02 M^{-1}$, $\Delta_{AB} \pm 0.02$ ppm, $\Delta H \pm 0.45$ kJ/mol, $\Delta S \pm 2$ J K $^{-1}$ mol $^{-1}$.

difference in the steric hindrance effect of the *ortho* substituents, but the ratios of the experimental Δ_{AB} to ΔH are in good agreement, indicating that the Δ_{AB} also correlates with the ΔH for minor structural changes in the proton donor. It is to be noted that in the case of pyridine as base, the experimentally observed Δ_{AB} is not the true hydrogen-bond chemical shift as it contains a component from the aromatic ring current effect of the pyridine.⁴ As the hydrogen bonding to pyridine is stronger in the case of the tri-*t*-butylphenol, the hydrogen bond must be shorter so that the phenolic proton is closer to the pyridine ring where the ring current effect is larger.⁵ The contribution to the experimental Δ_{AB} arising from the ring current effect should therefore be larger in the case of the tri-*t*-butylphenol. It is expected that if this component arising from the ring current effect were subtracted from the experimental Δ_{AB} , the resulting Δ'_{AB} value would yield ratios of Δ'_{AB} to ΔH that are more nearly equal than those shown in the Table for the interaction between the substituted phenols and pyridine. The effect of the ring current effect on the measurement of the hydrogen bonding to pyridine by NMR spectrometry is discussed elsewhere.⁶

REFERENCES

1. K.F. Wong, T.S. Pang and Soon Ng, J.C.S. Chem. Comm., 55 (1974).
2. T.S. Pang and Soon Ng, Spectrochim. Acta, 29A, 207 (1973).
3. Soon Ng, J.C.S. Perkin II, 1514 (1972).
4. P.J. Berkeley, Jr. and M.W. Hanna, J. Phys. Chem. 67, 846 (1963).
5. C.W. Haigh and R.B. Mallion, Org. Magn. Resonance, 4, 203 (1972).
6. T.S. Pang and Soon Ng, submitted to J. Magn. Resonance.

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