

Perhaps the simplest type of bonding would be "simple" donation of an electron pair by one of the nitrogen atoms of the tetrazole ring to the metal ion. If bonding occurred in this manner, one might expect copper to coordinate four ligands, as it does in its imidazole complexes.⁷⁻⁹

Since the tetrazolate anion seems to satisfy two coordination sites on the copper ion, coordination could occur by the formation of bonds to two distinct nitrogen atoms of the tetrazole ring. Coordination probably would not involve two adjacent nitrogen atoms of the tetrazole ring which means that if coordination occurs in this manner, the tetrazole rings would not be coplanar with the copper ion.

The electronic structure of the tetrazole ring has a marked similarity to the electronic structure of cyclopentadiene. Another possible mode of bonding is coordination of the metal ion to the π -electron system of the tetrazolate anion. If this type of bonding were encountered, one might expect the copper complexes to be soluble in organic solvents.

In fact, the almost complete lack of solubility of the copper complexes in a wide variety of solvents might suggest a polymeric structure in the solid state. There are several structures that one can visualize in which the tetrazolate anions are shared by more than one copper ion.

A determination of the structure of the solid complexes from X-ray data has not been made. The patterns indicate that the unit cell is large.

The dark blue solution obtained by mixing

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methanol solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{C}_7\text{H}_6\text{N}_4$ suggests that a soluble complex is formed on mixing the reactants. The intensity of the blue color remains constant until the solid complex begins to separate from the solution. The blue solid is not soluble in methanol. Such behavior suggests that the structure of the solid complex may be different from the structure of the complex in solution.

The "anion effect" observed in the reaction of Cu^{++} with CN_5H_3 is not well understood. The fact that SO_4^- is much more effective, in producing turbidity, than any of the other anions examined suggests that the anion plays a rather specific role in the reaction. The poor effectiveness of basic anions such as $\text{C}_2\text{H}_3\text{O}_2^-$ and $\text{PO}_4^{=}$ compared to SO_4^- indicate that the effect is not an acid-base phenomenon. The lack of effect by $\text{PO}_4^{=}$ leads one to believe the effect is not entirely one of coagulation of a colloidal material.

It is suggested, therefore, that rapid nucleation of the $\text{Cu}(\text{CN}_5\text{H}_2)_2$ requires a small amount of some complex which contains $\text{SO}_4^{=}$, Cl^- or NO_2^- and which may be insoluble. If that is the case the sulfate complex must form at once, but the chloride one only slowly, since the appearance of solid in the chloride case is slow and depends on (Cl^-) .

Although a systematic study of the roles of some anions on precipitation of tetrazole complexes has been made only with Cu^{++} and CN_5H_3 , one must point out that it seems to be quite general for metal ions and tetrazoles.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Chelate Stabilities of Certain Oxine-type Compounds. III. Schiff Bases¹

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The acid dissociation constants for three types of Schiff bases structurally similar to 8-hydroxyquinoline have been determined in 50% v./v. dioxane-water at 25° and the chelate stabilities of these ligands with $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cd}(\text{II})$ have been obtained by Calvin-Bjerrum potentiometric titration technique. The differences in values obtained for the basicities of the ligands have been explained by electron donating tendency of the substituents and by hydrogen bonding. The formation constants of these ligands with the metal ions studied are lower than those of the corresponding 8-hydroxyquinoline chelates due to unfavorable steric factors but are higher than those of the 4-hydroxybenzimidazoles because of more favorable nitrogen-oxygen distance. The stability constants for the metal chelates of the Schiff bases increase with increase in ligand basicity except when the size of the metal chelate ring or the presence of adjacent groups affects these values.

In the previous papers^{2,3} the chelate stabilities of 4-hydroxybenzimidazoles, 4-hydroxybenzoxazoles and 4-hydroxybenzothiazoles with divalent metal ions have been reported. In the present paper are presented and discussed the stability values obtained for the metal chelates of three

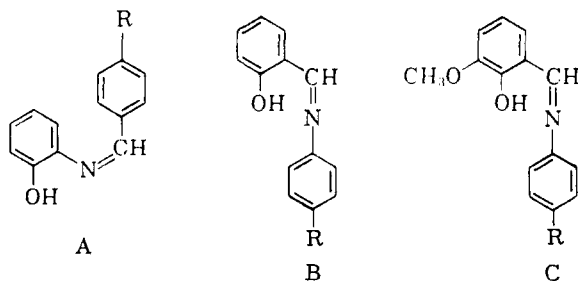
types of Schiff bases represented by the formulas where $\text{R}=\text{H}$, CH_3 , OCH_3 and OH . Compounds of type A are structural analogs of 8-hydroxyquinoline and contain the same chelating system $-\text{O}-\text{C}=\text{C}-\text{N}=\text{}$, the difference being that the nitrogen atom is not part of a ring. Type B and type C compounds have been included to study the effect of varying the size of the chelate ring and of introducing an *ortho* substituent, respectively.

Materials.—N-Benzylidene-*o*-hydroxyaniline (compound I, Table I), N-(4-methylbenzylidene)-*o*-hydroxyaniline

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(II), N-(4-methoxybenzylidene)-*o*-hydroxyaniline (III) and N-(4-hydroxybenzylidene)-*o*-hydroxyaniline (IV) were prepared by condensing an alcoholic solution of *o*-aminophenol with an equimolar amount of benzaldehyde, *p*-toluidaldehyde, *p*-anisaldehyde and *p*-hydroxybenzaldehyde, respectively.⁴ Reaction took place with the evolution of heat and with the elimination of water. The reaction mixture was cooled in an ice-bath for 0.5 hr., the product filtered, decolorized with charcoal and recrystallized several times from 50% alcohol.

N-Salicylideneaniline (V), N-salicylidene-*p*-toluidine (VI), N-salicylidene-*p*-anisidine (VII) and N-salicylidene-*p*-hydroxyaniline (VIII) were similarly prepared by condensing salicylaldehyde with aniline, *p*-toluidine, *p*-anisidine and *p*-aminophenol, respectively.

N-(2-Hydroxy-3-methoxybenzylidene)-aniline (IX), N-(2-hydroxy-3-methoxybenzylidene)-*p*-toluidine (X), N-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (XI) and N-(2-hydroxy-3-methoxybenzylidene)-*p*-hydroxyaniline (XII) were prepared by condensing, as above, 2-hydroxy-3-methoxybenzaldehyde with aniline, *p*-toluidine, *p*-anisidine and *p*-aminophenol, respectively.

The melting points of these compounds and the results of elemental analysis appear in Table I.

Apparatus, Procedure and Calculations.—The acid dissociation constants and stability constants were determined at 25° by the Bjerrum method⁵ of potentiometric titration in 50% *v/v*. dioxane-water. The titration apparatus and procedure have been described previously.⁶ Titrations were carried out using a ligand to metal ratio of 8:1. Stability values were calculated by the method described by Freiser, *et al.*,⁶ and in regions of metal hydrolysis were obtained by extrapolation from lower values.

Results

Acid dissociation constants of the various ligands and their formation constants with Cu(II), Ni(II) and Cd(II) appear in Table I.

It should be pointed out that none of the Schiff bases used in this study underwent hydrolysis under the experimental conditions described. This was indicated by the rapid attainment of equilibrium during the titration and by the absence of any significant drift in *pH* even after 3–4 hr. However, Schiff bases derived from aliphatic aldehydes and *o*-aminophenol could not be studied due to the hydrolysis of the ligands. Hovey, *et al.*,⁷ in discussing the hydrolytic tendencies of Schiff bases have attributed the higher stability of the aromatic derivatives to an increase of resonance energy in the system brought about by the presence of aromatic groups.

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TABLE I

VALUES OBTAINED FOR THE SCHIFF BASES

Compd. ^b	Type	R	Molecular formula	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %		Basicities ^a		Cu(II)		Ni(II)		Cd(II)		
					Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	<i>p</i> K _{SH}	<i>p</i> K _{OH}	Log K _f	2 Log K _{app.}	Log K _f	2 Log K _{app.}	Log K _f	2 Log K _{app.}	
I	A	H	C ₁₂ H ₁₁ NO	90	79.2	79.3	5.58	5.70	7.11	7.17	4.27	11.67	10.4	8.4	18.8	6.4	6.4	4.5	10.7
II	A	CH ₃	C ₁₄ H ₁₃ NO	107.5	79.6	79.4	6.16	6.16	6.64	6.55	4.28	11.79	10.8	8.4	19.2	6.8	6.8	4.7	11.6
III	A	OCH ₃	C ₁₆ H ₁₅ NO ₂	89.5	74.0	74.1	5.73	5.95	6.17	6.10	4.30	11.72	10.4	8.5	18.9	6.4	6.4	4.8	10.8
IV	A	OH	C ₁₂ H ₁₁ NO ₂	152	73.2	73.0	5.16	5.25	6.57	6.39	4.31	11.65	10.6	8.2	19.0
V	B	H	C ₁₀ H ₁₁ NO	51	79.2	79.4	5.58	5.75	7.11	7.18	3.83	9.99	8.4	6.9	15.3
VI	B	CH ₃	C ₁₂ H ₁₃ NO	95.5	79.6	79.6	6.16	6.14	6.64	6.68	4.23	10.37	8.8	7.5	16.2	5.9	5.9	4.5	10.3
VII	B	OCH ₃	C ₁₄ H ₁₅ NO ₂	84.5	74.0	74.2	5.73	5.70	6.17	6.22	4.28	11.03	9.3	8.1	17.3	6.2	6.2	4.8	11.0
VIII	B	OH	C ₁₂ H ₁₃ NO ₂	143	73.2	73.3	5.16	5.32	6.57	6.31	4.64	10.54	9.6	7.5	17.1	5.7	5.7	4.1	9.8
IX	C	H	C ₁₄ H ₁₃ NO ₂	83	74.0	73.3	5.73	5.62	6.17	6.27	3.84	9.72	9.2	7.0	16.3
X	C	CH ₃	C ₁₆ H ₁₅ NO ₂	101.5	74.7	74.6	6.22	6.21	5.81	5.82	4.25	10.27	9.5	7.7	17.4	6.3	6.3	4.8	10.9
XI	C	OCH ₃	C ₁₈ H ₁₇ NO ₂	94.5	70.0	70.1	5.84	5.95	5.45	5.44	4.37	11.10	10.7	8.3	18.9	6.7	6.7	5.2	11.8
XII	C	OH	C ₁₄ H ₁₃ NO ₂	81	69.1	68.8	5.35	5.65	5.76	5.64	4.57	10.49	10.2	7.0	17.9	6.0	6.0	4.5	10.4

^a Negative logarithms of the acid dissociation constants for the protonated ligands. ^b I, II, III, IV, IX, X, XI and XII are new compounds.

Discussion

Acid Dissociation Constants.—N-Benzylidene-*o*-hydroxyaniline (I) has a pK_{NH} of 4.27 (Table I). This value is not appreciably increased by the introduction of $-CH_3$, $-OCH_3$ and $-OH$ into position R (II, III, IV). Probably these groups are too far removed from the nitrogen atom to have any considerable influence on its electron cloud. Their pK_{NH} values, however, are higher than that reported for 8-hydroxyquinoline (3.97),⁸ in which compound the electron density of the nitrogen atom is lowered by contribution to aromatic ring resonance. This conclusion is in agreement with the higher pK_{NH} (4.52) of 1,2,3,4-tetrahydro-8-hydroxyquinoline⁹ where the nitrogen atom does not take part in ring resonance.

That the pK_{OH} values of these Schiff bases are higher than that of 8-hydroxyquinoline is probably due to stronger hydrogen bonding with the more basic nitrogen atom.

The low pK_{NH} (3.83) of N-salicylideneaniline (V) may be attributed to the electron-withdrawing tendency of the adjacent phenyl group. But the substitution of $-H$ in position R by $-CH_3$, $-OCH_3$, $-OH$ (VI, VII, VIII) increases this value to 4.23, 4.33 and 4.64, respectively, on account of the electron donating tendencies of these groups. The pK_{OH} of these compounds is lower than that of type A compounds due to better resonance stabilization of the phenolate anion.

The acid dissociation constants of N-(2-hydroxy-3-methoxybenzylidene)-anilines (IX, X, XI, XII) are practically the same as those of the corresponding N-salicylideneanilines (V, VI, VII, VIII) indicating that the $-OCH_3$ substituent in the 3-position has little effect on the electron densities of the chelating atoms.

Chelate Formation Constants.—The $2 \log K_{av}$ values for the copper(II) chelates of the Schiff bases derived from *o*-aminophenol (I, II, III, IV) are 18.8, 19.3, 18.9 and 19.0, respectively (Table I). These values are lower than that reported for 8-hydroxyquinoline (26.2)⁸ even though the basicities of these Schiff bases are higher. This lowering of formation constants can be attributed to the steric effect caused by the benzene rings of the aromatic aldehyde portion, as shown by molecular models (Fisher-Taylor-Hirschfelder).

The metal chelates of these Schiff bases are more stable than the corresponding chelates of 4-hydroxybenzoxazole, 4-hydrobenzimidazole and 4-hydroxybenzothiazole.^{2,3} In these 4-hydroxy compounds the N-O distance and the orientation of the donor electrons on the nitrogen atom are unfavorable for strong chelation.^{2,3} This conclusion seems to be in agreement with the results of Block's X-ray diffraction studies of N-salicylideneaniline copper(II) chelate.¹⁰ His value of 87° for N-Cu-O angle is close to a right angle required for a stable square planar copper chelate structure. Using his value of 2.11 and 1.91 Å. for Cu-N and Cu-O

bond lengths, respectively, a value of 2.8 Å. may be considered a favorable O-N distance for strainless copper chelates in the type of ligands under study. The estimated distance of 2.78 Å. in 8-hydroxyquinoline² would also explain the high stability values obtained for its metal chelates. The nitrogen-oxygen distance in these Schiff bases would be the same as that in 8-hydroxyquinoline, while the larger distance of 3.1 Å. in the 4-hydroxy compounds^{2,3} would result in strained chelate rings.

The stability constants calculated for the metal chelates of Schiff bases derived from salicylaldehyde (Type B) are lower than those for the corresponding chelates of *o*-aminophenol derivatives (Type A). This is explained by the lower basicity of these ligands and the diminished stability of 6-membered chelate rings.

The formation constants ($2 \log K_{av}$) for the copper(II) chelates of type C compounds are about one log unit higher than those of the corresponding type B compounds. This large increase in stability cannot be attributed to differences in ligand basicities but is possibly due to an increase in entropy caused by the blocking effect of the methoxy group in the 3-position. This interpretation is supported by data obtained by Calvin and Wilson¹¹ who found that stability values for the copper(II) chelates of 3-substituted salicylaldehydes increased with increase in size of the substituent. In addition, when two molecules of type C ligands are attached to a copper atom, the methoxy group of one ligand together with the N-phenyl group of the other would partially shield the central metal ion and render it less accessible to contacts with the solvent molecules.

As seen from Table I, nickel(II) and cadmium(II) chelates of type C compounds show an increase in stability but to a lesser degree than the corresponding copper(II) chelates. The square planar structure of copper(II) chelates would be expected to show a greater blocking effect than the tetrahedral structure of cadmium(II) complexes. As for nickel(II), definite discussion is difficult since it may form square planar or tetrahedral complexes.

The results of this study indicate that in general the formation constants of the chelates increase with an increase in the basicity of the nitrogen atom, except for *p*-methoxy and *p*-hydroxy derivatives. A similar inversion was observed by Calvin and Bailes¹² in their polarographic study of salicylideneanilines. This inversion may be attributed to differences in pK_{OH} values which are higher by about 0.5 log unit (VII, VIII and XI, XII, Table I). Freiser, *et al.*,¹³ have pointed out that it is difficult to justify the use of only one of the pK values when correlating chelate stabilities with ligand basicity.

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The Inductive Effect and Chemical Reactivity. V. Theoretical Dipole Moments of α,ω -Dichloroalkanes and α,ω -Dibromoalkanes¹

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The theory of earlier papers in this series^{3,4} has been applied to the calculation of dipole moments of α,ω -dichloroalkanes and α,ω -dibromoalkanes of up to ten carbon atoms. The molecules are assumed to be distributed over the possible staggered conformations; the excluded volume problem is handled by omitting the conformations for which there is appreciable atom interference. The few available experimental data are compared with the theory.

Introduction

The first paper of this series³ (I) presented a method for estimating charges on atoms in saturated organic molecules. In these molecules, the so-called inductive effect is predominant in determining the net charges on the atoms. After a readjustment of one of the parameters for the C-C bond in part IV of this series⁴ (IV), (this readjustment being in line with a reconsideration of the C-C bond longitudinal polarizability⁵), the theory successfully explained the charges in many halogenated hydrocarbons, as evidenced by the good agreement of calculated and observed dipole moments shown in I and IV. The success of the theory is exemplified by the close verifications of the predicted dipole moment of CH_2F_2 ⁶ and of the separate components, and hence angle with C-C axis, of the dipole moment of CH_3CHF_2 .⁷

So far, this series has been concerned only with halogenated alkanes for which there are no configurational problems, *i.e.*, molecules for which internal rotation, if present, does not affect the dipole moment. We now turn our attention to a class of molecules where the effect of internal rotation on dipole moment is very pronounced. The α,ω -dihaloalkanes have long been the subject of theoretical interpretation in this connection. Their dipole moments are strongly temperature dependent, and the moments of members of an homologous series vary in a way that appears irregular, although there are not enough reliable data to settle the problem of just how they do vary. Now, the theory and parameters of I and IV lead to a predicted dipole moment for any given α,ω -dihaloalkane configuration. Also, simple methods for tabulating and weighting *n*-alkane configurations have been reported from this

Laboratory⁸; as shown below, minor extensions allow the α,ω -disubstituted molecules to be tabulated and weighted. Therefore, we have performed the following calculations to determine how the experimental moments might be expected to vary with both temperature and chain length. We have confined ourselves to chlorine and bromine substituents, as there are practically no experimental data for the other halogens.

Recently, Hayman and Eliezer⁹ have considered the dibromoalkanes, using the theory of I and IV. However, the configurational problem is approached in the present paper in a way that permits the "excluded volume effect" to be taken into account; *i.e.*, geometrically impossible configurations are omitted. This was the case with neither the work of Hayman and Eliezer nor with earlier explorations of this problem.¹⁰ Also, both temperature and chain length are treated as variables in the present work.

Configurations.—Normal alkane chains may assume various configurations in which all bonds are staggered, which is equivalent to saying that the carbon atoms fit on a diamond lattice.^{9,10} The configurations which depart from complete staggering of all sets of bonds joined to all C-C bonds are not so stable and may be ignored. The staggered configurations may be described by codes in which the digit 2 represents a *trans* arrangement of three successive C-C bonds, and the digits 1 and 3 represent the two mirror-image gauche arrangements (*G'* and *G*, respectively, of Mizushima¹⁰). With this notation *n*-pentane, for example, has nine configurations which may be grouped into four sets as

22
11, 33
13, 31
12, 21, 32, 23

Here all configurations in each group are identical or mirror images. The smallest number in each group may be called the "standard configuration

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