A maximum value of K_2 for diphenylmethane of $^1/_3$ K_1 (for diphenylmethane) is predicted if it is assumed that the position sterically prohibited is the other side of the ring containing the first silver ion. The observed value of K_2 is 1.04 as compared to a maximum calculated value of 1.15.

In attempting to predict K_2 values for the fused ring systems, as represented by naphthalene and phenanthrene one cannot overlook the possibility that structures for Ag_2Ar^{++} in which two silver ions are coördinated with adjacent rings on the same side of the plane of the molecule are sterically unfavorable. Neglecting such structures values of K_2 may be calculated which are considerably less than the observed values. For fused ring systems, the structural nature of the Ag_2Ar^{++} complex may be somewhat different from those suggested for non-fused ring molecules.

Summary

By measurement of the solubilities of several aromatic hydrocarbons in aqueous silver nitrate solutions, evidence has been obtained for the formation of two water-soluble complexes, $AgAr^+$ and Ag_2Ar^{++}. Equilibrium constants for the reactions to form these complexes at 25° have been calculated. Structures for the complexes are suggested, and the tendencies for the various hydrocarbons to undergo argentation have been considered in terms of these structures.

A method of analysis for the aromatic hydrocarbon content of aqueous solutions is described in which the hydrocarbon is extracted from the solution with hexane, and its concentration in the hexane phase determined by spectrophotometric measurement.

DAVIS, CALIFORNIA RECEIVED MAY 3, 1949

Ag_2Ar^{++} in which one silver ion is coördinated with each ring. The method used in predicting a value for K_2 is similar to that used in approximating dissociation constants for dibasic acids; *cf.* Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, N. Y., 1945, p. 200.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Absorption Spectra of ortho-Substituted Aldehydes.
I. The *o*-Hydroxynaphthaldehydes[1]

BY NORTEN C. MELCHIOR[2]

The difficulties encountered in attempts to correlate the molecular structures of compounds with their absorption spectra makes careful comparisons of the spectra of closely related compounds important. During an investigation[3] of some of the metal derivatives of the *o*-hydroxynaphthaldehydes, the absorption spectra of these aldehydes and their negative ions was measured in methanol–water solutions. The striking differences in these spectra led to this extension of the measurements.

Experimental

Absorption Measurements.—All measurements were made with a Beckman model DU spectrophotometer in silica cells having a 10-mm. light path. The temperature of the cells was controlled by hollow metal plates, pierced by a small opening for the light beam, which were placed on opposite sides of the cell compartment. Water from a controlled temperature bath was circulated through these plates. A slow stream of dry air passed into the cell compartment prevented fogging of the cell windows at temperatures below the dew point of the laboratory air. Small differences in the measurements due to the volume change of the solvent were eliminated by making final dilutions at the temperature at which the spectrum was run, or by calculation from the measured temperature–volume coefficient of the solvent. Measurements at a given wave length were made with the same slit width, which was kept as small as possible.

Solvents.—Methanol was reagent grade, octane and heptane mixtures were purified by standard procedures. In all cases blanks were prepared from the same sample of solvent used for dissolving the compound studied.

Aldehydes.—The preparation of these compounds has been reported.[3,4] Each sample was sublimed several times at pressures below 0.001 mm., once immediately before use.

Results.—The more pertinent results are shown in Figs. 1 to 5. It is evident in Fig. 1 that the first band of the negative ion of 3-hydroxy-2-naphthaldehyde appears at a lower frequency but with considerably lower intensity, than do those of its isomers. It is easily seen by comparing Figs. 2, 3 and 4 that this is also the case in the neutral molecule, regardless of solvent. It is also apparent that solvent change has a greater effect on the spectrum of the 3-2-compound than upon that of either of its isomers. In addition, Fig. 5 shows the striking effect of temperature change on the absorption spectrum of the 3-2-compound in 80 mole per cent. methanol.

---

[1] Presented at the meeting of the American Chemical Society in San Francisco, March, 1949.

[2] Present address: Stritch School of Medicine, Loyola University, Chicago 12, Illinois.

[3] (a) Calvin and Melchior, THIS JOURNAL, **70**, 3273 (1948); (b) Thesis, N. C. Melchior, University of California, 1946.

[4] Arnold and Sprung, THIS JOURNAL, **60**, 1163–1164 (1938).

This effect is of a different order of magnitude than that shown by its isomers, or indeed by the compound itself in the other solvents studied. These latter effects would not be visible on the scale used.

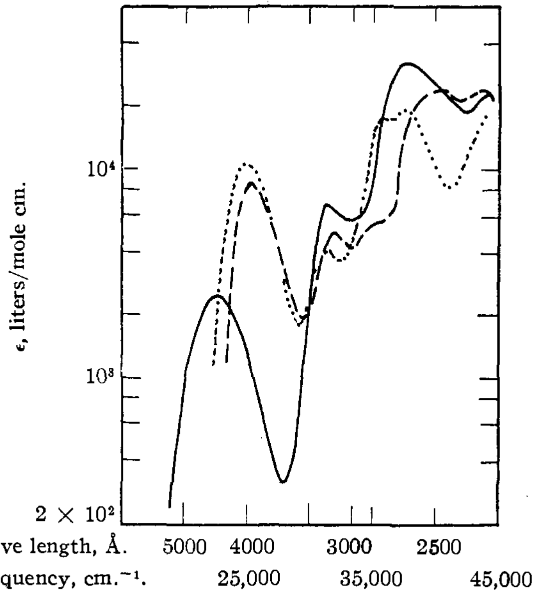


Fig. 1.—Absorption spectra of the negative ions of *o*-hydroxynaphthaldehydes at 35° in 95 mole % water, 5 mole % methanol, 0.1 *M* OH^-: solid line, 3-formyl-2-naphthoxide; dashed line, 1-formyl-2-naphthoxide: dotted line, 2-formyl-1-naphthoxide.

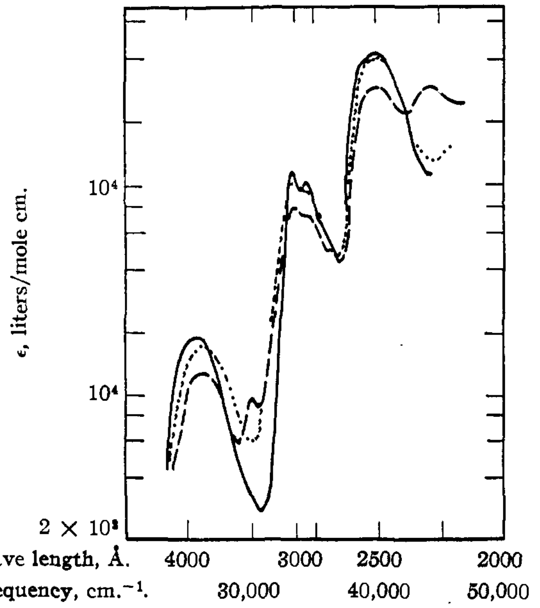


Fig. 2.—Absorption spectrum of 3-hydroxy-2-naphthaldehyde: solid line, in heptanes at 25°; dashed line, in 80 mole % methanol, 20 mole % water, 0.01 *M* hydrochloric acid at 35°; dotted line, in 5 mole % methanol, 95 mole % water, 0.01 *M* hydrochloric acid at 35°.

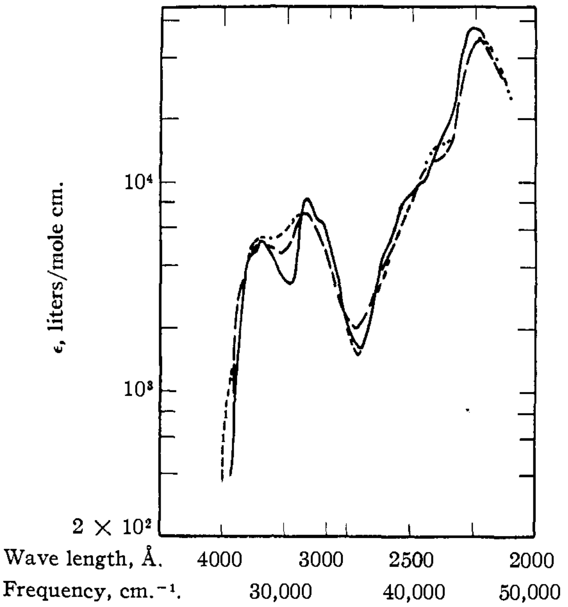


Fig. 3.—Absorption spectrum of 2-hydroxy-1-naphthaldehyde at 35°: solid line, in octane; dashed line, in 80 mole % methanol, 20 mole % water, 0.01 *M* hydrochloric acid: dotted line, in 5 mole % methanol, 95 mole % water, 0.01 *M* hydrochloric acid.

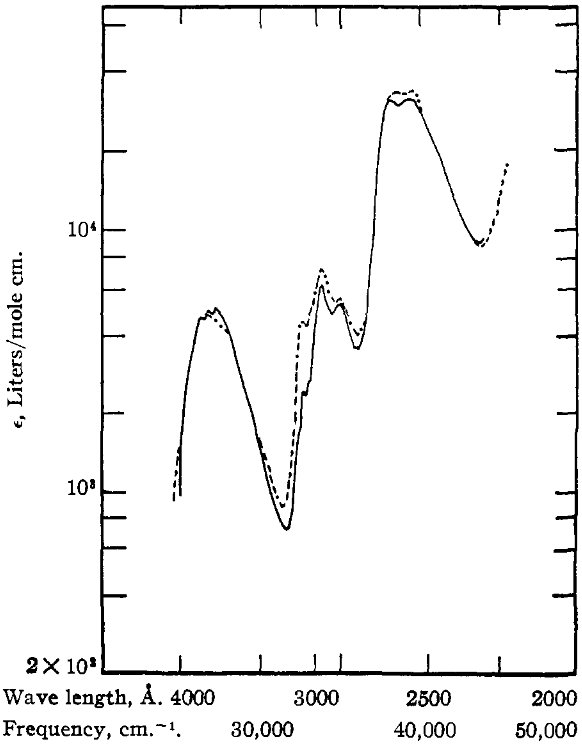


Fig. 4.—Absorption spectrum of 1-hydroxy-2-naphthaldehyde: solid line, in heptanes at 25°; dotted line, in 80 mole % methanol, 20 mole % water, 0.01 *M* hydrochloric acid at 35°.

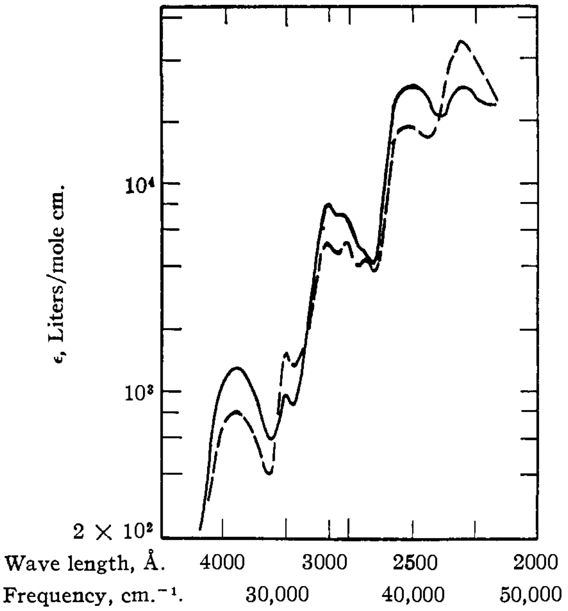
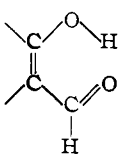
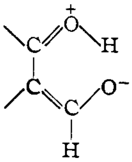


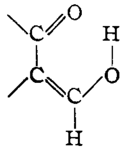
Fig. 5.—Absorption spectrum of 3-hydroxy-2-naphthaldehyde in 80 mole % methanol, 20 mole % water, 0.01 *M* hydrochloric acid; solid line, at 35°; broken line, at 2°.

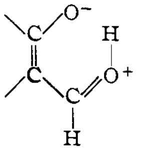
Discussion

It should be possible to account for some of the observed differences in the spectra of these compounds on the basis of reasonable assumptions concerning the nature of the ground and excited states of the molecules. If we consider their common naphthalene nucleus, we find that its major resonance forms are such that the bond between carbon atoms 1 and 2 has about $^2/_3$ double bond character while that between carbon atoms 2 and 3 has only about $^1/_3$ double bond character. In the molecules considered, hydrogen bonding will be an important additional factor, so that we may expect structures such as the following to make contributions to the ground state of the molecule[5]:


I

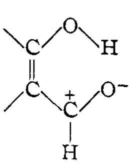

II

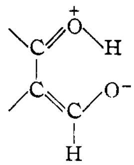

III

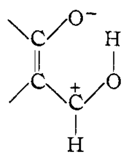

IV

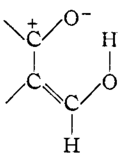
Structures I and IV do not require a double bond between the carbon atoms holding the functional groups, but structures II and III require that a double bond be available there. Therefore, as a first approximation, we would expect the contribution of forms II and III to the resonance hybrid to be less in the case of 2-hydroxy-3-naphthaldehyde than in either of its ortho-isomers, and that therefore its ground state would be of higher energy than those of its isomers.

It is reasonable to assume that the low energy absorption band (low frequency, long wave length) is associated with absorption by the carbonyl group and that the corresponding upper state may be the hybrid with important contributions from


V


VI


VII


VIII

It is reasonable to assume that structures VI and VIII are so much more important in the upper state than their analogs in the lower state, that, although one would still expect the upper state of the 3-2 compound to be of somewhat higher energy than that of either of its isomers, due in part to differences in the nuclear resonance forms, this energy difference will be reduced.

From this it follows that the energy difference between the upper and lower states of the 3-2 compound will be less than in its isomers; therefore its absorption maximum for this band should appear at a lower frequency, as observed. This postulated energy diagram is given in Fig. 6.

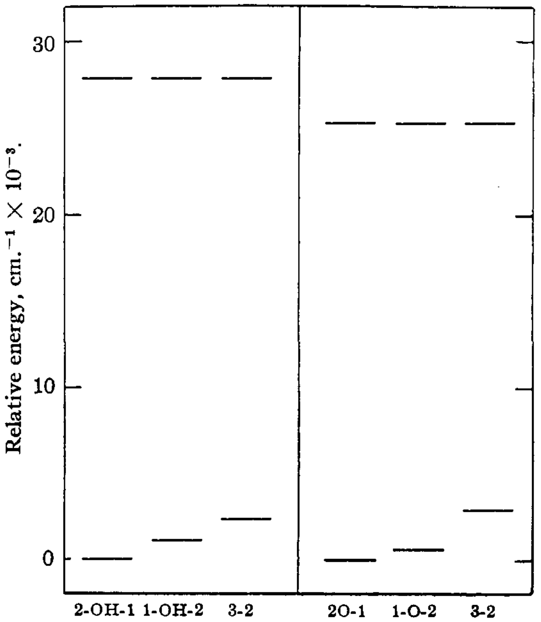


Fig. 6.—Energy diagram for the first absorption bands of hydroxynaphthaldehydes: left, in hydrocarbon solvents; right, in 0.1 *N* sodium hydroxide.

Second, from the author's assumption concerning the nature of the upper state of the low energy band of these compounds, it follows from resonance theory that the shape (*i. e.*, the bond distances and angles) of the ground state of the 1-2-

---

[5] Regardless of the fine structure of the hydrogen bond, its presence must decrease the energy of the molecule and this discussion does not postulate or depend on the fine structure.

and 2-1-compounds more closely approaches that of the upper state than does that of the 3-2-compound. From the Franck–Condon principle that the absorption of light occurs in a fraction of time much shorter than that required for atom vibrations, it follows that, other factors being equal, the more completely the shape of the molecule in the lower state corresponds to the shape of its upper state, the higher is the probability of light absorption. Thus one would predict that the probability of light absorption would be lower *for this band* in the 3-2 compound than for its isomers. This lowered probability would be reflected directly in the extinction coefficient if, as in this case, the bands are approximately the same shape.

This argument is applicable in its entirety to the corresponding absorption band of the negative ions of these compounds, with the resultant prediction that the first band of the negative ion of the 3-2 compound will appear at a lower frequency but with a lower extinction coefficient than those of its isomers. Both predictions are in agreement with the experimental results in Fig. 1. This relatively lower resonance interaction of the ground state of the ion of the 3-2 compound as compared with its isomers is in harmony with the results of Arnold and Sprung,[4] who found that it was a much weaker acid than its isomers, and with observations made on metal derivatives of these compounds.[3]

Extension of this reasoning to the closely related compounds, salicylaldehyde and the enol form of acetylacetone, leads to the prediction that the absorption probability for the low frequency bands of these compounds should increase in the order: 3-2, salicylaldehyde, [1-2, 2-1], acetylacetone; and that the same order should hold for the absorption probability of their negative ions. We are not, however, able to predict the energy of this transition. Table I indicates that the predictions of the order of the extinction coefficients is confirmed by experiment. The fact that the intensity of absorption in the first band of a series of diphenylpolyenes increases with the number of double bonded units in the chain[6] is in agreement with this idea. Table II shows some additional examples of variations in extinction coefficients of corresponding absorption bands in closely related compounds for which the idea of corresponding shapes may provide an explanation. In the absorption of light by a carbonyl group, the excited state is a hybrid which presumably has a single bond between the carbon and oxygen atoms. Thus any change in the molecule which would increase the C^+-O^- contribution in the ground state should, according to the idea of corresponding shapes, increase the absorption probability. The electron donating effects of the alkyl groups *and their steric effects would both increase the* C^+-O^- contribution in hexaethylacetone over that in acetone itself, and the expected increase in extrinction coefficient is found.

TABLE I

Compound	Hexane λmax. Å.	Hexane Log ε	0.1 *N* NaOH λmax, Å.	0.1 *N* NaOH Log ε	Double bond character[a]
3-Hydroxy-2-naphthaldehyde	3900	3.28	4420	3.73	1/3
Salicylaldehyde	3280	3.56	3820[b]	3.85[b]	1/2
2-Hydroxy-1-naphthaldehyde	3700	3.67	3950	3.90	2/3
1-Hydroxy-2-naphthaldehyde	3810	3.67	4050	4.02	2/3
Acetylacetone enol	2730[c]	>3.90[c]	2900[d]	4.38[d]	1

[a] Of the bond between the carbons holding the functional groups. [b] Lemon, THIS JOURNAL, **69**, 2998 (1947). [c] In absolute ethanol, Blout, Eager and Silverman, *ibid.*, **68**, 566 (1946). [d] Grossman, *Z. physik. Chem.*, **109**, 305 (1924).

TABLE II

Compound	λmax.	Log ε
Acetone[a]	2740	1.15
Hexaethylacetone[a]	3080	1.44
1,3-Butadiene[b]	2170	4.32
Piperylene[b]	2235	4.41
2,4-Hexadiene[b]	2270	4.41
Cyclohexadiene[b]	2560	3.90
Cyclopentadiene[b]	2385	3.53

[a] Lewis and Calvin, *Chem. Revs.*, **25**, 279 (1939). [b] Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940).

The data in Table II for the conjugated dienes may be interpreted similarly if we assume that the upper state of the absorption considered involves an oscillation of electrons over the four-carbon conjugated system. The preferred configuration approaches a line in this case, therefore the closer the lower state is to a linear system the higher should be its absorption probability. The straight chain dienes, it is seen, have similar extinction coefficients, while in the dienes where ring formation restricts the approach to linearity, the values are considerably lower. Moreover, the values decrease with decrease in ring size as expected.

It should be emphasized that the shape factor is only one of the factors which affect absorption probability, but these data indicate that it is important and might be used with due caution in drawing conclusions about the actual shapes of molecules.

Temperature Effects.—With the exception of the 3-2 compound, the temperature effects over the small range used (25°) are too small to be shown on these figures. The expected effect is a slight broadening of each band and a shift of the band toward the red. However, when two bands are sufficiently close together, these effects add on the low frequency band and oppose on the higher frequency band with the result that the low frequency peak will increase with temperature, while the higher frequency peak decreases. These effects, however, are slight. In the case of the 3-2 compound in 80 mole per cent. methanol–water solution (Fig. 5) an effect of a far different order

---

(6) Hauser, R. Kuhn and E. Kuhn, *Z. physik. Chem.*, **B29**, 391 (1935).

of magnitude is observed. This effect is attributed to the reversible formation of the acetal and will be discussed in paper II of this series.

Summary

The absorption spectra of the three *o*-hydroxynaphthaldehydes and their negative ions has been determined in a variety of solvents. A theory, based on resonance possibilities in the ground and excited states, accounts for the striking differences in the low frequency absorption bands of these compounds.

CHICAGO 12, ILL. RECEIVED APRIL 27, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Absorption Spectra of *o*-Substituted Aldehydes. II. Aldehyde–Acetal Equilibrium in Methanol–Water Solutions[1]

BY NORTEN C. MELCHIOR[2]

The striking effect of temperature change upon the absorption spectrum of 3-hydroxy-2-naphthaldehyde in acidified 80 mole per cent. methanol–water,[3] and the fact that temperature change had no such effect on the spectra of either 1-hydroxy-2-naphthaldehyde or 2-hydroxy-1-naphthaldehyde under identical conditions led to the extension of these studies to related compounds. Under the same conditions it was found that the spectrum of salicylaldehyde was somewhat affected by temperature, while that of *o*-methoxybenzaldehyde showed a pronounced temperature effect. Further experiments showed that the temperature dependence vanished when *neutral* methanol or methanol–water was used as solvent, and that temperature dependence appeared when acidified 98 mole per cent methanol was used as solvent for either 1-hydroxy-2-naphthaldehyde or 2-hydroxy-1-naphthaldehyde. These experiments suggested that the changes observed were caused by acid catalyzed formation of acetals or hemiacetals. To distinguish between these possibilities, and to define the differences existing among these related compounds, their spectra were determined in neutral and acid methanol–water solutions over a range of temperature and methanol concentration.

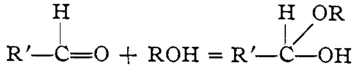
Experimental

Absorption Measurements.—A Beckman model D. U. spectrophotometer was used in all measurements. One-cm. fused silica cells with standard taper stoppers prevented solvent loss by evaporation. The temperature of the cells was controlled as previously described.[3] As a precaution, the previously purified aldehydes were distilled or sublimed immediately before use and were handled in nitrogen. Methanol was reagent grade, and blanks were prepared from the same sample of solvent in all cases.

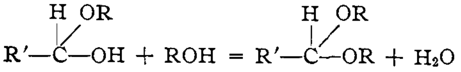
Preparation of Salicylaldehyde Methyl Acetal.—Twenty-five ml. (29 g.) of salicylaldehyde was dissolved in 100 ml. of methanol which contained 0.002 mole of hydrochloric acid. The solution was cooled in stages to Dry-Ice temperature and stored in Dry Ice for one week. It was then neutralized at that temperature with 1 *N* sodium hydroxide, and the methanol and water removed below 0.1 mm. as the mixture warmed to room temperature. The precipitated salt was filtered off with the aid of an anhydrous ether wash, and the product distilled at less than 0.01 mm. after removal of the ether below 25°. After the lapse of a week, this fraction was redistilled, and after preliminary evolution of a low-boiling liquid (possibly methanol), a 9-g. fraction (b. p. 64.5–65.0°, 0.01 mm.; d^{25}_{4} 1.107, n^{25}_{D} 1.5119) was obtained. The colorless residue weighed 9 g. Analysis of the distillate gave C, 64.8, 64.8; H, 7.2, 7.3. Calculated for $C_9H_{12}O_3$: C, 64.27; H, 7.19. This is apparently the same substance prepared by Pauley and v. Buttlar,[4] but these authors report only the boiling point.

Calculations and Results

The equilibria considered are



$$R'-CH=O + ROH = R'-CH(OR)-OH \quad (1)$$



$$R'-CH(OR)-OH + ROH = R'-CH(OR)-OR + H_2O \quad (2)$$

The equilibrium constant for the sum of reactions 1 and 2 is

$$K_{1+2} = \frac{a_{\text{acetal}}a_{\text{water}}}{a_{\text{aldehyde}}a^2_{\text{methanol}}} = \frac{\gamma_{Ac}N_{Ac}\gamma_{H_2O}N_{H_2O}}{\gamma_{Al}N_{Al}\gamma^2_{MeOH}N^2_{MeOH}} \quad (3)$$

If we assume that hemiacetal formation is small, the ratio N_{Ac}/N_{Al} can be obtained from the measured absorption spectra as

$$\frac{N_{Ac}}{N_{Al}} = \frac{\epsilon_0 - \epsilon}{\epsilon - \epsilon_1} \quad (4)$$

where, at a given wave length,[5] ϵ_0 is the measured extinction coefficient of the aldehyde in neutral methanol, ϵ_1 is that of the acetal in neutral methanol and ϵ is the apparent extinction coefficient of the aldehyde in a given acidified methanol–water solution. If ϵ_1 is zero or small compared to ϵ_0 and ϵ, the equation reduces to (1)

$$N_{Ac}/N_{Al} = \epsilon_0 - \epsilon/\epsilon \quad (5)$$

Measurements of the spectra of the acetals of salicylaldehyde and *o*-methoxybenzaldehyde showed that ϵ_1 was small at the wave lengths chosen in each case, and consideration of the spectra of α- and β-naphthol indicated that this

---

[1] Presented at the meeting of the American Chemical Society in San Francisco, March, 1949.

[2] Present address: Stritch School of Medicine, Loyola University, Chicago 12, Illinois.

[3] Paper I, THIS JOURNAL, **71**, 3647 (1949).

[4] H. Pauley and R. v. Buttlar, *Ann.*, **383**, 283 (1911).

[5] The preferred wave length is that of an absorption maximum which can be ascribed to the carbonyl group.