

The 1:2 Complex of Piperazine with Some Phenols: Hydrogen Bonding Pattern Involved in Transition States in Solution

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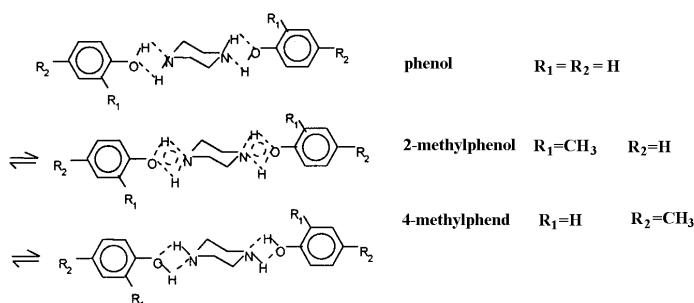
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Abstract: A novel model for the 1:2 complex of piperazine with some phenols in solution is established and verified. In CDCl₃ solution, one piperazine molecule is tied to two phenol molecules by hydrogen bonds of O—H---N and N—H---O. And the protons of >NH and -OH groups exchange quickly and simultaneously between the atoms of phenol oxygen and piperazine nitrogen.

Keywords: Piperazine, phenol, hydrogen bond, ¹HNMR, ESI-MS.

Previous calorimetric and IR studies¹ had showed that, in a system of secondary amine and unhindered phenol, hydrogen bonds of O—H---N and N—H---O concurred to appear. Fast proton exchange between proton donor and acceptor in solution is usual phenomenon²⁻⁴. Therefore, a novel model (**Scheme 1**) for the 1:2 complex of piperazine (Pip) respectively with phenol (Ph), 2-methylphenol (*O*-MPh), 4-methylphenol (*P*-MPh) (abbreviated generally as Pip·2XPh) in solution is now established. As showed in **Scheme 1**, one Pip molecule is tied to two XPh molecules by hydrogen bonds of O—H---N and N—H---O. And the protons of >NH and -OH groups exchange quickly and simultaneously between the atoms of XPh oxygen and Pip nitrogen.

Scheme 1. Arrangement of Pip·2XPh in CDCl₃ media



Crystals of Pip·2XPh in exact 1:2 molar ratio were prepared by recrystallization from ethanol. The ¹HNMR spectra of Pip·2XPh and the original constituents were recorded on a Bruker 500(MHz) spectrometer, using CDCl₃ as solvent at 20°C. The chemical shifts

are listed in **Table 1**. When one Pip molecule and two XPh molecules were kept in a complex, the original signals of >NH and -OH merged into a single signal. The proton exchange involved in hydrogen bonding was thus evidenced. Because the proton exchange too fast to be observed on NMR time scale, in the model, the protons of -OH and >NH are indistinguishable with each other, and appears as a merged signal in ^1H NMR spectrum. The great downfield-shifts of >NH in the spectra of Pip·2XPh, in comparison with that of the original Pip, inferred that the protons of >NH became largely deshielded. From this point of view, one can see further that the protons of >NH are held at the deshielded area of phenol benzene ring.

Table 1. Chemical shifts of Pip·2XPh, and the original constituents (20°C)

	Pip	Ph	<i>O</i> -MPh	<i>P</i> -MPh	Pip·2Ph	Pip·2 <i>O</i> -MPh	Pip·2 <i>P</i> -MPh
NH	2H, 1.81						
OH		1H, 5.20	1H, 4.34	1H, 4.78			
NH+OH					4H, 5.60	4H, 5.24	4H, 5.47
>CH ₂	8H, 2.69				8H, 2.93	8H, 2.90	8H, 2.92
C-H2		2H, 6.83		2H, 6.75	4H, 6.78		4H, 6.70
C-H3		2H, 7.23	1H, 6.75	2H, 7.05	4H, 7.20	2H, 6.66	4H, 7.00
C-H4		1H, 6.92	1H, 7.07		2H, 6.85	2H, 7.02	
C-H5			1H, 6.84			2H, 6.77	
C-H6			1H, 7.11			2H, 7.10	
CH ₃			3H, 2.24	3H, 2.28		6H, 2.23	6H, 2.25

The electrospray mass spectrum of Pip·2*P*-MPh was demonstrated on an Esquire spectrometer, and showed: m/z , 107($\text{C}_7\text{H}_8\text{O}^-$), 301.5 ($\text{C}_7\text{H}_8\text{OH}^- \cdot \text{C}_4\text{H}_{10}\text{N}_2 \cdot \text{C}_7\text{H}_8\text{O}^-$). The peak of 301.5 ($M-1$) was an irrefutable evidence of the negative ionized cluster of which the neutral origin had the same formula with that of the model. In a cluster of one Pip molecule and two *P*-MPh molecules, proton exchange can occur in the pattern showed in **Scheme 1**.

The ^1H NMR spectra of Pip·2*P*-MPh had been further performed at different temperatures. With the temperature changed from 40°C to -20°C, the merged signal remained uniform in shape, and shifted greatly from 4.68 to 6.18 ppm. The inert proton signals appeared approximately at the same region as that of original *P*-MPh and Pip. The downfield-shift of the merged signal suggests that the protons of >NH are held closer to the deshielded area of benzene ring upon cooling where the formation of hydrogen bond is favored.

References

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