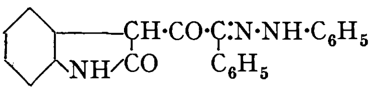
43. *The Absorption Spectra of Benzoylformyloxindole Phenylhydrazone and Some of its Derivatives.*

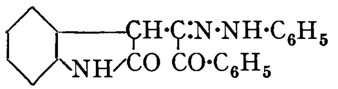
By F. W. Bergstrom and Robert Robinson.

The absorption spectra of solutions of arylhydrazones of benzoylformyloxindole have been examined in the hope of finding an explanation of the changes of visible colour observed in different solvents.

The phenylhydrazone of benzoylformyloxindole (Ainley and Robinson, J., 1934, 1510) may correspond to one of the structures (I) and (II), of which the former was preferred.

(I.)





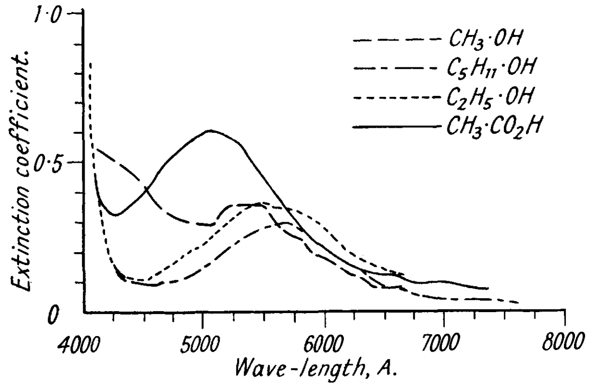
(II.)

The colours of solutions of this compound in different solvents vary widely. Solutions in dilute acids or in pyridine are yellow, in methyl alcohol violet-red, in amyl alcohol and, particularly, in *cyclo*hexanol almost pure blue, and in hot benzene practically colourless, if sufficiently dilute.

To find an explanation of these remarkable colour changes, the absorption spectra of benzoylformyloxindole phenylhydrazone and its derivatives in a variety of solvents have been examined. It was anticipated that substitution of nitroxyl and methoxyl groups for the hydrogens of the hydrazone phenyl would affect the absorption in a manner which might indicate the nature of the equilibrated systems.

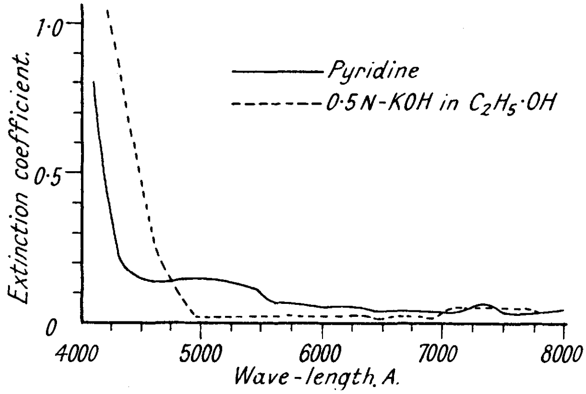
Influence of the Solvent on the Absorption of Benzoylformyloxindole Phenylhydrazone.—The solutions in acetic acid, which are orange-red to the eye, have an absorption maximum around 5050—5100 A. in the green, and a minimum at 4250—4300 A. in the blue. The absorption coefficient corresponding to the latter is relatively high. Methyl-alcoholic solutions have an absorption maximum at 5350 (0·0005M) (the curve at 0·0002M does not show as definite a maximum) and a minimum at 4800, both values being displaced towards longer wave-lengths compared with the acetic acid solutions. The methyl-alcoholic solutions therefore are more blue. The absorption maxima and minima of the solutions in ethyl and amyl alcohols are both displaced towards longer wave-lengths, and the absorption coefficient corresponding to both characteristics is decreased compared with the methyl-alcoholic solutions. This change is particularly noticeable in passing from methyl to ethyl alcohol. The amyl-alcoholic solutions are not pure blue because of the transmission of much red and some green. They are the bluest of those examined, having the greatest transmission in the region of 4750—5500.

FIG. 1.



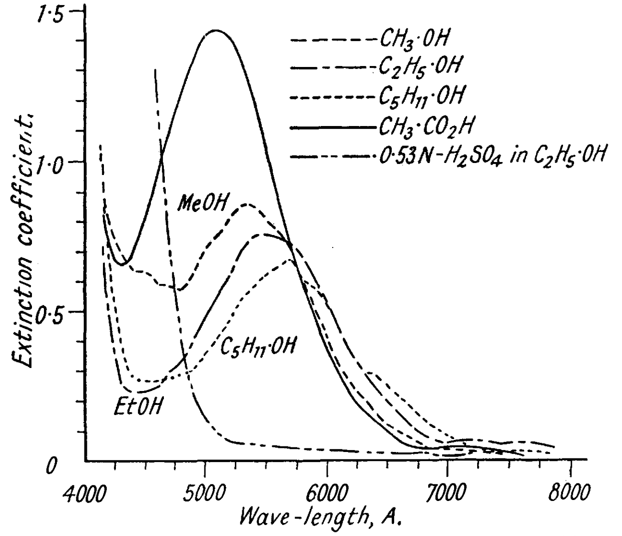
Absorption of benzoylformyloxindole phenylhydrazone, 0·0002M.

FIG. 2.



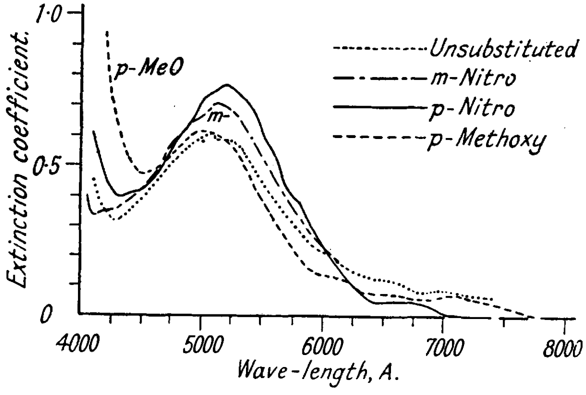
Absorption of benzoylformyloxindole phenylhydrazone, 0·0002M.

FIG. 3.



Absorption of benzoylformyloxindole phenylhydrazone, 0·0005M.

FIG. 4.

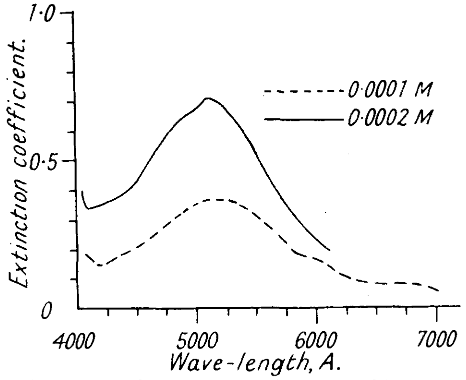


Absorption of the phenylhydrazones of benzoylformyloxindole glacial acetic acid, 0·0002M.

Effect of Substitution on the Colour of Benzoylformyloxindole Phenylhydrazone.—It has not been possible to compare the absorption spectra of the substituted and the unsubstituted benzoylformyloxindole phenylhydrazones in all solvents, owing to insolubility and the fact that the *p*-methoxyphenylhydrazone could not be obtained pure.

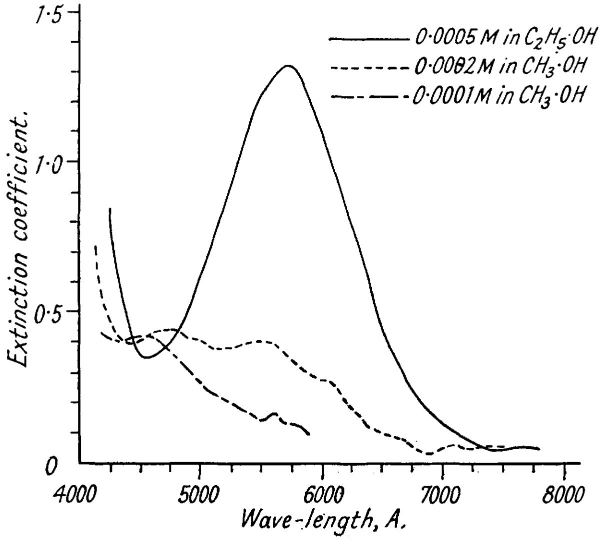
The position of the absorption maxima of all phenylhydrazones in ethyl alcohol is about 5500 or 5600. (The p-*nitrophenylhydrazone* is excluded because the specimens probably contained small quantities of acetic acid.) The position of the minimum varies between 4300 and 4600. The colours of the solutions to the eye are roughly the same, the variations doubtless largely being due to the relative magnitudes of the absorption coefficients corresponding to the maxima and minima.

FIG. 5.



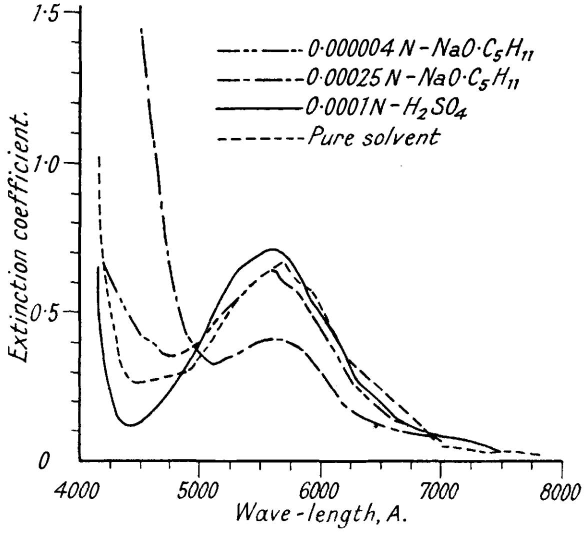
Absorption of the phenylhydrazones of benzoylformyloxindole in ethyl alcohol.

FIG. 6.



Absorption of the p-*nitrophenylhydrazone of benzoylformyloxindole (containing a small quantity of acetic acid of crystallisation).*

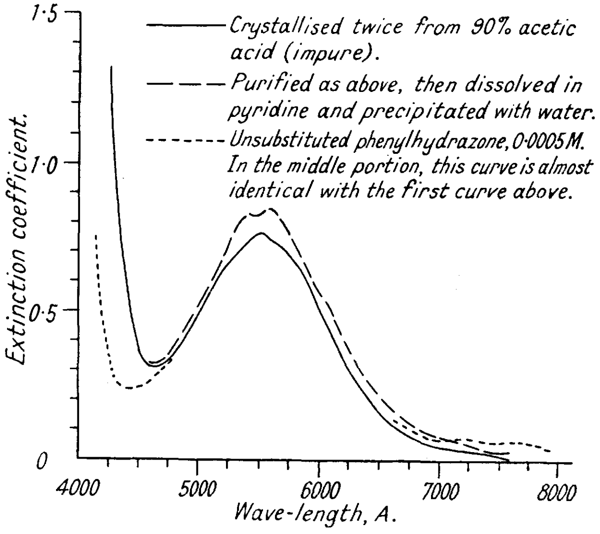
FIG. 7.



Absorption of benzoylformyloxindole phenylhydrazone in amyl alcohol, 0·0005M.

Effect of addition of acid and of alkali.

FIG. 8.



Absorption of p-*methoxyphenylhydrazone of benzoylformyloxindole in ethyl alcohol,* 0·0005M.

The absorption maxima and minima of the acetic acid solutions of all phenylhydrazones are, respectively, 5100—5200 and 4200—4300.

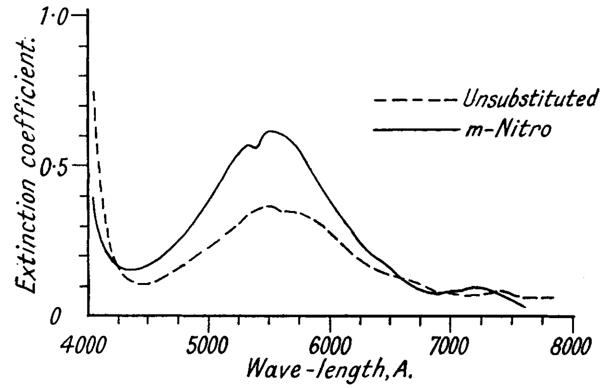
From the present work it can be concluded that substituents in the phenylhydrazine nucleus have such small effects on the colour as to render theoretical interpretation difficult.

The Effect of the Addition of Small Amounts of Acid or of Alkali on the Absorption Spectra of Solutions of Benzoylformyloxindole Phenylhydrazone in Amyl Alcohol.—The absorption spectra of 0·0005M-solutions of benzoylformyloxindole phenylhydrazone in *iso*amyl alcohol containing either sulphuric acid or sodium amyloxide in amounts insufficient to cause complete conversion into the yellow salts have been examined.

The addition of sodium amyloxide to the phenylhydrazone results in displacements of the absorption maximum (100—200 A.) towards shorter wave-lengths, and of the absorption minimum (300—600 A.) towards longer wave-lengths. Both of these shifts are in the directions observed when passing from a solution of the phenylhydrazone in pure amyl alcohol to one in methyl alcohol at the same concentration. Similarly, the absorption coefficients corresponding to the minima are lowered a little in both cases, but no regularity can be observed in the alteration of the absorption coefficients of the maxima.

Addition of sulphuric acid to the *iso*amyl-alcoholic solution of the phenylhydrazone produces a slight shift (about 100 A.) of both the maximum and the minimum towards shorter wave-lengths. More pronounced shifts in the same direction are noted in changing from the alcohols to acetic acid as a solvent. The very marked increase of the absorption maximum in acetic acid, above that in *iso*amyl alcohol, compared with the slight increase produced by adding sulphuric acid to the *iso*amyl-alcoholic solution (Fig. 7) should be noted, since it may signify the presence in solution of another coloured substance.

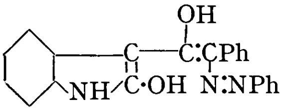
Fig. 9.



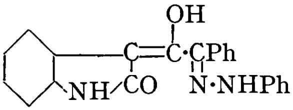
Absorption of the m-*nitrophenylhydrazone of benzoylformyloxindole in glacial acetic acid.*

The yellow solutions of the phenylhydrazone in acid and in alkali have somewhat different absorption spectra (Figs. 1, 2) and addition of acid or alkali affects the colour of the blue solutions in amyl alcohol differently. The absorption maximum is thus lowered by addition of small quantities of sodium *iso*amyloxide, and raised by addition of sulphuric acid.

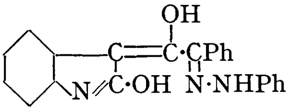
The only general deduction which can be made is that we are dealing with a complex mixture of tautomerides characterised by different colours, the equilibria being very sensitive to alterations in the solvent. A few of the possible formulæ (based on I) are shown below :—



(I*a*.)



(I*b*.)



(I*c*.)

Of these, (I*a*) is analogous to that of benzeneazoresorcinol and the substance might be orange-red; (I*b*) is the hydrazone form of the same azo-compound and there are no reasons for anticipating that this tautomeride would be blue. (I*c*) contains the longest conjugated system, but it is still doubtful whether a pure substance so constituted would be blue.

However, the structure of (I*c*) brings to mind the violet colour formed when isatin is dissolved in alkaline solutions and in the latter case the intense colour may be due to meriquinonoid association of isatin and ψ-isatin (or an anion derived therefrom). A similar conception can be applied to the present case, the intense colours being attributed, not to any one tautomeride, but to the association of two components of the system, for example, (I*b*) with (I*c*). This view may explain the influence of acids and bases, the former giving pure keto-modifications and the latter pure enols and so, in each case, hindering the contemplated association of two tautomerides.

EXPERIMENTAL.

Benzoylformyloxindole Phenylhydrazone.—The procedure of Ainley and Robinson (*loc. cit.*) was modified slightly. Benzoylformyloxindole (0·75 g.) was dissolved in acetic acid (30 c.c.), and phenylhydrazine (1·2 c.c.) added. The solution was boiled for about 5 minutes, cooled, and poured into an excess of cold water. The purple phenylhydrazone which was precipitated was collected, crystallised twice from aqueous acetic acid (75%), and dried in a vacuum over sulphuric acid (Found : C, 74·2; H, 4·8. Calc. for $C_{22}H_{17}O_2N_3$: C, 74·3; H, 4·8%). The same specimen was used in all of the absorption measurements reported.

An unsuccessful attempt was made to introduce a second phenylhydrazine residue by boiling phenylhydrazine (3 c.c.), acetic acid (15 c.c.), and benzoylformyloxindole (0·26 g.) under reflux for 8 hours. The product proved to be impure monophenylhydrazone (Found : C, 74·0; H, 4·7%).

The following solubilities and colour reactions have not hitherto been recorded : A yellow solution is formed at all temperatures in dimethylaniline. A fairly concentrated cold pyridine solution is red, and on dilution with water becomes orange and finally yellow. Very dilute pyridine solutions also are yellow. Addition of a large amount of water causes the slow separation of reddish-mauve flocks of the phenylhydrazone, indicating the formation with pyridine of a readily hydrolysed salt. Yellow solutions are formed at all temperatures in alkalis and in mineral acids, probably as a result of salt formation. A yellow solution is likewise formed in concentrated aqueous ammonia, but the original material separates on dilution, indicating, as above, a readily hydrolysed salt.

Benzoylformyloxindole m-*Nitrophenylhydrazone.*—Benzoylformyloxindole (0·53 g.) and *m*-nitrophenylhydrazine (0·55 g.) were dissolved in warm acetic acid (15 c.c.) and boiled for about 10 minutes. The cooled solution was poured into an excess of water; the purplish-red solid then precipitated was crystallised three times from aqueous acetic acid (90% by vol.) (two crystallisations are insufficient) and dried in a vacuum over sulphuric acid (Found : C, 66·1; H, 4·2. $C_{22}H_{16}O_4N_4$ requires C, 66·0; H, 4·0%).

It was found impossible to prepare a 0·0005M-solution of the m-*nitrophenylhydrazone* in acetic acid; but a 0·0002M-solution could be made and the colour of this solution was red with a purplish tinge that disappeared when small amounts of water were added.

The substance was soluble in boiling benzene to a light yellow solution. The acetic acid filtrate from the above preparation of the *m*-nitrophenylhydrazone was diluted with a large volume of water; the amorphous brown precipitate which separated was collected, dried, and washed with hot benzene; m. p. 223—224°. The substance may be the isomeric phenylhydrazone, but only a very small quantity was obtained. The colours of solutions were as follows : acetic acid, deep red; concentrated sulphuric acid, orange; ethyl alcohol (0·0002M), purple; ethyl alcohol (0·0005M), deep blue with a purplish tinge; hot dilute amyl alcohol, green and purplish-red when cooled.

Benzoylformyloxindole p-*Nitrophenylhydrazone.*—Benzoylformyloxindole (1·6 g.) and *p*-nitrophenylhydrazine (3·2 g.) were dissolved in glacial acetic acid (75 c.c.) and heated at b. p. for 40 minutes (15 minutes would probably suffice). No marked colour changes were observed, the solution having a reddish-brown appearance. The deep purple needles which separated on cooling were recrystallised twice from a large volume of acetic acid and dried for a week in a vacuum over sodium hydroxide (Found : C, 64·3; H, 4·6. $C_{22}H_{16}O_4N_4$ requires C, 66·0; H, 4·0; N, 14·0. $C_{22}H_{16}O_4N_4,0·33C_2H_4O_2$ requires C, 64·9; H, 4·2; N, 13·4%).

In an attempt to remove the acetic acid, which this material evidently contained, the crystals were dissolved in a small volume of pyridine, and the filtered solution added to a large volume of water. The mauve precipitate which slowly separated on keeping was collected, washed with water and dried in a vacuum over sulphuric acid (Found: C, 66·2; H, 4·3%).

The deep brownish-red acetic acid filtrate from the purple crystals contained a secondary reaction product, which was precipitated by the addition of a large amount of water as a flocculent yellow-brown solid. It was recrystallised twice from dilute alcohol and dried in a vacuum over sulphuric acid; m. p. 224—225° (Found: C, 65·8; H, 4·2; N, 14·0. $C_{22}H_{16}O_4N_4$ requires C, 66·0; H, 4·0; N, 14·0%). Apparently this is the isomeric p-*nitrophenylhydrazone*, which must have a structure analogous to (II), if the purple compound is assumed to be analogous to (I).

It is difficult to prepare a solution of the nitrophenylhydrazone in cold glacial acetic acid, although a 0·0002M-solution (reddish in colour) was made in the gently heated solvent. It was impossible to prepare a 0·0005M-solution of the pure purple *p*-nitrophenylhydrazone in either methyl or ethyl alcohol. The most concentrated ethyl-alcoholic solution was purple, the most concentrated amyl-alcoholic solution blue with a purplish tinge. When the latter was warmed, the colour became lighter and more nearly a pure blue, and at the b. p. the colour was still lighter and green. The reverse changes took place on cooling.

The *p*-nitrophenylhydrazone dissolved readily in pyridine in the cold, forming a deep red or reddish-brown solution. A mauve-coloured precipitate slowly separated on dilution with water. Hot concentrated pyridine solutions were deep green. Hot benzene dissolved very little of the nitrophenylhydrazone, the extremely dilute solution having a pale yellow colour. From a solution in aqueous sodium hydroxide (orange-red or red at moderate concentration) acetic acid threw down a purple precipitate.

Positions of the Maxima and Minima of Absorption.

			Maximum.		Minimum.	
Curve.		Fig.	A.	Abs. coeff.	A.	Abs. coeff.
Unsubstituted Phenylhydrazone.						
$CH_3{\cdot}OH$	0·0002M	1	5300—5500	0·35	5100	0·28
$C_2H_5{\cdot}OH$	,,	,,	5500	0·37	4500	0·10
$C_5H_{11}{\cdot}OH$	,,	,,	5700	0·30	4600	0·09
$CH_3{\cdot}CO_2H$	,,	,,	5050	0·60+	4250	0·32
$CH_3{\cdot}OH$	0·0005M	3	5350	0·86	4800	0·58
$C_2H_5{\cdot}OH$	,,	,,	5500	0·76	4400	0·24
$C_5H_{11}{\cdot}OH$	,,	,,	5700	0·67	4500	0·26
$CH_3{\cdot}CO_2H$	,,	,,	5100	1·43	4300	0·66
m-*Nitrophenylhydrazone.*						
$C_2H_5{\cdot}OH$	0·0002M	5	5500	0·62−	4400	0·15
$C_2H_5{\cdot}OH$	0·0005M	(impure specimen)	5600	1·33	4300	0·34
$CH_3{\cdot}CO_2H$	0·0002M	9, 5	5100	0·71	4100	0·34
$CH_3{\cdot}CO_2H$	0·0001M	9	5100	0·37	4200	0·14
p-*Nitrophenylhydrazone.*						
Pure material.						
$CH_3{\cdot}CO_2H$	0·0002M	4	5200	0·77	4300	0·40
Material containing a small amount of acetic acid.						
$CH_3{\cdot}OH$	0·0001M	6	No sharp maximum or minimum.			
	0·0002M		,,	,,	,,	,,
$C_2H_5{\cdot}OH$	0·0005M	6	5700	1·32	4500—4600	0·36
Maximum and minimum closely checked after standing overnight.						
p-*Methoxyphenylhydrazone* (both specimens somewhat impure).						
$C_2H_5{\cdot}OH$	0·0005M	8	5500	0·76+	4600	0·31
$C_2H_5{\cdot}OH$	,,	,,	5600	0·85	4600	0·28
Unsubstituted Phenylhydrazone, 0·0005M in $C_5H_{11}{\cdot}OH$. Effect of the addition of small quantities of $C_5H_{11}{\cdot}ONa$ and of H_2SO_4. Normality of solution with respect to						
$C_5H_{11}{\cdot}ONa$	0·000004	7	5600	0·64	4800	0·36
$C_5H_{11}{\cdot}ONa$	0·00025	,,	5500, 5600	0·41	5100	0·33
H_2SO_4	0·0001	,,	5600	0·71+	4400	0·12
Pure solvent		8	5700	0·67	4500	0·26

Benzoylformyloxindole p-*Methoxyphenylhydrazone.*—A mixture of benzoylformyloxindole (0·8 g.), *p*-methoxyphenylhydrazine (1·75 g.), and glacial acetic acid (30 c.c.) was boiled for 15 minutes, cooled, and poured into water. The purplish-red precipitate was crystallised twice from 90% acetic acid and dried successively in a vacuum over sulphuric acid and sodium hydroxide. The solid was dark purplish-red (Found : C, 71·0, 72·3; H, 5·1, 5·2. $C_{23}H_{19}O_3N_3$ requires C, 71·7; H, 5·0%). A second specimen was made by dissolving the first in a small volume of pyridine and precipitating it with a large volume of water, but neither was pure, possibly because of contamination with small quantities of solvent.

At a concentration of 0·0005M the methyl-alcoholic solution was deep red, and the more concentrated solutions had a purplish cast. A 0·0005M-solution in ethyl alcohol was red with a purplish tinge. A 0·0002M-solution in glacial acetic acid was orange-red.

Purification of Solvents.—Pyridine and the alcohols were refluxed for several hours over calcium oxide, kept overnight, and distilled. Acetic acid was kept for a day with a mixture of anhydrous sodium acetate and potassium permanganate, distilled, and then crystallised three times. All solvents were redistilled through a Young column, the middle fraction boiling over a range of 0·1—0·3° being collected.

The Absorption Measurements.—All absorption measurements were made in the visible region with a Hilger–Nutting spectrophotometer. Solutions were made up to 0·0005M and to 0·0002M. The measurements were carried out in fused quartz absorption cells, 2·00 cm. long internally, with two small side tubes which were loosely capped during an experiment. The absorption spectrum on occasions slowly changed with time, because of contamination from the atmosphere. In most cases, the absorption spectrum was checked after the cells had stood capped for a day. If it was apparent that the absorption had changed in a manner not explicable by atmospheric contamination, the experiment was repeated. A glass cell was also tried but was found unsatisfactory.

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