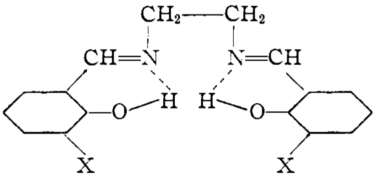
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HOWARD UNIVERSITY]

Chelation and Association of Some Ethylenediamine Schiff Bases[1]

BY LLOYD N. FERGUSON AND IRENE KELLY[2]

It is suggested that the 410 mμ absorption band of bis-(salicylal)-ethylenediamine (I) is due to intramolecular hydrogen bond formation, or chelation, since bis-(*o*-methoxybenzal)-ethylenediamine and bis-(*p*-hydroxybenzal)-ethylenediamine, for which chelation is impossible, do not have absorption bands above 320 mμ. It is observed that the substitution of a halogen atom in the second ortho position to the OH group of I increases the intensity of this 410 mμ band but a nitro group in this position increases the wave length and intensity of absorption. It is proposed that the charge distribution in the excited states of these Schiff bases leads to a stronger hydrogen bond and thereby stabilizes the excited states relative to the ground states. Consequently, the energy difference between the excited and ground states is diminished through chelation and absorption takes place at longer wave lengths. Using a method of dry and wet melting points to distinguish between chelation and association, the wet and dry melting points of several *o*- and *p*-formylated halogenophenols were determined. The *o*-hydroxy aldehydes were found to have smaller wet-melting point depressions.

Several investigators[3,4,5] have reported that certain aromatic compounds with an *o*-hydroxyl group absorb light at longer wave lengths than do the corresponding *m*- and *p*-hydroxy derivatives. It has been suggested that the bathochromic effect of the *o*-hydroxyl group is due to intramolecular hydrogen bond formation,[3] which can be referred to as chelation.[6] In the present study, it is proposed that the 410 mμ band of bis-(salicylal)-ethylenediamine (I, X = H), is due to a chelated structure, inasmuch as bis-(*p*-hydroxybenzal)-ethylenediamine and bis-(*o*-methoxybenzal)-ethylenediamine, for which chelation is impossible, do not have absorption bands above 320 mμ. There is a marked visible change upon methylating the hydroxyl groups of bis-(salicylal)-ethylenediamine, for the latter compound is bright yellow while its methyl ether is pure white.



I

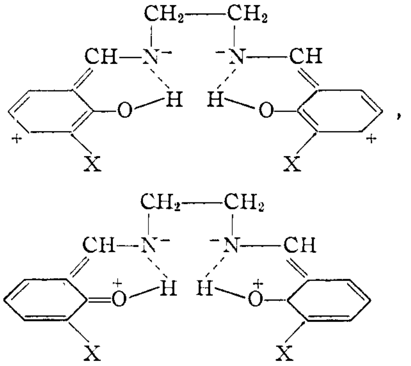
It might be of interest to note the effect of substitution in I of a second group at X which is also capable of forming a hydrogen bond with the OH group. For this purpose, derivatives of I, where X represents a chlorine, bromine, or iodine atom, or a nitro group, were prepared and their ultraviolet spectra measured. Spectral characteristics of the compounds studied are listed in Table I and their spectra are drawn in Figs. 1 and 2.

A suggested explanation of the bathochromic effect of chelation in these Schiff bases may be given in terms of molecular structures that contribute to the resonance of these molecules. The chief polar structures contributing to their resonance hybrids are probably of type II.

TABLE I

SPECTRAL CHARACTERISTICS OF SCHIFF BASES OF ETHYLENEDIAMINE

Aldehyde	$\lambda_{max.}$, mμ	$\epsilon_{max.}$
Salicylaldehyde	410	1,200
3-Chlorosalicylaldehyde	410	4,600
3-Bromosalicylaldehyde	410	2,000
3-Iodosalicylaldehyde	410	4,000
3-Nitrosalicylaldehyde	440	11,000
o-Methoxybenzaldehyde	320	8.600
p-Hydroxybenzaldehyde	290	2.616



II

These are important primarily in the excited states of the molecules. It is generally being accepted that a hydrogen bond, A–H ··· B, is largely due to electrostatic attraction between atom B and the proton, and the greater the electron density about B, the greater will be the bond energy. The charge distribution in II is more favorable for hydrogen bond formation than in I and, therefore, a stronger hydrogen bridge is formed in II than in I, with the result that chelation stabilizes II to a greater extent than I. Consequently, the energy difference between the ground and excited states is diminished and absorption takes place at longer wave lengths than for similar compounds lacking intramolecular hydrogen bonds.

The surprising fact that compounds I, where X = H, Cl, Br and I, all have maximum absorption bands at the same wave length, is interpreted by saying that X has not altered the energy difference between the ground and first excited states of these substances. However, the effect that substitution

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[1] Presented before the Organic Division of the American Chemical Society at Boston, April, 1951. Part of the material in this paper is taken from the M.S. thesis of I. Kelly.

[2] Atlantic Yeast Corporation, Brooklyn, N. Y.

[3] E. D. Bergmann, Y. Hirshberg and S. Pinchas, *J. Chem. Soc.*, 2351 (1950).

[4] L. Dede and A. Rosenberg, *Ber.*, **67**, 147 (1934); R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

[5] E. R. Blout and R. M. Gofstein, THIS JOURNAL, **67**, 13 (1945).

[6] It also has been observed that many *o*-substituted compounds have two bands in place of the one of the correspondingly *m*- and *p*-substituted compounds. The double maxima have been attributed to inter- and intramolecular hydrogen bonding[4] and to resonance among forms arising from non-colinear electron oscillations.[5]

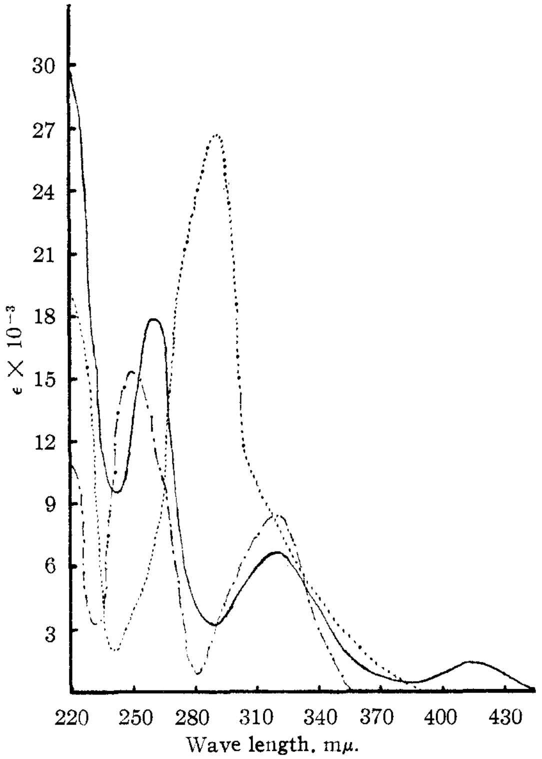
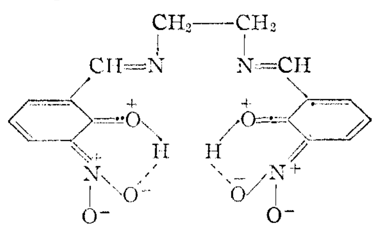


Fig. 1.—Ultraviolet absorption spectra of: bis-(salicylal)-ethylenediamine ——; bis-(*p*-hydroxybenzal)-ethylenediamine . . . . . . ; and bis-(*o*-methoxybenzal)-ethylenediamine —·—·—.

has on the intensity of the 410 mμ band is not clear. It is in the opposite direction from that which would be anticipated on the basis of the population of molecules with the O–H···N or O–H···X hydrogen bond.

The absorption by bis-(3-nitrosalicylal)-ethylenediamine is at a longer wave length and of greater intensity than that by the other Schiff bases. This suggests that chelation with the nitro group produces a stronger chromophoric system. That is,



the difference in energies between the ground and excited states is smaller than for the Schiff bases with O–H···N hydrogen bonds.

Intermolecular hydrogen bond formation, or association, is usually accompanied by an increase in both boiling point and solubility in water. In contrast to this, chelation brings about just the opposite effect. A method[7] of differentiating between the two has grown out of some solubility studies of Sidgwick.[8] It consists of determining the differences in melting point of a substance when dry and when in contact with water. The depression in melting point of chelated compounds when wet is much smaller than that of associated compounds when wet. Presumably this is because associated molecules can also associate with water and thereby their mutual solubilities are increased, with the result that the melting points of the eutectic mixtures are considerably lower than those of the pure compounds. Since water will be much less soluble in the chelated compounds, because of the small degree of association between the two, the water content of the eutectic mixture will be relatively small and so will the wet-melting point depression.

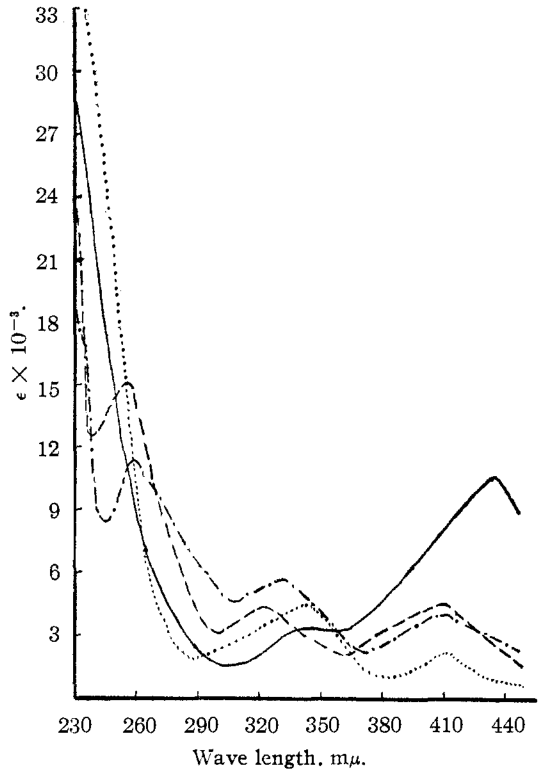


Fig. 2.—Ultraviolet absorption spectra of: bis-(3-chlorosalicylal)-ethylenediamine — — — —; bis-(3-bromosalicylal)-ethylenediamine . . . . ; bis-(3-iodosalicylal)-ethylenediamine— · — · —; and bis-(3-nitrosalicylal)-ethylenediamine ——.

The present authors have made such a study of some ethylenediamine Schiff bases and it is observed from Table II that, although the separation is not great, there is a distinct difference in ranges of the melting point depressions of the chelated and associated compounds.

TABLE II

WET AND DRY MELTING POINTS OF CERTAIN HYDROXY SCHIFF BASES OF ETHYLENEDIAMINE

Aldehyde	M.p., °C. Dry	M.p., °C. Wet	Approx. diff. deg.
Salicylaldehyde	126–127	120–123	5
o-Methoxybenzaldehyde	115.5–116.5	100–103	14
3-Chlorosalicylaldehyde	160–161	153–156	7
3-Bromosalicylaldehyde	176–177	172–175	5
p-Hydroxybenzaldehyde	212–213	176–179	35
3-Chloro-4-hydroxybenzaldehyde	221–222	170–180	46
3-Bromo-4-hydroxybenzaldehyde	235–236	177–192	50

Preparation of Compounds.—The compounds were all prepared by mixing ethanol solutions of equivalent quantities

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(7) R. D. Amstutz, I. J. Chessick and I. M. Hunsberger, *Science*, **111**, 305 (1950).

(8) N. V. Sidgwick and R. K. Callow, *J. Chem. Soc.*, 527 (1924).

of the respective aldehydes and ethylenediamine. The Schiff bases were then recrystallized to constant melting points.

Measurements.—The spectra were measured with a Beckman model DU spectrophotometer, using fused-silica cells. The solvent was commercial ethanol in all cases. The wet melting points were determined in sealed glass tubes from Size 7 glass tubing, with one end drawn to a 2-cm. capillary of about 1 mm. i.d. Several measurements were made for each compound with varying amounts of water and the value chosen that was the most reproducible. The proportion of water used was found to have only a small effect on the melting range.

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Liquid Complexes of Lower Olefins with Anhydrous Metal Salts[1]

BY ALFRED W. FRANCIS

Anhydrous silver nitrate forms liquid complexes with propylene and 1-butene containing over 1.3 moles of olefin to one of salt. These are stable only under pressure near the vapor pressure of the olefin, and below 36 and 25°, respectively. At lower pressures or higher temperatures evolution of the olefin is complete. Propylene forms an equimolar liquid complex with anhydrous mercuric acetate. This liquid does not evolve propylene on evacuation or moderate heating, but does so with addition of hydrochloric acid.

The solvent power of aqueous solutions of silver, mercury, and cuprous salts for the lower olefins is well known[2a,b] although the decided differences in properties and operation for different solutions are not so well understood. For example, it is not generally realized[2a,b,3,4] that the absorption of olefins by most mercury solutions is irreversible[5,6] except with destruction of the reagent by addition of certain substances such as hydrochloric acid.

Solid anhydrous cuprous chloride has been shown to form solid complexes with ethylene,[7,8,9] propylene,[8,9] and isobutene[8,9] and cuprous bromide with ethylene.[8] These have definite equimolar compositions, but are stable only under high partial pressures of the respective olefins. Soday[4] suggested that many other solid dry salts of monovalent copper, mercury and silver might form similar complexes with olefins and diolefins. There seems to be no mention in the literature of a *liquid* complex of an olefin with an anhydrous metal salt (excluding halides of amphoteric elements like aluminum).

In this investigation anhydrous crystalline silver nitrate was agitated with liquid propylene under pressure and was found to give a separate liquid phase of unusual properties.

The new liquid phase is colorless, not very viscous, insoluble in excess of propylene, but miscible with water (with slight decrease in its propylene content). Its density is 1.83 to 1.95 depending on its composition. It is stable only under pressure approaching the vapor pressure of the olefin, since at lower pressure it dissociates quantitatively to propylene and crystalline silver nitrate. Even in contact with pure liquid propylene it dissociates with rising temperatures, and is not stable above 36° although it may be superheated for a few seconds up to 60° or for several hours at 40°. The lower layer reappears when it is cooled and shaken. The liquid thus shows the paradoxical behavior of seeming to freeze on warming and to remelt on cooling. A tube containing a sample in contact with liquid propylene has been kept more than five years. It shows only a slight yellow color in spite of frequent exposure to light and in spite of previous heating to complete dissociation and cooling to regeneration.

Phase relations in the binary system are shown in Fig. 1, and observations of the points are recorded in Table I. The liquid complex exists in the area ABC. The line AB shows the composition of this liquid in equilibrium with pure liquid propylene. It has metastable extensions above 36° and below the freezing point, −26°, both of which are readily observable because of superheating and subcooling. The line AC shows the composition of the liquid in equilibrium with silver nitrate crystals. This equilibrium can be readily subcooled, but not superheated. The straightness of the lines is due to the short range in composition.

When the liquid complex is frozen, crystals may appear as rapidly growing seemingly regular tetrahedra, as much as a centimeter on a side, but these are usually interfered with by conglomerates. These crystals must be solid solutions of at least two different propylates because they melt over a nine or ten degree range except when the composition is above 60 mole % propylene. The composition is non-stoichiometric in spite of well formed crystals, and the crystal shape is independent of composition. They are probably not mixtures of different crystals because on gradual melting from the top down without agitation no trace of crystals (*e.g.*, silver nitrate) remains. Free silver nitrate is not a physical component of the solid solution since

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 117th Meeting of the American Chemical Society, Detroit, Mich., April, 1950.

(2) (a) C. Ellis, "The Chemistry of Petroleum Derivatives," Chem. Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1934, pp. 142, 582. There are at least twenty-one patents for absorbing olefins in solutions of cuprous salts, seven for silver salts, and one for mercury salts. (b) R. N. Keller, *Chem. Revs.*, **28**, 229, especially p. 245 (1941).

(3) J. Chatt, *ibid.*, **48**, 32 (1951).

(4) F. J. Soday, U. S. Patents 2,373,715; 2,389,647 (1945); 2,395,956 (1946).

(5) A. W. Francis and S. J. Lukasiewicz, *Ind. Eng. Chem., Anal. Ed.*, **17**, 703 (1945).

(6) A. W. Francis and co-workers, U. S. Patents 2,077,041 (1937); 2,377,221 (1945); 2,463,482 (1949).

(7) H. Tropsch and W. J. Mattox, THIS JOURNAL, **57**, 1102 (1935).

(8) E. R. Gilliland, J. E. Seebold, J. R. Fitz Hugh and P. S. Morgan, *ibid.*, **61**, 1960 (1939).

(9) E. R. Gilliland and Standard Oil Development Co., U. S. Patents 2,209,452 (1940); 2,289,773 (1942); British Patents 537,468; 537,497 (1941).