

Richardson for certain absorption measurements in the ultraviolet region.

Summary

1. The absorption spectrum of a merocyanine dye has been determined for the gaseous state (*in vacuo*).

2. The displacement of the absorption band (or bands) in various solvents is referred to that *in vacuo*.

3. It is shown that, with certain families of compounds, there is a definite correlation of the displacement (to longer waves) with: (a) the re-

fractive index and dielectric constant for non-polar solvents; (b) the polar moment for polar solvents.

4. With ionized (cyanine) dyes, it is shown that no displacement is effected by change of polar moment, but definite changes occur in non-polar solvents of increasing refraction and dielectric strength.

5. Theoretical considerations of the solvent effects are given in relation to the structures of the dyes. The exceptional behavior of the alkyl halides is discussed.

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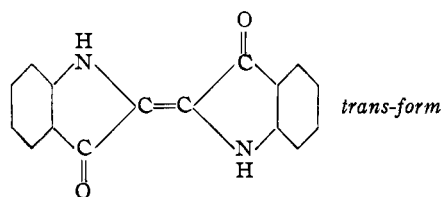
[COMMUNICATION NO. 869 FROM THE KODAK RESEARCH LABORATORIES]

The Effect of Solvents on the Absorption Spectra of Dyes. II. Some Dyes Other than Cyanines

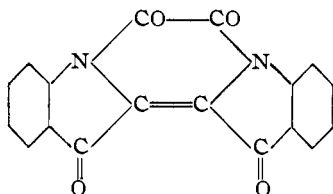
BY S. E. SHEPPARD AND P. T. NEWSOME

We have made some investigation of dyes other than the cyanines, and of which two can be vaporized and the absorption determined *in vacuo* (*i. e.*, as gas at low pressure) for comparison with solutions. These are *indigo* and *diaminoanthraquinone*, and they are of particular interest in comparison with the *merocyanines* since they are both non-ionic.

Indigo.—The formula usually assigned is



Evidence for a *cis*-form is mostly based on the production of cyclized derivatives of the *cis*-form, such as *oxalyl indigo*¹ and *N,N-styrolin-indigo*.²

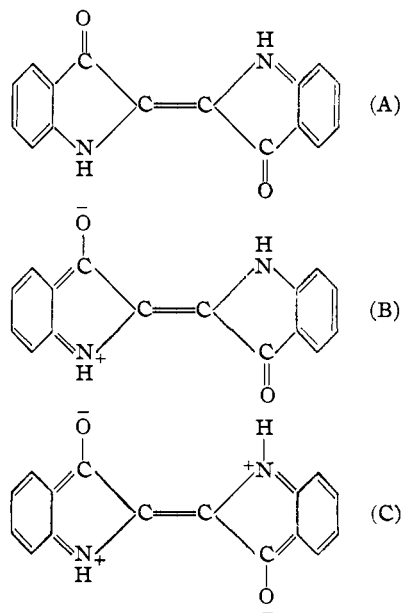


For the solid, crystalline form, the evidence favors the presence of the *trans*-form.² Apart from the

(1) Cf. R. Pummerer, H. Fiesselmann and O. Müller, *Ann.*, **544**, 206 (1940).

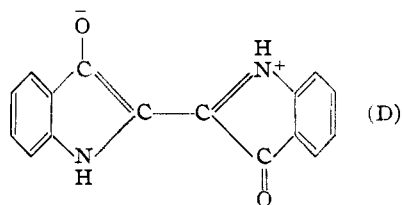
(2) A. Reis and W. Schneider, *Z. Krist.*, **68**, 543 (1928).

steric variation, which in the case of the stilbenes³ appears to affect the intensity of the absorption more than the location of the absorption bands, the nature of the "limit configurations" corresponding to the resonance and the color is not completely decided. For a review of the subject, papers by J. van Alphen⁴ may be consulted. This author has suggested that indigo is a resonance hybrid having the following principal "limit structures"



(3) A. Smakula and A. Wassermann, *Z. physik. Chem.*, **155A**, 353 (1931). There is some hypsochromic displacement in the *cis*-derivative relative to the *trans*-form.

(4) J. van Alphen, *Rec. trav. chim.*, **60**, 138-152 (1931).



A similar view was expressed by F. Arndt⁵ and expanded by B. Eistert.⁶ The latter considered the resonance A \longleftrightarrow D of principal importance, and form D, allowing "free" rotation about $>C-C<$ according with the actual existence of only one form (*trans*) but with the possibility of *cis*-derivatives.

We have measured a number of absorption spectra of indigo in various solvents with the spectrophotometer; to conserve space the extinction curves are not given here but, as in Part I, only the absorption maxima and the corresponding "displacements." Compared with the merocyanines, the behavior of indigo in non-polar sol-

TABLE I
INDIGO IN NON-POLAR SOLVENTS

Solvent	K	n_D	$\mu \times 10^{18}$	$1/\lambda_m$ in cm.^{-1}	$\Delta 1/\lambda$
Vacuum	1.0	1.0	0	18315	0
Hexane	1.87	1.375		insufficiently soluble	
Carbon tetra- chloride	2.20	1.458	0	16667	1648
Benzene	2.38	1.498	0	16800	1515
<i>p</i> -Xylene		1.496	0	16800	1515
<i>o</i> -Xylene		1.503	0.5	16800	1515
<i>m</i> -Xylene		1.496	0.4	16800	1515
Carbon disulfide	2.65	1.629	0	16610	1704

TABLE II
INDIGO IN ALIPHATIC POLAR SOLVENTS

Solvent	$\mu \times 10^{18}$	$1/\lambda_m$ in cm.^{-1}	$\Delta 1/\lambda$
Hexane	0	insufficiently soluble	
Diethyl ether	1.12	16892	1423
Methyl acetate	1.74	16800	1515
Isoamyl acetate ^a	1.70	16450	1865
Acetone	2.74	16751	1564
Nitromethane	3.80	16751	1564
Methyl alcohol	1.68	16529	1786
Isoamyl alcohol ^a	1.70	16450	1865
Formic acid	1.77	15949	2366
Acetic acid	1.63	16260	2055
<i>n</i> -Valeric acid		16260	2055
Diethylamine	0.9	16340	1975
<i>n</i> -Butylamine	1.3	16393	1922
<i>n</i> -Propylamine	1.4	16393	1922

^a The marked effect of the isoamyl group is noteworthy.

(5) F. Arndt, *Ber.*, **72**, 860 (1939).

(6) B. Eistert, "Tautomerie und Mesomerie," F. Enke, Stuttgart, 1938, p. 189; also *Ber.*, **72**, 860 (1939).

TABLE III
INDIGO IN AROMATIC SOLVENTS

Solvent	$\mu \times 10^{18}$	$1/\lambda_m$ in cm.^{-1}	$\Delta 1/\lambda$
Benzene	0	16800	1515
<i>p</i> -Xylene	0	16800	1515
Diphenyl ether	1.05	16610	1704
Phenyl methyl ether	1.20	16667	1648
Phenyl acetate	1.52	16667	1648
Acetophenone	2.94	16529	1786
Benzophenone	2.95	16584	1731
Nitrobenzene	3.90	16529	1786
Aniline	1.52	16129	2186
<i>o</i> -Chloroaniline	1.77	16129	2186

TABLE IV
INDIGO IN HETEROCYCLIC SOLVENTS

Solvent	$\mu \times 10^{18}$	$1/\lambda_m$ in cm.^{-1}	$\Delta 1/\lambda$
Pyridine	2.11	16340	1975
Quinoline	2.16	16260	2055
Piperidine	1.17	16340	1975

vents is anomalous, in giving a smaller displacement in benzene and xylene than in carbon tetrachloride, although their dielectric constants are higher as are also the refractive indices. The solubility of indigo in this group of solvents is too low to permit extensive measurements.

On comparing these results with the data for the merocyanines XXIII and XXXI (Part I), the following conclusions were reached: (i) the behavior in non-polar solvents seems less simple, but owing to restricted solubilities the data are very scant; (ii) in the typical aliphatic and aromatic series of polar solvents, there appears to be no definite displacement of λ_m with change of polar moment as was found with the merocyanines (Part I); (iii) no regularity was apparent with amines of different polar moments, but both aliphatic and aromatic amines, as well as heterocyclic nitrogenous bases, show considerably greater displacements than other solvents of the same polar moment. Scheibe, Dörfling and Assmann⁷ concluded that *aniline* is outstanding as a solvent for indigo and derivatives, in respect of "red displacement" of the spectrum. Our observations (*cf.* Tables I to IV) show others of equal potency, *formic acid* giving the greatest displacement. The behavior of indigo in the *associated* solvents, the alcohols and fatty acids, and in the tautomeric acetoacetate, is similar to that of merocyanine.

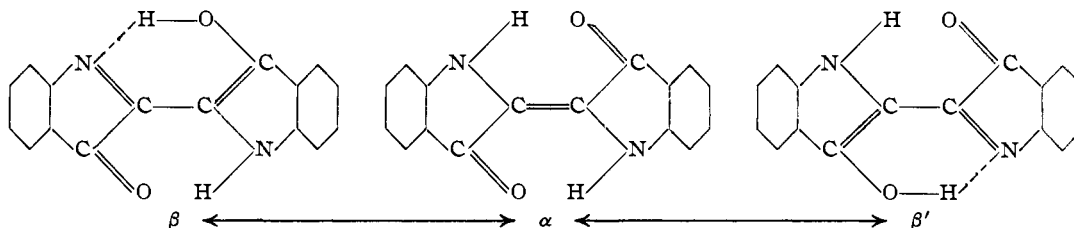
Scheibe and his co-workers concluded, particularly from the behavior of indigo in mixtures of non-polar and polar solvents, that no grounds exist for assuming specifically different structures in

(7) G. Scheibe, H. Dörfling and J. Assmann, *Ann.*, **544**, 240 (1940).

equilibrium as responsible for the color differences (tautomerism) nor for assuming molecular aggregation as a principal factor. As *positive* conclusions, they consider that the color changes are explainable "by displacement of the electron clouds within the molecules under the action of different solvents," and also that solvent molecules "whose dipoles are most strongly active outwardly (alcohols) displace the absorption most to the long waves."

The slight to inappreciable effect which a change of polar moment *per se* of a solvent has on the absorption spectrum indicates that the hybrid ion or bipolar (and quadrupolar) structures suggested by Eistert⁶ and by van Alphen⁴ are probably contributing little to the resonance system responsible for the first electronic transition band of indigo.

It seems possible that the resonance system in question is that indicated in the structural formulas



β and β' are similarly hydrogen-bonded structures which are suggested as the two identical most stable structures, *i. e.*, energetically lowest.

The normal structure α conventionally assigned to indigo would then represent an intermediate (mesomeric) state of higher energy.

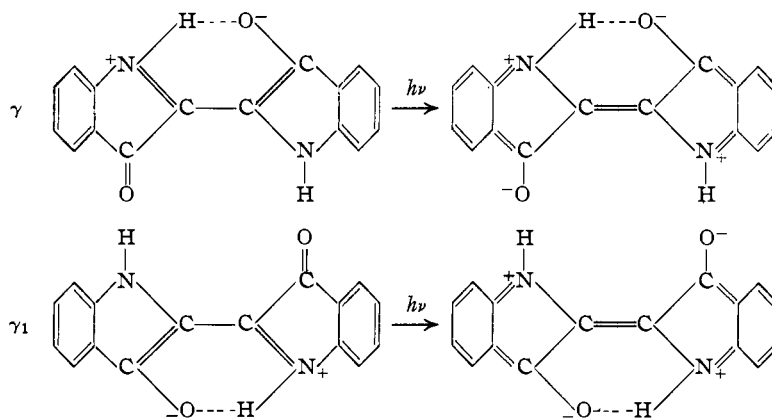
It may be supposed that in associating solvents the structures β and β' would be less stable, producing a reduction in the energy difference from the splitting of levels, and hence displacement of the absorption band to longer waves.

The figures in Table V show the considerably lower sensitivity to solvent influence exhibited by indigo as compared with the merocyanine.

It may be pointed out here that any effect of solvent upon the absorption of light must involve a "solvation" preceding the act of light absorption, in accordance with the Franck-Condon principle that no movements of atomic nuclei can be

concerned in it. On the resonance theory this is quite consistent with the solvent shifting, so to say, the center of gravity of the resonance system of the molecule.

In discussion with Dr. M. L. Huggins, he has suggested as alternatives or modifications of the formulations β and β' the structures γ and γ_1



thus indicating a certain ionic strength of the hydrogen bridge. The structures γ and γ_1 approach the structure D favored by Eistert (see above) but with diminished ionic strength (polar-

ity) suggested; the structures indicated for excited states produced by absorption of light from γ and γ_1 similarly approach the structure C of van Alphen (as above).

TABLE V

	XXIII $\Delta I/\lambda, \text{cm.}^{-1}$	Indigo $\Delta I/\lambda, \text{cm.}^{-1}$
Benzene	2408	1520
Alcohol	3300	1786
Formic acid	3258	2366

The hydrogen bonding possibilities of a solvent are undoubtedly very important for the spectrum of such molecules as indigo. The capability of such dye molecules to effect H-bridging *inter se* in condensed states might be expected therefore to be indicated in the spectrum of the *solid* state (*cf.* later, Fig. 7).

1,4-Diaminoanthraquinone.—Spectrophotometric absorption measurements were made in a

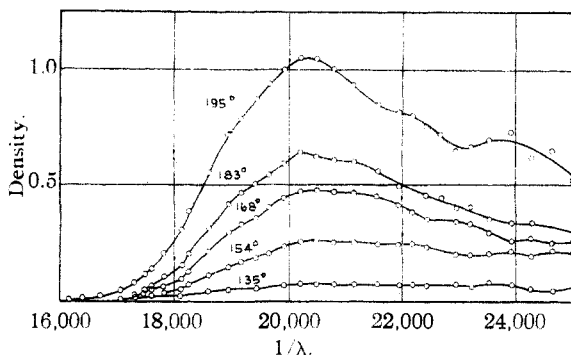


Fig. 1.—1,4-Diaminoanthraquinone vapor at various temperatures.

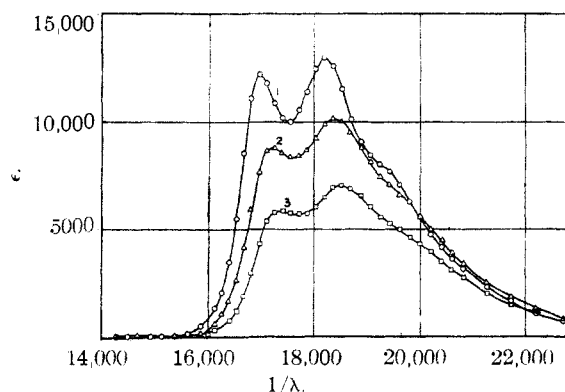


Fig. 2.—1,4-Diaminoanthraquinone in: 1, methyl alcohol; 2, benzene; 3, carbon tetrachloride.

number of non-polar and polar solvents. The absorption shows three fairly pronounced maxima, which have been termed α , β and γ , the α -band being of longest wave length (*cf.* Figs. 1 and 2).

TABLE VI

1,4-DIAMINOANTHRAQUINONE IN NON-POLAR MEDIA

Medium	n_D	K	α -Band		β -Band		γ -Band	
			λ	$\Delta 1/\lambda$	λ	$\Delta 1/\lambda$	λ	$\Delta 1/\lambda$
Vapor	1.000	1.00	525	0	492	0	470	0
<i>n</i> -Hexane	1.375	1.87	575	1657	535	1628	500	1276
<i>n</i> -Decane	1.409	1.95	575	1657	535	1628	500	1276
Carbon tetrachloride	1.458	2.24	576	1846	540	1801	508	1591
Benzene	1.498	2.28	580	1807	545	1972	510	1668
Carbon disulfide	1.629	2.65	587	2012	550	2138	515	1859

TABLE VII

1,4-DIAMINOANTHRAQUINONE IN ALIPHATIC SOLVENTS

Solvent	$\mu \times 10^{18}$	α -Band		β -Band		γ -Band	
		λ	$\Delta 1/\lambda$	λ	$\Delta 1/\lambda$	λ	$\Delta 1/\lambda$
Vapor		525	0	492	0	470	0
<i>n</i> -Hexane	0	575	1657	535	1628	500	1276
Diethyl ether	1.12	582	1868	542	1870	510	1668
Methyl acetate	1.74	580	1807	545	1972	510	1668
Acetone	2.74	585	1954	547	2039	510	1668
Nitromethane	3.80			550	2138		
Diethylamine	0.90	595	2248	552	2204	510	1668
Triethylamine	.90	590	2099	555	2302	510	1668
<i>n</i> -Butylamine	1.3	595	2248	555	2302	517	1934
Acetic acid	1.63	590	2099	550	2138	510	1668
Propionic acid	1.68	590	2099	550	2138	510	1668
Methyl alcohol	1.68	590	2099	550	2138	515	1859
Water	1.90	582	1866	545	1972	505	1474

The values for the maxima in non-polar media have been plotted as a function of the refractive index (Fig. 3). While they fall on fairly smooth curves, they do not give a linear relation, as in the case of the merocyanine, though there is approach to this with increasing index.

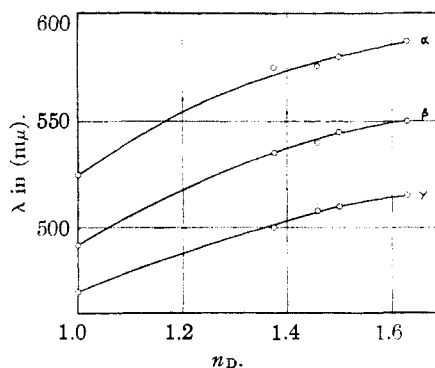


Fig. 3.—1,4-Diaminoanthraquinone in non-polar media.

In polar solvents, both aliphatic and aromatic, there is a very definite tendency for the displacement to increase with increase of polar moment of the solvent (*cf.* Figs. 4 and 5). The displacement,

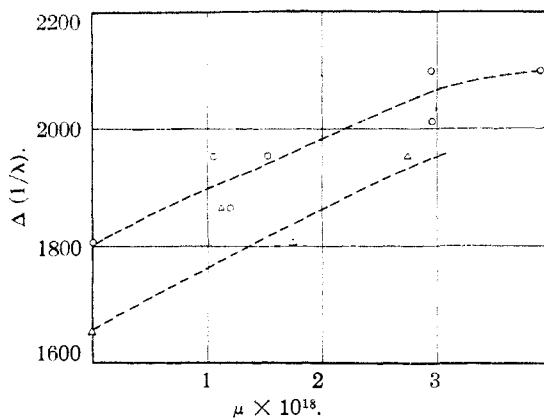


Fig. 4.— α -Band of 1,4-diaminoanthraquinone in polar media: Δ , aliphatic solvents; O , aromatic solvents.

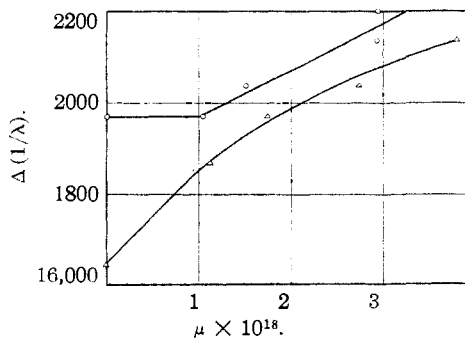


Fig. 5.— β -Band of 1,4-diaminoanthraquinone in polar media: Δ , aliphatic solvents; O , aromatic solvents.

in general, is greater in aromatic solvents than in aliphatic solvents of the same moment (*cf.* Table VIII and Figs. 4 and 5). The behavior is more like that of the merocyanines than is that of indigo.

TABLE VIII

1,4-DIAMINOANTHRAQUINONE IN AROMATIC SOLVENTS

Solvent	$\mu \times 10^{18}$	α -Band		β -Band		γ -Band	
		λ	$\Delta 1/\lambda$	λ	$\Delta 1/\lambda$	λ	$\Delta 1/\lambda$
Benzene	0	580	1807	545	1972	510	1668
Diphenyl ether	1.05	585	1954	545	1972	510	1668
Anisole	1.20	582	1866	545	1972	510	1668
Phenyl acetate	1.52	585	1954	547	2039	510	1668
Acetophenone	2.94	590	2099	550	2138	515	1859
Benzophenone	2.95	587	2012	552	2204	515	1859
Nitrobenzene	3.90	590	2099	550	2138	510	1668
Aniline	1.52	590	2099	552	2204	515	1859
<i>o</i> -Chloroaniline	1.77	590	2099	552	2204	515	1859
Quinoline	2.16	598	2326	560	2463	520	2045

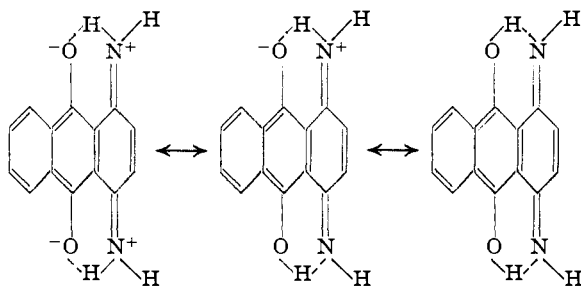
The normal constitution assigned to 1,4-diaminoanthraquinone readily admits hydrogen-bonded structures, such as were previously cited for the dioxanthraquinone.⁸ In recent papers on the constitution of certain (acid) anthraquinone dyes,⁹ C. F. H. Allen, C. V. Wilson and G. F. Frame have given an interpretation of certain characteristics of their spectra based on hydrogen bonding in 1,4- and 1,5-diaminoanthraquinone derivatives. One feature in particular is thus explained "when there are in the 1- and 4-positions two groups which are able to furnish electrons by a mesomeric shift, the main band of absorption will have a double head. If but one group of this type is present, only a single head will be observed." This appears to be in agreement with the secondary characteristic of the evolution of the spectrum of 1,4-diaminoanthraquinone, *via* 1-aminoanthraquinone illustrated in Part I; the second amino group in the 4-position produces not only a considerable displacement of the longest wave band toward the red, but a splitting of the band. Actually, however, there are present in most absorption spectra of 1,4-diaminoanthraquinone three fairly well-marked sub-bands. The question as to whether these are independent electronic transitions or are due to superpositions of vibrational quanta on a main electronic transition is perhaps not yet clear.

It is evident from the normal valence formula that a large number of structures could be written, not all of equal probability, but there are at present insufficient data to estimate more than

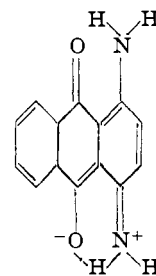
(8) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 329.

(9) C. F. H. Allen, C. V. Wilson and G. F. Frame, *J. Org. Chem.*, **7**, 169 (1942).

roughly the energy differences implied. As in the case of indigo, we suppose hydrogen-bonded structures to be chiefly contributing to a lower state and normal and quadrupolar structures to higher levels. The structures of lower energy may be represented as follows



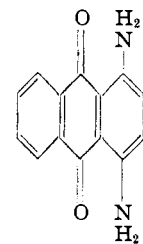
These represent three possible structures contributing to the resonance of the two parallel hydrogen bonds. As chiefly contributing to the first excited state, we may suggest such structures as



and the alternate: also, but chiefly contributing to a higher excited state, the structure shown.

We have again to thank Dr. Huggins for very helpful suggestions in regard to the formulation of the hydrogen-bonded structures. The interpretation proposed is quite tentative and purely qualitative.

In Part I, in the discussion of the behavior of the merocyanines, there was reproduced a diagram from a paper of Th. Förster¹⁰ indicating the participation of polar and non-polar structures of a dye in the principal lower and upper states corresponding to the main electronic transition, or absorption band. Förster indicated that *a priori* there would be a possibility of molecules in which (di)polar structures made the larger contribution to the ground state, these being more stable. We regarded this as improbable, in fact, because of the large coulombic energy in the separation of charges. However, it is possible that we were too hasty in this conclusion.



(10) Th. Förster, *Z. Elektrochem.*, **45**, 548 (1939).

Hydrogen bonding can effect a relative stabilizing of (di)polar structures, which may lead to increased contribution of such structures to the ground state, though it may not allow the complete inversion suggested in Förster's discussion.

From the solvent data recorded in Part I for merocyanine (dye XXIII) and in this paper for *indigo* and 1,4-diaminoanthraquinone, as well as from the resonance systems indicated, we suggest the following approximate scheme for the polar, non-polar balance in the molecules of these dyes in the gas state (*in vacuo*). The diagram is based on that of Förster (Fig. 6) and expresses approximately the findings that the effects of increasing dielectric constant of non-polar liquids and of polar moment of polar liquids (normal or non-associated) are greatest with *merocyanine*, considerable with *diaminoanthraquinone*, and least (approaching zero) with *indigo*. From these considerations,

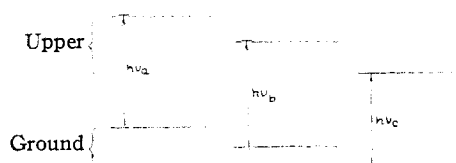


Fig. 6.—Polar non-polar characters of dyes in gaseous state:

Merocyanine (XXIII)	1,4-Diaminoanthraquinone	Indigo
$h\nu_a = 2.63$ ev.	$h\nu_b = 2.51$ ev.	$h\nu_c = 2.26$ ev.
λ_m in $m\mu = 470$	492	544
$1/\lambda$ in $\text{cm.}^{-1} = 21,276$	20,320	18,315

it appears probable that the "associated" liquids (alcohols, aliphatic acids, acetoacetate, etc.) which give "high" displacements with merocyanine (dye XXIII) do so because, having "high" dielectric constants in the liquid state or because developing effective polar moments two to three times that of the gaseous molecule. The relatively lower effect of these solvent liquids with 1,4-diaminoanthraquinone and with indigo may be explained perhaps by the following considerations. (a) Their dipole moment will have some positive weight for the anthraquinone dye, practically none for the indigo. (b) Their tendency to form hydrogen bonds may reduce the stability of internal structures of this type in a dissolved dye molecule. This could lessen the energy difference between the upper and lower levels and, hence, displace the absorption to longer wave lengths. The relative tendencies to intermolecular combination in these three dyes are indicated to some extent by comparison of the vapor spectra of the dyes with the spectra of solid films sublimed on

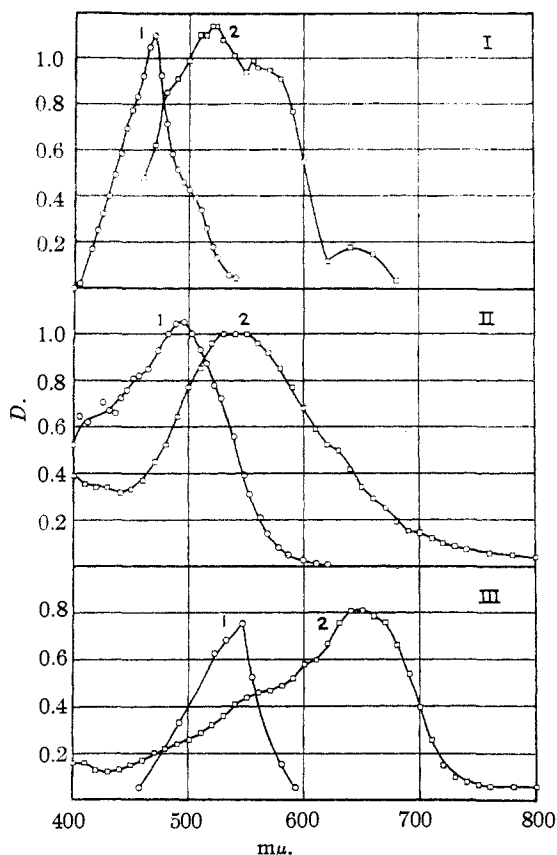


Fig. 7.—I, Merocyanine XXIII; II, 1,4-diaminoanthraquinone; III, indigo (1, vapor; 2, solid).

glass (*cf.* Fig. 7). The positions of the maxima in the solid films, also the wave number differences between λ_m (solid) and λ_m (gas) are given below:

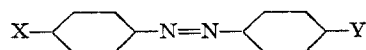
Merocyanine (XXIII)	1,4-Diaminoanthraquinone	Indigo
λ (solid) 520 $m\mu$	540 $m\mu$	650 $m\mu$ (670 $m\mu$) ^a
$\Delta 1/\lambda$ 2036 cm.^{-1}	1820 cm.^{-1}	3015 cm.^{-1}

^a From J. Königsberger and K. Küpferer (*Ann. Physik*, 37, 601 (1912)).

There is a considerable change in each case, but largest for indigo. In view of the complications in the spectra of crystalline dyes¹¹ it appears premature to draw any very definite conclusions from these observations.

Azobenzene Derivatives

Molecules of the type



where X and Y are relatively basic and acidic (electropositive and electronegative) groups (Dilthey and Wizinger's auxochrome and antauxo-

(11) *Cf.* E. E. Jelley, *Ind. Eng. Chem. (Anal. Ed.)*, 13, 196 (1941).

chrome) give well-marked absorption bands in the near ultraviolet or the visible spectrum; the position varies with the potential drop between X and Y, being displaced farther to the long waves the greater the drop.

We have examined the influence of solvent (and of pH) on the following: (a) benzeneazodiphenylamine; (b) *p*-dimethylaminoazobenzene; (c) *p*-hydroxy-*p'*-nitroazobenzene; (d) *p*-amino-*p'*-nitroazobenzene; (e) *p*-dimethylamino-*p'*-nitroazobenzene.

The general character of the absorption spectra remains much the same with change of auxochrome groups. The long wave band is broad and considerably diffused, and this makes the assignment of values of λ_{\max} (or ν_{\max}) rather uncertain. Moreover, the addition of a proton (H^+) makes a large change in the resonance system, and consequently a large displacement of the absorption band. Since both bases and cations are "colored," overlap when conversion is incomplete can complicate the picture further. We shall give data only for *p*-dimethylamino-*p'*-nitroazobenzene, which are fairly representative of the group behavior.

The character of the absorption band and the shift with proton addition can be seen in Fig. 8. There can be discerned two major overlapping bands, α at longer, β at shorter wave lengths.

In Table X are given for λ_{α} and λ_{β} , the corresponding wave numbers for non-polar solvents, normal aliphatic and aromatic solvents of increasing polar moment.

Solvent	n_D	$\mu \times 10^{18}$	α -Band $1/\lambda$	β -Band $1/\lambda$
Non-polar Solvents				
<i>n</i> -Hexane	1.375	0	(21400)	22720
Carbon tetrachloride	1.458	0	(21400)	22200
Benzene	1.498	0	20800	21740
Carbon disulfide	1.629	0	20400	21700
Aliphatic Solvents				
Diethyl ether	1.351	1.13	21400	22500
Methyl acetate	1.361	1.74	20600	21500
Acetone	1.356	2.74	20200	21300
Nitromethane	1.381	3.80	18900	19800
Aromatic Solvents				
Diphenyl ether	1.576	1.05	19600	20840
Phenyl acetate	1.500	1.52	20000	20840
Acetophenone	1.534	2.94	19600	20400
Nitrobenzene	1.553	3.90	19600	20300

Further, in Table XI are given the values for:

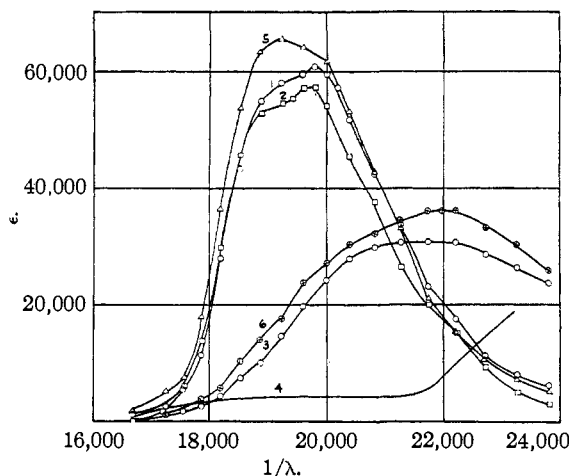


Fig. 8.—*p*-Dimethylamino-*p'*-nitroazobenzene in: 1, formic acid; 2, acetic acid + dilute H_2SO_4 ; 3, propionic acid; 4, concd. H_2SO_4 ; 5, dilute H_2SO_4 ; 6, diethylamine.

(i) normal aliphatic monocarboxylic acids; (ii) sulfuric acid and fatty acid with sulfuric; (iii) alcohol and acetone with sulfuric acid and with diethylamine, respectively; (iv) phenol, acetophenone, diethylamine.

TABLE XI
p-DIMETHYLAMINO-*p'*-NITROAZOBENZENE IN ACIDS, ALCOHOLS AND AMINES

Solvent	$\mu \times 10^{18}$	α -Band $1/\lambda$	β -Band $1/\lambda$	
i	Formic acid	1.77	19160	19800
	Acetic acid	1.63	20400	21740
	Propionic acid	1.68	20400	21740
	<i>n</i> -Butyric acid	1.9	20400	21700
ii	Concd. H_2SO_4		>23260	
	Dilute H_2SO_4 (1:1)		19200	20000
	Acetic acid + drop of dil. H_2SO_4		19000	19700
	Butyric acid + drop of dil. H_2SO_4		18800	19600
iii	Methyl alcohol	1.68	20200	21300
	Methyl alcohol + drop of dil. H_2SO_4		18600	19600
	Methyl alcohol + drop of diethylamine		20400	21300
	Acetone + drop of formic acid		20200	21300
iv	Acetone + drop of dil. H_2SO_4		18860	19800
	Acetone + drop of diethylamine		20400	21740
	Phenol	1.70	18200	19100
	Phenol + drop of dil. H_2SO_4		18200	19200
	Acetophenone + drop of dil. H_2SO_4		18300	19100
	Acetophenone + drop of diethylamine		19300	20400
Diethylamine	0.9	20900	22000	

The base, *p*-dimethylamino-*p'*-nitroazobenzene obeys Beer's law, *e. g.*, in benzene and in acetone, but in accord with the breadth and diffuseness of the absorption, the extinction coefficients are relatively low: benzene $E_{\max} = 2.40 \times 10^4$; acetone $E_{\max} = 2.56 \times 10^4$. The base in normal aliphatic and aromatic solvents shows "red displacement" with increasing polar moment of the solvent (Figs. 9 and 10), but the magnitude of the displacement is not large, and, as in the case of

merocyanine XXII (Part I), the behavior is complicated by the incidence of halochromy.

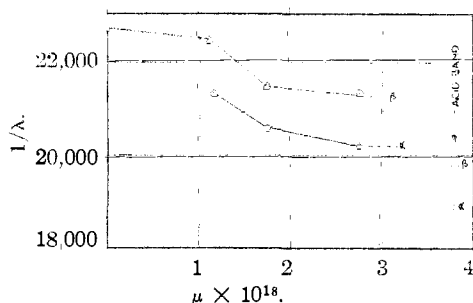


Fig. 9.—*p*-Dimethylamino-*p'*-nitroazobenzene (base) in aliphatic solvents.

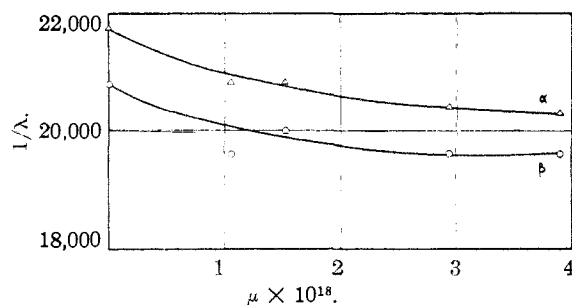


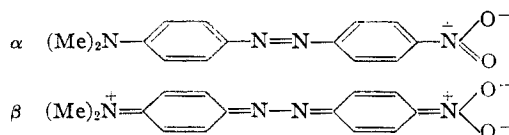
Fig. 10.—*p*-Dimethylamino-*p'*-nitroazobenzene (base) in aromatic solvents.

Addition of Proton

The weak acids, acetic, propionic and *n*-butyric, do not show the effect observed with merocyanine, with indigo, and 1,4-diaminoanthraquinone, of associating hydroxylated solvents. In fact, they behave as normal aliphatic solvents for the base. Formic acid, however, as found previously, behaves as a "strong" acid able to add a proton to the base.

The effect of this addition is quite strongly bathochromic, as may be seen from Fig. 8 and from the tables.

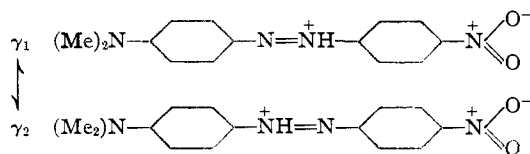
The two structures principally concerned in the resonance system of the base are very feasibly¹²



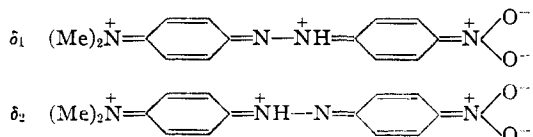
The upper structure α would be stabilized by the Kekulé resonance forms in the benzene rings, and perhaps, slightly by resonance in the $-\text{N}^+\text{C}(\text{O})_2\text{O}^-$ group. Perhaps the transition which arises from

(12) Cf. G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 305 (1939), for the similar system of *p*-nitro-aniline.

the splitting of the energy of these structures might give rise to an absorption of somewhat longer wave length than that of benzene, or rather of nitrobenzene itself, but it seems doubtful if we can assign even the shorter wave region of the main band of the base to this alone. The lower structure β is one of considerably lower stability, or of higher energy, than α , and as in the case of the merocyanines, may be considered as principally contributing to the first excited state. The effect of polarity of solvent on the "red displacement" is in accord with this interpretation. On adding a proton to the base we have two very similar but not identical alternates



γ_1 and γ_2 are tautomeric, and each structure is stabilized, as in α , by the Kekulé resonance, etc. To these there similarly correspond structures of higher energy



All these will have a single net positive charge, and consequently, as observed with the ionic cyanines, little effect of polar moment of the solvent is to be expected. The addition of still another proton would block the resonance, and this possibly accounts for the decolorization produced in concentrated sulfuric acid (*cf.* Fig. 8).

Hydrocarbons

The dye molecules may be considered as derived from certain hydrocarbon protomorphs, which are, however, already resonance systems, by substitutions of reactive atoms and/or groups (*cf.* Part I). It has appeared well, therefore, to include for comparison some data: (a) on the behavior of a visible colored polyene—*diphenyl-octatetraene*—which has a constitution with some affinity to that of the polymethine dyes. It is usually formulated as $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_4-\text{C}_6\text{H}_5$. (b) On the behavior of the aromatic hydrocarbons, benzene, naphthalene and anthracene.

Diphenyl-octatetraene

The absorption data are compiled from the

paper of Hausser, Kuhn and Kuhn,¹³ (cf. Tables XII and XIII).

TABLE XII

DIPHENYL-OCTATETRAENE (BAND I) IN NON-POLAR MEDIA

Medium	n_D	K	$1/\lambda$	$\Delta 1/\lambda$
Vacuum	1.000	1.00	27933	
Hexane	1.375	1.87	25380	2553
Decalin	1.483		24938	2995
Benzene	1.498	2.28	24752	3181
Carbon disulfide	1.629	2.65	23923	4010

TABLE XIII

DIPHENYL-OCTATETRAENE (BAND I)

Solvent	$\mu \times 10^{18}$	$1/\lambda$	$\Delta 1/\lambda$
Aliphatic			
Hexane	0	25380	2553
Ethyl ether	1.12	25252	2681
Acetic acid	1.63	25252	2681
Methyl alcohol	1.68	25445	2488
Ethyl alcohol	1.70	25252	2681
Formic acid	1.77	25189	2744
Acetone	2.74	25189	2744
Aromatic			
Benzene	0	24752	3181
Xylene	0.4	24752	3181
Pyridine	2.11	24510	3423
Nitrobenzene	3.9	24332	3601

In non-polar solvents, the displacement increases continuously with increasing dielectric constant and refractive index (Fig. 11).

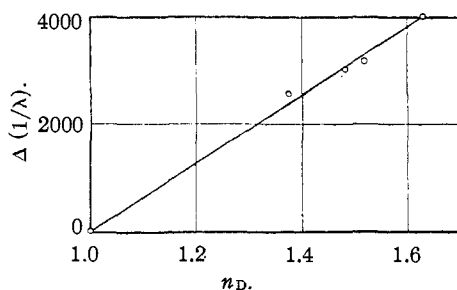
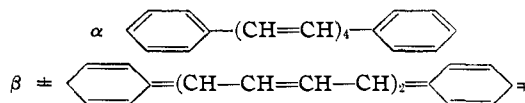


Fig. 11.—Diphenyl-octatetraene in non-polar media.

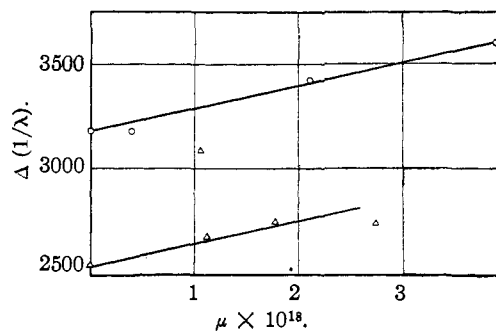
Data for the behavior in aliphatic and aromatic solvents of increasing polar moment are rather scant, and hardly permit definite conclusions. Certainly, it may be said that the displacement is greater in aromatic than in aliphatic solvents of comparable polar moment, but, while there are some indications of an influence of polar moment (cf. Fig. 12), they are not conclusive. Chloroform gives an apparently unduly large, methyl alcohol an unduly small displacement. The sensitivity to polar moment appears in any case to be small. The resonance system for the diphenyl polyene is

(13) K. W. Hausser, R. Kuhn and E. Kuhn, *Z. physik. Chem.*, **20B**, 417 (1935).

probably somewhat similar to that of the azobenzenes



The upper structure α is stabilized by the Kekulé resonance of the terminal phenyl groups, and would contribute mostly to the ground level. The lower structures β are dipoles of considerably higher energy and would be expected to contribute mostly to the (first) excited level. Such effect as there is of polar moment would be in accord with this.

Fig. 12.—Diphenyl-octatetraene in polar media (Band I): Δ , aliphatic solvents; \circ , aromatic solvents.

Data on the solutions of benzene in different solvents are given by Lauer and Oda¹⁴ for the absorption bands in the near ultraviolet. The first and second bands (the first band being of longest wave length and so on) show small *negative* displacements (*i. e.*, to shorter wave lengths) in solutions as compared with the vapor. These displacements—of the order of 300 cm^{-1} —are much the same for the solvents tested, with the exception of water, in which it is smaller. The higher frequency bands show small *positive* displacements of the same order of magnitude, and again practically independent of the solvent, except that the shift in water is again smaller. The behavior of liquid benzene indicates an effect of the congener molecules little, if at all, different from that of the other solvents.

The insensitivity to solvents is in accord with the resonance system attributed to benzene,¹⁵ and to the quantum mechanical theory developed by Sklar¹⁶ and Förster.¹⁰

Similar in some respect to the aromatic fused-ring hydrocarbons are the phthalocyanine dyes

(14) K. Lauer and R. Oda, *Ber.*, **69**, 851 (1936).

(15) Cf. L. Pauling, *op. cit.*, p. 128.

(16) A. L. Sklar, *J. Chem. Phys.*, **5**, 606 (1937).

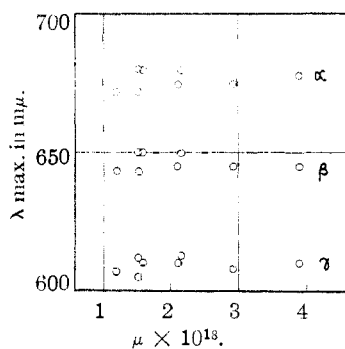
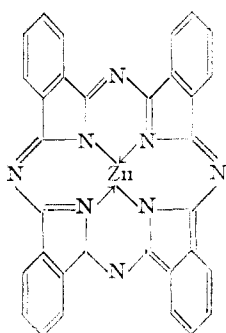


Fig. 13.—Zinc phthalocyanine in polar media.

(and thereby the porphine macrocyclic compounds in general).

Our spectrophotometric measurements on the phthalocyanines, exemplified by *zinc phthalocyanine*



nine show no definite effect of polar moment of solvent on the absorption (Fig. 13). This indifference may be taken to mean that no ionized (dipolar) structures are represented in the first excited state; the resonance system is presumably by way of the two alternately covalently and coordinately

linked pairs of the four interior N-atoms,¹⁷ through

(17) The conjugation extends, of course, through the external —N= links.

the central atom, making the system resemble benzene with its basic Kekulé resonance. A notable difference from benzene, however, is the great intensity (extinction) of the longest wave absorption band.

Acknowledgment.—We desire to express our thanks for helpful suggestions and criticisms to Dr. M. L. Huggins, and to Mr. H. R. Brigham for the preparation and spectrophotometry of sublimed solid films of certain dyes.

Conclusion

The results presented in this paper extend the tentative conclusions expressed in Part I. So far as these orienting investigations go, they indicate that the sensitivity of the absorption spectra of dyes to solvent influence is rather closely related to the resonance system of the dye, and may throw some light upon this. Correlatively, it appears possible that, with increased investigation, the effect of given solvents on the absorption spectrum of selected dyes may improve our understanding of the molecular structure of liquids. The rather notable behavior of halogenated alkyls suggests a promising field for further investigation as also the observations on hydroxylated solvents.

ROCHESTER, N. Y.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Solubility of Calcium Oxalate Monohydrate in Pure Water and Various Neutral Salt Solutions at 25°

BY WILBUR H. MCCOMAS, JR.,¹ AND WM. RIEMAN III

Because of the importance of calcium oxalate in analytical work, accurate data on its solubility are very desirable. A survey of the literature reveals, however, very discordant figures for the solubility in pure water and very few reliable data on the effect of neutral salts.² Table I summarizes the previous work on the solubility in pure water. Since the equilibrium between calcium oxalate and its saturated solution is established rather quickly, the major source of error in

the solubility determinations probably lies in the failure to obtain pure calcium oxalate.

Solubility in Pure Water

Experimental.—Calcium oxalate monohydrate, product A, was prepared as follows:^{2a} fifty mmol. of ammonium oxalate contained in 400 ml. was added slowly (twenty-five minutes) with vigorous stirring to 60 mmol. of calcium chloride contained in 1600 ml. at room temperature. Then 200 ml. of 0.1 *N* hydrochloric acid was added with vigorous stirring. The precipitate was digested for one day at 95–100°. After cooling, the precipitate was washed by centrifugation until a negative test for chloride ion was obtained in the wash water. It was stored under water until used.

(1) This paper is taken from part of a thesis submitted by Wilbur H. McComas, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Hammersten, *Compt. rend. trav. lab. Carlsberg*, **17**, 11 (1929), has studied the effect of several salts at 37°, mostly at ionic strengths below 0.2.

(2a) Kolthoff and Sandell, *J. Phys. Chem.*, **37**, 459 (1933).