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The Absorption Spectra of Derivatives of Phthalic Anhydride

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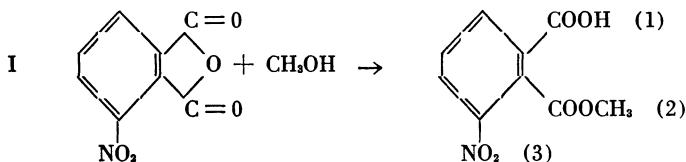
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The Absorption Spectra of Derivatives of Phthalic Anhydride

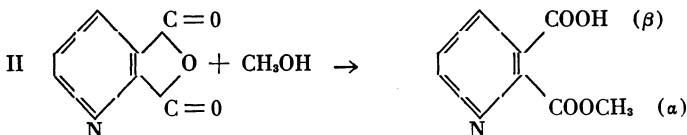
By CALVIN HANNA and W. T. SMITH, JR.

INTRODUCTION

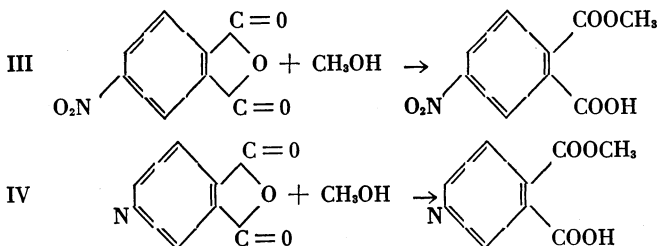
The organic qualitative reagent 3-nitrophthalic anhydride has been found useful in the characterization of alcohols and mercaptans. It is of particular interest to note that in the products formed by the reaction of this reagent with alcohols the ester group is uniformly *ortho* to the nitro group rather than *meta*. For example, methyl alcohol reacts with 3-nitrophthalic anhydride to form the 2-methyl ester according to the following equation (Wegscheider and Lipschitz, 1900) :



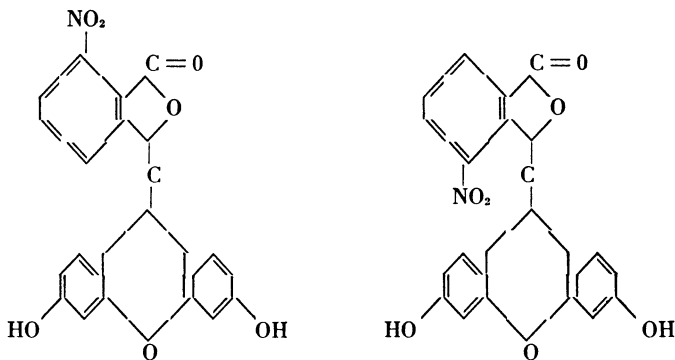
Similarly it has been noted that the reaction of quinolinic anhydride with methyl alcohol likewise gives the α -methyl ester (Kirpal, 1907) :



On the other hand, the reaction between methyl alcohol and 4-nitrophthalic anhydride or cinchomeric anhydride results in the formation of derivatives in which the ester group is *para* to the nitro group or to the heterocyclic nitrogen (Wegscheider and v. Dubrav, 1903; Goldschmiedt and Strache, 1889).



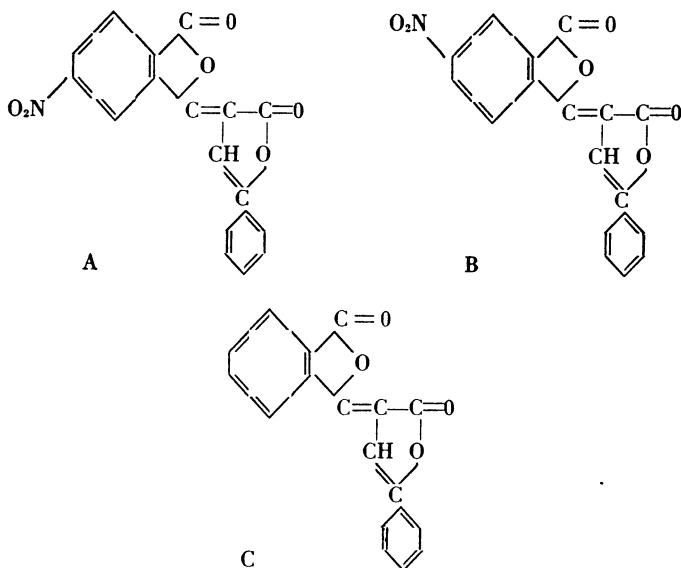
While the determination of the position of the ester group in the above examples has been worked out, many other reactions involving these reagents yield products in which the influence of the nitro- or heterocyclic nitrogen is unknown. For example, 3-nitrophthalic anhydride forms a nitro substituted fluorescein. Even though Underwood and Wakeman (1931) name this compound resorcinol-3-nitrophthalein the position of the nitro is unknown.



This is the case with a number of reactions with any of the four mentioned anhydrides.

An examination of structures I-IV indicates that the carboxyl group which is esterified is uniformly the carboxyl group which is in resonance conjugation with the nitro- or heterocyclic nitrogen group. A technique which has found abundant application in the measurement of the extent of resonance conjugation in various materials in recent years is the determination of absorption spectra. On the basis of a preliminary study of some of the above mentioned esters and anhydrides it was felt that the direct determination of the absorption spectra of these compounds would not lend itself well to a determination of the position resonance relationship. On the other hand, if these anhydrides could be reacted with other materials so that the resulting products possessed an additional double bond capable of resonance conjugation with the aromatic ring of the anhydride then the absorption spectra studies on these products might be useful in the determination of the position of reaction.

For example, consider the reaction of 4-nitrophthalic anhydride with β -benzoylpropionic acid in the presence of acetic anhydride to yield a lactone possessing two possible isomeric structures A and/or B:



From the standpoint of electronic chemistry the nitro group in structure B would tend to contribute to the lengthening of the resonance conjugation chain and thereby result in a bathochromic shift in its absorption spectra relative to C. The structure A would contribute little to the lengthening of the resonance conjugation chain and its absorption spectra should be little different from that of the unsubstituted phthalyl derivative C.

EXPERIMENTAL

Preparation of Fluorescein—A mixture of phthalic anhydride and resorcinol was pulverized and transferred to a large test tube. The test tube was inserted inside the neck of a flask fitted with a sidearm for refluxing. Benzaldehyde (B.P. 179°C) was refluxed in the flask forming a constant temperature bath. When the contents of the test tube melted anhydrous zinc chloride powder was added slowly with stirring. After thirty to sixty minutes the reaction mixture became too viscous to stir. The test tube was removed from the heat, water and conc. hydrochloric acid was added with stirring. The product was filtered and purified by dissolving in sodium hydroxide solution and reprecipitating it with hydrochloric acid.

Preparation of Resorcinol-3-Nitrophthalein (Underwood, Jr. and Wakeman, 1931)—When 1.93 g. (0.01 mole) of 3-nitrophthalic anhydride and 2.2 g. (0.02 mole) of resorcinol was reacted by the

above procedure there was obtained 2.5 g. (66%) of resorcinol-3-nitrophthalein melting at 260°C.

Preparation of Resorcinolquinolinein (Berntsen and Mettegang, 1887)—When the above procedure for the preparation of fluorescein was run with 1.49 g. (0.01 mole) of quinolinic anhydride it was noted that some decomposition took place. The best temperature found for this preparation was that of refluxing cyclohexanol (B.P. 161°C). The product was soluble in both acid and alkali, thus in each step of the purification the product was reprecipitated by neutralization. The yield was 1.1 g. (33%) of resorcinolquinolinein melting at 266-7.5°C with decomposition.

Preparation of Rhodanine Derivatives—Rhodanine was prepared by the method of Redemann, Icke and Alles (1947). The 5-substituted rhodanines were prepared by the following general procedure: A mixture of the aldehyde, rhodanine, freshly fused sodium acetate and glacial acetic acid was heated in a beaker until the solution became yellow. The reaction mixture was then cooled and the solid product filtered with suction, washed with water and recrystallized from alcohol. The following four compounds were prepared: 5-Benzylidene rhodanine, 5-(2-Nitrobenzylidene) rhodanine, 5-(3-Nitrobenzylidene) rhodanine, 5-(4-Nitrobenzylidene) rhodanine.

Preparation of α -(Substituted)- γ -Phenylcrotonlactones (Smith and Hanna, 1951)—The lactones were prepared by the following general procedure: A mixture of β -benzoylpropionic acid, freshly fused sodium acetate and acetic anhydride was heated until solution was complete. The substituted phthalic anhydride or the aldehyde was added in one portion and heating continued until a precipitate formed. The solid product was filtered with suction, washed with water and dried. The lactones were recrystallized from the minimum amount of chlorobenzene.

Preparation of 2-Phenyl-4-(Substituted)-5-Oxazolones (Smith and Hanna, 1951)—By using the above procedure for the preparation of the lactones with hippuric acid in place of β -benzoylpropionic acid.

When quinolinic anhydride or 3-nitrophthalic anhydride was reacted in this manner the reaction mixture decomposed with the evolution of heat to form a black tar. To prepare an azlactone from these two compounds the anhydride was heated with sodium acetate in acetic anhydride until complete solution was obtained. Then hippuric acid was added with vigorous stirring, the color of the reaction was watched and when the color of the reaction became a light red, the reaction was stopped with water. In this manner the condensa-

tion product from hippuric acid and 3-nitrophthalic anhydride was prepared in 10-32% yield. The corresponding product from quinolinic anhydride was obtained in such low yields that this compound was not investigated further. When 4-nitrophthalic anhydride was reacted in this manner no decomposition took place.

Determination of Absorption Spectra—All spectra were determined with a Beckman quartz spectrophotometer model DU. Measurements of optical densities were made regularly at 2 $m\mu$ -intervals within the range 220 to 230 $m\mu$, at 5 $m\mu$ -intervals between 320 and 400 $m\mu$, and at 10 $m\mu$ -intervals above 400 $m\mu$; except in the neighborhood of maxima and minima where the interval was reduced to 1 $m\mu$. Silica cells of a path length of 1cm. were employed in the determinations. Ethanol (95%) was used as a solvent for the samples as well as for the blank. All samples were dissolved in the solvent to a concentration of 10 mg. per liter. In the curves obtained from this data, the molar extinction coefficient was plotted against the wave length in $m\mu$.

Ultraviolet Absorption Spectra—A preliminary study of the absorption spectra of some of the compounds mentioned in the introduction held little promise of helping to answer the problem of position resonance relationship, for example, the spectra of phthalic anhydride, quinolinic anhydride and dimethyl quinolate. This study also included resorcinolphthalein, resorcinol-3-nitrophthalein and resorcinol-quinolinein which give two bands exhibited by many conjugated systems (Booker, *et. al.*, 1940). These three compounds were not useful because the corresponding first maxima were close to each other, and the second maxima were broad and could not be used for the purpose of comparison.

The fact that the position of the nitro group can be determined by absorption spectra in compounds which possess conjugated systems was shown by Bellis (1950), with the nitro substituted *trans*-stilbenes (Table I). The *ortho* nitrostilbene is slightly hypsochromic, this effect is to be expected since the resonance in an *ortho* substituted compound is not as strong as that of the corresponding *para* substituted compound. The *meta* nitro group is not conjugated with the double bonds of the stilbene molecule and, therefore, cannot be expected to contribute significantly to the resonance of the molecule. For this reason the absorption spectra of the *meta* nitrostilbene should be similar to those of stilbene. The same pattern holds for a number of nitro substituted conjugated systems as shown by Schueler and Wang (1950) with the azlactones (Table I). This

Table 1
Spectral Data

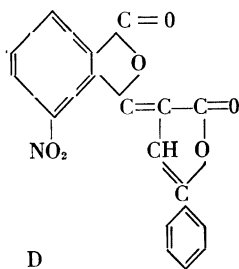
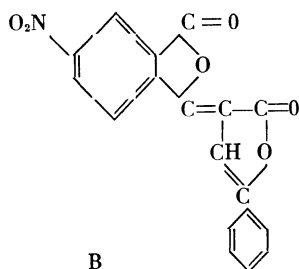
Graph No.	Compound	Max. 1 m μ $\epsilon \times 10^4$		Max. 2 m μ $\epsilon \times 10^4$		Max. 3 m μ $\epsilon \times 10^4$	
	Phthalic anhydride	288	0.08				
	Quinolinic anhydride	263	0.33				
	Dimethyl quinolinate	263	0.26				
	Resorcinol-3-nitrophthalein			277	1.55	456	0.31
	Resorcinolphthalein	226	6.80	277	1.05	458	0.45
	Resorcinolquinolinein			275	0.17		
	<i>trans</i> -2-nitrostilbene			273			
	<i>trans</i> -3-nitrostilbene			296			
	<i>trans</i> -4-nitrostilbene			350			
1	5-Benzylidene rhodanine	237	1.15	265	1.04	374	3.84
1	5-(2-nitrobenzylidene) rhodanine	235	1.47	263	1.08	365	2.17
1	5-(3-nitrobenzylidene) rhodanine	240	1.73			370	3.13
1	5-(4-nitrobenzylidene) rhodanine	227	0.86	271	1.02	396	2.54
2	α -Benzal- γ -phenylcrotonlactone	248	1.87	384	2.97		
2	α -(3-Nitrobenzal)- γ -phenylcrotonlactone	254	1.67	385	1.67		
2	α -(2-Nitrobenzal)- γ -phenylcrotonlactone	246	2.52	380	1.99		
2	α -(4-Nitrobenzal)- γ -phenylcrotonlactone	256	0.76	415	0.72		
3	2-Phenyl-4-(3-nitrobenzal)-5-oxazolone	228	2.03	272	2.14		
3	2-Phenyl-4-(3- or 6-nitrophthalal)-5-oxazolone	224	3.15	335	0.19		
3	2-Phenyl-4-(phthalal)-5-oxazolone	244	1.65	365	0.74		
3	2-Phenyl-4-(4- or 5-nitrophthalal)-5-oxazolone	224	2.68	335	0.45	430	0.06
4	α -(3- or 6-Nitrophthalal)- γ -phenylcrotonlactone	316	0.91	364	1.24		
4	α -(3- or 6-Quinolinal)- γ -phenylcrotonlactone			365	0.79		
4	α -Phthalal- γ -phenylcrotonlactone	258	1.03	424	1.71		
4	α -(4- or 5-Nitrophthalal)- γ -phenylcrotonlactone	226	2.46	360	1.66	450	0.72

is also shown by the nitro substituted lactones and the nitro substituted rhodanine in Table I.

Since the corresponding phthalal azlactone and lactone (Table I) are known it was of interest to try to see if information about the position of the nitro group from the corresponding 3-nitrophthalal azlactone and lactone could be determined by absorption spectra studies. First, consider the absorption spectra of the substituted phthalal lactones (Table I). The phthalal derivatives give the characteristic two band absorption spectra, while the 4-nitrophthalal derivative gives a third band. Compare the second and third maxima of phthalal-3-nitrophthalal-, quinolinal- and 4-nitrophthalal lactones. It can be seen that only the phthalal lactone has a second maximum near $424\text{ m}\mu$ while both the 3-nitrophthalal- and quinolinal lactones have a second maxima at $364.5\text{ m}\mu$. In the case of 4-nitrophthalal lactone the second maximum is at $360\text{ m}\mu$ and there is a third maximum at $450\text{ m}\mu$.

Now consider the absorption spectra of the substituted phthalal azlactones (Table I). Again the phthalal azlactone gives the two band absorption spectra while the 4-nitrophthalal azlactone gives a third band. Only the phthalal azlactone has a second maximum near $365\text{ m}\mu$ while the 3-nitrophthalal azlactone has a second maximum at $335\text{ m}\mu$. In the case of the 4-nitrophthalal azlactone the second maximum is at $335\text{ m}\mu$ with a point of inflection at $430.6\text{ m}\mu$.

From the seven cases of the phthalal- and substituted phthalal derivatives which were studied it is probable that the position of the nitro group in these compounds is either *ortho* or *para* to the conjugated chain. The reasons are as follows: First, both of the 3-nitrophthalal derivatives have a second maxima hypsochromic to the corresponding phthalal derivatives, as might be expected with the nitro group *ortho* to the conjugated chain. The third maxima of both of the 4-nitrophthalal derivatives were bathochromic to the second maxima of the corresponding phthalal derivatives, as might be expected with the nitro group *para* to the conjugated chain. This may be seen more clearly in the examples B and D:



Secondly, the azlactone from 3-nitrophthalic anhydride (Table I) shows a marked depression of the second maximum just as does the corresponding azlactone from o-nitrobenzaldehyde. In the latter compound this depression has been attributed to steric effects (Brown and Reagan, 1947), and the same reasoning may be applied by analogy to the azlactone from 3-nitrophthalic anhydride.

FIGURE I. ABSORPTION CURVES

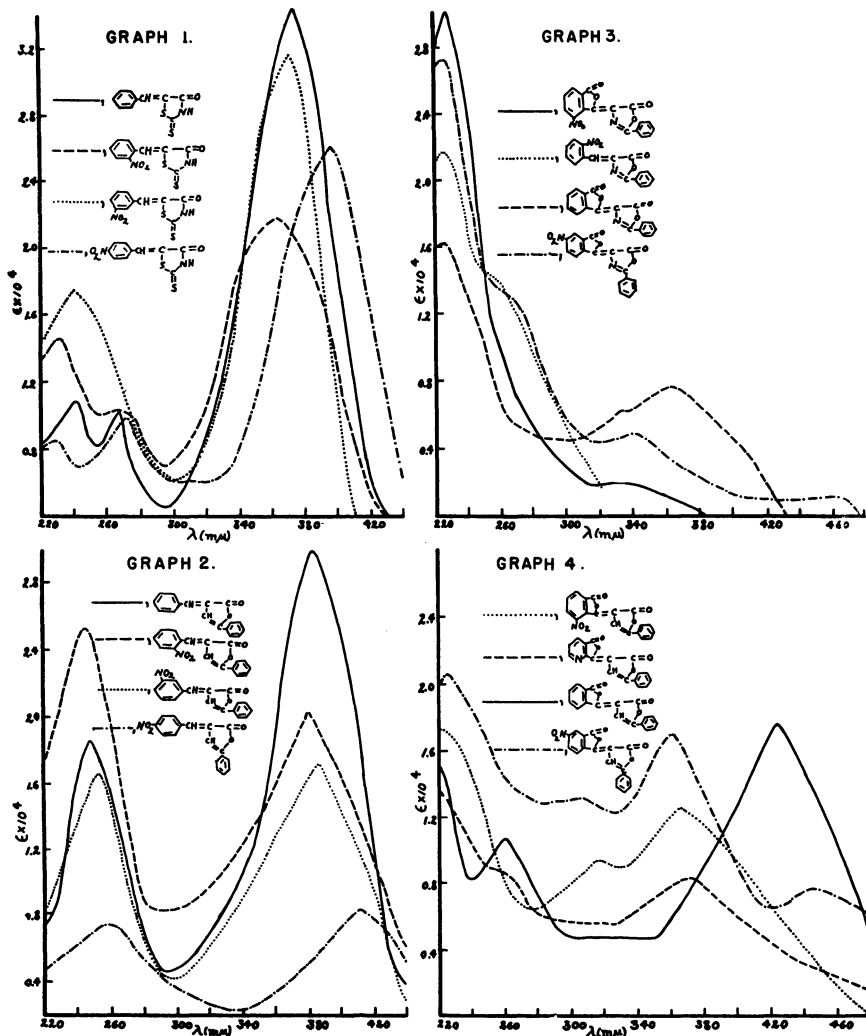


Figure 1. Absorption Curves. These curves are referred to in Table 1 by graph numbers.

DISCUSSION OF RESULTS

Preparation—Fluorescein, resorcinol-3-nitrophthalein and resorcinolquinolinein were prepared by the general method of Vogel (1948). The best yields of resorcinolquinolinein were obtained by carrying out the reaction at the temperature of refluxing cyclohexanol (B.P. 161.5°C). Rhodanine was prepared by the methods of Redemann, Icke and Alles (1947). Rhodanine was condensed with aromatic aldehydes by heating in glacial acetic acid and sodium acetate. The azlactones were prepared by heating hippuric acid and sodium acetate in acetic anhydride, followed by the addition of the aldehyde or substituted phthalic anhydride. The corresponding lactones were prepared in an analogous manner only using β -benzoylpropionic acid instead of hippuric acid.

When 3-nitrophthalic anhydride or quinolinic anhydride is reacted in this manner with hippuric acid and sodium acetate the reaction mixture decomposes. To prepare an azlactone from these two compounds the anhydride is heated with sodium acetate in acetic anhydride, then hippuric acid is added. The color of the reaction must be watched and when the color of the reaction becomes a light red, warm water is added to stop the reaction. In this manner the condensation product from hippuric acid and 3-nitrophthalic anhydride can be prepared in 10-32% yield. The corresponding product from quinolinic anhydride was obtained in such low yields that this compound was not investigated further. When 4-nitrophthalic anhydride is reacted in this manner no decomposition takes place. The azlactone from *o*-nitrobenzaldehyde and hippuric acid undergoes extensive decomposition when heated with alkali and yields *o*-nitrotoluene. The corresponding azlactone from *m*-nitrobenzaldehyde under these same conditions gives no nitrotoluene (Burton, 1935). Thus in the case of the 3-nitrophthalal azlactone, the decomposition may be due to the carboxyl group *ortho* to the nitro group being attacked. This is in support of the evidence shown by the absorption spectra of the azlactone from 3-nitrophthalic anhydride.

SUMMARY

Absorption spectra of twenty-five related compounds in the ultraviolet and visible regions are reported. Correlations between chemical constitution of these compounds and their absorption spectra are discussed.

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