

nitrate added to 0.083 *m* dodecanesulfonic acid which was also 0.0035 *m* in hydrochloric acid caused a drop in *e. m. f.* of 11.2 millivolts (Fig. 3, upper curve), corresponding to an increase in  $\log \gamma_{H^+}\gamma_{Cl^-}$  of  $11.2/59.1 = 0.190$ . Neglecting, as a first approximation, the increase of ionic strength caused by the salt addition, and ascribing this increase simply to the displacement of hydrogen ions from the micelles, the concentration of free hydrogen ions has been multiplied by (antilog 0.190) or 1.55. If, after adding excess of salt, the concentration of free hydrogen ions is equal to the stoichiometric concentration, which is 0.087 *m*, the concentration of free hydrogen ions before adding the salt was  $0.087/1.55 = 0.056$  *m*. The proportion of hydrogen ions of the sulfonic acid which are bound in the micelle is  $(0.087 - 0.056)/0.083$ , or 37%.

This is a lower limit to the proportion of bound hydrogen ions, since no account was taken of the increase of ionic strength caused by salt addition. It is consistent with the upper limit estimates of 50% from *e. m. f.*, and 70% from freezing point, made by McBain and Betz.<sup>1</sup>

It is noteworthy that hydrogen ions seem to be displacable from the micelles over the whole concentration range studied. This gives no

evidence either for or against the view of McBain<sup>5</sup> that there are two or more kinds of micelle whose proportions change with concentration.

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### Summary

1. The activity coefficient of hydrochloric acid in solutions of 1-*n*-dodecanesulfonic acid has been measured by an electromotive force method. The activity coefficient-concentration curve is of the form characteristic of colloidal electrolytes.

2. The ratio of activity coefficients of chloride ion and dodecanesulfonate ion in these solutions has been evaluated.

3. Addition of neutral salt causes an increase in the activity of hydrochloric acid. This is interpreted as a displacement of hydrogen ions from the colloidal micelles and, from the magnitude of the effect, a lower limit of 37% for the proportion of bound hydrogen ions in 0.083 *m* sulfonic acid is estimated.

(5) McBain, Laing and Titley. *J. Chem. Soc.*, **115**, 1279 (1919), also ref. 3.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

## The Absorption Spectra of Some Para Substituted Aniline Derivatives. The Presence of $x'$ Bands

BY W. D. KUMLER

Lewis and Calvin<sup>1</sup> and Lewis and Bigeleisen<sup>2</sup> have given evidence for the existence of second order  $x$  bands in carotinoids, polyenes and several types of dyes. These second order  $x$  bands have been designated  $x'$  bands and result from an electronic oscillation along the long axis of the molecule but are an "octave" higher than the main  $x$  band. The compounds in which such bands have been found absorb mainly in the visible and are symmetrical or nearly so.

In this communication evidence is presented for the existence of  $x'$  bands in a series of highly unsymmetrical compounds all but two of which absorb mainly or entirely in the ultraviolet. All of these compounds are of the type A——B in which A is an electron donating group and B is an electron attracting group. The A group in the series is amino or alkyl substituted amino and the B group is nitroso, nitro, aldehyde, acetyl, carboxyl and sulfonamide.

**Evidence for  $x'$  Bands.**—Two criteria for  $x'$  bands have been set up by Lewis and co-workers<sup>1,2</sup> by noting the characteristics of an oscillator of

varying anharmonicity. One criterion is that the ratio of the frequencies of the short to the long wave length band  $\bar{\nu}'/\bar{\nu}$  should be less than two and increase in a series of compounds as the wave length  $\lambda$  increases, the other that the ratio of the extinction coefficients  $\epsilon'/\epsilon$  should decrease as  $\bar{\nu}'/\bar{\nu}$  increases.

For a perfect harmonic oscillator  $\bar{\nu}'/\bar{\nu}$  is two but  $\epsilon'/\epsilon$  would be zero because the probability of the 0-2 jump is zero. As the anharmonicity increases  $\bar{\nu}'/\bar{\nu}$  would decrease from two and  $\epsilon'/\epsilon$  increase from 0. The relative anharmonicity depends on the amplitude of the electronic oscillations relative to the dimensions of the molecule. The amplitude depends on the polarizability and the latter is greater for those compounds whose bands come at long wave length. Hence  $\bar{\nu}'/\bar{\nu}$  should decrease and  $\epsilon'/\epsilon$  increase as we go down a series of compounds arranged in descending order of  $\lambda$ .

The spectra of the eighteen compounds studied are given in Figs. 1-6. In spite of the fact that the compounds contain B groups that have quite different chemical properties, the spectra of all these compounds are very similar, being characterized by two bands, a long wave length band of

(1) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(2) Lewis and Bigeleisen, *This Journal*, **65**, 2107 (1943).

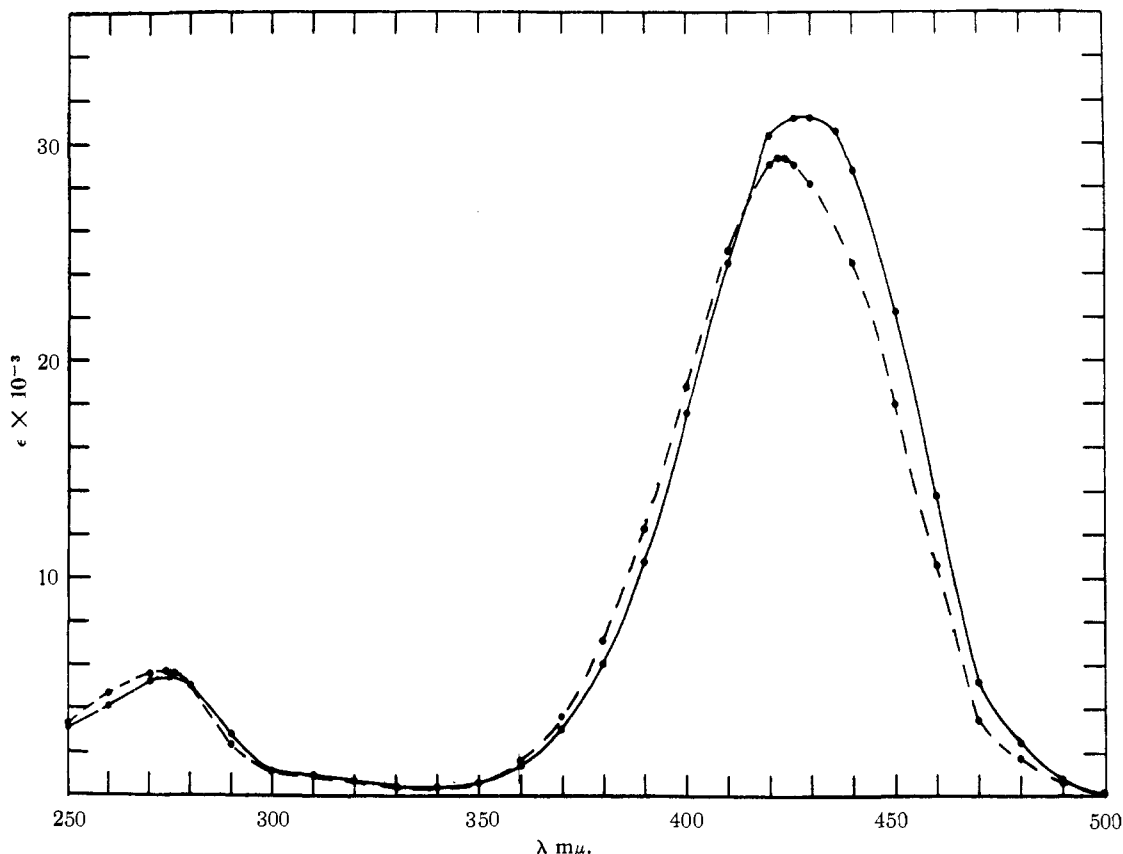


Fig. 1.——— *p*-Nitrosodiethylaniline; - - - *p*-nitrosodimethylaniline.

high extinction and a short wave length band of low extinction. Although the wave lengths of maximum absorption of the main bands vary from 428 to 262  $m\mu$  the extinction coefficients of both the main and the secondary bands vary only by a factor of approximately two over the whole series.

In Table I the compounds are arranged in the

order of decreasing wave length of the main band. If we exclude the nitro compounds,  $\bar{\nu}'/\bar{\nu}$  decreases fairly regularly and  $\epsilon'/\epsilon$  in general increases as we go down the table. In Fig. 7 the ratio of the frequencies  $\bar{\nu}'/\bar{\nu}$ , which has the same numerical value as  $\lambda/\lambda'$ , is plotted against  $\lambda$ . It will be noticed that  $\bar{\nu}'/\bar{\nu}$  is virtually a linear

TABLE I

In 95% alcohol	$\lambda$	$\lambda'$	$\bar{\nu}$	$\bar{\nu}'$	$\epsilon$	$\epsilon'$	$\bar{\nu}'/\bar{\nu}$	$\epsilon'/\epsilon$
<i>p</i> -Nitrosodiethylaniline	428	275	23,300	36,400	31,100	5,470	1.56	0.176
<i>p</i> -Nitrosodimethylaniline	423	273	23,600	36,600	29,400	5,750	1.55	.195
<i>p</i> -Nitrodiethylaniline	400	236	25,000	42,400	21,550	8,850	1.70	.412
<i>p</i> -Nitrodimethylaniline	390	232	25,600	43,100	19,020	9,300	1.68	.488
<i>p</i> -Nitroethylaniline	390	231	25,600	43,250	19,000	7,500	1.69	.395
<i>p</i> -Nitromethylaniline	386	230	25,900	43,400	18,430	7,470	1.68	.405
<i>p</i> -Nitroaniline	375	227	26,700	44,100	15,450	7,180	1.65	.465
<i>p</i> -Diethylaminobenzaldehyde	348	243	28,700	41,100	32,800	6,010	1.43	.183
<i>p</i> -Dimethylaminobenzaldehyde	342	241	29,200	41,500	29,800	7,390	1.42	.248
<i>p</i> -Dimethylaminoacetophenone	337	239	29,700	41,800	25,600	6,340	1.41	.248
<i>p</i> -Ethylaminoacetophenone	332	238	30,100	42,000	25,900	6,030	1.40	.233
<i>p</i> -Aminoacetophenone	317	233	31,500	42,900	20,100	6,750	1.36	.336
<i>p</i> -Diethylaminobenzoic acid	312	227	32,100	44,000	30,650	8,260	1.37	.270
<i>p</i> -Dimethylaminobenzoic acid	308	227	32,400	44,000	25,400	7,450	1.36	.293
<i>p</i> -Aminobenzoic acid	288	220	34,700	45,500	17,400	8,220	1.31	.472
<i>p</i> -Diethylaminobenzenesulfonamide	280	213 <sup>a</sup>	35,700	46,800	26,600	10,200	1.31	.383
<i>p</i> -Dimethylaminobenzenesulfonamide	276	211 <sup>a</sup>	36,300	47,300	24,500	9,400	1.30	.384
<i>p</i> -Aminobenzenesulfonamide	262	204 <sup>b</sup>	38,200	49,000	17,700		1.28	

<sup>a</sup> Estimated from curve. <sup>b</sup> Estimated using Spekker and I. O. Plates.

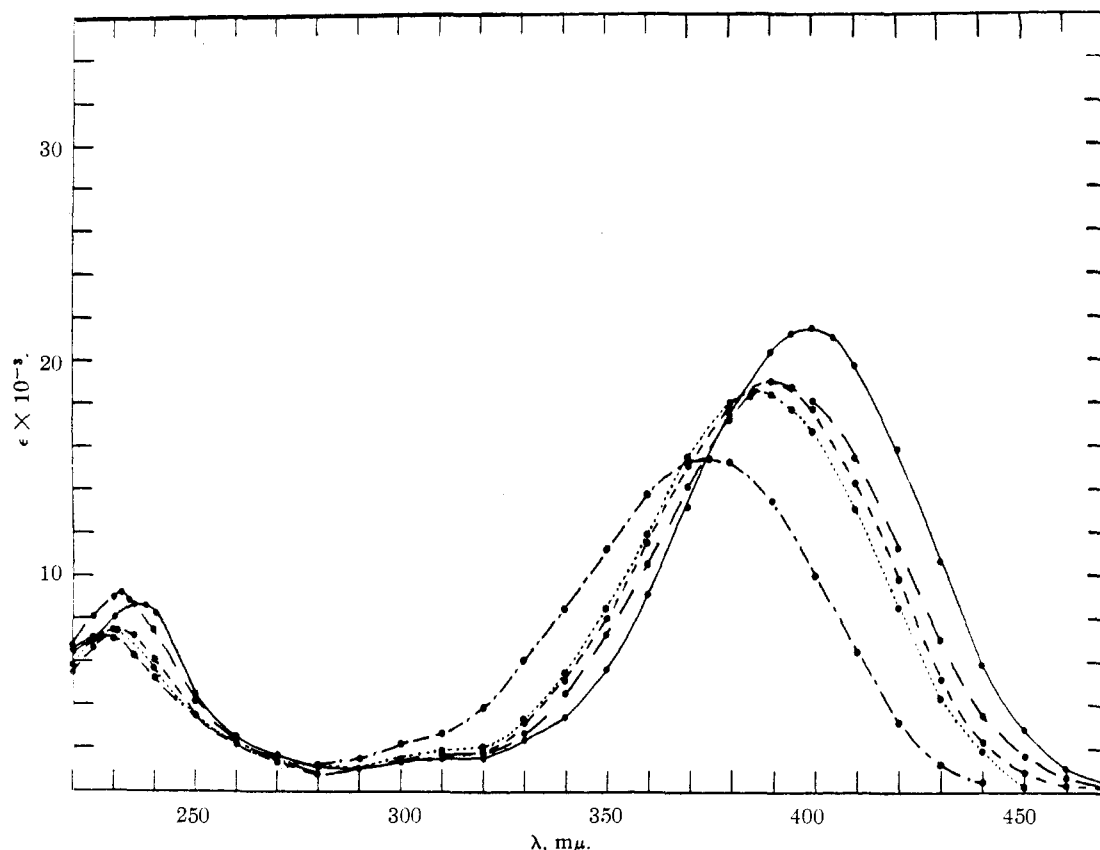


Fig. 2.— ——— *p*-Nitrodiethylaniline; — — — — *p*-nitrodimethylaniline; - - - - - *p*-nitroethylaniline; · · · · · *p*-nitromethylaniline; · · · · · *p*-nitroaniline.

function of  $\lambda$  for all thirteen compounds without nitro groups. This rather remarkable fact demonstrates that the two bands in these compounds are very intimately related and the only interpretation appears to be that they are  $x$  and  $x'$  bands. This interpretation is further strengthened by the observation that when the absorption spectra of one of these compounds is measured in a different solvent the point still falls on the same line. Thus the square near the top in Fig. 7 is *p*-nitrosodimethylaniline in hexane while the same compound in alcohol is represented by the second circle from the top. The square near the middle of the line is *p*-dimethylaminobenzaldehyde in hexane and the third circle above it is the same compound in alcohol. Thus although there is considerable shift to shorter wave length in the main absorption band in going from alcohol to hexane the other band shifts in a comparable manner so the straight line relation is maintained between  $\lambda$  and  $\lambda/\lambda'$ .

In Fig. 8 the plot of  $\epsilon'/\epsilon$  against  $\bar{\nu}'/\bar{\nu}$  shows that the thirteen compounds also fulfill the second criterion<sup>2</sup> for  $x$  and  $x'$  bands in that  $\epsilon'/\epsilon$  diminishes as  $\bar{\nu}'/\bar{\nu}$  increases. The value of  $\epsilon'/\epsilon$  appears to be approaching zero as  $\bar{\nu}'/\bar{\nu}$  becomes two as predicted by the theory.<sup>2</sup> In this plot again the nitro compounds are far off the curve.

**The Anomalous Behavior of the Nitro Compounds.**—The abnormal behavior of the nitro compounds is undoubtedly associated with the resonating semipolar double bond that is present in these compounds and in none of the others. The spectra of the nitro compounds differ from the others in that the high frequency bands appear at shorter wave lengths by 25–30  $m\mu$  compared with the position required to fit in the series; the extinction coefficients of these bands are high, and the extinction coefficients of the main bands are low, and both bands are abnormally wide. This results in high  $\bar{\nu}'/\bar{\nu}$  and  $\epsilon'/\epsilon$  values for these compounds.

It will be noted that the curves for the nitro compounds (Fig. 2) show a third weak band between the other two bands at about 310  $m\mu$ . The band appears to be real for it appears in all the nitro compounds and is still present when a compound is measured in a different solvent. It shifts very little with a change in solvent. This band may be a  $y$  band. It comes at too long a wave length and has too low an extinction coefficient to be considered an  $x'$  band for this series of compounds.

The most probable explanation for the high frequency band around 230  $m\mu$  in the nitro compounds is that it is a combination of a "partial"

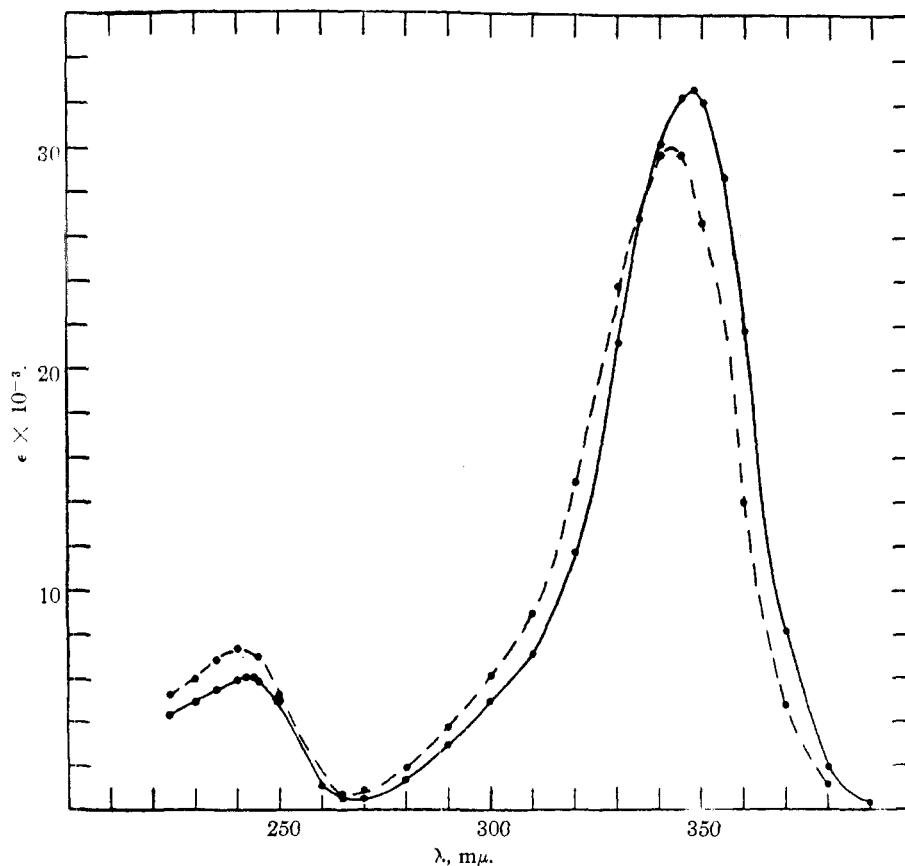
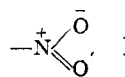


Fig. 3.— ——— *p*-Diethylaminobenzaldehyde; - - - *p*-dimethylaminobenzaldehyde.

with the  $x'$  band. The "partial" would be expected to result from electronic oscillations in the nitro group itself due to the resonance



If this is the case then an aliphatic nitro compound which does not have a group that can resonate with the nitro group should have an absorption band somewhere in this region. The spectrum of 2-nitropropane was investigated and very little absorption was found from the red down to 230  $m\mu$  where the beginning of a band was detected. The extinction coefficient increased as one went to shorter wave length until it reached a value of 2100 at 216.5  $m\mu$  which was the limit of the instrument. The curve was still rising rapidly at this point so the peak is somewhere below this, possibly around 210  $m\mu$  with an extinction coefficient considerably higher than 2100. This comes at too short a wave length to account for the observed band unless the peak is shifted about 20  $m\mu$  when the isopropyl group in 2-nitropropane is replaced by the substituted phenyl group. The heavier group would be expected to cause a shift to longer wave length and the magnitude of the shift does not appear unlikely for such a substitution. The peak of acetone<sup>1</sup> for instance

is shifted about 45  $m\mu$  to longer wave length when its hydrogen atoms are replaced with ethyl groups.

The nitro "partial" could thus account for the band at 230  $m\mu$ , however, the observed band is probably not due exclusively to this "partial" for then one is confronted with the problem of explaining the disappearance of the  $x'$  band and there appears to be no good reason why it should do so. If the observed band is a combination of the "partial" with the  $x'$  band then the observed band should be abnormally high and abnormally wide as has been observed to be the case.

The  $x'$  bands in the nitro compounds would have to come at 255–260  $m\mu$  and have extinction coefficients of 3500–3800 if these compounds were to fall on the lines with the other compounds in Figs. 7 and 8. The observed extinction coefficients at 255 and 260  $m\mu$  are less than this, varying from 2200–3400 as seen in Fig. 2. However, if the  $x'$  bands come 3 or 4  $m\mu$  toward shorter wave length they could account for the observed extinctions and still be very near the lines in Figs. 7 and 8.

The tentative explanation is that the observed high frequency band in the nitro compounds results from a combination of the nitro "partial" with the  $x'$  band. The "partial" having a higher extinction is chiefly responsible for the maximum,

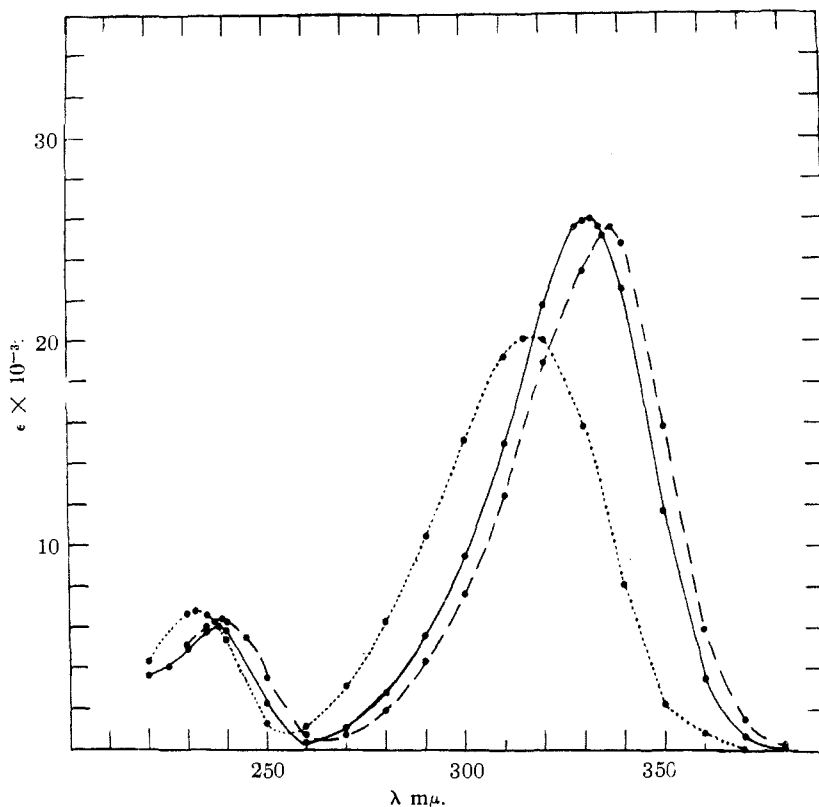


Fig. 4. ——— *p*-Dimethylaminoacetophenone; ——— *p*-ethylaminoacetophenone; - - - - - *p*-aminoacetophenone.

and the  $x'$  band is mainly responsible for the absorption on the long wave length side of the observed band. The combination of the "partial" with the  $x'$  band results in the observed band being both abnormally high and wide.<sup>3</sup>

**The Effect of Solvent on the Wave Length.**—Kumler and Strait<sup>4</sup> pointed out that the shift in  $\lambda$  with different solvents in the case of *p*-nitroaniline is much better correlated with the ability of the solvent to form hydrogen bonds with the solute than it is with the dielectric constant of the solvent. Thus in going from hexane to dioxane the shift in  $\lambda$  is 35  $m\mu$ , and from dioxane to water 38  $m\mu$ . The difference in the dielectric constant of the solvents in the first case is 0.3 and in the second 78.9. On the other hand *p*-nitroaniline can form no hydrogen bonds with hexane but can form them at one end of the molecule with dioxane and at both ends with water.

If hydrogen bonds are responsible for the solvent effect then one would expect a smaller shift when *p*-nitrodimethylaniline, which can form hydrogen bonds at only one end, goes from hexane to alcohol than when *p*-nitroaniline, which can form

(3) Another possible explanation is that the resonance due to the nitro group interacts with the over-all resonance in some way so that the anharmonicity is considerably reduced. This could account for the high  $\bar{\nu}/\bar{\nu}$  values but it would demand low  $\epsilon'/\epsilon$  values and the observed  $\epsilon'/\epsilon$  values are high instead of low.

(4) Kumler and Strait, *THIS JOURNAL*, **65**, 2349 (1943).

hydrogen bonds at both ends, goes from one solvent to the other. This is observed to be the case, the shift with the former is 38  $m\mu$  and with the latter 55  $m\mu$ .

Furthermore, if hydrogen bonds are the only contributing factor, *p*-nitrodimethylaniline should absorb at approximately the same wave length in both hexane and dioxane for it can form hydrogen bonds with neither. However this is not the case. This compound absorbs in hexane at 352  $m\mu$ , in dioxane at 380  $m\mu$ , and in alcohol at 390  $m\mu$ . Thus there is a much greater shift in going from hexane to dioxane than in going from dioxane to alcohol. This is probably due to a dipole interaction between dioxane and the *p*-nitrodimethylaniline. Although dioxane has zero dipole moment there are appreciable dipoles in the molecule between the oxygen and carbon atoms. The molecule must be in the *trans* form  $\leftarrow \rightleftarrows \rightarrow$  so

that these dipoles are opposed. However, there is room for the negative oxygen atom to approach fairly close to the positive amino nitrogen atom thus giving rise to fairly large dipole interactions

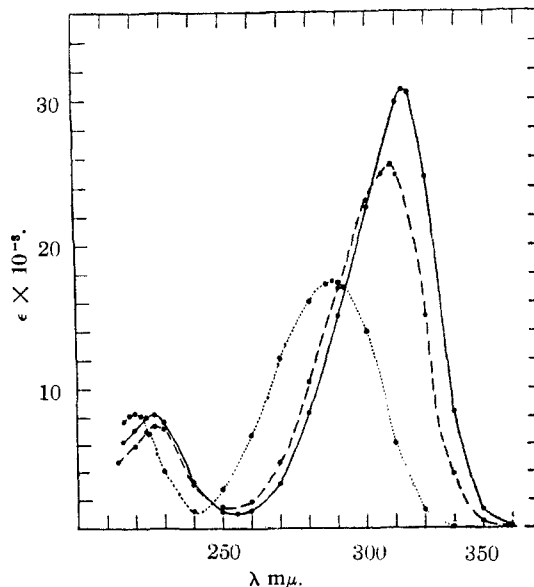


Fig. 5. ——— *p*-Diethylaminobenzoic acid; - - - - - *p*-dimethylaminobenzoic acid; - - - - - *p*-aminobenzoic acid.

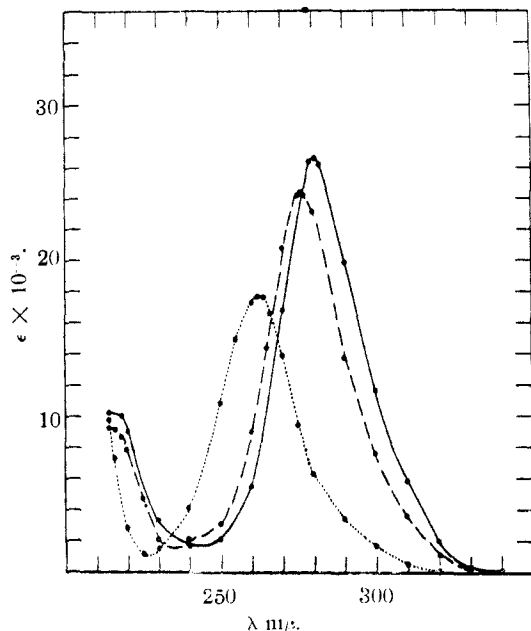
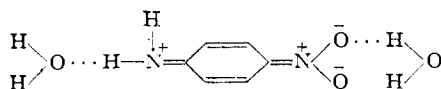


Fig. 6.——— *p*-Diethylaminobenzenesulfonamide;  
 - - - *p*-dimethylaminobenzenesulfonamide; ·····  
*p*-aminobenzenesulfonamide.

at this end of the molecule. Smaller dipole interactions may also take place at the nitro end between the negative oxygens in this group and the more positive  $\text{CH}_2$  groups in the dioxane.

If we think of the hydrogen bond itself as arising from ionic or dipole interactions as has been assumed by some workers, all of the solvent effects can be explained on this same basis. The reason such pronounced effects are obtained with compounds that can form hydrogen bonds is due to the fact that hydrogen is much smaller than other atoms and hence can approach much closer, giving rise to larger dipole interactions.

Of the various solvents hexane is the one that has the least interaction with the solute molecules. As the solvent is changed to those that interact more and more the absorption shifts to longer wave lengths. This can be considered as resulting from the loosening up of the electrons by the interacting solvent resulting in more nearly harmonic oscillations and consequently absorption at longer wave lengths. When hydrogen bonds are formed with the solvent giving rise to structures such as



the plus charge that is built up on the amino nitrogen and the negative charge on the nitro oxygens are somewhat relieved thus permitting longer oscillations than were possible without solvent interaction.

A change of solvent with some of these compounds results in a larger shift in  $\lambda$  than replacing

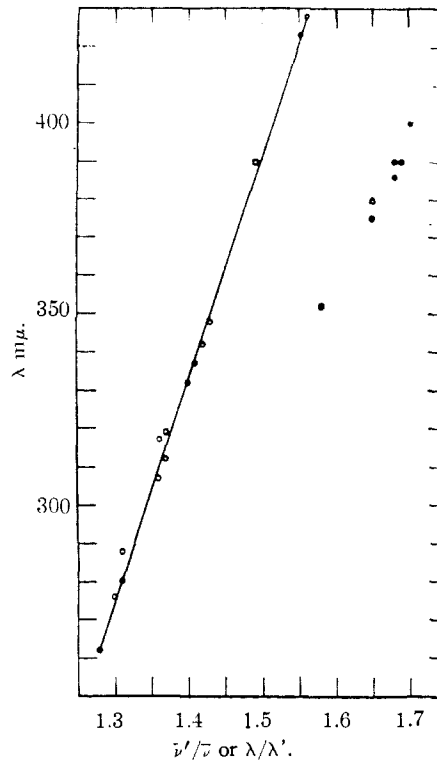


Fig. 7.—The hollow circles on or near the line are the thirteen compounds without nitro groups listed in Table I. Their order on the line is the same as the order in the Table. The solid circles to the right of the line are the five nitro compounds. The square near the top of the line is *p*-nitrosodimethylaniline in hexane. The square near the middle of the line is *p*-dimethylaminobenzaldehyde in hexane. The square off the line is *p*-nitrosodimethylaniline in hexane and the triangle is the same compound in dioxane.

one B group by the next one in the series. Thus *p*-dimethylaminobenzaldehyde has a  $\lambda$  of 342  $\text{m}\mu$  in alcohol and 319  $\text{m}\mu$  in hexane while *p*-dimethylaminoacetophenone has a  $\lambda$  of 337  $\text{m}\mu$  in alcohol. In fact a displacement of two groups in the series to *p*-dimethylaminobenzoic acid with a  $\lambda$  of 312  $\text{m}\mu$  in alcohol is necessary to get a comparable shift in wave length.

Considering the thirteen compounds that fall on the straight line in Fig. 7 the order of decreasing harmonicity is from the top to the bottom. This is the order in which the compounds are arranged in Table I, if the nitro compounds are neglected. This would also be the order of decreasing resonance in these compounds. One might expect a greater shift in  $\lambda$  on change of the solvent with those compounds near the top in which the electronic oscillations are more nearly harmonic and extend over a longer portion of the molecule than in those near the middle whose electronic oscillations are more restricted. This is the case, the change in  $\lambda$  in going from hexane to alcohol is 33  $\text{m}\mu$  for *p*-nitrosodimethylaniline which is near the top while the change is 23  $\text{m}\mu$

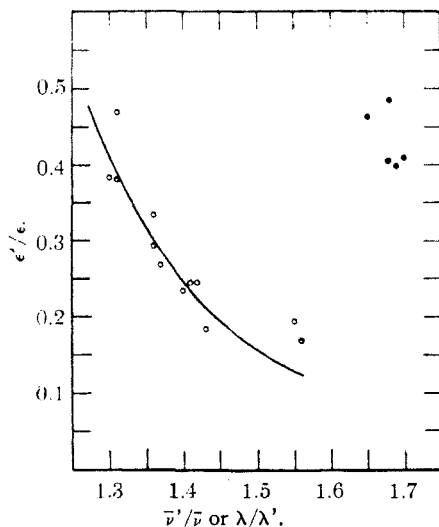


Fig. 8.—The hollow circles near the line are the compounds in Table I that do not contain nitro groups. The solid circles to the right of the line, nitro compounds.

for *p*-dimethylaminobenzaldehyde which is near the middle.

**Effect of the A Groups.**—In Figs. 1–6 and Table I it is seen that substitution in the A group of a methyl for a hydrogen or an ethyl for a methyl results both in an increase in  $\lambda$  and an increase in the extinction coefficient. The basicity of the A group is related to the resonance which has an effect on  $\lambda$  and  $\epsilon$ . The order of basicity is  $(C_2H_5)_2N- > (CH_3)_2N- > C_2H_5N- > CH_3N- > H-N-$  with the possible exception that  $(CH_3)_2N-$  and  $C_2H_5N-$  may have nearly the same basicity. This is also the observed order of  $\lambda$  and  $\epsilon$  in these compounds. The more basic the A group the greater the contribution made by the form  $>N^+=\text{C}_6\text{H}_4=\text{B}$  because the nitrogen here is essentially being neutralized just as it is when it combines with an acid to form a salt. The greater contribution from this form then results in higher  $\lambda$  and  $\epsilon$ .

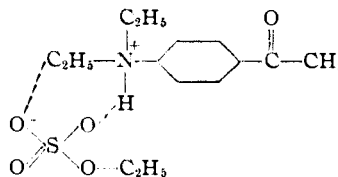
Lewis<sup>5</sup> found an average shift of 13  $m\mu$  in a large number of dyes when an alkyl group replaced a hydrogen. The same substitution in these compounds results in an average shift of 11  $m\mu$ . Substituting ethyl for methyl caused a small shift in the dyes and here such a substitution results in an average shift of 3  $m\mu$ .

**Correlations with Chemical Reactivity.**—It was observed in the process of preparing some of these compounds by treating the free amino compounds with ethyl sulfate that while the diethyl compounds could be easily prepared in the cases in which the B group was sulfonamide or carboxyl only the monoethyl compounds were obtained when the B group was acetyl or nitro. This can be accounted for on the basis of the

(5) Lewis, THIS JOURNAL, 67, 770 (1945).

greater amount of resonance in the acetyl and nitro compounds preventing the formation of the activated complex for the addition of the second ethyl group. Thus after substitution of

one ethyl group the form  $C_2H_5-N^+=\text{C}_6\text{H}_4=\overset{\ominus}{\text{C}}-CH_3$  contributes enough to the structure to prevent the formation of the activated complex



which also has a plus charge and four bonds on the nitrogen. In the case of the first ethyl group the free amino group is sufficiently weaker than the ethylamino group so the form

$H-N^+=\text{C}_6\text{H}_4=\overset{\ominus}{\text{C}}-CH_3$  does not contribute enough to prevent formation of the activated complex for the introduction of one ethyl group.

That the corresponding dimethyl compound can be made from the free amino compound and methyl sulfate results from the weaker basicity of methylamino as compared with the ethylamino group plus the greater reactivity of methyl sulfate as compared with ethyl sulfate.

It was observed that whereas the ester  $CH_3-N^+=\text{C}_6\text{H}_4-\overset{\ominus}{\text{C}}-O-CH_3$  hydrolyzes with comparative ease the corresponding triethyl compound had to be refluxed for several hours with 1 *N* sodium hydroxide to effect hydrolysis. This difference is too great to be due only to the difference in ease of hydrolysis of a methyl ester compared with an ethyl ester. The additional factor is the greater basicity of the diethylamino group increasing the contribution of the form with

a separation charge  $(C_2H_5)_2N^+=\text{C}_6\text{H}_4=\overset{\ominus}{\text{C}}-O-C_2H_5$  which decreases the formation of the activated

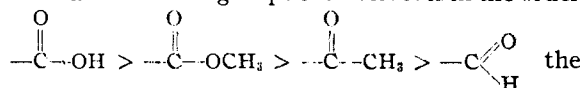
complex  $(C_2H_5)_2N-\text{C}_6\text{H}_4-\overset{\ominus}{\text{C}}-O-C_2H_5$  for the

alkaline hydrolysis.

The methyl ester of *p*-dimethylaminobenzoic acid was measured and it was found to absorb at slightly longer wave length than the free acid. The order of  $\lambda$  maximum for the compounds con-

taining a carbonyl group is then  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} > -\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 > -\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3 > -\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ . This is also

the order of the reactivity of these groups with a nucleophilic reagent such as cyanide ion. The resonance in these groups themselves is in the order



ketone having more than the aldehyde due to hyperconjugation with the  $\text{---CH}_3$ . The more resonance within the group itself the less the overall resonance responsible for the main absorption and hence the observed order of  $\lambda$  maximum. Likewise, more resonance in the group itself reduces the electrophilic character of the carbonyl carbon atom and hence the observed order with cyanide ion.

### Experimental

The spectra were obtained with a Beckman Quartz Spectrophotometer, Model DU. The setting of the wave length scale of the instrument was checked using several of the mercury lines. The solutions were made up in volumetric flasks from weighed quantities of the compounds. One or two volumetric dilutions were carried out to obtain the final concentration of 0.001% which was used in the measurements.

In the case of the sulfonamides the instrument was not sensitive at short enough wave length to show the presence of the second maximum. These compounds were also measured with the Hilger Medium Quartz Spectrograph in connection with the Hilger Spekker Photometer.<sup>6</sup> It was found that the two beams did not balance at these short wave lengths around 200–215  $\mu$ , possibly due to the different absorption characteristics of the quartz in the two paths. (At these wave lengths quartz itself has appreciable absorption.) This was remedied by placing plates of quartz in one beam until a fair match was obtained in this region. With this arrangement it was found that the curves for all three sulfonamides went through a maximum, although it was not possible to tell where the maximum occurred with any degree of precision because of the inability to get the beams balanced over the whole region. However, knowing that the curves did go through a maximum it was possible to estimate where this occurred in the case of the diethyl and dimethyl compounds from the shape of the curves obtained with the Beckman Spectrophotometer. In the case of *p*-aminobenzenesulfonamide the position of the maximum was arbitrarily taken where it appeared on the plate made with the Hilger instrument. It will be noticed in Fig. 7 that this point falls directly on the line. It possibly should be slightly above the line since the other two compounds with free amino groups, *p*-aminobenzoic acid and *p*-aminoacetophenone have their points slightly above the line.

(6) Both instruments used in this investigation were in the Spectrographic Laboratory of the University of California Medical Center.

### Materials

Commercial 95% alcohol and Eastman Kodak Co. pract. hexane from petroleum were used as solvents. The transparency of both solvents was satisfactory without further purification.

*p*-Nitromethylaniline.—The Eastman Kodak Company product was treated with charcoal and recrystallized twice from alcohol, m. p. 150–151°; lit. 150–151°, 152°. The melting points marked lit. both here and in the following are from Beilstein.

*p*-Nitroaniline.—The Eastman Kodak Company product was treated with charcoal and recrystallized twice from alcohol, m. p. 148–149°; lit. 146°, 147°.

*p*-Diethylaminobenzaldehyde.—The Eastman Kodak Company product was used, m. p. 40–41°; lit. 41°.

*p*-Dimethylaminobenzaldehyde.—The Kahlbaum product was used, m. p. 73–74°; lit. 74–75°.

*p*-Aminoacetophenone.—The Eastman Kodak Company product was recrystallized from alcohol, m. p. 105–106°; lit. 106°.

*p*-Aminobenzoic Acid.—The Eastman Kodak Company product was treated with charcoal and recrystallized from alcohol, m. p. 187–188°; lit. 186–187°.

*p*-Aminobenzenesulfonamide.—The commercial product was recrystallized twice from alcohol, m. p. 165–166°; lit. 163°.

The following eight compounds were made using standard methods.

*p*-Nitrosodiethylaniline.—M. p. 83–84°; lit. 84°.

*p*-Nitrosodimethylaniline.—M. p. 84–85°; lit. 85°, 85.5°.

*p*-Nitrodiethylaniline.—M. p. 77–78°; lit. 77–78°.

*p*-Nitrodimethylaniline.—M. p. 162–163°; lit. 162.5°, 163°, 163–164°.

*p*-Nitroethylaniline.—M. p. 95–96°; lit. 95–95.5°, 96°.

*p*-Dimethylaminoacetophenone.—M. p. 103–104°; lit. 103°, 105.5°.

*p*-Diethylaminobenzoic Acid.—M. p. 192–193°; lit. 188°, 193°.

*p*-Dimethylaminobenzoic Acid.—M. p. 236–237°, 234°, 235–236°, 238–239°, 240°.

The next three compounds are believed to be new.

*p*-Ethylaminoacetophenone.—Ten grams of *p*-aminoacetophenone was placed in 50 cc. of water and 50 cc. of ethyl sulfate added dropwise while 40% sodium hydroxide was added at such a rate the solution was kept basic. The solution was stirred mechanically and heated to 70–80° during the addition. Heating was continued until the excess ethyl sulfate was destroyed, the solution was then cooled, the product filtered and recrystallized three times from alcohol, m. p. 101–102°. Calcd. for  $\text{C}_{10}\text{H}_{14}\text{O}_2$ : N, 8.58. Found: N, 8.56, 8.48.


*p*-Diethylaminobenzenesulfonamide.—To 20 g. of sulfanilamide was added 50 cc. of water then 125 cc. of ethyl sulfate was added drop by drop with mechanical stirring while the solution was heated to 70–80° and 40% sodium hydroxide was likewise added at such a rate that the solution was kept slightly basic. After the excess ethyl sulfate was destroyed the solution was cooled, the product filtered, treated with charcoal and recrystallized twice from alcohol, m. p. 132–133°. Calcd. for  $\text{C}_{10}\text{H}_{16}\text{O}_2\text{N}_2\text{S}$ : N, 12.27. Found: N, 12.31, 12.31.

*p*-Dimethylaminobenzenesulfonamide.—To 10 g. of sulfanilamide was added 50 cc. of water. The solution was heated to 70–80°, stirred mechanically and 50 cc. of methyl sulfate was added drop by drop together with 40% sodium hydroxide at such a rate that the solution was kept slightly basic. After all the excess methyl sulfate was destroyed by continued heating and addition of sodium hydroxide the solution was cooled, filtered, and the product recrystallized twice from alcohol, m. p. 208–210°. Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ : N, 13.99. Found: N, 13.97, 14.00.

**Acknowledgment.**—I am greatly indebted to Professor G. N. Lewis for a discussion of the paper and to Professor L. A. Strait for a number of discussions relating to the problem.



### Summary

The absorption spectra of eighteen compounds of the type A——B have been measured in which A is amino or alkyl substituted amino and B is one of six different electron attracting groups. The spectra of the compounds are very similar, being characterized by two bands, a long wave length band of high extinction and a short wave length band of low extinction.

It has been found for thirteen of the compounds (all those without nitro groups) that the ratios of the frequencies of the two bands are a linear function of the wave length of the main bands. These compounds fulfill the criteria for  $x'$  bands and it is concluded the two bands are  $x$  and  $x'$  bands. The ratio of the frequencies of the short to the long wave length band  $\bar{\nu}'/\bar{\nu}$  is less than two and increases in the series as  $\lambda$  increases. The ratio of the extinction coefficients  $\epsilon'/\epsilon$  decreases as  $\bar{\nu}'/\bar{\nu}$  increases.

The nitro compounds are anomalous, the second bands coming at too short a wave length and having too high an extinction to fit in the series. It

is proposed that the second band in these compounds is a combination of the  $x'$  band and the "partial" due to the nitro group.

A change in solvent results in a big shift in  $\lambda$  with some of these compounds. The shift is correlated with the ability to form hydrogen bonds with the solvent and the possibility of dipole interactions between solvent and solute.

The basicity of the A group is related to  $\lambda$  and  $\epsilon$ , the more basic this group the higher  $\lambda$  and  $\epsilon$ . This fact is correlated with resonance.

Substitution of an alkyl group for hydrogen in the A group results in an average shift in  $\lambda$  of 11  $m\mu$  toward longer wave length.

The relative chemical reactivity of some of the compounds bears a relation to where they absorb and both observations have been correlated with resonance.

Three new compounds, *p*-ethylaminoacetophenone, *p*-dimethylaminobenzenesulfonamide and *p*-diethylaminobenzenesulfonamide, have been made.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SIENA HEIGHTS COLLEGE]

## The Spectrophotometric Estimation of Methoxy-cinchona Alkaloids<sup>1</sup>

BY MIRIAM MICHAEL STIMSON AND MARY AGNITA REUTER<sup>2</sup>

In the past, spectra of various cinchona alkaloids in ethanol, ether or dilute acid solutions have been reported<sup>3</sup> in the range 2250–4000 Å. To facilitate the estimation of methoxyl cinchona alkaloids in crude extracts the spectra of the four common natural occurring alkaloids and some related compounds have been measured over a *pH* range 1–10.

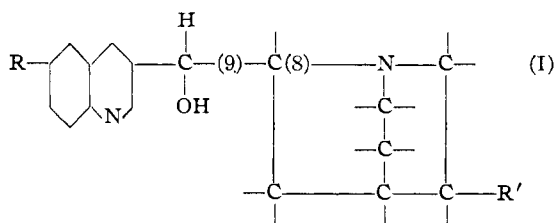
### Discussion

The general uniformity of the spectra of quinine (Fig. 1), quinidine (Fig. 2), epiquinine (Fig. 3), epiquinidine (Fig. 4), dihydroquinine (Fig. 5) and dihydroquinidine (Fig. 6) indicates that there is little effect on the spectrum if the group substituted at  $R'$  in (I) is varied because the contribution of  $R'$  is isolated from the aromatic ring system by the spectroscopically ineffective piperidine ring, thus preventing either conjugation or interaction through resonance. The changes observed in the spectra of these alkaloids are

(1) This work was conducted as part of the research program of Institutum Divi Thomae, with which this Laboratory is affiliated.


(2) Sister Miriam Michael Stimson, O. P., and Sister Mary Agnita Reuter, O. P.

(3) Fischer, "Die physikalische Chemie in der gerichtlichen Medizin und in der Toxikologie mit spezieller Berücksichtigung der Spectrographie und der Fluorescenz-Methoden," Zurich, 1925; Manta, *Z. physik. Chem.*, **B22**, 465 (1933); Heidt and Forbes, *This Journal*, **56**, 2701 (1933); Fuchs and Kamptisch, *Sci. Pharm.*, **6**, 125 (1935); Carol, *J. Off. Agri. Chem.*, **26**, 238 (1943); Mead and Koepfli, *J. Biol. Chem.*, **154**, 507 (1944).



thus attributed to changes in electronic configuration of the quinoline ring, either by introduction of an auxochrome, by weighting, or by variation in the average planarity of the molecules as controlled by epimerism at  $C_8$  and  $C_9$ , or at  $C_6$ .

Although the effect is slight it will be noted that in quinine and its three epimers there is some variation in the effect of *pH* on the 2800 Å. maximum. In the case of quinine all indications of an absorption band have disappeared and a well-defined minimum appeared at *pH* 4. In quinidine this becomes evident at *pH* 3, while in both epiquinine and epiquinidine no clear cut minimum is observed until *pH* 1.0. It is of interest also to note that though both epiquinine and epiquinidine have lower over-all absorption curves than the parent compounds, epiquinidine

with the same quinoline ring  arrangement