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# 2-Phenyliminomethylphenols, 2-Phenylaminomethylphenols and their Copper(II) Complexes

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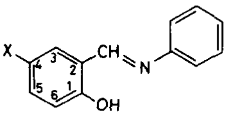
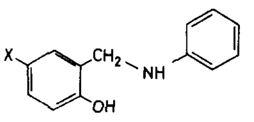
*Syntheses of 2-phenyliminomethylphenols (I) and 2-phenylaminomethylphenols (II) are described. Acid dissociation constants, determined potentiometrically, for the amines (II) are related to substituent constants; values are not obtained for Schiff bases(I) due to their hydrolysis. IR spectra of the amines (II) indicate chelate ring formation via O–H···N hydrogen bonding. NMR spectra for Schiff bases (I) are consistent with the phenol-imine tautomer, not the ketone-amine tautomer. Ligands (I) form bis-complexes with copper(II) while the amines (II) form copper(II) complexes in the presence of acetate anion; magnetic measurements for these indicate no metal–metal interaction in the solid state.*

## Introduction

Schiff bases, derived from the condensation of aldehydes or ketones with ammonia or primary amines, are well known and in 1840, Ettling [1] reported the copper(II) complex formed from copper(II) acetate, salicylaldehyde and aqueous ammonia. This and other allied work are excellently reviewed by Holm [2]. This earlier work includes the formation of metal chelates of Schiff bases derived from salicylaldehyde and aniline. These bases (*I*) and their reduced products (*II*) are both potentially bidentate chelating agents. We report here the synthesis and properties of a series of 4-X-substituted derivatives and their copper(II) complexes.



(I)



(II)

## Experimental

### Preparations

The Schiff bases (*I*) were prepared by warming stoichiometric amounts of aniline with the 4-substituted salicylaldehyde dissolved in ethanol. The products crystallized from the reaction mixture, were then separated and recrystallised from ethanol. Melting points agreed with published values (*I*, X = H, Cl, Br, $NO_2$ [3] ; *I*, X = $CH_3$ [4]). The new ligands had melting points 330–331 K (*I*, X = $OCH_3$) and 371–373 K (*I*, X = $C_6H_5$). Aniline was freshly distilled before use. Salicylaldehydes (*I*, X = H, Br, $OCH_3$) were available commercially (Aldrich) or were prepared by the Duff reaction [5] (*I*, X = Cl, $CH_3$, $C_6H_5$) or the Sommelet reaction [6] (*I*, X = $NO_2$).

Reduction of Schiff bases (*I*) to the amines (*II*) was achieved using sodium borohydride in anhydrous methanol [7]. After the initial vigorous reaction, the mixture was refluxed for fifteen minutes. The amine was liberated on addition of water. After filtration, the products were recrystallised from ethanol or aqueous ethanol. The melting point for amine (*II*, X = H) was 385–6 K agreeing with the published value [8]. Others had melting points 373–4 K (X = $CH_3$), 355–6 K (X = $OCH_3$), 394–5 K (X = $C_6H_5$), 388–9 K (X = Cl), 388–9 K (X = Br) and 377–8 K (X = $NO_2$); yields were high (*ca.* 90%).

### Acid Dissociation Constants, $pK_a$

These were determined potentiometrically in 50 percent (v/v) aqueous dioxan. pH-readings were obtained using a cell of a glass electrode combined with a saturated calomel electrode, standardized by acetate and aniline buffers as described previously [9]. $pK_a$ values were obtained only for the amines (*II*); the Schiff base ligands (*I*) were found to hydrolyse too rapidly.

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### *Hydrolysis of Schiff Bases (I)*

Decomposition of ligands (*I*) was studied spectrophotometrically (Unicam SP 800) in cells thermostatted at 298.2 K. Ligand concentrations were 5 X $10^{-4}$ mol $dm^{-3}$ in 50 percent aqueous dioxan.

### *Infra-red Spectra of Ligands (II)*

Spectra of KBr discs, Nujol mulls and hexachlorobutadiene mulls were obtained using the Perkin Elmer 237 Spectrophotometer. To investigate hydrogen bonding, the spectra of solutions in tetrachloromethane were obtained for the range 3000–4000 $cm^{-1}$, using the Unicam SP 700 Spectrophotometer with cells thermostatted at 298.2 K. Ligand concentrations in the range 5–10 X $10^{-3}$ mol $dm^{-3}$ were used.

### *NMR Spectra*

The Perkin Elmer 60 was used on 10 percent solutions in trichlorodeuteromethane ($CDCl_3$), with an internal standard of tetramethylsilane. We are indebted to Dr. J. D. Hepworth of Preston Polytechnic, England for these spectra.

### *Preparation of Copper(II) Complexes*

Schiff base (*I*) solutions in ethanol were added to hot solutions of copper(II) acetate in hot aqueous ethanol in molar ratio of 2:1. The bis-ligand complex precipitated and was recrystallised from trichloromethane or ethanol.

Amine ligands (*II*) only form complexes in the presence of acetate. These were difficult to purify due to very low solubility in many solvents.

Determination of Bohr Magneton number for the complexes was carried out by the Gouy method, using copper(II) sulphate pentahydrate as a reference standard.

## Results and Discussion

### *Acid Dissociation Constants*

$pK_a$ values for the amines (*II*) are presented in Table I, together with values for analogous phenols [10] and analogous acetoacetanilides [11]. By direct comparison of these $pK_a$ values there is good correlation between the amines (*II*) and phenols. In previous work in this laboratory, Smith [11] found good correlation between $pK_a$ for acetoacetanilides and Hammett $\sigma$-constants derived for phenols, but poor correlation using $\sigma$-values derived from $pK_a$ values for benzoic acids.

### *Hydrolysis of Schiff Bases*

Rate of decomposition, measured as the absorbance at the peak wavelength of 32,500 $cm^{-1}$ (*I*, X = H), was first order with respect to concentration of *I*. The first order rate constant in neutral 50 percent aqueous dioxan was 2.1 X $10^{-4}$ $sec^{-1}$. It was approximately ten times faster when the ligand was made up in 5 X $10^{-4}$ mol $dm^{-3}$ KOH and $10^{-6}$ mol $dm^{-3}$ HCl (1.9 X $10^{-3}$ $sec^{-1}$, 2.5 X $10^{-3}$ $sec^{-1}$, respectively).

TABLE I. Acid Dissociation Constants ($pK_a$) in 50 Percent Dioxan at 298.2 K for X-Substituted Amines (*II*) and 4-Substituted Phenols (in Water) and Acetoacetanilides (in 50 Percent Dioxan).

| X | $pK_a$ (*II*) | $pK_a$ (phenol) | $pK_a$ (acetoacetanilide) |
|---|---|---|---|
| $CH_3$ | 12.73 | 16.26 | 11.62 |
| $CH_3O$ | 12.68 | 10.21 | 11.73 |
| H | 12.31 | 9.98 | 11.45 |
| $C_6H_5$ | 11.95 | 9.95 | |
| Cl | 11.46 | 9.38 | 11.17 |
| Br | 11.38 | 9.36 | 11.15 |
| $NO_2$ | 8.65 | 7.15 | 10.07 |

### *Infra-red Spectra*

Spectra for the amines (*II*) as discs and mulls showed strong sharp peaks in the region 3258 $cm^{-1}$ (X = H) to 3400 $cm^{-1}$ (X = $NO_2$). These correspond to N–H stretching frequencies. A broad band in the 3200–2000 $cm^{-1}$ range is attributed to hydrogen-bonding effects; N–H····O or N·····H–O interactions could both result from either inter-molecular or intra-molecular reactions. Studies on solutions of *II* (X = H) gave an N–H stretching peak at 3352 $cm^{-1}$ and O–H stretch at 3604 $cm^{-1}$. These sharp peaks were accompanied by a broader peak at 3254 $cm^{-1}$ assigned to O–H···O and/or O–H····N stretching. With changing concentration of ligand, the peak positions were unaltered, indicating an intramolecular and not intermolecular H-bonding. This is consistent with chelate ring formation involving O–H····N.

The variation of $\nu_{O-H\cdots N}$ with ring substitutent was found to correlate quite well with Hammett $\sigma$ constants, as did $\Delta\nu$ (difference between $\nu_{OH}$ and $\nu_{O-H\cdots N}$). $\Delta\nu$ can be considered as a measure of relative strength of hydrogen bonding in the series. The latter is, not surprisingly, related to the acidity of OH of (*II*). Indeed, there is a good linear relationship between $\Delta\nu$ and $pK_a$. In all these correlations the nitro-derivative shows deviations.

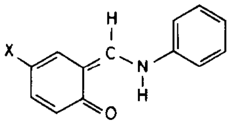
### *NMR Spectra*

The ligands (*I*) all gave a sharp singlet at or near 8.5 $\delta$, assigned to the -CH=N-proton. The phenolic proton signal occurs at high $\delta$ values in the range 12.72 ppm (X = $CH_3O$) to 14.40 ppm (X = $NO_2$); this peak disappears on addition of deuterium oxide due to isotopic replacement. These spectra are consistent with the structure (*I*), the phenol-imine tautomer as opposed to the ketone-amine tautomer

(*III*), which would require splitting of the -CH= signal.

There is increased broadening of the phenolic proton peak for the more electron-withdrawing substituents; this suggests that broadening accompanies increasing strength of hydrogen bonding.

In the spectrum of the parent reduced compound (*II*, X = H), the main feature of difference from the Schiff base (*I*, X = H) is the presence of the $-CH_2-$ singlet at $\delta = 4.35$ ppm. That this signal is not split by the neighbouring -NH- proton suggests this latter proton is strongly H-bonded, probably intramolecularly to the phenolic oxygen, a possibility strengthened by the broad peak covering 4.8 to 6.6 ppm and which integrates to two protons. Apart from aromatic protons, no further signals were found down to $\delta = 20$ ppm.



(III)

## Copper(II) Complexes

Of the chelates of Schiff bases (*I*), only the parent and bromo-derivatives were previously reported [12]. Determination of copper content, by atomic absorption spectrophotometry agreed within 0.2 percent to the value calculated for the bis-chelate. The products were characterised by melting point (Table II). No satisfactory solvent was found to recrystallise the nitro-derivative.

Amine ligands (*II*) gave rise to mixed chelates of the type Cu(chelate)(Acetate) where (chelate) represents the phenolate anion of II. Again, the nitro-derivative gave poor analysis (Table II). Previous work by Beretka and West [13] on the parent amine (*II*, X = H) also gave a poor copper analysis. Other transition metal ions, M(II) did not form analogous complexes, nor did copper(II) in the absence of acetate.

Magnetic measurement of the copper complex of the parent amine gave a Bohr Magneton number of 1.98, giving no indication of spin-pairing of copper(II) ions. This suggests the formation of a dimer by acetate bridging is unlikely; this is a feature of copper(II) acetate dihydrate dimer [14].

TABLE II. Copper Complexes of Substituted Schiff-base Ligands (*I*) and Substituted Amine Ligands (*II*).

(a) Schiff-base complexes, Copper(II) (ligand *I*)$_2$

| Substituent X | Colour | m.pt (K) | % Copper | |
|---|---|---|---|---|
| | | | found | required |
| $CH_3O-$ | v. dk. brown | 476–7 | 12.5 | 12.3 |
| $CH_3-$ | dk. brown | 485–7 | 12.9 | 13.1 |
| H- | brown | 508–10* | 13.8 | 13.9 |
| $C_6H_5-$ | brown | 510–1 | 10.4 | 10.4 |
| Cl- | brown | 538–40 | 12.0 | 12.1 |
| Br- | brown | 547–50 | 10.2 | 10.4 |
| $NO_2-$ | lt. brown | 558–63 | 11.0 | 11.6 |

*Lit. value 503 K (ref. 15).

(b) Amine complexes, Copper(II) (ligand *II*) (Acetate)

| Substituent | Colour | % Copper | |
|---|---|---|---|
| | | found | required |
| $CH_3O-$ | dk. green | 19.8 | 18.1 |
| $CH_3-$ | dk. green | 20.6 | 19.0 |
| H- | green | 19.6 | 19.8 |
| $C_6H_5-$ | green | 16.1 | 16.0 |
| Cl- | green | 18.1 | 17.9 |
| Br- | green | 15.9 | 15.9 |
| $NO_2-$ | light tan | 12.1 | 17.4 |

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