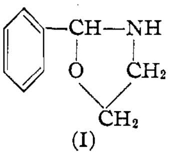
[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Infrared Spectra and Structure of Reaction Products of Ethanolamine and Aromatic Aldehydes[1]

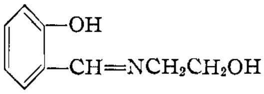
BY L. W. DAASCH AND URHO E. HANNINEN

In the course of studies on aldehyde–amine condensation products for use as rubber vulcanization accelerators, the structure of the products of ethanolamine and aromatic aldehydes assumed importance in the work of correlating structure with accelerator activity. The reaction between ethanolamine and benzaldehyde, for example, could lead either to a Schiff base or to an oxazolidine ring system.

Meltsner and co-workers[2] reported the products obtained from the reaction of aromatic aldehydes with ethanolamine to be oxazolidine ring systems of Type I.



(I)



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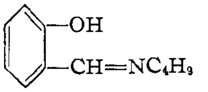

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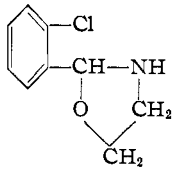


(IV)

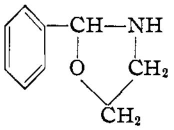
Recently, Goodson and Christopher,[3] in studying condensation reactions of ethanolamine with salicylaldehyde and *o*-chlorobenzaldehyde, reported ultraviolet absorption spectra for these products. The reaction product of salicylaldehyde and ethanolamine was assigned a Schiff base structure (II) from a comparison of its ultraviolet absorption spectrum with that of a known Schiff base (III). The reaction product of *o*-chlorobenzaldehyde with ethanolamine was reported to be 2-(2-chlorophenyl)-oxazolidine (IV) from a similar comparison with 2-phenyloxazolidine (I) whose structure was assigned by analogy with known oxazoles and by its method of preparation.[4]

Five aromatic aldehyde–ethanolamine condensation products, including those prepared by Goodson and Christopher, have been investigated. The structure of these compounds was obtained through a study of their infrared spectra.

Discussion

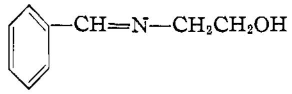
Considering first the reaction product of benzaldehyde and ethanolamine, the problem is to decide between the two structures

(I)



Oxazolidine ring structure

and (V)



Schiff base structure

This can be done by means of well-established relationships which exist between molecular structure and infrared absorption, such as have been found for hydrocarbon groups and for many other molecular groups both at this laboratory and elsewhere.[5] On this basis it may be said that structure (I) will exhibit: (1) absorption characteristic of an N–H link but none characteristic of an alcoholic O–H link, (2) no absorption characteristic of the C=N link, (3) a group of fourteen bands which will be identical with those which characterize an aromatic ring attached to a secondary carbon atom of an alkyl group; and that structure (V) will exhibit: (1) characteristic O–H absorption but no N–H absorption, (2) characteristic C=N absorption, (3) a group of about fourteen bands which will be similar but *not* identical with those for a mono-alkyl-substituted aromatic ring. Further, both structures will exhibit similar absorptions due to the presence of the C—O— link and CH_2 groups, but it may be expected that structure (I) will exhibit a greater number of strong bands which cannot be accounted for by various groups since (I) has a five-membered ring structure (which produces strong bands not easily correlated) while (V) has not.

As shown in Fig. 1, the reaction product has a strong band at 3280 cm^{-1}. This must be due to free N–H, to hydrogen-bonded N–H or to hydrogen-bonded O–H. To differentiate between these possibilities the product was examined in very dilute carbon tetrachloride solutions so as to decrease the effect of hydrogen bonding. Under these conditions the intensity of the band was greatly diminished (showing that intermolecular hydrogen bonding had existed), and a strong sharp band appeared at 3625 $cm.^{-1}$. According to previous experience at this laboratory and to the correlations of Barnes[5a] and of

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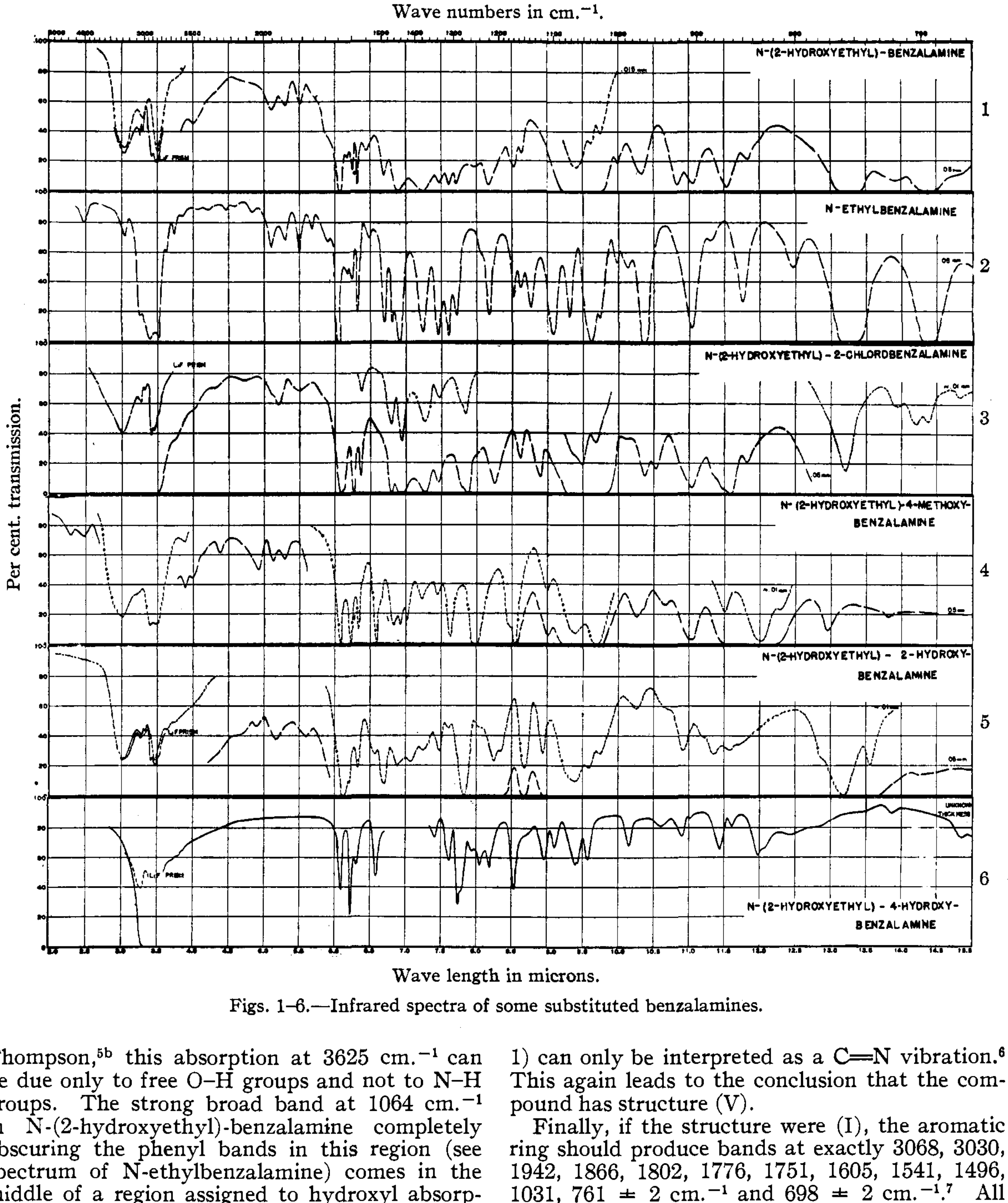
[1] The opinions contained herein are the authors' and are not to be construed as official or reflecting the views of the Department of the Navy. Article not copyrighted.

[2] Meltsner, Waldman and Kremers, THIS JOURNAL, **62**, 3494 (1940).

[3] Goodson and Christopher, *ibid.*, **71**, 1117 (1949).

[4] Knorr and Matthes, *Ber.*, **34**, 3487 (1901).

[5] (a) Barnes, Gore, Stafford and Williams, *Anal. Chem.*, **20**, 402 (1948); (b) Thompson, *J. Chem. Soc.*, 328 (1948).



Figs. 1–6.—Infrared spectra of some substituted benzalamines.

Thompson,[5b] this absorption at 3625 cm.$^{-1}$ can be due only to free O–H groups and not to N–H groups. The strong broad band at 1064 cm.$^{-1}$ in N-(2-hydroxyethyl)-benzalamine completely obscuring the phenyl bands in this region (see spectrum of N-ethylbenzalamine) comes in the middle of a region assigned to hydroxyl absorption[5] and is therefore additional evidence for this grouping and structure (V).

The characteristic absorption of a C=N structure may next be considered. Compounds that contain this group always exhibit a strong band in the region 1667 to 1587 cm^{-1}.[5] Since other structural groups which also have characteristic absorption in this region (the olefinic C=C group, for example) are not present in either (I) or (V), the strong band at 1645 cm.$^{-1}$ (Fig. 1) can only be interpreted as a C=N vibration.[6] This again leads to the conclusion that the compound has structure (V).

Finally, if the structure were (I), the aromatic ring should produce bands at exactly 3068, 3030, 1942, 1866, 1802, 1776, 1751, 1605, 1541, 1496, 1031, 761 ± 2 cm.$^{-1}$ and 698 ± 2 cm.$^{-1}$.[7] All of these bands can be identified in the spectrum of the compound (Fig. 1) but it will be noted that several of them have slightly different positions, particularly the last two. This is exactly what

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[6] The condensation products from secondary amines must have the oxazolidine structure (Schiff base is not possible). The absence of the 1645 cm.$^{-1}$ absorption in a sample of 2-phenyl-3-ethyl-oxazolidine, which was kindly supplied by Dr. L. H. Goodson of Midwest Research Institute, substantiates the assignment of the C=N group frequency.

[7] Unpublished work by Dr. D. C. Smith of this laboratory.

TABLE I

SCHIFF BASES

Products	B. p. °C.	B. p. Mm.	M. p., °C.	$n^{25}D$	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
N-(2-Hydroxyethyl)-benzalamine (V)[a]	114–115	1.8	22.5–23.5	1.5728	$C_9H_{11}NO$	9.39	9.27
N-(2-Hydroxyethyl)-benzalamine (V)[b]	115–117	2	24–25[c]	1.5727			
N-(2-Hydroxyethyl)-2-hydroxybenzalamine (II)	143–144	1.6		1.6049	$C_9H_{11}NO_2$	8.48	8.46
N-(2-Hydroxyethyl)-4-hydroxybenzalamine			169–170[d]		$C_9H_{11}NO_2$	8.48	8.51
N-(2-Hydroxyethyl)-2-chlorobenzalamine	132–135	1.6	35–36	1.5792	$C_9H_{10}ClNO$	7.63	7.72
N-(2-Hydroxyethyl)-4-methoxybenzalamine	147–148	1.6	35–36	1.5840	$C_{10}H_{13}NO_2$	7.82	7.91
N-Ethylbenzalamine	58–60	2		1.5371	$C_9H_{11}N$	10.52	10.29

[a] Preparation according to Method (A). [b] Preparation according to Method (B). [c] Mixed melting point of the products obtained by Methods (A) and (B) was 24–25°. [d] Ref. 2 gives m. p. 169°. This compound was recrystallized from a mixture of butyl ether and butyl alcohol.

would be expected for structure (V) where the mono-substituted ring is conjugate to a double bond. Similar deviations are noted in the spectrum of styrene[8] and even more clearly in the spectrum of N-ethylbenzalamine, which is shown in Fig. 2. In fact, the correspondence of the spectra in Figs. 1 and 2 is so great as to remove any doubt that the compound in question is structure (V), particularly when it is realized that most of the spectral differences in Figs. 1 and 2 are due to the presence of a —CH_2OH group in (V) as compared to a —CH_3 group in N-ethylbenzalamine. The reaction product of benzaldehyde and ethanolamine is thus identified clearly as structure (V) and is labeled accordingly in Fig. 1.

The correspondence between the spectrum of N-ethylbenzalamine (Fig. 2) and the spectra of the other compounds investigated (Figs. 3, 4, 5 and 6) indicates likewise that all have the Schiff base structure. However, if any of the three characteristics enumerated above for structure (V) can be shown present, the structure will be established. Referring to Figs. 3 and 4 the strong bands at 3280 and 1064 cm.$^{-1}$ are again present. The carbon tetrachloride solution again displayed a decrease at 3280 cm.$^{-1}$ and the free hydroxy band at 3625 cm.$^{-1}$ was strong and sharp. The C=N grouping is also present, as evidenced by the absorption at 1640 cm^{-1}. Accordingly, there is no doubt that N-(2-hydroxyethyl)-2-chlorobenzalamine and N-(2-hydroxyethyl)-4-methoxybenzalamine also have the Schiff base structure.

N-(2-Hydroxyethyl)-2-hydroxybenzalamine and N-(2-hydroxyethyl)-4-hydroxybenzalamine (Figs. 5 and 6) contain the additional hydroxyl group on the ring so that for either the Schiff base or the oxazolidine structure the spectrum should contain bands at 3280 and 1064 cm^{-1}.[9] However, the C=N group will only be present in the Schiff base structure and the band at 1640 cm.$^{-1}$ in both spectra is sufficient evidence to label these compounds according to the Schiff base structure.

In conclusion it may be mentioned that certain spectral differences in the 833 to 666 cm.$^{-1}$ region for the disubstituted aromatic compounds (Figs. 3, 4, 5 and 6) as compared to the monosubstituted compounds (Figs. 1 and 2), are due to the particular type of substitution. Monosubstituted benzene rings have two strong characteristic bands at 746 and 694 cm.$^{-1}$ (Figs. 1 and 2). The absence of the 694 cm.$^{-1}$ band and the shift of the 746 cm.$^{-1}$ band to 757 cm.$^{-1}$ in Figs. 3 and 5 are expected changes due to ortho substitution.[5] Likewise the absence of the 694 cm.$^{-1}$ band and the new band at 833 cm.$^{-1}$ in Figs. 4 and 6 are indications of para substitution.

Experimental

The preparation of the compounds presented in Table I consisted of heating an aldehyde with ethanolamine or ethylamine as exemplified by Method (A).

Method (A).—To 21.2 g. of benzaldehyde, 12.2 g. of ethanolamine was slowly added with stirring and the mixture heated several minutes. Redistillation gave a colorless product. Compound (V) was also prepared by an alternate Method (B).

Method (B).—A mixture of 12.2 g. of benzaldehyde (redistilled) 12.2 g. of ethanolamine and 100 ml. of benzene was refluxed for one hour during which time 3.5 ml. of water was collected in an attached water trap. After removing the benzene and water, the product was distillled. Redistillation gave a colorless product.

Spectroscopic Equipment and Methods.—The spectra were obtained on a large prism spectrometer described in detail elsewhere,[10] using a rocksalt prism for the 670 to 5000 cm.$^{-1}$ range. In some cases (see figures) a lithium fluoride prism was also used in the 2500 to 4000 cm.$^{-1}$ region to obtain higher resolution in this range.

All liquid samples were in stoppered cells of appropriate thickness with potassium bromide windows. In most cases, due to high viscosity, the very thin films were obtained by placing a small amount of liquid between two polished potassium bromide plates. Only approximate values of the thickness are given for these films (see figures). The one solid sample [N-(2-hydroxyethyl)-4-hydroxybenzalamine] was ground to a fine slurry with liquid petrolatum and pressed between potassium bromide plates (Fig. 6). Very dilute solutions in carbon tetrachloride were used to investigate hydrogen bonding in the region 3625 to 3150 cm.$^{-1}$. Cells of 10, 21 and 52 mm. thickness were used in this phase of the work.

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(8) National Bureau of Standards A. P. I. Project 44, Catalogue of Infrared Spectrograms, Serial No. 170, contributed by The Dow Chemical Company.

(9) N-(2-Hydroxyethyl)-4-hydroxybenzalamine was in the solid state. It is well known that shifts in group frequencies can occur in changing the state of a sample and these shifts will be especially noticeable for groups involved in bonded structure. Apparently the OH valence frequency in this compound has shifted and is obscured by the petrolatum absorption in the 2860 to 3030 cm.$^{-1}$ region.

(10) Nielsen, Crawford and Smith, *J. Opt. Soc. Am.*, **37**, 296 (1947).

Acknowledgment.—The guidance and advice of Dr. D. C. Smith are gratefully acknowledged.

Summary

The reaction of benzaldehyde and certain substituted derivatives with ethanolamine gives compounds with the Schiff base structure rather than the oxazolidine ring structure previously assigned to these compounds.

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Properties of Electrolytic Solutions. XLVI. Conductance of Long Chain Salts at Low Concentration in Water[1]

BY DONALD W. KUHN[2] AND CHARLES A. KRAUS

I. Introduction

In the limit, the conductance of ordinary salts in aqueous solution changes with concentration in accordance with Onsager's theory, in that the conductance is a linear function of the square root of concentration. The slope of this line is predetermined by the limiting conductance, Λ_0, the charges on the ions and the dielectric constant and the viscosity of the solvent.

It has commonly been assumed that solutions of long chain salts conform to this relation from the lowest concentrations up to the critical point where the course of the conductance curve changes abruptly. If the critical concentration is high, deviation occurs as in the case of ordinary salts. In brief, it has commonly been assumed that long chain salts behave like normal electrolytes at concentrations below the critical.

It should be noted, however, that up to now, there have been no measurements with long chain salts of sufficient precision to warrant any definite conclusion as to the course of the conductance curve at low concentrations. While the indications are that the conductance varies linearly as a function of the square root of concentration, the measurements have been carried out at relatively high concentrations and the experimental data are not sufficiently precise to fix the slope of the straight line with certainty. Chance observations in this laboratory have led us to suspect that the slope of the $\Lambda - \sqrt{C}$ curve might be greater than the theoretical, particularly in the case of salts with very long chains. Accordingly, it was thought worth while to investigate the precise course of the conductance curve of long chain salts at concentrations below the critical.

Since the critical concentration of salts with very long chains is often quite low (2.0×10^{-4} N), it was necessary to devise suitable techniques for carrying out conductance measurements at very low concentrations. The specific conductance of ordinary distilled water is of the order of 1×10^{-6} mho. The equivalent conductance of long chain salts is in the neighborhood of 100. The specific conductance of a 5×10^{-5} N solution is, therefore, 5×10^{-6}, or 5000×10^{-9} mho. It is obvious that if the conductance of the salt is to be determined with precision, the conductance of water must be known to a few units in the ninth place of decimals.

Shedlovsky and his co-workers have elaborated a technique that has proved quite successful with solutions of ordinary salts in water. This technique, however, is not readily applicable to solutions of long chain salts, chiefly because bubbles formed in stirring are very stable and cling tenaciously to the electrodes and the walls of the cell. It appeared desirable, therefore, to devise a technique adapted to solutions of long chain salts.

The method, as finally employed, consists in carrying out all manipulations with the conductance cell in a closed chamber similar to the well-known "dry box." The carbon dioxide content of the atmosphere within this chamber is controlled and manipulations are carried out within the box by means of long-sleeved rubber gloves. An attempt was first made to absorb all the carbon dioxide but this did not prove successful. It was found, however, that by passing the air from the atmosphere through an aspirator pump and then through the box, water in equilibrium with this air had a specific conductance of approximately 0.4×10^{-6} which was very constant. The pH of the tap water was 9, which accounts for the low value of the specific conductance of water in equilibrium with air from the aspirator pump.

II. Apparatus and Procedure

1. **The Conditioning Box.**—As a chamber within which to carry out manipulations, a stainless steel "dry box" was employed; the top of the box consisted of a sheet of lucite. The box was provided with an air-lock which was provided with a movable platform and closures to the box and to the external atmosphere. These devices could be conveniently manipulated from without the box. Air from without the laboratory was passed through three aspirator pumps, the air and water being discharged into a chamber of about 5 gallons capacity. From this chamber the air was piped into the box as well as into the air-lock. From the chamber the air passed out through three cylindrical metal guard chambers each of about 2 gallons capacity. The purpose of the guard chambers was to ensure that no air from without was introduced into the box during manipulations with the rubber gloves.

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(1) This paper is based on a portion of a thesis presented by Donald W. Kuhn in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1949.

(2) Du Pont Postgraduate Fellow in Chemistry, Brown University, 1947–1948.