

Experimental

Materials.—The amines were all Eastman Kodak Co. products, and they were carefully fractionated before use. The aluminum chloride, ferric chloride, zinc chloride and sulfuric acid were anhydrous c. p. products and were used without further purification.

Experiments in Open Vessels.—The catalyst and amine were mixed, with considerable evolution of heat, and the resulting mixture was heated under reflux. In almost every case a two-phase system was obtained. In experiments for which a constant temperature was desired, a large electrically heated oil-bath was used and the solution was frequently shaken. At the end of a definite period the mixture was cooled in an ice-bath and a considerable excess of aqueous sodium hydroxide was added. The amine layer was separated, washed with water, dried over potassium carbonate and finally fractionated.

For large quantities a fractionating column, 40 cm. long, 13 mm. i. d., electrically heated, and packed with glass helices was used. However, many runs were made using only about 30 cc. of solution, and in such cases a Vigreux column, 25 cm. long, and of 8 mm. i. d., was used. The column was very efficient, and, in general, a reflux ratio of 30 to 1 was maintained.

Experiments in Sealed Vessels.—Pyrex bomb tubes were used in this work. Ammonia, if required, was added to mixtures by condensing the gas in the tubes, using a dry ice-alcohol bath. Sealed tubes containing the reactants were heated in an electric furnace. After heating, the tubes were cooled in a dry ice-alcohol bath and then opened. The contents of the tubes were poured into an excess of cold aqueous sodium hydroxide, and the amine layer was separated. The aqueous layer was extracted twice with ether, the ether extracts being added to the

amine layer. The aqueous layer was then distilled into a standard hydrochloric acid solution and the ammonia concentration was determined from the amount neutralized. The amine-ether fraction was dried over potassium carbonate and fractionated, using one of the columns described above.

Preparation of Picrates.—Although the boiling points of the amine fractions indicated that no rearrangements within the alkyl groups had occurred during redistribution, a check was desirable. This was done by preparing the picrates of amine fractions obtained by redistribution. Mixed melting point determinations with picrates prepared from amines obtained from the Eastman Kodak Co. indicated that no changes had taken place within the alkyl groups. The picrates were prepared by mixing 1 g. each of picric acid and the amine and heating until a brown solution was obtained. Six cc. of ethanol was then added and the mixture cooled. The fine yellow crystals which formed were filtered, washed and finally recrystallized from ethanol. The picrates of *n*-butylamine, di-*n*-butylamine and tri-*n*-butylamine melted at 151, 59 and 105°, respectively.

Summary

It has been found that when aliphatic amines are heated with metal halide catalysts, the groups attached to the nitrogen are redistributed. This redistribution reaction has been studied with respect to the catalytic activity of several substances and the order of the reaction with respect to catalyst concentration. The mechanism of the reaction has been discussed.

DAVIS, CALIFORNIA

RECEIVED FEBRUARY 24, 1942

[COMMUNICATION NO. 827 FROM THE KODAK RESEARCH LABORATORIES]

Some Effects of Solvents upon the Absorption Spectra of Dyes. I. Chiefly Polymethine Dyes

By S. E. SHEPPARD, P. T. NEWSOME AND H. R. BRIGHAM

Introduction

To examine the effect of solvents upon the absorption spectrum of a substance, it is desirable that the spectrum should be measured originally for the substances present as a gas at low pressures and at temperatures comparable with those of the solutions. This is far from easy with dyes, which possess rather large and complicated polyatomic molecules. Low pressures and rather high temperatures are required to volatilize them. Also, they are very liable to decomposition (pyrolysis) with formation of colored (yellow to brown) reaction products.

Experimental

The dyes in which we are primarily interested

are photographically active sensitizing and desensitizing dyes such as cyanines (polymethine dyes), and xanthene and phenazine derivatives. Most of these are salts, and, while it was found possible to volatilize (sublime) a number of them, there was generally too much decomposition for satisfactory spectral measurement. Certain non-saline *merocyanines* first prepared by Brooker¹ could be volatilized at low pressures without contamination. Because of the low pressures necessary, a quite long optical path was used, *viz.*, a 15-ft. tube, operated as an electrical resistance heater furnace by wrapping it with nichrome wire and asbestos (*cf.* Fig. 1).

(1) L. G. S. Brooker, U. S. Patents 2,177,401-2-3.

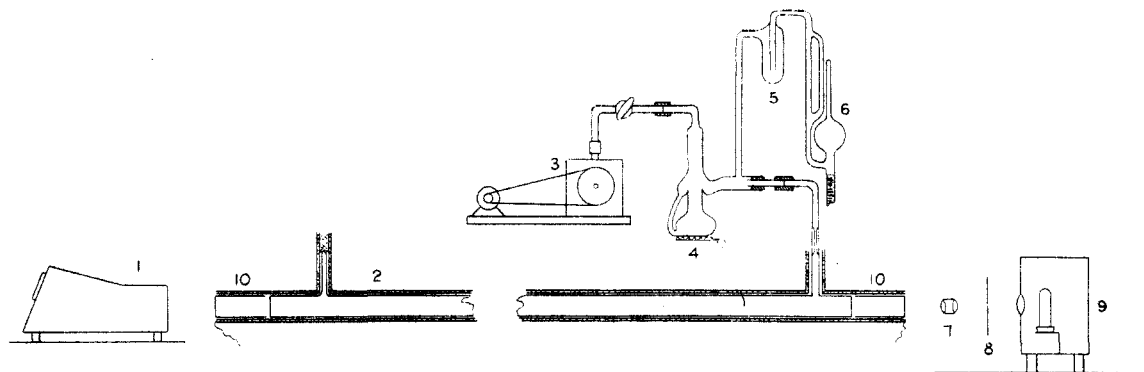


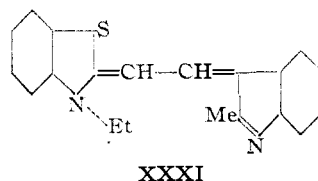
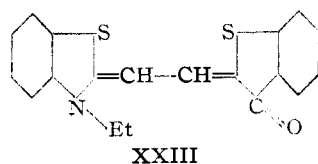
Fig. 1.—Diagram of vapor absorption apparatus: 1, spectrograph; 2, absorption tube with heating coils and insulation; 3, Hyvac pump; 4, condensation pump; 5, trap; 6, McLeod gage; 7, lens; 8, diaphragm; 9, light source; 10, end guards.

The total pressure was about 0.1μ ; the partial pressure of the dye was not measured. Consequently, we were unable to measure actual extinction coefficients, defined as

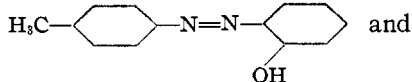
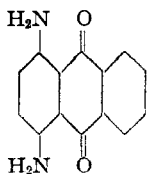
$$\epsilon_{\lambda} = \frac{1}{cd} \log \frac{I_0}{I}$$

where c = molar concentration, and d = thickness in cm.

However, the envelope of the band spectrum could be measured spectrophotometrically in terms of optical density; after analysis, the relative extinctions of the band maxima were obtained.



Beside the *merocyanines*, XXIII and XXXI (see above), measurements in the gas phase were made of *1,4-diaminoanthraquinone*, of *p-toluidine azo-β-naphthol*,



of *indigo*. It is to be noticed further that, while absorption measurements were made at low pressures, the *temperatures* were much higher than those in the solutions. This is more or less inevitable, since rough calculation shows that to obtain an

optical density of 1.0 at 25° , lengths of tube of the order of 10^7 to 10^{16} would be necessary.

Previous measurements on some vaporized dyes (indigo, alizarin, dianilidoanthraquinone) have been made by Koenigsberger and Küpferer.²

Representation and Analysis of Extinction Curves

A common graphic representation is a plot of $\epsilon_{\lambda} \sim D_{\lambda}$ against λ (wave length in $m\mu$ or \AA). Curves of this type are shown for gaseous *merocyanine* (dye XXIII) and *1,4-diaminoanthraquinone* at different temperatures (*cf.* Fig. 2). Similar curves for *merocyanine* (dye XXIII) dissolved in various solvents are shown in Fig. 3. However, for comparison and analysis of the effects of structural and environmental changes, there are many advantages in taking reciprocal values of the wave length as abscissas, as wave numbers $1/\lambda$ in cm.^{-1} . The use of $\log \epsilon$ as ordinate is frequently useful, either to obtain compactness, or to enhance the apparent strength of minor bands³; ϵ_{λ} is a quantity having no dimensions, and representing the *probability* of the event occurring at the value λ .

The curves shown in Figs. 2 and 3 are only the envelopes of a definite group of related bands; in some cases, one or more of the subsidiary peaks are clearly defined; in others, they may be present only as a hump or shoulder, or merely as a strongly marked asymmetry of the extinction curve. Changes of environment may affect the relative sharpness and strength of the individual bands.

Such band complexes may be analyzed by semi-empirical methods, assuming that the ϵ (\sim prob-

(2) J. Koenigsberger and K. Küpferer, *Ann. Physik*, [4] **37**, 601 (1912).

(3) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 310 (1939).

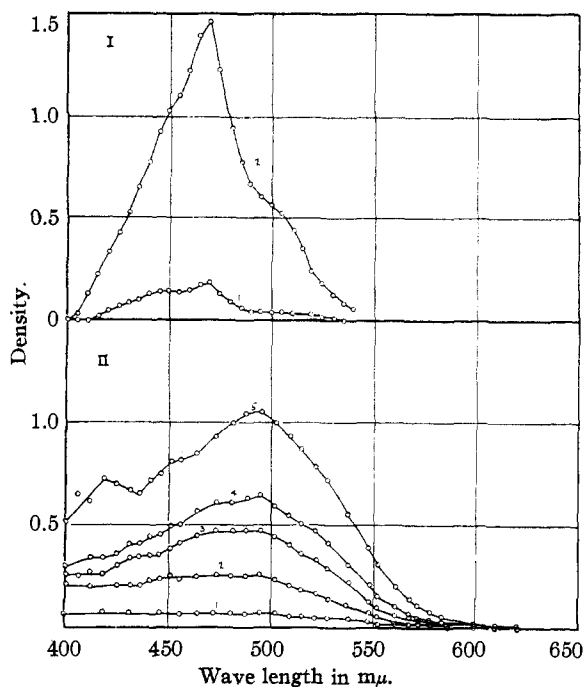


Fig. 2.—I, Merocyanine gas at 1, 228°; 2, 250°. II, 1,4-diaminoanthraquinone gas at 1, 135°; 2, 154°; 3, 168°; 4, 183°; 5, 195°.

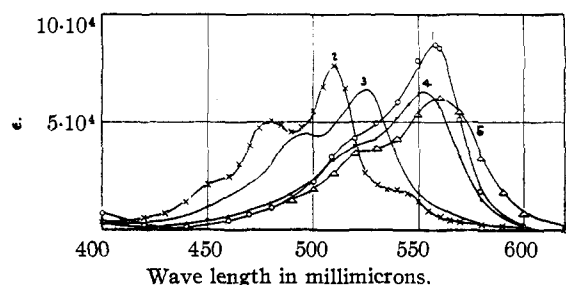


Fig. 3.—Merocyanine in 1, methyl alcohol; 2, *n*-hexane; 3, carbon tetrachloride; 4, quinoline; 5, methylene iodide.

ability of absorption) values are distributed about a maximum, usually according to a Gaussian function. We have used the method originally introduced by Henri,⁴ and by Henri and Bielecki.⁵ Their function

$$\epsilon_\nu = ke^{-[(\nu_0 - \nu)^2]/2a^2} \text{ or } y = ke^{-x^2/2a^2}$$

where k is the ordinate, ϵ_{ν_0} , at the center of the distribution curve, *i. e.*, when $x = \nu_1 - \nu = 0$ and $2a$ is the breadth at a value $0.606k$, and ϵ_ν = the molar extinction coefficient.

It was observed that in the organic solvents employed, Beer's law is generally followed by these dyes.

In Figs. 4 and 5 are presented comparative extinction curves for the *merocyanine* dye—and *di-*

(4) V. Henri, *Physik. Z.*, **14**, 516 (1913).

(5) J. Bielecki and V. Henri, *Comp. rend.*, **158**, 1114 (1914).

aminoanthraquinone—in which the analyzed components of the envelope are indicated.

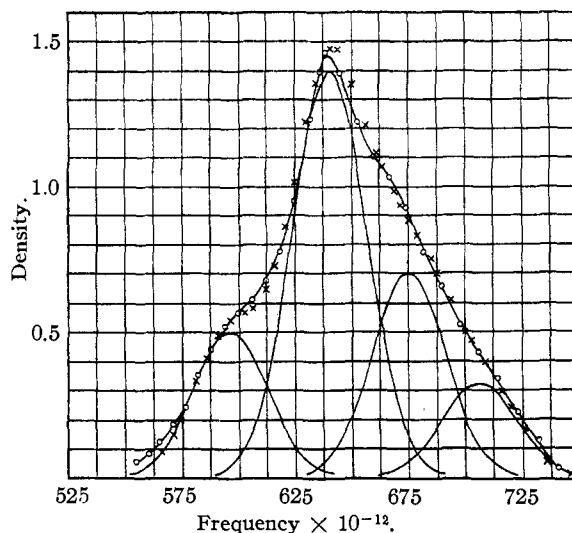


Fig. 4.—Analysis of merocyanine absorption.

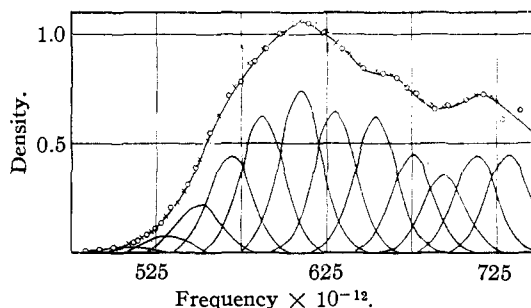


Fig. 5.—Analysis of 1,4-diaminoanthraquinone absorption (gaseous).

The data indicate that the band group persists as a whole in different media, and is displaced as a whole, not only with the merocyanine XXIII, a polymethine dye, but with diaminoanthraquinone, representing a quite different class. This conclusion is supported by graphic representation of the intensity ratios in the spectrum shown elsewhere.⁶

The persistence of this group of bands, adjacent to the band of maximum intensity, in the gaseous state, and in organic solutions, wherein Beer's law is followed, is of considerable importance. In aqueous solutions the ratio of intensities of the bands may change with the concentration. The auxiliary bands have been attributed to polymers of the single dye molecules.⁷ But it is evident that this is incorrect, since these bands are

(6) S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **9**, 96 (1941).

(7) G. Scheibe, *Kolloid-Z.*, **82**, 1-14 (1938).

definitely present both in the gaseous state and in organic solutions following Beer's law. They correspond, therefore, to electronic transitions proper to the individual molecule, and all that can be said is that aggregation or polymerization may change the relative probabilities of these transitions.

The wave-number differences between successive bands in the polymethine dyes range from 900 cm.^{-1} to 1700 cm.^{-1} ; these are of the same order as such differences in the polyenes and linear benzenes.

Effect of Temperature on Solutions

A considerable range of temperature is open to study with solutions of dyes in organic solvents. A mixture of ethyl alcohol and ether is a good solvent for many cyanine (polymethine) dyes. The most evident effect is to sharpen the band components as the temperature is lowered, or conversely, increased diffusion as it is raised. This can be expressed to some extent quantitatively as the change of ϵ_{max} with temperature. Here it is most useful to plot $\log \epsilon_{\text{max}}$ against $1/T$, where T is the absolute temperature, and characteristic curves are shown for several cyanine (polymethine) dyes (Fig. 6). The increased sharpening at lower temperature is due to reduction of rotational and vibrational energies, which cause the diffusion of the individual band. As very low temperatures are approached, this elimination becomes less, and the sharpening—shown by increase of ϵ_{max} and

reduction of the half-width of the band—asymptotically approaches a limit, or a maximum. This latter phenomenon is very possibly due to separation of the dye from solution, but further study is required.

There is liable to be a specific effect in aqueous solution, namely, a redistribution of intensities in the band complex. In consequence of this, the extinction coefficient ϵ_{max} of the long wave band tends to increase with rising temperature.

Comparison of Solvent Effects

There are at least two parameters for which solvent effects on absorption could be evaluated, *viz.*, in respect of band strength $\int \epsilon d\nu$ and band position— ν_{max} or λ_{max} . In regard to the former, Chako⁸ made a comparison of expressions for band strength for a large variety of organic substances, but not including dyes, in various solvents. The principal expression, derived from classical theory, evaluates the influence of neighboring molecules due to the Lorentz-Lorenz force, *i. e.*, the force coming from the polarization of the surrounding molecules. According to this, if F_s is the transition probability in solution, and F_g , that in the gas state, then

$$F_s = F_g \left(\frac{9}{(n_0^2 + 2)^2} \right)$$

where n_0 is the refractive index of the solvent. Chako concluded from his review that "it is impossible to account for the influence of the solvent through the Lorentz-Lorenz force."

If the width of the absorption band in the different solvents is constant, we can substitute ϵ_{max} for $\int \epsilon d\nu$, and should have

$$\epsilon_{\text{max}} \frac{9}{(n_0^2 + 2)^2} = \epsilon_{\text{gas}} = \text{constant}$$

This has been computed for the merocyanine in various solvents having values of n_0 ranging from 1.327 to 1.576. The calculated values of ϵ_{gas} varied from 3×10^4 to 6×10^4 . Some improvement occurs by evaluating the band strength F_s , but far from sufficient to account for 100% variation of ϵ_{gas} .

Displacement of Bands

In 1878 Kundt⁹ concluded that with increasing (partial) dispersion of the solvent the absorption maximum of a dye is shifted toward longer wave lengths. Usually, the refractive index n_D is

(8) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934); *cf. also*, R. S. Mulliken and C. A. Rieke, "Reports on Progress in Physics," Vol. VII, 1941, pp. 234-236.

(9) A. Kundt, *Ann. der Physik und Chemie*, **4**, 34-54 (1878).

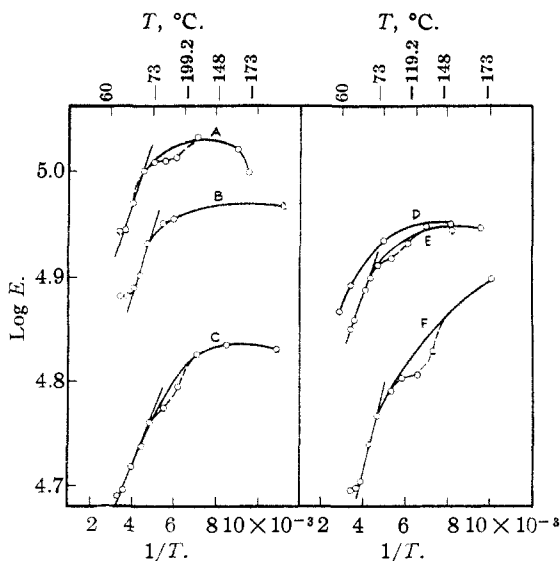


Fig. 6.—A = Dye XVIIIa; B = Dye XVIa; C = Dye XIXa; D = Dye Va; E = Dye XXa; F = Dye XVIIa.

TABLE I
 DISPLACEMENT $\Delta\nu$ IN CM.^{-1} CALCULATED FROM $\Delta\nu = a(1 - 1/K)$

Solute	Vapor ν_{max} in cm.^{-1}	Solvent									
		C_6H_{14}		C_8H_{18}		CCl_4		C_6H_6		CS_2	
		obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.
Benzene	39540	278	320	278	350	440	380	365	400		
Diphenyl-octa- tetraene	27933	2566	2760					3166	3450	4033	3710
<i>p</i> -Toluidine-azo- <i>p</i> - naphthol	25000	3261	3100			3724	3660	3495	3880	4167	4170
Merocyanine XXIII	21276	1668	1920	1859	2110	2228	2260	2408	2400	2928	2570
Cyanine IVb (18692)						1240	1260	1240	1350	1539	1450

considered instead of the dispersion. Numerous exceptions were observed, but chiefly for the ultra-violet absorption bands of substances other than dyes.

However, we found that if we definitely separate non-polar from polar solvents, Kundt's rule holds quite well, not only for dyes but for certain hydrocarbon prototypes, such as the polyenes, polyphenyls, and *lin*-benzenes. In many cases, the relation of γ_{max} to n_D is approximately linear—including the gaseous state with $n_D = 1.00$ (cf. Fig. 7). A relation between λ_{max} and the dielectric constant K was examined also for the merocyanines in non-polar media.

Simple electrostatic considerations¹⁰ suggest that the change of energy required to displace an electron in a medium of dielectric constant K compared with that in a vacuum would be given by the relation

$$\Delta E = \frac{e}{2r^2} \left(1 - \frac{1}{K} \right)$$

Hence, for the displacement of an absorption band in a solvent of dielectric constant K , we should have $\Delta\nu = a(1 - (1/K))$, for constant r . Keeping to non-polar solvents, values are given in Table I for near ultraviolet bands for aromatic hydrocarbons, and a diphenyl polyene, and for visible bands of certain dyes.

It is thought that somewhat better agreement might be obtained if variation of a , the molecular radius parameter, could be allowed for. One or two calculations for benzene, using the volume change on mixing, indicate this.

Effect of Polar Moment

An over-all survey of our data for the merocyanine seemed to indicate that no direct and simple relation between the band displacement and the polar moment could be observed. However, on analyzing the results in terms of families of homol-

(10) A. F. Joffe, "The Physics of Crystals," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 140.

ogous compounds, in general, of increasing chemical complexity, certain regularities became ap-

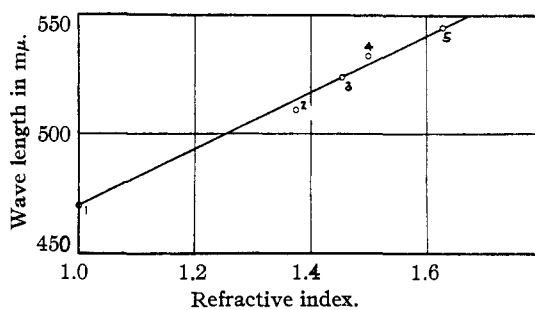


Fig. 7.—1, Merocyanine (gas) *in vacuo*; 2, in *n*-hexane; 3, in CCl_4 ; 4, in C_6H_6 ; 5, in CS_2 (non-polar solvents).

parent, as exhibited in Tables II, III, IV, and V. The displacement changes but slightly in this series and accords with the change of dielectric constant.

 TABLE II
 ALIPHATIC HYDROCARBONS

Substance	λ_{max} in $\text{m}\mu$	$\Delta\nu$ in cm.^{-1}	n_D	K	μ
<i>n</i> -Pentane	510	1668	1.358	1.80	0
<i>n</i> -Hexane	510	1668	1.375	1.87	0
<i>n</i> -Octane	514	1821	1.394	1.96	0
<i>n</i> -Decane	515	1859	1.409	1.95	0
<i>n</i> -Dodecane	515	1859	1.423		0
<i>n</i> -Tetradecane	517	1934	1.430		0
Cyclohexane	515	1859		2.05	0
Carbon tetrachloride	524	2192	1.458	2.20	0
Carbon disulfide	545	2928	1.629	2.65	0

 TABLE III
 ALKYL ETHERS

Ether	λ_{max}	$\Delta\nu$ in cm.^{-1}	n_D	K	$\mu \times 10^{18}$
Diethyl	520	2045	1.351	4.33	1.12
Dibutyl	520	2045	1.398		

 TABLE IV
 ACETATES

Acetate	λ_{max}	$\Delta\nu$ in cm.^{-1}	n_D	K	$\mu \times 10^{18}$
Methyl	530	2408	1.361	7.30	1.74
Ethyl	530	2408	1.374	6.40	1.81
<i>n</i> -Propyl	530	2408	1.384	6.30	1.78
<i>n</i> -Butyl	530	2408	1.394	5.0	1.84
<i>n</i> -Amyl	530	2408	1.405	5.1	1.91

TABLE V
ALKYL KETONES

Ketone	λ_{\max}	$\Delta\nu$ in cm.^{-1}	n_D	K	$\mu \times 10^{18}$
Acetone	535	2584	1.356	21.4	2.74
Diethyl	535	2584	1.393	17.3	2.74
Di- <i>n</i> -propyl	535	2584	1.407	12.6	2.73
Methyl- <i>n</i> -hexyl	535	2584	1.416	10.7	2.70

To these series the alcohols (Table VI) form an exception in the sense that they give a larger displacement while having a lower polar moment than the acetates, ethers and ketones.

TABLE VI
ALIPHATIC ALCOHOLS

Substance	λ_{\max}	$\Delta\nu$ in cm.^{-1}	n_D	K	$\mu \times 10^{18}$
Methanol	558	3355	1.327	33.1	1.68
Ethanol	555	3258	1.360	26.5	1.70
<i>n</i> -Propanol	555	3258	1.383	26.0	1.66
<i>n</i> -Butanol	555	3258	1.397	17.8	1.65
Iso-amyl alcohol	555	3258	1.408	15.3	1.70
<i>n</i> -Heptanol	555	3258	1.425	6.7	1.71

It is interesting to compare the values for aliphatic with aromatic groups of the same character.

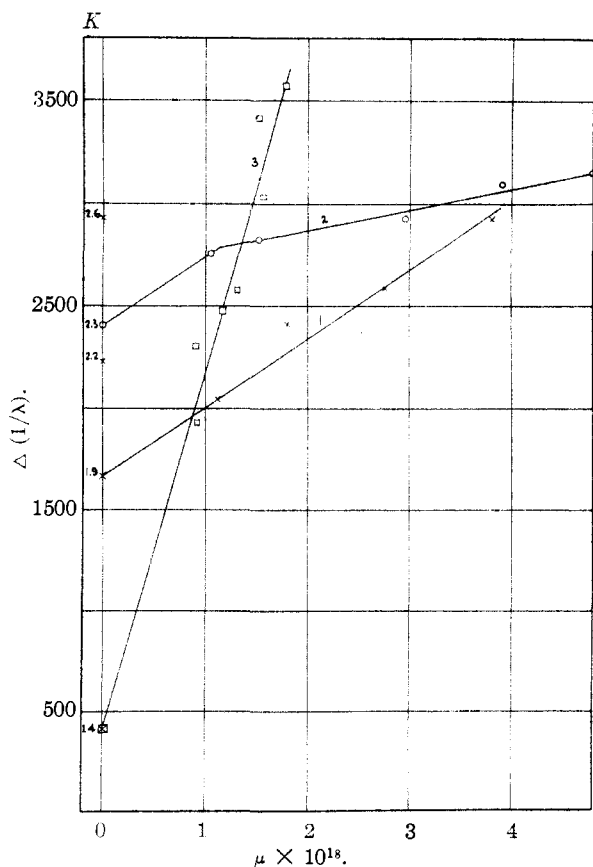


Fig. 8.—Merocyanine in polar solvents: 1, aliphatic series; 2, aromatic series; 3, amino bodies.

TABLE VII

	Aliphatic		Aromatic		$8(\Delta\nu)$ cm.^{-1}
	ν in cm.^{-1}	μ	ν in cm.^{-1}	μ	
Hydrocarbon	19600	0	18868	0 to 0.4	732
Ether	19231	1.12	18519	1.05	712
Ketone	18692	2.73	18348	2.74	344
Alcohol	18018	1.70	17689	1.69	329

A fairly regular progression of the displacement with the polar moment was observed with the amines (including certain heterocyclic bases—piperidine, pyridine).

TABLE VIII

DYE XXIII IN AMINES AND NITROGENOUS BASES

Solvent	μ	λ	$1/\lambda$	$\Delta 1/\lambda$
(Nitrogen) ^a	0		20876	400
Triethylamine	0.8	517	19342	1934
Diethylamine	1.0 to 0.90	527	18976	2300
Piperidine	1.17	532	18797	2479
<i>n</i> -Amylamine	1.30	532	18797	2479
<i>n</i> -Butylamine	1.30	532	18797	2479
<i>n</i> -Propylamine	1.30	532	18797	2479
Ethylamine	1.30	535	18692	2548
Ammonia	1.50	548	18248	3028
Aniline	1.54	560	17857	3419
<i>o</i> -Chloroaniline	1.77	565	17699	3577
α -Picoline	1.72	542	18450	2826
Quinoline	2.16	553	18083	3193
Pyridine	2.11	550	18182	3094

^a Values for N₂ (nitrogen) by extrapolation.

A plot of the results so far is shown in the following graph (Fig. 8). This exhibits the following features: (i) progressive increase of the displacement Δ with K , (dielectric constant) for non-polar liquids ($\mu \cong 0$); (ii) progressive increase of Δ with μ for the aliphatic series Hydrocarbon \rightarrow Ethers \rightarrow Alkyl acetates \rightarrow Ketones \rightarrow Nitro- C_nH_{2n+1} . The alcohols form an outstanding exception. There is a distinct tendency for the sequence to give either two lines of different slope or perhaps to approach a "saturation" value. (iii) Starting with benzene ($\mu = 0$), the same types of compounds give, in part, a linear array of the same slope, but with a constant difference. Again, there is a well-marked trend or branch, of lower slope; the convergence of this with the "aliphatic" series, at the nitro-anisole "value" may be coincidental. It seems possible, however, that with the higher bond moments, e. g., $\text{>C}(-\text{NO}_2)$, this becomes of preponderant effect, and that a "saturation" limit is approached.

(iv) The series of amines, $\text{N} \begin{matrix} \text{R}_1 \\ \text{R}_2 \\ \text{R}_3 \end{matrix}$ (including NH_3 and $\text{HN} = \text{C}_5\text{H}_{10}$ (piperidine)), gives a linear series; the line extrapolated back to $\mu = 0$ gives a

displacement corresponding approximately with that to be expected for liquid nitrogen ($K = 1.47$). While these results indicate definite regularities, it must be noticed that very definite exceptions occur. Thus, the *alcohols* give values quite out of proportion to their mean (molecular) moments: Aliphatic $\mu = \sim 1.70 \Delta = 3260 \text{ cm.}^{-1}$, aromatic $\mu = \sim 1.70 \Delta = 3240 \text{ cm.}^{-1}$. (Roughly as though the aliphatic alcohols had *three* times the monomeric moments, the aromatic, *twice* the measured moment.) Another group of related compounds which appears at first to defy reduction to order is that of the alkyl halides. The measurements so far obtained are given in Table IX.

TABLE IX
HALIDES OF METHANE AND ETHANE

	ΔCl	ΔBr	ΔI
CH_3X	..	992	2757
CH_2X_2	2757	3094	3419
CHX_3	2928	2479	..
CX_4	2228
CH_3CH_3
$\text{CH}_3\text{CH}_2\text{X}$	2408	2300	2689
CH_3CHX_2	2584	2757	..
CH_3CHX_3	2408
$\text{CH}_2\text{XCH}_2\text{X}$	2757	2757	..
CH_2XCHX_2	2826	2995	..
CH_2XCH_3
CHX_2CX_3	2654
CX_3CX_3

When these are plotted as functions of the average moments (best available values at 25°), it will be seen that something like a peculiar "shot-gun pattern" is obtained. (The oblique line is the principal aliphatic line repeated from Fig. 9.) It

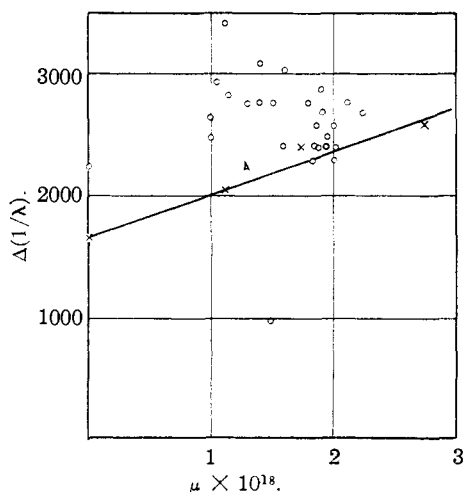


Fig. 9.—Merocyanine in alkyl halides: A, principal aliphatic curve.

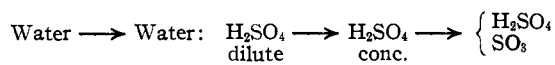
would appear evident that very specific—even individual—combinations of the molecular forces are required to account for these results.

Basicity and Acidity of Solvents

The avidity of a molecule for a proton (H^+ ion) is termed its basicity,¹¹ and, conversely, its facility in donating one to another molecule, its acidity. As is well known, quantitative measures of these values depend upon the solvent. For example, in water there is possible a *pH* range from 0 to 14; superacid solutions can be made in acetic acid plus acetic anhydride, but the relating of these to the water scale values is a matter of considerable uncertainty.

The relations of proton addition to the constitution and color of dyes is *per se* outside our subject.¹² However, two aspects of it affect the question of solvent influence, in particular with certain dyes which we have used.

Evidently a comparison of the basicities or acidities of our "solvents" obtained with these as "solutes" in a common, solvent medium, *e. g.*, water, or acetic acid will only give their relative order in the common medium. It will not give much, if any, information as to the absolute basicities or acidities of these solvent molecules in the presence only of their own congeners. It is none the less interesting to note that with two merocyanines (XXIII and XXXI) the displacement parameter varies in a very similar fashion with the (aquo) basicity figure.¹³ The behavior of merocyanine XXIII with definitely acidic solutions and solvents may throw some light on the problem. First, in the series of media



the curves in Fig. 10 show a certain swing between two systems. Thus, in *water* the absorp-

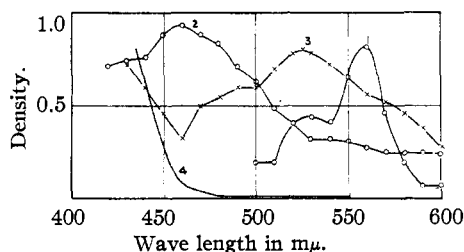


Fig. 10.—Absorption curves of merocyanine XXIII: 1, in water; 2, H_2O and H_2SO_4 ; 3, H_2SO_4 ; 4, H_2SO_4 and SO_3 .

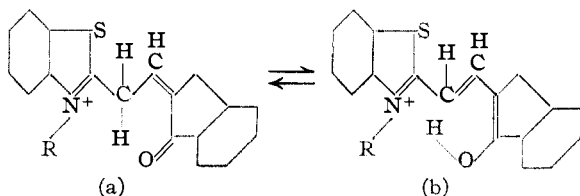
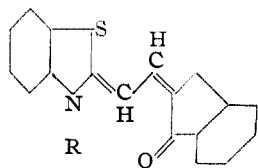
(11) J. N. Brønsted, *Z. angew. Chem.*, **43**, 229 (1930).

(12) G. Schwarzenbach, *Z. Elektrochem.*, **47**, 40-52 (1941).

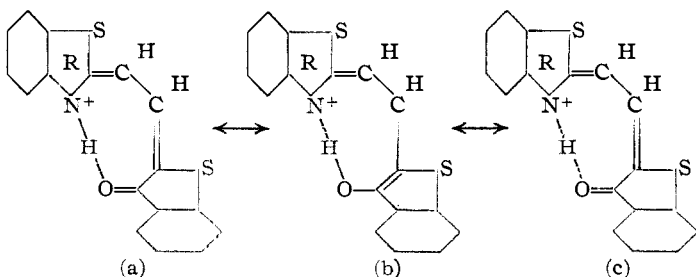
(13) N. F. Hall, *THIS JOURNAL*, **52**, 5115 (1930).

tion curve is much the same as in alcohol or other hydroxylated solvent. And this is also the case *initially* in concentrated sulfuric acid, which is perhaps behaving as $O_2S \begin{matrix} OH \\ \diagup \\ \diagdown \\ OH \end{matrix}$. However, on standing, the absorption system in the visible region disappears, to be replaced by a powerful system on the violet edge of the visible region and in the ultraviolet with its longest wave band at 4150 Å. By neutralization, the absorption in the visible region is restored, but to that in dilute sulfuric acid rather than to that in water alone. The absorption in *dilute* sulfuric acid is remarkable as giving a maximum at *ca.* 4600 Å. (see Fig. 10) which appears identical with that given by the dye in *formic acid*—but not in the other fatty acids.

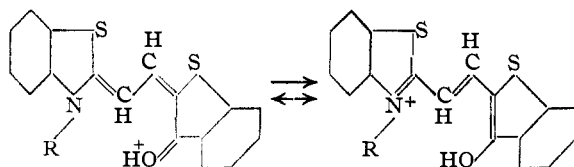
On considering the formula for merocyanine XXIII, it seems possible that the initial addition of a proton can give the alternative structures (a) and (b).



And there might be actually resonance (mesomerism) between these structures, by which is developed the band at 4600 Å. in dilute sulfuric acid and in formic acid. M. L. Huggins has suggested the alternative possibility of the 8-ring shown below



with the same type of mesomerism over a wider circuit. This requires a slightly greater strain on the bond angles involved, to about 129°. Another configurational treatment is suggested in the following resonance scheme.



Owing to the instability of the $=OH^+$ grouping, the left-hand configuration would have considerably higher energy, and the passage from the merocyanine would involve "reversed halochromy"—hence the band at shorter wave length, 4600 Å. The behavior of the lower homologous fatty acids is interesting; the absorption curves are shown in Fig. 11. In order to remove traces of water, a small amount of acetic anhydride was added. It will be seen that the spectrum in formic acid is quite distinct from that in the higher homologs, while that in acetic acid shows a tendency to an intermediate type, with enhancement of a band at about 4800 Å. The position of the longest wave band, as shown in the table (Table X) is practically the same as that in the alcohols (588–555 $m\mu$) so that these "associating" acids show the same tendency to behave as if having a much higher moment than that of the monomeric mole-

TABLE X
MERCOCYANINE XXIII IN FATTY ACIDS

Acid	λ_m in $m\mu$	$\Delta\nu$	μ
Formic	460 (1.2)
Acetic	480	557	3350 1.4
Propionic		555	3258 1.74
<i>n</i> -Butyric		555	3258 1.4
<i>n</i> -Valeric		560	3419 (0.9)

cule. Usually it appears that the moments of the polymers in associated liquids are reduced or entirely internally compensated. It is interesting that abnormal "displacements" of the same order are produced by *ethyl acetoacetate*, *acetylacetone*, and *acetonyl acetone*—all liquids in which the existence of similar configurations, potentially mesomeric, is highly probable. This general similarity is brought out in Table XI.

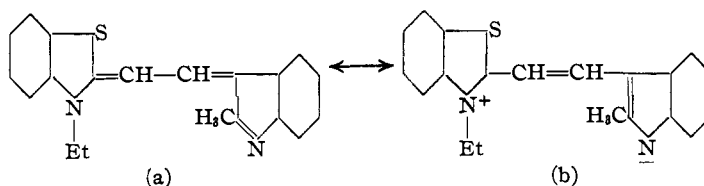
The "odd" behavior of formic acid is perhaps to be attributed to much higher "acidity" in the dimeric state, with ionization of the $-CH$ and forma-

tion of dicarbeniate ions $H^+ \left[\begin{matrix} O \\ \diagup \\ C \\ \diagdown \\ O \end{matrix} \cdots \begin{matrix} H \\ \diagup \\ O \\ \diagdown \\ O \end{matrix} \right] H^+$ also, *ethyl acetoacetate*, if accounted as acetate ester, has a high moment—2.93 compared to 1.8.

TABLE XI
"HIGH" DISPLACEMENTS

Substance	Tautomer or Polymer	Dipole moment μ	Δ Observed	Δ calcd. from μ
Water		1.84	3419	2200
Alcohols		1.70	3258	2300
Fatty acids		1.4 to 1.70	3258	2300
Ethyl acetoacetate		(2.93)	2757	2400
Acetylacetone		3.00	3193	2750
Acetylacetonone		2.8	2757	2680

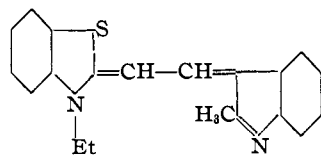
Its "displacement" is about normal for its moment, but abnormal as an ester. Acetylacetone, so near in structure, has a slightly high moment as a ketone, but a "displacement" which is high both for the keto structure and for its moment.



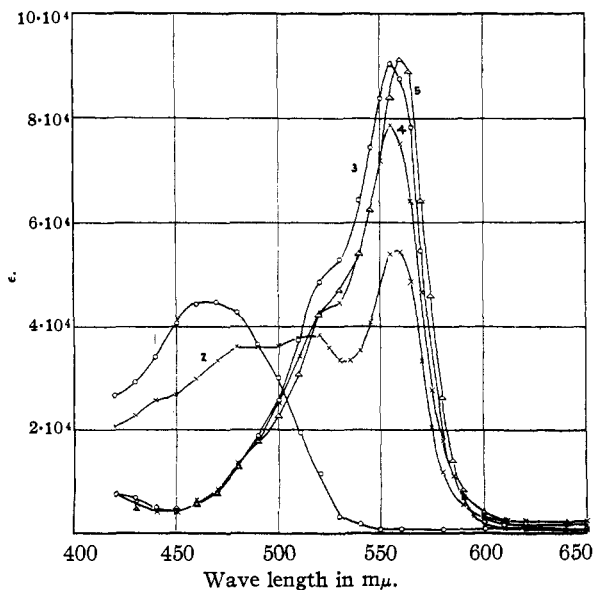
Although having a very similar configuration to merocyanine XXIII, with the same length of conjugate chain between the key atoms in each case, the maximum absorption is very definitely dis-

Some Observations with Merocyanine Dye XXXI

We come now to some observations on a dye, representative of a class first prepared by Brooker, Sprague, Smyth and Lewis¹⁴ which, while specifically a merocyanine, is especially interesting as being at the same time an ansolvo-base of an actual cyanine; Dye XXXI is



Brooker and his collaborators have shown that this base gives rise to "reversed halochromy," in that, on salt formation, by combination either with alkyl halide, or with acid (thus forming a cyanine), the main absorption shifts not to longer but to shorter wave lengths than for the base itself. To the base can be attributed two principal limit structures



(14) L. G. S. Brooker, R. H. Sprague, C. P. Smyth and G. L. Lewis, THIS JOURNAL, **62**, 1116 (1940).

Fig. 11.—Merocyanine XXIII in fatty acids: 1, formic; 2, acetic; 3, propionic; 4, *n*-butyric; 5, *n*-valeric.

placed to higher frequencies than that for XXIII, a fact which may be attributed to the lower stability of the negatively charged N atom in (b) compared with the negatively charged O atom of XXIII. While XXXI can be volatilized at low pressures, so far we have not succeeded in obtaining a satisfactory value for the absorption curve *in vacuo* because of too considerable decomposition. At present actual "displacement" values cannot be given for the solvent influence, but instead the absolute values of $1/\lambda_m$ may be compared; and, owing to the complexity of the absorption spectrum, it is not always easy to be sure that the comparison is being made for the same member of the band complex.¹⁵ The largest complicating factor is the "acidity" of the solvent, whether derived from extrinsic hydrogen ions (acid) or the intrinsic "acidity" of the liquid solvent molecules. It is a complicating factor because, by salt formation and development of one full charge, a true cyanine is developed, which, however, (reversed halochromy) has its absorption at higher frequencies than the base. The addition of another proton, giving two full charges, results in discharge of visible color, by blocking the resonance. Where possible, to assure the presence of the dye as free base, we may add a small amount, comparable with that of the dye, of a base such as diethylamine, following the procedure of Brooker, *et al.*, for methyl alcohol. The following table (XII) shows that in non-polar solvents the absorption band is displaced steadily toward the red with increase of dielectric constant (and refractive index) of the solvent.

The values with "+ d. e." indicate controls with the addition of diethylamine to ensure removal of the "acid" form. In order to control the origin of such values, some of the free base

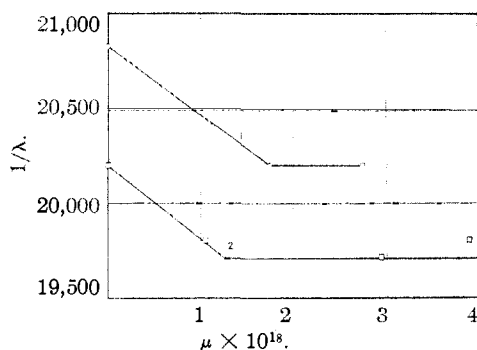


Fig. 12.—Merocyanine XXXI in polar solvents: 1, aliphatic series; 2, aromatic series.

(15) Compare the band system of merocyanine XXXIII.

TABLE XII

DYE XXXI IN NON-POLAR SOLVENTS				
Solvent	K	$\mu \times 10^{18}$	λ_m, α	λ_m, β
n-Hexane + d. e.	1.87	0	480	450
n-Decane + d. e.	1.95	0	482	455
Cyclohexane + d. e.	2.05	0	480	455
			480	455
Decalin	2.15	0		460
Carbon tetrachloride	2.20	0	490	465
Benzene + d. e.	2.38	0	495	470
			495	470
Carbon disulfide	2.65	0	510	478

was converted to the methiodide, as described by Brooker, Sprague, Smyth and Lewis. As they observed, the absorption of the "salt" is generally identical with that of the alkyl halide, but in certain solvents the methiodide gave a maximum at a somewhat longer wave length than the simple salt. It may be noted in advance that both the H-salt and the methiodide behaved like other full cyanine dyes in showing very little effect of polarity of solvent on the position of the absorption maximum.

In the following table (XIII) are summarized positions of the α -band maximum in a series of aliphatic solvents used with Dye XXIII.

TABLE XIII

DYE XXXI IN ALIPHATIC SOLVENTS				
Solvent	$\mu \times 10^{18}$	$\frac{1}{\lambda_m}$	λ_m Base	Trace λ_m Acid
Hexane	0	20833		
Ethyl ether	1.12	20408	490	475
Alkyl Acetate	1.74 to 1.90	20202	495	
Alkyl ketone	2.7	20202	497	478
Propionitrile	3.4 to 3.66	20000	500	
Nitromethane	3.8	[20000]	?	

In the next table (XIV) a comparable series of aromatic solvents is presented.

TABLE XIV

DYE XXXI IN AROMATIC SOLVENTS				
Solvent	$\mu \times 10^{18}$	$\frac{1}{\lambda_m}$	λ_m Base	Trace λ_m Acid
Benzene	0	20202	495	
Diphenyl ether	1.05	19800	505	
Phenyl acetate	1.50	19608		
Benzophenone	2.95	19724	507	495
Nitrobenzene	2.90	[20202]		

The "aliphatic" and "aromatic" series plotted in Fig. 12 show a general similarity with the corresponding series for merocyanine XXII; some deviations may be due to incomplete suppression of the salt form of XXXI. For example, in *nitromethane* the dye is definitely present for the most part in that condition. The addition of a drop of

diethylamine produces a quite transient deepening (reddening) of color. In *nitrobenzene* this deepening is more persistent and allows a value for XXXI (base) in this solvent. We have assembled also the results with Dye XXXI in associated and tautomeric solvents (Table XV).

TABLE XV

Solvent	$\mu \times 10^{18}$	$\frac{1}{\lambda_m}$	Trace	
			λ_m Base	λ_m Acid
Water	1.90	19800	505	
Alcohol	1.68	19800	505	482
Benzyl alcohol	1.69	19417	515	
Ethyl acetoacetate	2.93			
Acetyl acetone	3.00		490	

As in the case of merocyanine XXIII, the frequency is much lower than would correspond with the moment, except for *benzyl alcohol*.

It seems reasonable to regard the initial red displacement (bathochromy) as the same effect of the solvent as that upon merocyanine XXIII. This is supported by the fact that the slopes $\delta\nu/\delta\mu$ are the same in both cases, *viz.*, $350 \text{ cm.}^{-1}/1\mu$. But in the case of merocyanine XXXI, the solvents with the higher moments tend to stabilize the acid, or rather salt, form of the dye.

Ionized Cyanine Dyes

Dye XXII—the methiodide of XXXI—and the H-salt behave as cyanine dyes with a one full positive charge in respect of solvent action. Features of this behavior are low solubility in non-polar solvents (but increasing somewhat with increase of dielectric constant) and relative *independence* of the spectrum of the moment of polar solvents (see Tables XVI and XVII).

TABLE XVI

DYE XXXII IN SOLVENTS			
Solvent	K	$\mu \times 10^{18}$	$1/\lambda_m \text{ (cm.}^{-1}\text{)}$
Carbon disulfide	2.65	0	20000
Benzene	2.38	0	20202
Ether	..	1.12	Insoluble
Alkyl acetate	..	1.74	20620
Ketone	..	2.74	20747
Propionitrile	..	3.50	20830
Nitromethane	..	3.80	20620

Comparing a symmetrical with an unsymmetrical dye, the independence of the band position in polar solvents was confirmed.

TABLE XVII

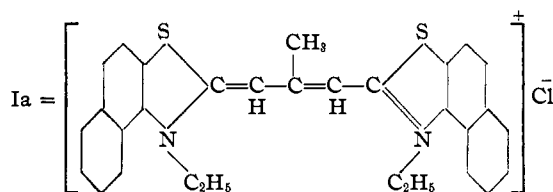
Dye	$1/\lambda \text{ (Aliphatic)}$	$1/\lambda \text{ (Aromatic)}$
(Sym.) Ia	17270 (± 100) cm.^{-1}	16960 (± 260) cm.^{-1}
(Unsym.) XVb	20000 (± 90) cm.^{-1}	19600 (± 94) cm.^{-1}

The possibility that the solvent effect (of polar

moment) might vary with the length of the conjugated chain between the nuclei was tested with three thiocyanine homologs. No difference was observed.

Alkyl Halides

In this group of solvents the behavior of the cyanine (ionized) dyes is more analogous to that of the merocyanines. The displacement is very variable, and seems to bear no direct relation to the dipole moment of the solvent nor to the dielectric constant. Using the (symmetrical) dye



Ia, there appears to be a rather significant advance in the magnitude of the "displacement" on passing from chloride \rightarrow bromide \rightarrow iodide, as shown in Table XVIII.

TABLE XVIII

	HALIDES OF METHANE		
	ΔCl	ΔBr	$\Delta\text{I in cm.}^{-1}$
CH_3X	..	610	1182
CH_2X_2	550	844	1400
CHX_3	990	1400	..
CX_4	1130
HALIDES OF ETHANE			
$\text{CH}_3\text{CH}_2\text{X}$	550	786	844
$\text{CH}_2\text{XCH}_2\text{X}$	550	1030	..
CH_2XCHX_2	610	844	..
CHX_2CHH_2	640	1130	..

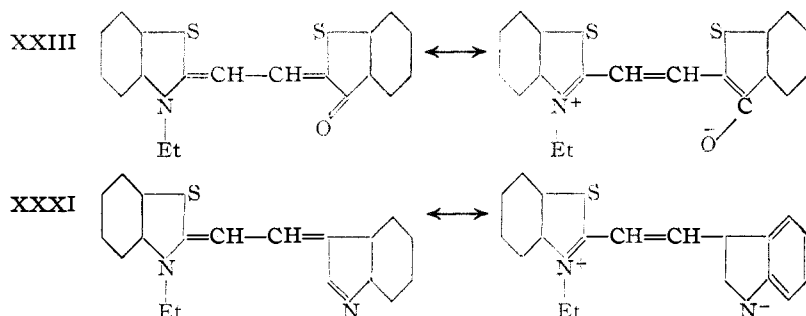
Discussion

The effect of solvents in displacing an absorption band may be attributed to van der Waals forces of three principal types: (i) dipole induction; (ii) orientation of permanent dipoles; (iii) mutual induction of electron clouds (dispersion forces). Of these, the first should be effective with dye molecules capable of a dipolar structure. The distance law is $F \propto 1/r^6$, and the electric forces operative between solute and solvent are not very powerful. The temperature coefficient is slight. The behavior of merocyanines in "non-polar" solvents may derive largely from this, but in part from "dispersion" forces, and to some extent from partial moments of the solvent molecule made effective by specific orientation.

The orientation of permanent dipoles permits more powerful intermolecular electric forces, the

distance law being $F \propto 1/r^3$. The temperature coefficient would be large; rise of temperature would disrupt orientation, and lower the "displacement" produced. This effect might be expected to diminish, the higher the polar moment of the solvent, and the nearer to saturation. How far "dispersion" forces can be expected to produce a displacement is uncertain. They have been invoked as favoring dimerization of dye cations, and thereby (in dimerization) coupling of vibrations with electronic transitions. The characteristic difference between aromatic and aliphatic solvents of the same chemical type certainly seems to indicate a specific "displacement" effect, which indeed persists with ionized cyanine dyes.

The merocyanines XXIII and XXXI are dyes of the type termed by Dilthey and Wizinger¹⁶ "intramolecular ionoid," that is, they can be ascribed in ordinary valence symbols two structures; one a hybrid ion and the other neutral.



In general, in such molecules the two structures represent considerably different energy levels; depending upon the characters of the terminal nuclei A and B, one or the other may principally constitute the ground level, the other a relatively high excitation level, or the two configurations may be sufficiently near in energy for quantum mechanical resonance to occur.

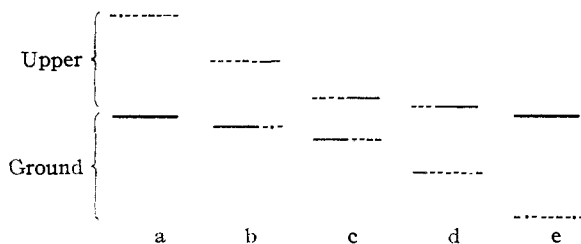


Fig. 13.—Energy levels of an intramolecular ionoid dye, with polar character increasing from *a* to *d*: ---- proportion of polar; —, proportion of non-polar contribution to the ground and excited states.

(16) R. Wizinger, "Organische Farbstoffe," F. Dummlers Verlag, Berlin, 1933, p. 44.

The various possibilities have been discussed by Th. Förster¹⁷ (*cf.* Fig. 13). In the case represented by (a) the polar form has a much higher energy than the non-polar form, and represents an excited state which would only be produced by absorption of relatively short wave radiation or by an equivalent activation energy. As the energies of the two configurations are brought closer, the energy difference between the ground state and the lowest excited state is reduced, and absorption occurs at longer wave lengths. This is expressed in the diagram by a more equal "weighting" of the two limit structures in the ground and excited states, corresponding to increasing resonance. Such a progressive change could be brought about by change in the character of the auxochrome A and anti-auxochrome B (in the language of Dilthey and Wizinger), or more analytically, as pointed out by L. G. S. Brooker, *et al.*,¹⁴ by change in the basicities of the terminal

groups. Förster suggests that this progression might be carried over to an inverse state, in which the non-polar configuration became increasingly the *less* stable, or of higher energy than the dipolar form. This is indicated in the diagram for *d* and *e*, with reversion to shorter wave absorption. The tendency to reduction

of the electrostatic energy of the dipole, with consequent relaxation to the non-polar form seems to make this little likely. Instead of the progression toward greater resonance $a \rightarrow b \rightarrow c$ being effected by internal change in the molecule, it could be brought about by change in the immediate environment, *e. g.*, of solvent.

Assuming that the action of induced and permanent solvent dipoles upon such "intramolecular ionoids" is to approach the energy states of the dipolar and non-polar configurations, the actual effect should be less, the nearer these two energies are in the isolated dye molecule. But a solvent effect still remains with dyes whose constitution guarantees equality of the energies of the limiting structures, and which, moreover, are not susceptible of dipole exaltation. Such for example are the ionized cyanine dyes.

With dyes carrying a full ionic charge, little or no effect of induced or permanent dipoles of the

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

solvent molecules is to be expected, but, in terms of van der B. Houckgeest's theory,¹⁸ there is a large effect upon solubility. However, there can be notable changes in the absorption with change of solvent for such dyes.¹⁹ It seems unlikely to be due to dipole induction, and is at present most conveniently plotted as a function of refractivity (cf. Fig. 14). This effect—with ionized dyes—may be caused by the dispersion forces, as a resonance effect between the mobile electron cloud of the solvent and that of the dissolved dye. The increased "displacement" for a cyanine dye in alkyl halides in passing from the *chloride* to the *bromide* to the *iodide* is consistent with this view.

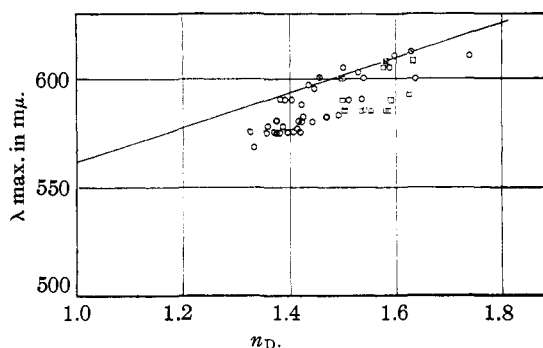


Fig. 14.—Dye Ia in polar O, aliphatic liquids; □, aromatic liquids. Line refers to non-polar liquids.

The "dispersion" contribution is also manifest in the difference between aliphatic and aromatic solvents of the same polar moment. Polar solvents of the same refractive index show, in general, a lower displacement than the non-polar ones. This is brought out in Fig. 14, which shows a reference line for non-polar solvents, and the generally lower group of polar ones. The effect of polar character is to reduce the displacement effect corresponding to a given refractive index, but is not expressible by a simple subtractive quantity. It appears indeed to be pronouncedly individual. Empirically, the nearest approximation is found in the expression

$$\lambda_s = \frac{kN^p}{\sqrt{1 + \mu}}$$

where p is an integer. Since N^2 has some theoretical basis we illustrate the correlation in that case (Fig. 15).

Structure of Bands

The origin of the auxiliary bands of dye absorption in the optical region is not too clear at pres-

(18) J. P. W. A. van B. Houckgeest, *Rec. trav. chim.*, **59**, nos. 7/8, 560 (1940).

(19) S. E. Sheppard, *J. Chem. Soc.*, **95**, 15 (1909).

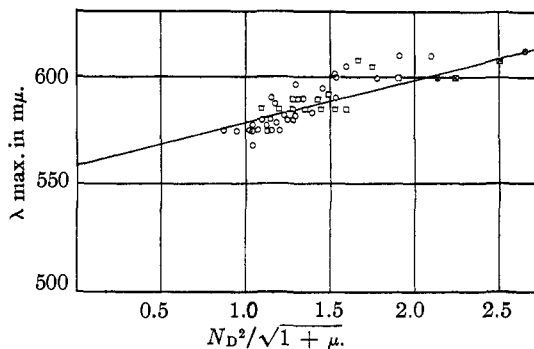
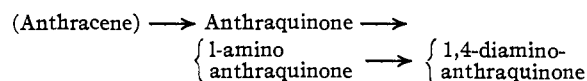


Fig. 15.—Dye Ia in polar O, aliphatic liquids; □, aromatic liquids.

ent. The principal band, *i. e.*, generally the long wave band of maximum extinction, is assigned to an electronic transition or charge transfer determined by the resonance structure of the dye.²⁰ A dye can be regarded as derived from an aromatic hydrocarbon or chain of conjugated ethylene bonds as a prototype (or a hybrid of these two types) by the introduction of auxochromes and anti-auxochromes.¹⁶ The principal ultraviolet spectrum of anthracene—as a homolog of benzene—was first derived on quantum mechanical grounds by Sklar¹⁹ and Förster,¹⁶ with the important corollary of the displacement of the absorption to longer wave lengths with the number of linearly conjugated benzene nuclei. Similar considerations obtain for the polyenes. Development of the theory for the introduction of auxochromes has been carried out by Förster¹⁷ with particular application to the triphenylmethane cation on substitution of $-\text{NH}_2$ groups. The conditions are not unlike the substitution of $-\text{NH}_2$ groups into anthraquinone



In Fig. 16 are given very approximate term-diagrams for the evolution of the spectrum of anthraquinone with increase of auxochromic groups.

With the introduction of the auxochromes there appear not only new electronic transition bands, but increasing diffusion of the structure of the pre-existing shorter wave bands, owing to the increase in the number of vibrational levels and to the increased change of coupling of π -electrons (concerned in transitions) with others of anti-parallel spin. The influence of solvents upon the structure of the absorption bands of dyes requires further investigation.

(20) A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937).

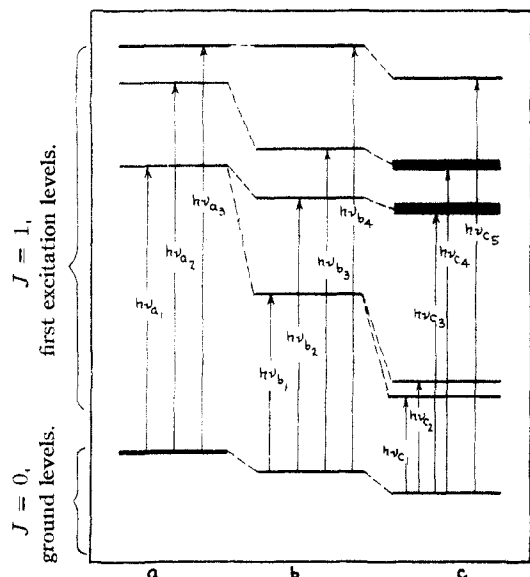


Fig. 16.—a, Anthraquinone; b, 1-aminoanthraquinone; c, 1,4-diaminoanthraquinone.

Associating Solvents

A systematic divergence in the effect of polar moment upon the merocyanine absorption spectrum was shown by "associating" solvents. This behavior is not shown by ionized cyanine dyes. It seems to be connected with the potential dipolar character of the merocyanines, and may indicate either an effectively higher dipole moment of these solvents in the liquid state, an effectively higher dielectric constant (than for individual molecules of the gas), or a marked effect of dispersion forces. Investigation of the temperature coefficient should help to decide.

Behavior of Alkyl Halides

A rather considerable degree of variation of the polar moment with temperature has been noted with these compounds, also a number of deviations from the theoretical values.²¹ These derivations, however, are inadequate to explain the large variations of "red displacement" observed in these solvents. We believe that a rather definite approach to explanation of the facts is indicated in two articles by J. P. W. A. van B. Houckgeest¹⁷ on the "Solvent and Dissociating Power of Chlorinated Hydrocarbons"—as exhibited in respect of quaternary ammonium salts. The "red displacement" with a merocyanine may be regarded as due to an "intramolecular ionization" or predissociation of a compound which is a potential or

(21) C. P. Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monographs, Chem. Catalog Company, 1931.

inner salt of a quaternary ammonium base. The arguments by which Houckgeest is able to place the alkyl halides in relative order as to their solvent powers are applicable to their displacement of the merocyanine spectrum, and we find that our results are concordant therewith. We have not space to detail the argument.²² It deals in each

case with orientation in the molecule of C^+-Cl^- dipoles, of which the positive end is regarded as more active than the negative. The purely qualitative order was derived from stereochemical and energetic considerations alone. In the second paper the author derives a quantitative theory in terms of the thermodynamic potentials. This is perhaps less relevant to the displacement effect at one temperature, since then considerations as to change of number of molecular species are not involved. It may have definite application to the effects of temperature change upon the "displacement" in these solvents. In any case, the "solvation energies" calculated from the more complete theory fall in much the same order as our "displacements" of the merocyanine spectrum (cf. Table XIX). From the very specific be-

TABLE XIX
SOLVENT POWER OF CHLORINATED ETHANES

Solvent	According to van B. Houckgeest ^a			$\Delta\nu$ obs. cm. ⁻¹	$\mu \times 10^{18}$	K
	Cl	Br	I			
CH ₂ CH ₂ Cl	100	92	82	2408	2.02	~11.0
CH ₂ CHCl ₂	104	96	85	2584		10.8
CH ₂ ClCH ₂ Cl	122	114	102	2757	2.0	10.4
CH ₂ CCl ₃	78	72	65	2408	1.60	7.2
CH ₂ ClCHCl ₂	126	112	99	2826	1.15	7.1
CH ₂ ClCCl ₃	75	70	63			5.8
CHCl ₂ CHCl ₂	127	117	104	3028	1.60	8.2
CHCl ₂ CCl ₃	66	61	55	2654	1.00	3.6

^a The halide ions above refer to respective salts of quaternary ammonium bases.

havior of the alkyl halides we suggest that with polar solvents and the merocyanine type of dye, there is formed an addition or molecular compound. This may be subject to a general "field" of the solvent molecules, but if there is only displacement, without radical transformation of the spectrum, it is probable that no quantum mechanical resonance occurs between the components.

Acknowledgments.—The cyanine and merocyanine dyes employed were prepared by Dr. L. G. S. Brooker and his staff, who synthesized them and determined their constitution. Our thanks are also due Dr. L. A. Jones and Mr. E. E.

(22) If not available, copy may possibly be obtainable through the American Documentation Institute.

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.

ROCHESTER, NEW YORK

RECEIVED MARCH 25, 1942

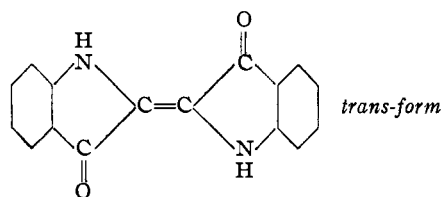
[COMMUNICATION NO. 869 FROM THE KODAK RESEARCH LABORATORIES]

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

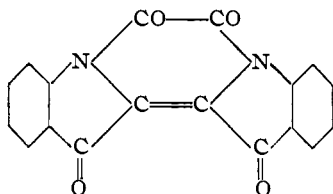
BY S. E. SHEPPARD AND P. T. NEWSOME

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

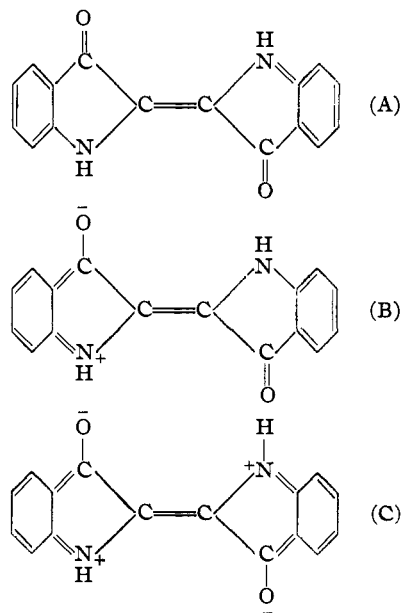


For the solid, crystalline form, the evidence favors the presence of the *trans*-form.² Apart from the

(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).