The Effects of Environment and Aggregation on the Absorption Spectra of Dyes*

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SECTION I. GASEOUS AND DISSOLVED STATES

(with H. R. Brigham and P. T. Newsome)

THE vaporization of dyes requires rather high temperatures and low pressures, and the range of temperature free from decomposition is quite limited. By and large, the behavior in solution (in organic solvents) resembles that in the gaseous state, and the temperature effect can be studied better.

In solution (ether-alcohol) cyanine dyes show over the range 313°K to 83°K increased extinction of the principal long wave band, with falling temperature. This is due to reduction of population density of vibrational-rotational levels, as shown by sharpening of the spectrum. This behavior resembles that of benzene, anthracene, and phenanthrene. There are no pronounced effects such as new bands or displacements, but a general sharpening of the structure.

Solution and Solvents

It is desirable when possible to compare the solution with the vapor—at similar temperatures and low enough pressure for collisional effects to be small. The former condition is not possible but many dyes can be volatilized under reduced pressure, without decomposition. Spectral meas-



FIG. 1. Analysis of merocyanine absorption (gaseous). \bigcirc = experimental. \times = calculated.

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urements in the gaseous state are of value in determining the energies of adsorption and of solvation. The absorption curves of two dyes in the gaseous state are shown in Figs. 1 and 2. Since the partial pressures and concentrations were not known the curves show only optical density = log (I_0/I) vs. wave-length and not the molecular extinction coefficients. This prevents comparison of band strengths but not comparisons of positions. The absorption curves shown in Figs. 1 and 2 are for:



first prepared by L. G. S. Brooker and christened 2-(3-ethyl-2(3)-benzothiazolylidene) ethylidene-2(3)-thianaphthenone, and for:



These curves are only the envelopes of a definite group of bands. In view of statements, noted later, concerning the supposed origin of auxiliary bands in dimerization and polymerization, it is desirable to point out that the same band group, with approximately the same frequency interval or intervals between maxima, persists as a whole both in the gaseous state and in solutions. This is illustrated in Fig. 3 by absorption curves for the merocyanine in various solvents, and in Fig. 4 which gives the ratios of the intensity (extinction or density) at the maxima to the intensities of other bands of the group. The



FIG. 2. Absorption of vapor of 1,4-diaminoanthraquinone at various temperatures.



FIG. 3. Absorption of merocyanine in (1) methyl alcohol, (2) *n*-hexane, (3) CCl₄, (4) quinoline, (5) methylene iodide.

the common structure in varying environment. They are definitely related to the principal electronic transition responsible for the long wave band of maximum intensity. In the polymethine dyes, the frequency difference between the heads of the component bands may vary from 800 cm⁻¹ up to 2000 cm⁻¹, the most usual values being around 1200 cm⁻¹ to 1600 cm⁻¹. There seems little doubt that these values represent certain fundamental vibration frequencies of the molecule as a whole or in part, and that it is the coupling of these vibrations with the principal electronic transition which

gives rise to the auxiliaries.

parallelism of these curves is further evidence of

Solutions

Inductively, there are two principal parameters for which solvent effects on the spectrum could be evaluated, *viz.*, band strength $\int \epsilon a\nu$, and band position ν_{max} or λ_{max} . Chako (1)¹ has made a comparison of various "band strength" expressions for a large variety of organic substances, but not dyes, in various solvents. According to the classical theory for the Lorentz-Lorenz force from the polarization of neighboring molecules if F_s is the transition probability in solution, and F_o that in the gas state, then

 $^{^{1}\}operatorname{References}$ in parentheses are given at the end of the paper.



FIG. 4. Merocyanine: ratios of extinction of subsidiary and main band in different solvents. $\triangle =$ methylene iodide, $\bigcirc =$ methyl alcohol, $\square =$ quinoline, $= CCl_4$, $\times = n$ -hexane, $\otimes =$ vapor.

 $F_s = F_g(9/(n_0^2+2)^2)$, where n_0 is the refractive index of the solvent. Chako concluded that no proposed rules were valid without many exceptions. The influence of the solvent could not be accounted for adequately through the Lorentz-Lorenz force.

The foregoing expression was not confirmed for the dyes tested, an over-all variation of about 100 percent being found.

More definite results were obtained for solvent influence on ν_{max} or λ_{max} , the position of greatest transition probability. In 1878 Kundt concluded that with increasing dispersion of the solvent, the absorption maximum of a dye is shifted toward longer wave-lengths. Generally, the refractive index N_D has been taken instead of the dispersion. Numerous exceptions were urged against "Kundt's rule," but chiefly for the ultraviolet absorption bands of substances other than dyes.

If non-polar solvents are separated from polar solvents, then we have found so far Kundt's rule to hold without exception for different dyes and types of dyes, such as: merocyanines, indigo, and diaminoanthraquinone, all non-ionic, cyanines and thiazines ionic, basic, and xanthenes, ionic, acid.

The relation between the displacement and the refractive index appears to be steady, and in some cases linear from the base value (vacuum), as for the merocyanine XXIII (cf. Fig. 5). This relation is empirical; a relation having more theoretical significance may be found between the displacement $\Delta \nu$ —representing an energy—and the dielectric constant K. From the simple expression for the work of displacement of an electron $\Delta E = (e/2r^2)[1-(1/K)]$ we should have, for constant r, the equivalent $\Delta \nu_m = a[(1-(1/K))]$ for the shift of the frequency. The values of $\Delta \nu$ showed, generally, a tendency to increase more rapidly than corresponds to this expression, and it may be suspected that partial polar moment is indicated in solvents such as benzene, carbon tetrachloride, and bisulfide.

Polar Solvents

We must greatly condense a large amount of experimental material. With the merocyanine XXIII it was found:

(a) In a homologous series of solvents, e.g., alkyl acetates, alkyl ketones, etc., the polar moment is constant, while the refractive index increases, the dielectric constant decreases. In all these solvents, the "red" displacement $\Delta \nu \sim \Delta 1/\lambda$ remains constant.

(b) Passing from one such group of solvents to another, $\Delta \nu$ increases with the polar moment.

(c) With normal, non-associated liquids, $\Delta \nu$ increases at first about linearly, then less rapidly approaches a "saturation" value (cf. Fig. 6).



FIG. 5. Variation of refractive index in non-polar solvents. (1) Merocyanine (gas) in vacuum, (2) merocyanine in *n*-hexane, (3) merocyanine in CCl₄, (4) merocyanine in C₆H₆, (5) merocyanine in CS₂.

(d) The displacement $\Delta \nu$ is greater by an approximately constant amount for aromatic solvents of the same type and same polar moment (cf. Fig. 6).

(e) The amines, including heterocyclic bases such as pyridine, etc., show a very steep rate of increase of $\Delta \nu$ with polar moment (cf. Fig. 6).

These results are exhibited graphically in Fig. 6. Although these figures show a relation between the displacement $\Delta \nu$ and the polar moment of the solvent measured as gas, or in dilute solution, we know that it is unsafe to conclude from the polar moment in the gas state to that in the liquid state. It is not surprising that the behavior as dye solvents of such "associated" liquids as the alcohols, the fatty acids, appears abnormal (cf. Table I). It is possible that they possess effectively higher polar moments in the liquid state or that their constitution allows of higher "dispersive" forces being brought to bear on the dye solute (cf. Table I).

A group of related compounds which appears at first to defy any reduction to order in respect of their influence upon the displacement $\Delta \nu$ is that of the alkyl halides. $\Delta \nu$ bears no appreciable relation to the polar moment measured in the gas state. But it is found that a theory developed by a Dutch investigator, van B. Houckgeest (2), for their solvent and dissociative effect upon solid quaternary ammonium halides applies rather accurately to their displacing effect upon the absorption spectrum of merocyanine. We cannot discuss this now, but will note that it takes account of the relative screening effect of the atoms of the halide upon a $C^+ - Cl^-$ dipole, and its orientation to a soluble (or solute) molecule.

Acidity and Basicity of Solvents

A factor which cannot be disregarded in relation to the spectral effects of solvents is



FIG. 6. Variation of refractive index of merocyanine in polar solvents. (1) Aliphatic series, (2) aromatic series, (3) amino.

Substance	Tautomer or polymer	Dipole moment µ	Δ Observed	Δ Calc. from μ
Water	R-0-R	1.84	3419	2200
	(or chain)			
Alcohols	R H R O O H H H R H R	1.70	3258	2300
Fatty acids	$R \rightarrow C$ $O \rightarrow H \rightarrow O$ $O \rightarrow H \rightarrow O$ $C \rightarrow R$	1.4 to 1.70	3258	2300
Ethyl aceto-acetate	CH₃—C==CH—C—O Et │	(2.93)	2757	2400
Acetyl acetone	$CH_3 - C = CH - C - CH_3$ $ \qquad \\O - H \cdots O$	3.00	3193	2750
Acetonyl acetone	CH ₃ C=-CHCH=-CCH ₃ OHOH	2.8	2757	2680

TABLE I. "High" displacements.

acidity, or inversely, basicity. The characteristic of an acid is a tendency to donate a positron, generally in company with a hydrogen atom, as a proton. It is essential to differentiate actual proton transfer-producing a new resonance system in a dye-from the solvent effects proper. These effects may be provisionally classified under three heads: (i) induction effect between polarizable molecules: solute: solvent; (ii) mutual orientation of permanent dipoles; (iii) quantum mechanical interaction of mobile electrons, sometimes termed dispersion effect. The first of these is exemplified by the effect of non-polar solvents of increasing dielectric constant. The temperature influence is slight. The second is illustrated by the increasing "red displacement" of merocyanine in normal liquids of increasing polar moment. The temperature coefficient is large. The third effect is perhaps shown by the greater displacement produced by aromatic compared with aliphatic solvents. The temperature influence is small or nil.

Resonance Systems in Relation to Solvent Effect

The two most probable configurations for the merocyanine XXIII are



These are non-identical structures, structure (a) being preferred as of lower energy; (b) will be



FIG. 7. 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 .

more heavily represented in the excited state; (a) in the ground state. The behavior of both non-polar and polar solvents, in displacing λ_m to the longer waves, is in accord, as bringing the energies of the excited and ground states nearer to each other.

The addition of a proton produces a complete change in the absorption, a band appearing at much shorter wave-length (cf. Fig. 7). This is what Brooker, who first observed it in another merocyanine (dye XXXI), has termed "reversed halochromy." (3) It appears possible that the two structures



being mesomeric phases of a hydrogen-bonded structure, contribute chiefly to the ground state of the new transition, for which the structure of higher energy:



participates chiefly in the excited state. To this resonance system may be assigned the band at 4600A in aqueous sulfuric acid and in formic acid. This leaves the band shown in curve 3 (Fig. 7) in concentrated sulfuric unaccounted for. An additional proton would block the resonance, as shown in curve 4 (Fig. 7). The band at 4800A may be a composite, or there may be an alternative hydrogen-bridged structure between the N atom and the O atom. This was suggested by M. L. Huggins.

We may note in passing the behavior of another merocyanine (dye XXXI) which corresponds, as base, to the resonance system:



The long arrow pointing to the left, following Brooker's notation, is to indicate his observation that the right-hand form—because of the instability of the negatively charged nitrogen would be of much higher energy than the left. Hence also a higher frequency of the absorption band than for the nearly equivalent merocyanine XXIII. It is curious that after eliminating acidic effects, this "base" shows very much less solvent sensitivity, e.g., in polar solvents, than merocyanine XXIII. It is suggested that this is due to a large degree of "screening" of the $-\overline{N}$ — atom by the adjacent methyl group. This "screening" might be equivalent even to a sort of subsidiary



FIG. 8. Extinction curve of indigo in (1) benzene, (2) α -chloronaphthalene, (3) aniline.

resonance cycle, involving a hydrogen bridge between the carbon of the methyl group, and the pyrrolic nitrogen.²



The great increase of energy thus demanded would be partly compensated by the stabilization of the onium nitrogen, while the structure, with two full charges, would be very insensitive to solvent influence.

Ionized Cyanines

The addition of a hydrogen or alkyl halide to merocyanine XXXI produces a cyanine (polymethine) dye with a full (positive) charge. For this, as for other such ionized cyanines, the solvent effects are very limited; this is to be expected, since the limiting valence structures are both equally charged, and this whether the dye is symmetrical or non-symmetrical.

Another "neutral" dye somewhat unexpectedly shows little polar solvent influence. This is indigo, readily obtained in the vapor state; extinction curves in solution are shown in Fig. 8. However, both aliphatic and aromatic amines, also heterocyclic bases, show considerably greater "red displacement" than other solvents of the same polar moment. Moreover, alcohols again show relatively large displacement, as also the fatty acids. In fact, formic acid shows the largest displacement measured.

The absorption band of indigo, for which the *trans*-form is to be preferred (4), has been explained by Arndt and Eistert (5) and by Van Alphen (6) in terms of resonance between the accepted valence structure



and dipolar structures of higher energy. In view of the insensitivity to purely polar solvent influence, it seems that the contributions of such structures to the excited state must be small or negligible, and it is suggested that the actual

² The structure in question might indeed be written as a doubly (positive) charged ion as:

resonance system is more nearly the following :



The normal valence structure α assigned to indigo would then represent an intermediate (mesomeric) structure of higher energy than the identical β , β' semihydrogen-bonded structures of equal (lower) energy. According to this, associating solvents (and those with high dispersive force) make the structures β and β' less stable, producing a reduction in the energy difference from the splitting, and hence a displacement to long waves. On the other hand, the dye 1,4-diaminoanthraquinone



which also admits of hydrogen-bonded structures shows: (i) in non-polar solvents "red displacement" smoothly increasing with the refractive index and dielectric constant; (ii) definite increase of the displacement, with polar moment, in both aliphatic and aromatic solvents. The displacement is greater in aromatic solvents of the same polar moment. While the constitution of 1,4-diaminoanthraquinone readily admits of hydrogen-bonded structures similar to the dioxyanthraquinones (7), it must be concluded that these have a more ionic (dipolar) structure than is the case for indigo, and a resonance system based on this has been suggested (8).

A group of dyes which also approach the merocyanine XXIII in behavior derives from azobenzene. Typical is p-dimethylamino-p'-nitroazobenzene; the two structures principally concerned in the resonance system of the base



FIG. 9. Absorption spectrum of pinacyanol chloride at various concentrations in water.

	С	Thickness		С	Thickness
×	2.57×10^{-3} molar	0.1 mm	Ø	2.57×10 ⁻⁵ molar	1.0 cm
0	1.28×10^{-3} molar	0.1 mm		6.4 ×10 ⁻⁶ molar	4.0 cm
\triangle	2.57×10 ⁻⁴ molar	1.0 mm	\odot	2.57×10 ⁻⁷ molar	10.0 cm
	1.28×10 ⁴ molar	1.0 mm	\div	6.4×10^{-7} molar	40.0 cm
\oplus	6.4 ×10 ^{−5} molar	4.0 mm	+	3.2×10^{-7} molar	40.0 cm

are very feasibly like those indicated by G. N. Lewis and M. Calvin (9) for p-nitroaniline. Thus



The upper structure would be stabilized by the Kekulé resonance of the two benzene nuclei, and perhaps also by that of the $-NO_2$ group, and would contribute chiefly to the ground state, the lower β -structure contributing chiefly to the

excited state. The dye base shows strong progressive "red displacement" in non-polar solvents of increasing refractive index and dielectric constant. It also shows well-marked increase of "displacement" with polar moment in aliphatic solvents, but a lower sensitivity in aromatic solvents of increasing polar moment. Fatty acids above formic acid behave, like the alcohols, in line with their polar moment, but formic acid behaves as a strong acid, giving positive halochromy by addition of a proton.

It is of interest to note the behavior of related hydrocarbon resonating molecules. The visibly colored polyene—diphenyloctatetraene—has a constitution with some affinity to that of the polymethine dyes. Its resonance system may be formulated as





FIG. 10. Extinction coefficient of pinacyanol in alcohol.

The upper structure α is stabilized by the Kekulé resonance of terminal phenyls, 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 excited state.

"Red displacement" increases steadily in non-polar solvents of increasing refractive index and dielectric constant. There is some evidence of increase of displacement in polar solvents with increased polar moment, and aromatic solvents have a larger effect than aliphatic ones of the same polar moment.

Benzene, in full accord with the resonance system assigned to it, shows great indifference in solvents. There are small hypsochromic displacements of the first and second (long wave) ultraviolet bands, which are nearly independent of the solvent, and similar small positive (bathochromic) displacements of the shorter wave bands. The behavior of liquid benzene is the same.

SECTION II. AQUEOUS SOLUTIONS AND AGGREGATION

(with H. R. Brigham, A. L. Geddes, and R. H. Lambert)

Dyes in solutions in organic solvents, in general, obey Beer's law, and behave as though

molecularly dispersed. Any "cooperative spectral effects" are those arising from the interaction of solute and solvent.

But in aqueous solution a great many dyes show a behavior indicating aggregation and interaction of the solute molecules, sometimes with interesting effects upon their spectrum. These spectral characteristics began to be noticed rather more than thirty years ago when Sheppard made a study of solutions of cyanine dyes (10) and found that:

(i) In organic solution, e.g., alcohol, the absorption obeyed Beer's law, not only for the main α -band, but for subordinate β - and γ -bands at shorter wave-length.

(ii) In water, Beer's law was not obeyed, but the ratio of band intensities (extinctions) depended on the concentration. With increasing concentration the shorter wave bands gained in strength at the expense of the α -band. This behavior was reversible.

(iii) On raising the temperature, the aqueous solution became more like the organic, i.e., with rising temperature the α -band gained intensity and the shorter wave bands lost. This behavior was reversible also. Sheppard concluded that the spectral changes in water were due to a reversible molecular aggregation, whereas in organic solvents the dye was molecularly dispersed. At high concentrations in water, and by addition of salts, colloidal particles of the dye were produced.

This was in 1906 to 1907. Although thereafter considerable investigation was made of the dispersity of dyes in aqueous solution, considered as colloidal electrolytes, nothing to speak of was done in connection with the spectrum for many years. In 1936 G. Kortüm (11) published work on deviations from Beer's law in aqueous



FIG. 11. Partition of dye between hexyl alcohol and water.

solutions of dyes such as sodium eosinate. The deviations, however, are not large, compared with those shown by the cyanines. In 1937 G. Scheibe, of Munich (12), discussed such variations ascribing them to secondary valence forces, and in 1938, in conjunction with several co-workers, gave an account of quantitative work on the spectra of polymethine dyes in aqueous solutions.

The nature of the changes is shown specifically in Fig. 9 for the variation of the absorption of pinacyanol (chloride) dye VIIa



in water with change of concentration, while in Fig. 10 is shown the molecular extinction curve in alcohol, which is invariant with concentration. It is evident that the same structure is present in both cases, there being three bands indicated— α , β , and γ . In water the strength passes to the shorter wave bands as the concentration rises. This is general for most cyanines, although not all show a well-marked third (γ) band.

In connection with these and other phenomena Scheibe introduced the term "reversible poly-



FIG. 12. Λ , Total (equivalent) conductance of pinacyanol chloride. λ_a , conductance of cation; λ_r , conductance of anion.



FIG. 13. A, total (equivalent) conductance of dye Xa. λ_a , conductance of cation; λ_r , conductance of anion.

merization." Whether this is an improvement upon "reversible aggregation" is no matter. Of more importance was the introduction of new quantitative methods for studying the degree of aggregation or polymerization. One of these is to measure the partition of the dye between water and an immiscible organic solvent.

The equilibrium of the dye with hydrogen ion must be controlled. The cyanine dyes can add on a proton, with complete change of the resonance system, and the band in the visible disappears. It follows that for spectrophotometric observations the pH must be maintained sufficiently high to obviate any effect from this direction. It is a complication which is not entirely easy to control experimentally, because buffering is liable to introduce "salting out" effects.

The simple theory of the partition experiments proposed by Scheibe is based on the expression

$$[D_s]/[D_w]^n = K \text{ (constant),}$$

where $[D_s]$ = concentration of dye in solvent, $[D_w]$ = concentration of dye in water, n = order of aggregation. Scheibe considered that his results, e.g., with *pinacyanol*, supported the conclusion that n=2, i.e., that the dye molecules were "dimerized" in aqueous solutions—at least at sufficiently low concentrations!

There is, of course, no basis for the assumption that a process of aggregation reversible with dilution would proceed in discontinuous stages, except for radical changes of state (solubility) dealt with later. There is, moreover, even supposing only one change of aggregation to occur, e.g., dimerization, a neglect in the expression given, of the mobile equilibrium in water.

We have carried out numerous determinations of such partitions with cyanine dyes, but were unable to confirm Scheibe's conclusions. The simple expression can be formulated

$$\log \left[D_s \right] = n \log \left[D_w \right] + K,$$

whence *n* should be the slope of a linear relation between $\log [D_s]$ and $\log [D_w]$ and be an integral value. We did not find such linear relations, nor did the (averaged) slopes at lower concentration ranges give integral values. An example from the partition of pinacyanol between hexyl alcohol and water is shown in Fig. 11. Actually, in this case the tangent slope is always less than unity, so the simple expression is obviously unsatisfactory. We may now take account of a mobile equilibrium in the aqueous phase. Using a formulation as for organic acids given by Smith and Elgin (13) we have

$$C_{\rm H,0}/C_a = nK_1P^nC_a^{n-1} + P,$$

where n = order of aggregation in water, $C_p = \text{concentration}$ of polymer in water, C = concentration of monomer in water, $C_1 = \text{concentration}$ of monomer (total), $K_1 = C_p/C_1^n$, P = partition coefficient of monomer, $= C/C_a$. From this the value of n may be found by choosing arbitrary values until the plot of $C_{\text{H}_2\text{O}}/C_a vs. C_a^{n-1}$ gives a straight line, when the intercept P is the partition coefficient of the monomer while n of course should be an integer. It must suffice



FIG. 14. Transport numbers. $-\bigcirc -\bigcirc -$ dye VIIa (pinacyanol chloride); $-\times -\times -$ dye X_a.

to state here that no integral value of n could be found which gave a straight line; the nearest actual value was 1.5. The further assumption that dimers and trimers are in equilibrium requires that the plot of the second derivative $(1/C_a)(dC_w/dC_a)$ vs. C_a should be linear, but this was remote from the facts.

The inadequacy of direct mass law considerations in the partition analysis for two phases to support a simple molecular aggregation hypothesis was confirmed by analysis of the spectrophotometric dilution data in water alone.

Scheibe supposed that the auxiliary bands— β and γ for pinacyanol—were new bands, the β -band peculiar to a dimer, the γ -band to a higher polymer, while the α -band is ascribed to the monomer. Neglecting, for a certain concentration range, the γ -band, an expression is developed for the extinction coefficient of the α -band as a function of concentration in water; the extinction at infinite dilution ϵ_{∞} being taken as equal to $\epsilon_{alcohol}$. On application of the mass law it was considered that the results indicated an aggregate of two cations.

We have made a large number of measurements of absorption curves of cyanine dyes in water without being able to get satisfactory confirmation of Scheibe's equation. In most cases the graph of the "dissociation residue" is curved, instead of straight; the tangential slope increased from $\equiv 1$ at low concentration to sometimes approach 2 at the highest.

E. Rabinowitch and L. F. Epstein (14) have developed a mathematical process of approximation to determine the "fraction x of monomer" in the mass law expression $nCx^n/(1-x)=K$, where C = total concentration of dye, $K = \text{con$ $stant of equilibrium, and } n = \text{order of molecular}$ aggregation. We propose to discuss elsewhere in detail our reasons for disagreement with their analysis, and the conclusion that the mass law applies to the aggregation of thionine to dimers in aqueous solution.

Electrochemical Considerations

The attempts to determine the order of aggregation not succeeding in this way, recourse was had to investigations of the electrical conductance of the solutions and of the transport numbers as functions of concentration. Full



FIG. 15. *n* Molecular aggregation values μ . \triangle dye VIIa (Pinacyanol chloride); \bigcirc dye Va (Diethyl-cyanide chloride); \land dye Vd (Diethyl-cyanide sulfate); \Box dye Xa.

details will be published elsewhere;³ we shall note briefly the results.

It is not possible at present to determine from such measurements directly the integral order of aggregation, but only the average order of aggregation at any concentration.

In Fig. 12 are shown the conductance data at 25°C for pinacyanol chloride, and again in Fig. 13 the data for dye Xa:

Dye Xa



The significance of the sharp breaks in the conductance curves will be considered shortly. The region of concentration with which we are concerned for the spectral shift in water covers the range below the critical concentrations. For any dye D⁺X⁻ if λ_c = equivalent conductance of cation, λ_a = equivalent conductance of anion, T_c = transport number of cation, T_a = transport number of anion, and Λ = total equivalent



FIG. 16. Schematic arrangement of molecules.

conductance, then $\lambda_c = \Lambda T_c$ and $\lambda_a = \Lambda T_a$ and data are shown graphed for T_c as function of concentration for two dyes in Fig. 14. The data indicated aggregation of the cations, increasing in degree with the concentration. The decrease of Λ and of λ_a might indicate some removal of counter ions, but is more probably an effect of ionic atmosphere, since there is evidence that the order of aggregation is low and counter ion inclusion unlikely. Values for the fraction of free counter ions (4) in solution may be obtained from the equation $(f = \Lambda/\lambda_a^1 + \lambda_c)$, where λ_a^1 = conductance of free counter ions and is obtained from data on a simple electrolyte with this same anion. The average degree of aggregation n of the cations is calculated from the Stokes relation $\lambda_c = f \lambda_c^{-1} n^{\frac{2}{3}}$, where λ_c^{-1} is the equivalent conductance at infinite dilution.

Values of n thus obtained are shown graphically as function of the concentration in Fig. 15.

³ With A. L. Geddes.



FIG. 17. Spectral reflection data. Dye IVb adsorbed to cuprous chloride. 1—0.1-cc dye; 2—1.0-cc dye; 3—10.0-cc dye; 4—saturated.

The values of n are in no case greater than 2, which indicates a low order of aggregation. While not conclusive for dimerization, since a few larger aggregates might produce the same effect as many smaller ones, it is actually in good support of this.

This conclusion was confirmed by diffusivity measurements. There are many difficulties in determination of particle size of basic dyes, with the aggregation reversible with dilution (15). But for two cyanine dyes in water at 25°C for which reliable measurements with correction for disgregation on dilution have been made, the values for n, the mean degree of aggregation, while approaching 2 at the highest concentration 4×10^{-4} molar, did not exceed this value.

Nature of the Aggregate in Water

The balance of the evidence favors the view that in aqueous solutions of many cyanines as well as of the thiazines—the aggregated particle contains two dye cations. This appears to be in reversible equilibrium with the simple cations, although thus far the applications of the mass law appear to be inadequate to complete quantitative description of the equilibrium. The formation of these double ions is favored by the fact that these molecules have a large organophile portion with a small hydrophile edge. This dorsi-ventral anatomy is schematically illustrated in Fig. 16 and we have given evidence for it from experiments on first-stage irreversible and second-stage reversible adsorption of cyanine dyes to silver halide (16). In the first, monomolecular layer, the dye cations are held, in more or less vertical orientation, by the ionizable ventral edge to the ionic lattice. The adsorption is irreversible, and water hardly wets the dye layer as shown by contact angle measurements.

It is further evident, from the spectral sensitizing and spectral reflection data, that the adsorbed dye cations are increasingly ordered in a manner similar to that occurring in water in increasing concentration. This is shown by the increase in strength of the higher frequency γ -and β -bands at the expense of the α -band—an example of which is shown in Fig. 17. It appears probable then that the doublet cations (or dimers) comprise two dye cations with the molecular planes about 3.8A apart. It can be shown that optical doublet formation hardly occurs when the minimum distance is much greater than this. The cyanine dye "Astra-phloxin" has the formula:



and was found by Scheibe to obey Beer's law in aqueous solution.⁴ This Scheibe attributes to the



TABLE II. Characteristics of dyes.

	<i>pK</i> a	€m	λ_m	Dye
Planar	4.79	8.70×104	5530A	XVIIIa
Non-planar	4.30	4.77×10^{4}	5350A	XIXa

⁴ Later measurements of Ecker show some deviation at very high concentrations.

linkages reducing the resonance, but since dyes with S and O links at the same position show the spectral deviation in water, this seems unlikely. Actually, the voluminous dimethyls would prevent sufficiently close side-by-side approach of the molecular planes, as can be demonstrated with an atomic model of the structure. Other examples on the relation of molecular orientation and steric hindrance can be cited. Erythrosin, and related fluorescein dyes, have the structure



in the erythrosinate ion (and the alternative resonance form). The attached phenyl group, with the $-COO^-$ group, cannot, except under great strain, be in the plane of the main resonance system, but would, as in *diphenyl* normally be rotated some 40° to 50° out of this plane to secure a clearance of 3.1 to 3.2A. This would tend to produce sufficient steric hindrance to the minimum necessary apposition of the two resonance planes to allow doublet formation. It is not surprising that these dyes do not show much spectral anomaly in water.

Steric hindrance of optical doublet formation in these cases derives from accessory groups outside the main resonance system. But the same effect can occur, and with even stronger impedance of optical coupling, when stereochemical factors prevent planarity of the potential resonance system of the component molecule itself. Examples of this in the cyanine dyes have been described by the author and co-workers elsewhere (17). Since the matter has further importance for the "cooperative spectra" of dyes, we may note a characteristic example. The two dyes whose normal valency formulae



FIG. 18. Suggested structure of dimer.

are given below:

and



are isomers, first prepared by L. G. S. Brooker and G. H. Keyes (18) from β -naphthoquinoline and from phenanthridine, respectively. Dye XVIII can be shown to be readily capable of a planar structure, whereas in dye XIX planarity is not possible without the 3 : 4 benzo-radical approaching within 1.7A of the opposite β -naphthoquinoline group. A difference appears in the absorption spectra (in alcohol), the wave-length of maximum absorption being at a longer wave-length for the planar isomer, and the extinction at the peak being much greater as is indicated in Table II. The spectral



FIG. 19. Absorption of zinc phthalocyanine sodium sulfonate. Concentration $c=4.53\times10^{-3}M$. $\bigcirc =pH$ 4.2; $\times =pH$ 6.1; $\bigtriangleup =pH$ 7.95; $\cdot =pH$ 10.0; $\square =pH$ 11.85.

differences are consequences of the reduction or impedance of resonance in the non-planar form, as also the lower value of the pK_a for the nonplanar isomer, this value corresponding to the free energy of proton (H+ ion) addition. Still more notable differences are the following: (i) Both types of dye are strongly adsorbed to silver halide, but the non-planar isomers reach a lower saturation for a primary monomolecular layer (17). (ii) The planar isomers are powerful optical sensitizers, but the non-planar isomers show practically no sensitizing ether photographically or photolytically (17). (iii) The planar isomers adsorbed to silver halide readily develop strong "extra" long-wave bands. These will be referred to shortly, as J bands, in connection with meso-phase formation. (iv) Although all these benzocyanines have rather low solubilities in water (because of the accretion of benzene nuclei) the addition of water to alcoholic solutions of the planar dyes produces considerable intensification of the higher frequency components at the expense of the α -band. This indication of doublet formation in water is shown only in small degree by the non-planar isomers, apparently because of the difficulty of coupling in parallel apposition the resonance systems of the non-planar molecules, and effectively, by steric hindrance to near enough approach.

Other examples of the relation of the stereochemical factors to intermolecular organization of cyanine dyes could be cited, but it is apparent that this evidence supports certain aspects of the dimerization theory.

Nature of Forces in Aggregation

The formation of such intermolecular aggregates is usually ascribed to van der Waals forces. The spectral effect is supposed to be due to the mutual induction of the electron "clouds" of the parallel molecules. But it appears questionable whether this mutual induction is sufficient alone to account for the actual binding of two dye molecules in a doublet. There is a notable temperature coefficient, for purely dispersion forces (14).

This suggests that the dimerization equilibrium involves the participation of a water molecule in the structure of the aggregate. A feasible structure among others is that represented in Fig. 18. The H_2O molecule is supposed to be



FIG. 20. Absorption of zinc phthalocyanine sodium sulfonate in water at pH 4.2. $\bigcirc =1$ in 25,000; $\times =1$ in 400,000.

centrally coordinated between two cyanine cations. The electrical structure of the water molecule is discussed in the next section. The axis of negative electrification is indicated between the median -CH+- groups, which, in consequence of the resonance, is attributed the main positive charge density. Coordination of the nitrogens is also shown. The formation of such hemi-hydrates may explain the considerable temperature-coefficient for the process of "dimerization." Rabinowitch and Epstein (14) from their data on thionine obtained a value of $\Delta H = 6.82$ kcal./mole for the heat of dimerization. If this value, per mole dye, be referred to mole water involving two dye molecules, it should be doubled, giving 13.64 kcal./mole, which is sufficiently higher than the latent heat of vaporization to be reasonable. The heat of dimerization, on the present hypothesis, would include an energy term for the polarization of the water molecule by the two dye cations, and this might vary somewhat with the constitution of the dyes.

Although in some disagreement with G. Scheibe, and with E. Rabinowitch and L. Epstein as to the validity of the mass law applied to the process, we consider that doublet or dimer formation accounts for the spectral deviation. But this is not because the auxiliary



FIG. 21. Absorption of zinc phthalocyanine sodium sulfonate. 1 : 25,000 in water at pH 9.8: $\triangle = 2^{\circ}C$; $\bigcirc = 25^{\circ}C$; $\times = 75^{\circ}C$.

 β - and γ -bands of higher frequency are new bands peculiar to "polymers," but because doublet formation enhances the transition probability of bands produced in the molecule by coupling of the electronic transition with vibrations.

Another important group of dyes which when water-soluble show the spectral redistribution associated with "dimerization" is that of the porphyrins, at least the azaporphyrins termed phthalocyanines (19). Phthalocyanine and its metal derivatives are normally insoluble in water, but can be made soluble by sulfonation, when three or four sulfonic groups enter. The sodium tetrasulfonate of zinc phthalocyanine has the structure shown.



The phthalocyanines have a planar structure. The sodium sulfonate of the zinc compound in water at constant concentration and temperature shows signs of increasing aggregation as the pH is lowered (Fig. 19). Also at constant pH and temperature, the indications of aggregation increase with concentration (Fig. 20), while at constant pH and concentration, aggregation is clearly increased with fall of temperature from 75°C to 2°C (cf. Fig. 21).

Quantitative analysis of the data has not been made yet, but the qualitative indications point to a similar behavior to that of the cyanines and thiazines. At highest dilutions and temperatures, the spectrum approaches that in organic solvents, in which Beer's law is followed. As the concentration is increased and the temperature lowered, the intensity of the α -band, which may be



FIG. 22. Adsorption isotherms of (a) erythrosin, (b) dichlorfluorescein. x/m = amount dye adsorbed per gram silver halide. Cr = residual (equilibrium) concentration of dye.

ascribed to an electronic transition involving no vibration,⁵ passes to β - and γ -bands of higher frequency, in which one or more units of vibration are associated with the normal electronic state. Certain similarities of the phthalocyanine spectrum in this respect to that of the polyenes have been pointed out by Hausser, Kuhn, and Kuhn (20).

It is probable that in the aggregated state in water pairs of molecules are held in parallel apposition with an interplanar distance of about 3.8A. It is possible that the structure does not require a water molecule link, being maintained by intermolecular hydrogen bridges, e.g., of the sulfonic groups.

SECTION III. ADSORBED AND PARACRYSTALLINE STATES

(with A. L. Geddes, R. H. Lambert, and R. D. Walker)

We come now to a field of higher organization or cooperation of dye molecules or ions in the production of spectra, and in which the orientation of the dye molecules is still more strongly emphasized.

Adsorption of Dyes

The relations of adsorption to the optical behavior of dyes, will be limited to two groups of dyes, viz., (i) derivatives of fluorescein, acid dyes, i.e., dye anions; (ii) polymethine or cyanine dyes, basic dyes, i.e., dye cations. They are the groups from which the principal optical sensitizers for the silver halides have been drawn, though the property is not exclusive to these groups (21). Optical sensitizing can give information on the state of a dye, because the latter can, so to say, autograph a spectral record on the photographic emulsion. We must summarize briefly some principal results from several investigations, mostly from our own laboratory and some not yet published.

With regard to the adsorption of acid dyes to silver halides and certain cognate compounds, we may consider the group: dichlor-, dibrom-, diiodo-, tetrabrom-, and tetraiodofluorescein

⁵ Actually, it is only required that it be the band with lowest vibration coupling which is permitted.



 62×10^{-7} normality of Ag 5 $\times 10^{-7}$ normality of Ag

derived by halogen substitution in the structure



The chain of conjugated double bonds shows the resonance path between the key oxygen atoms. Substitution of electronegative halogens at positions in it not only influences, by "weighting," the locus of maximum absorption, but also progressively diminishes the solubility of the silver compound. Thus only the last three dyes found photographic use; of these erythrosin or tetraiodofluorescein is the most important. The lower the solubility, the higher the absorption density possible on the silver halide surface, for the same residual concentration in the solution. The adsorption is reversible, approaching a monomolecular layer according with a Langmuir isotherm (22), as shown in Fig. 22.

In the figure, curve (a) indicates the (fluorescein) dye with a silver compound of higher, (b) erythrosin with lower solubility. The limiting adsorption-density with these acid dyes (anions) is greater, according as the surface of the silver halide is populated with silver ions, hence, as the pAg of the solution in equilibrium is raised.

The adsorption of these xanthene (acid) dyes is not quite a simple case of reversible electrostatic adsorption. The spectral absorption maximum of the adsorbed dye and the sensitizing maximum are identical with each other. But they are considerably displaced toward the red compared with that of, e.g., sodium erythrosinate in solution, and are, in fact, identical with that of solid silver erythrosinate.

The "solubility" of the silver erythrosin compound involves the complete dissociation: $Ag_2E \rightarrow 2Ag^+ + E^-$ and there is no existence of the ion $(AgE)^-$ in solution. The characteristic absorption of the silver erythrosin compound and of adsorbed erythrosin—is, therefore, peculiar to the solid phase (cf. Fig. 23). The absorption shift from sodium erythrosinate to silver erythrosinate has been attributed by Fajans to deformation of the erythrosin ion by the large silver cation. We believe we can be more specific than this, in view of the fact that the



FIG. 24. Silver erythrosin structure in solid.

ion $(AgE)^{-}$ does not exist independently, and that this characteristic absorption is shown only by the adsorbed and solid phases. We have given already evidence that the erythrosin ions cannot approach each other closer than some 5 to 6A between the molecular planes. If we suppose the silver ion affected to the phenolicquinone oxygen atoms to be at a point midway between these two oxygen atoms of the same molecule, the interval is too great-about 5 to 6A-for any deforming or other action to be exerted. It is logical, therefore, to suppose that the arrangement is one in which each of these two silver ions is intercalated between two similarly placed oxygens of two erythrosin molecules, as shown in Fig. 24. The silver ion has a radius of 1.26A, so that this arrangement would bring it nicely within electronic interchange distance of the key oxygen atom-ions of two parallel erythrosin molecules. A complex resonance system is now possible, in which the molecular resonance in the plane of the molecule supports (and is supported by) intermolecular, or rather interatomic resonance, via the intercalated silver ions, which are in the oscillating state $Ag^+ + \theta \rightleftharpoons Ag$. The great mobility of the lone outermost electron of an isolated silver atom is attested by the work of Hilsch and Pohl (23) on the photoconductivity of the silver halides.

We have now two coupled resonance systems, one molecular, of the erythrosin ion (molecule), the other intermolecular, between the erythrosin oxygens via the silver atom-ions. We suggest that the displaced, or rather new silver, erythrosin absorption band, is due to an electronic transition made possible by this arrangement.

The effective light vibration might be in the plane of the erythrosin ion, or perpendicular thereto, between the molecules, or either might be possible according to the orientation of the ensemble and the polarization of the light ray of the appropriate (lower) frequency. Thus although erythrosin is a strong optical sensitizer for silver halides, solid silver erythrosin is practically insensitive to the light which it absorbs (16). It is not decomposed to form metallic silver, except by very high intensities of light, when the *heat* developed is considerable, or by heat itself.

The hypothesis seems also to be in accord with the color-deepening effect of several heavy metal ions forming solid complexes with certain organic compounds. Silver is notorious in this connection, as in Feigl's reagent with rhodanine (24) and in the organic reagent for silver discovered by Sheppard and Brigham (25). A point to be remembered in dealing with erythrosin and the cognate fluoresceins is that the acid absorbs differently than the salts. The acid is relatively insoluble in water but soluble in alcohol; according to pH and solvent, it gives bands at longer and at shorter wave-length than the erythrosinate ion. This is because of hydrogen bond interaction of the carboxyl group with the phenolic hydroxyl, and cannot be discussed here. The characteristic bands are given in Table III.

The "chelation" of heavy metal ions between molecules to produce deepening of color has evident relation with the "mordanting" of certain types of dyes by metal salts and oxides (26). Originally supposed limited to oxyanthraquinones having two orthohydroxy groups in the alizarin 1,2-position, it became clear that other groups ($-NH_2$, etc.) could also function, and the field was further generalized by Werner (26) in terms of inner complex formation. However, it remained a matter of "chelation" by the metal ion between sufficiently contiguous oxygroups of the same molecule, in a co-planar structure.

The porphyrins, including the phthalocyanines, also have a coordinating metal ion as an important element of the structure of dyes. In this

TABLE III. Characteristic bands.

	Erythrosin acid	Erythrosin alkali	Erythrosin silver	Erythrosin adsorbed	Optical sensitizing
Solution	{4900A 5370	5270A			
Solid	5000		5650A	5650A	5650A

group its position is central to the macromolecule (cf. Section II). At first sight it does not appear greatly to affect the color (in the sense that change of the metal ion produces only a small displacement). There is, however, a radical change when the metal ion is removed and hydrogens take its place (19). We must suppose that the whole spectrum is displaced to the long wave-lengths—with some change of frequency differences—or that a new band of longer wave-length is produced, while the shorter wave bands are displaced to still higher frequencies.

Basic Cyanine Dyes

The adsorption of basic cyanine dyes to silver halides (and cognate metal halides of low solubility in water) differs in important respects from that of the acid phthaleins. First the influence of pAg is antibat to that with the acid dyes, since the electrostatic attraction is to the negative halide ion; the octahedral surfaces of the silver halide crystals (16) will at sufficiently high pAg be covered with halide ions. Secondly, under these conditions, it is observed that the cyanine dyes are irreversibly adsorbed from water in a first stage (of added dye), which, if further dye is added, gives a second reversible stage. This behavior is illustrated in Fig. 25.

We have found that the first stage from water produces a monomolecular layer with the molecules oriented edge-on, either vertically or tilted at an angle probably not greater than 30° from the vertical. From calculations of the area covered by the molecules in this orientation, it was found that in approximately closest packing the interval between the dye molecules would be about 3.8A. The second, bimolecular, layer is in reversible equilibrium with residual dye molecules. From this and other related facts it appears that the primary monomolecular layer is held to the lattice at the ionic, positively charged, hydrophile edge, the organophile "backs" of the dve molecules (or cations) turned to the water. In the second layer the orientation is reversed, the organophile edges being held dos-à-dos, and the polar aspect in contact with the water. Hence the reversible adsorption of this layer. Quite similar arrangements have been observed with soap micelles (27) and with the polymolecular films of fatty acid salts



FIG. 25. Effect of dye concentration on amount of dye adsorbed for dye IIb for precipitated silver bromide. \triangle dyed from water; \bigcirc dyed from butyl alcohol.

studied by Trillat (28) and by Langmuir and Blodgett (29). This second layer has no immediate importance for the optical and spectroscopic behavior of the adsorbed dye. Photochemical and photographic sensitizing efficiency usually reaches an optimum well before completion of the monomolecular layer, i.e., primary saturation. With many cyanines, not all, the condition in the primary monolayer is complicated by the fact that the adsorbed dye cations may be assembled in different states of mutual relation or aggregation : monodisperse, dimerized, and in a more highly aggregated state which we will term a mesophase. The evidence is spectrophotometric and photographic.

(1) Monodisperse State

This is produced out of anhydrous alcohol on pure precipitated silver chloride or bromide, and out of dilute aqueous solution. With the dyes investigated the adsorption density in this state at saturation did not reach much more than half that possible (from water). The adsorption is irreversible in both water and alcohol. It is distinguished, spectrophotometrically (reflection spectra) and photographically (in sensitizing), by giving a strong long wave α -band, a weaker auxiliary β -band of higher frequency, and, with some dyes, e.g., pinacyanol, a still weaker but definite γ -band. The spectrum (absorption) is similar to that in organic solvents, or in dilute aqueous solution.

Compared with the latter, or that in alcohol, the spectrum is displaced toward the red by amounts, varying with the dye, from 150A to



FIG. 26. Separation of Mesophase (dye V Cl). \bigcirc = data of Scheibe et al ; \times = data of Sheppard and Lambert.

350A (16). This displacement on adsorption cannot be so specifically accounted for as that of erythrosin; but must be assigned to interaction with the crystal lattice as a whole—perhaps related to what Pauling (30) has termed "the electron affinity of the crystal." Referred to the spectrum of a dye in vacuum, the displacement should give a measure of the "adsorptionenergy." We have not been able to measure the spectrum of the ionized cyanines in the gaseous state, but, as noted in Section I, have done so for the merocyanine (dye XXIII). Comparison with this dye adsorbed to silver bromide gives for λ_m (gas) 4700A and for λ_m (adsorbed) 6390A. The difference is 0.69 ev as the total adsorptionenergy, and this, plus the amount of a quantum absorbed by the (adsorbed) dye molecule $\lambda_m = 639 \text{ m}\mu = 1.93 \text{ ev}$, would be sufficient to provide the energy necessary in optical sensitizing, i.e., to transfer an electron to a silver ion (17). Another way of stating this is that on adsorption of the merocyanine dye electrons of the "filled" levels of the silver halide crystal are raised by some 0.69 ev nearer the conductance level.

We cannot say that this is the sole factor in optical sensitizing of the silver halides, because we have not got the absorption spectrum of the ionized cyanines in the gaseous state. But we may note, in confirmation of the argument, independent measurements of the change in free energy of cyanine dye in water and adsorbed: The free energy of the reaction $D^++H^+ \rightleftharpoons^+ D^+H$ can be determined by spectrophotometric titration of the *p*H function. It was found that for the same dye adsorbed to silver bromide the acid sensitivity is less than when dissolved in water. The difference in free energy in the two cases represents the difference between the adsorption and hydration energies

$\Delta F = RT \ln (a_s(\mathrm{H}^+)/a_a(\mathrm{H}^+)),$

where $\ln a_s(H^+) = \operatorname{activity}$ in solution $= pK_s$, $\ln a_a(H^+) = \operatorname{activity}$ adsorbed $= pK_a$. Hence ΔF $= RT\Delta pK$, $= 2.3\Delta pK$, which at 298° abs. = 0.36 $\times 10^{23}\Delta pK$ ev. For cyanine dye IVb (1,1'diethyl-2,2'-cyanine bromide), pK (water) = 2.90 and pK (ads.) = 1.05. Whence $\Delta pK = 1.85$ kcal./mole or $\Delta F = 0.109$ ev. On the other hand, when dye IVb is adsorbed to silver bromide there is a shift of the α -absorption from 5430A in water to 5700A. The shift in energy $h\Delta \nu = \Delta F$ is (2.272-2.164) ev = 0.106 ev. The agreement is good, and it is observed with other adsorbed dyes not yet measured that qualitatively the red shift of the absorption band is accompanied by lower pK of the adsorbed dye.

This reduction of pK points to a resonance stabilization of the adsorbed dye as compared with the dissolved (hydrated) dye molecule. From the heats of hydration and solution and the heat of condensation (from the gaseous state) it may be possible to determine the total energies of adsorption for the ionized cyanines.

(2) Dimerized State

As the concentration in water of many cyanine dyes is raised, and therewith the adsorption-density (always for the primary monolayer), the reflection and sensitizing spectrum show increasing strengthening of the auxiliary β - and γ -bands of higher frequency. This is well illustrated in Fig. 17. The behavior is quite similar, therefore, to what we have considered already for aqueous solutions, and shows that in an adsorbed monolayer those dyes, which can, couple as previously discussed. It is perhaps further confirmation of the "edge-on" orientation. Also it is interesting that out of anhydrous alcohol, in which the dye does not "dimerize," it is not adsorbed in the dimerized condition.



FIG. 27. Separation of mesophase dye V. Anion effects.

(3) Mesophases

The rather qualitative evidence for aggregation and "colloid" formation in sensitizing dye solutions (22), with associated spectral changes, had raised relatively early the question of these playing a role in optical sensitizing. This was supported by certain peculiarities in sensitizing spectra. But the first definite evidence in this sense was given by Leermakers, Carroll, and Staud (31) in 1938. This indicated two forms of optical sensitizing by certain cyanine dyes, distinguished by two spectral regions found both in sensitizing (spectrum photographs) and in the absorption (reflection) spectra of these dyes adsorbed to silver halide. They suggested that one of these corresponded with the molecular state in solution, the other with a state of polymolecular aggregation. Evidence for the formation of such aggregates was obtained on saturating certain cyanine dye solutions with salts. They suggested that this aggregate sensitizing was related to a remarkable new long wave absorption (and resonance-fluorescence) band discovered in 1936 by E. E. Jelley (32) on precipitating the so-called diethyl- ψ -cyanine, 1,1'-diethyl-2,2'-cyanine iodide, (dye Vc) and which was independently observed about the same time by G. Scheibe (33). Jelley observed with this dye coming out of solution the transient production of a very intense new band of considerably longer wave-length than that given by the dye in solution. Not only was it intense in absorption, but also in emission, as resonancefluorescence. As the dye definitely crystallized, the band became fainter and disappeared. Jelley at first attributed the band to a transient "molecular" state of the dye, while Scheibe proposed the formation of a new kind of giant polymeric molecule. In a further publication (34) Jelley gave account of new observations on the appearance of the band on "salting out" the dye from aqueous solutions. He noticed that the appearance of the band-observed spectrographically—was followed by the separation of a strongly birefringent thread-like phase, as seen in the ultramicroscope. He found that: (i) the threads were strongly fluorescent, the fluorescence being polarized with vibrations in the length of the thread; (ii) the absorption of light vibrating parallel to the length of the thread at first gave a very sharp maximum at 573 m μ , which, however, became more diffuse and displaced somewhat to the red as the preparation aged. It became identical with a weak band at 579 m μ assigned to the y axis of the crystal;⁶ (iii) the birefringence was of the same sign for all orientations of the threads; for threads crossing at very acute angles it was additive, but with random orientation of needle

⁶ See later, Section IV.

crystals, partial or complete neutralization occurred for crossing points. Jelley concluded that the threads were true crystals in one dimension—the y axis of the crystal—and regarded them as analogous to a nematic phase of liquid crystals, in contra-distinction from Scheibe's "polymerization of dye cations."

With this dye (and other cyanines) adsorbed at sufficient concentration to silver bromide a sensitizing band is observed, e.g., at about 577 m μ (31) which indicates the adsorption of the mesophase. From their investigation of adsorption to silver halide, Sheppard, Lambert, and Walker (16) concluded that nearing saturation much of the adsorbed dye must be present in extended card-pack like aggregates of parallel planar dye cations, with an interval between the cations of the order ~3.8A. They suggested that the "threads" of Jelley's "nematic" phase were constituted essentially by such extended card-pack aggregates.

Scheibe and his co-workers (35) carried out a number of valuable quantitative investigations on the production of this mesophase. They investigated its appearance spectrophotometrically as a function of temperature and concentration, and obtained a sharp limiting curve, similar to a solubility-temperature curve (cf. Fig. 26). The points on this curve represent the concentration-temperature at which the new band just appears or disappears. Scheibe concluded that this limit curve was independent of the anion associated with the dye cation. In this our own results (cf. Fig. 27) are not in full agreement. Not only does dye V-sulfate show systematic deviation from the chloride, though the J-band wave-length remains the same, but dye V-phosphate showed larger systematic deviations, and also displacement of the J-band maximum. Considerable displacements have also been noted by Jelley-particularly with iodate. This anion influences would signify inclusion of anions in the new phase. contrary to Scheibe's contention that it consists solely of polymerized cations. A further argument against this can be drawn, however, from the conductivity-concentration curves. In Fig. 28 three such curves are shown: (a) for dye V-Cl, which gives a strong J band and a mesophase; (b) for dye V $\frac{1}{2}$ SO₄, which does so also; (c) for



FIG. 28. Variation of specific conductance with dye concentration. $\times =$ dye V Cl at 20°C (Scheibe); $\bigcirc =$ dye V Cl at 25° C.; $\triangle =$ dye VII Cl (pinacyanol); $\square =$ dye V SO₄ at 25° C.

pinacyanol, dye VIIa, which gives, if at all (cf. later), a very weak J band, and no definite evidence of mesophase formation. The sharp break in the conductivity curve for pinacyanol is associated with the immediate appearance of a crystalline phase; this is at once apparent in the ultramicroscope (and confirmed by x-ray diffraction) just beyond the transition point as brilliant threads, similar to those described by Jelley. On the other hand, at the same stage immediately beyond the transition point, dye V Cl, which prior to that had also been optically clear, only showed a bright unresolved ground. It appears definite that at this stage the mesophase is below resolution in at least two dimensions.

Not only is the anion effect confirmed by this method, but the break in the conductivity—in all cases—shows clearly that we are not dealing with the formation of large cationic micelles, as claimed by Scheibe, but with a new phase, in which anions are removed from solution with the cations. Otherwise, $d\lambda/dc$ would have risen, not fallen. Jelley's conclusion that the J band is due to a mesophase on the border line of the crystalline state seems borne out.

On the other hand, the fact that with dye V, and with a number of others, this mesophase is

stabilized at the surface of silver halide and other crystals in a monolayer argues against a nematic phase. The latter is distinguished by a constraint of long molecules to remain in parallel, but with no other reduction of degrees of kinetic freedom (36). Much evidence points to the molecules in this new mesophase remaining in fixed positions parallel to each other, and with a new electronic transition perpendicular to the planes of the parallel molecules.7 This conclusion drawn from the production of the J band with dyes adsorbed to silver halide is further borne out by Scheibe's (33) investigation of dye V adsorbed to fresh surfaces of mica (muscovite). He showed that in this state, and in a monolayer, the typical J band is developed in both absorption and emission (resonance-fluorescence). He concluded, in agreement with our results on silver halide, that the dye cations are adsorbed in edge-on and parallel orientation, and at an interval of about 3.8A. However, from the presumption that the K⁺ ion positions on splitting the mica crystal would on an average be vacated about 50 percent on each new surface. and assuming that the single positive charge on the ventral edge of the dye cation could be treated as a half-charge at each nitrogen atom, he concluded that the planar cations were arranged in parallel, but in staggered array, each cation alternately displaced sideways by a considerable interval.

The dye cation is not necessarily located exactly in respect of one available anion of a lattice and the argument has no significance for the silver halide and cognate crystals.

Origin of J Bands

Scheibe (35) proposed for the *J*-band transitions direct electronic interchanges between the "electron clouds" of the resonance systems of the parallel dye cations. This interchange is supposed to permit a new "electron cloud" common to all component molecules of a thread, which may number many thousands. This conception of a totalitarian or collectivist electronic state was supported by important observations of Scheibe, Schöntag, and Katheder (37) on the quenching of fluorescence in the

meosphase of dye Va. Quenching was found to be very intense with OH ions, with phenols, and particularly with pyrocatechol. Usually, considerable excess of the quenching molecule over the fluorescing one is necessary. With quinoline red, a cyanine dye, but one not giving a mesophase, to produce a just measurable quenching -about 5 percent reduction-some 5 to 10 pyrocatechol molecules were required to 1 dye molecule. With dye Va, only 1 pyrocatechol molecule to $10^{3} \sim 10^{6}$ dye molecules, depending upon the concentration of dye, was necessary to give noticeable quenching. In explanation Scheibe et al. suggest that in chains of thousands of molecules, light energy—a quantum—can be taken up at any point, and given up by collision at any point of attachment of the quenching molecule. Unaffected propagation of energy must take place over thousands of dye molecules. The probability of collisions between fluorescing aggregates and quenching molecules increases with the chain length, and this again with the concentration. Hence the amount of quenching molecules decreases with concentration of dye, contrary to the behavior of molecular fluorphores. Experiments also indicated that any "afterglow' or phosphorescence lasted less than 5×10^{-9} second.

Scheibe pictures the mesophase as consisting of polymers of dye cations loosely held by van der Waals forces, emanating from the hydrocarbon residues. The parallel dye molecules are assumed to form a thread-like aggregate but in staggered array. The electronic collectivity is such that "in the giant molecules every electron taking part in the absorption knows what other molecules are participating in the formation of the polymer and in what number." To such subjective "Anschauungen" one can but say that these co-conscious electrons bespeak the domination of a certain "Zeitgeist" still, at this writing, geographically limited.

An important point is whether the unique assemblage of plane-parallel molecules necessarily forms a straight-line arrangement or not. Here an observation by Scheibe and Kandler (38) is illuminating. They remark "Wären die Fadenmoleküle von vornherein geradlinig, so wäre danach zu erwarten, dass bei regeloser Verteilung (z. B. im frischpolymesierten Zustand)

⁷ Modification of this argument is noted below.

linear polarisierten Licht nur von den entsprechend gelagerten Molekülen aufgenommen werden könnte und zur Fluoreszenz von in gleichen Richtung polarisierten Licht führen wurde. Wider Erwarten tritt in diesem Fall völlig Depolarisation ein. Hieraus muss geschlossen werden, dass die Moleküle bei gewöhnlicher Polymerisation in regelos gebogenen Form enstehen. Sie können Licht bestimmter Schwingungsrichtung bei paralleler Lage des elektrischen Vektors zur Tangente an diese gebogenen Moleküle aufnehmen. Dieses Licht kann nur durch das Fadenmolekul und an anderer Stelle mit anderer Richtung wieder ausgestrahlt werden. So kommt im Mittel völlig Depolarisation zustande." This observation is very important, but does it necessarily impose the idea of a peculiar metal-like molecular filament-more metallic than any metal? It is probable that the length or continuity of a thread is important for certain behavior, e.g., fluorescence-quenching but not for all, e.g., for the position and intensity of absorption and fluorescence in depolarized light. However, unless there be admitted some degree of interfibrillar transfer of energy, of the same efficiency as resonance-fluorescence itself, the depolarization of polarized light would require a considerable degree of parallel shifting or sliding of the component dye molecules of a filament, such that large degrees of curvature or bending be possible, albeit only in a plane common to all the molecules of a filament. With this, and admitting unlimited transfer of excitation in a filament or fibril, polarized exciting radiation could be re-emitted completely depolarized. This would cease to be the case if tangential shear, as in laminar flow, straightened out the filaments and also brought them into parallel alignment. Then excitation (in the J band) would be limited to suitably polarized rays, and would be re-emitted as such, so that selection occurs from natural light. The behavior is similar to that shown by dye molecules oriented in Cellophane or polyvinyl alcohol sheets by stretching the sheets when swollen, then drying them. Light vibrating in the plane of the dye molecule is selectively absorbed, as illustrated in Fig. 29. (This behavior with cyanine dyes confirms the view that the absorption bands in solution-

the α -, β -, and γ -bands—are due to transitions in the plane of the molecule.) With this qualification the coarser structure of the mesophase can be rather definitely envisaged. Also, it is evident that the "giant polymeric molecule" of Scheibe does not differ considerably from Jelley's "nematic thread," since there is admitted in the former a certain degree of lateral mobility of the molecules (or cations) which, however, is much below that of the component molecules of a true nematic swarm (36). The evidence, however, from conductance and transition temperatures, and from anion influence, makes us conclude that anions are also removed from solution and integrated in the thread. We are still left with two unsettled points, viz.: (i) the nature of the bond between the molecules in the polymer or aggregate; (ii) the nature of the electronic transition responsible for J bands.

As to (i) Scheibe considers that the cations are held in parallel by relatively weak van der Waals forces, of the dispersion type, principally due to the p electrons of the nuclei. He is not specific as to the exact process involved in (ii) but for the J band of dye V notes the low half-width of 180 cm⁻¹ or less. From this, and the resonance-fluorescence, it is argued that the electronic transition involved must be extremely well shielded, and practically free from coupling with vibrations. Also, except for a slight asymmetry, the band can be represented by dispersion theory equation of the form а $\epsilon_{\nu} = a/[(\nu_0 - \nu)^2 + b]$, where ϵ_{ν} is the frequency of the absorption maximum, a and b are constants. This type of equation holds for the



FIG. 29. Dichroism of cyanine dye in an anisotropic medium. Density D measured for λ_m . Curves are for increasing stretch.

absorption bands of atomically dispersed alkali metal atoms in halide crystals (23) (F centers), also one in which practically no coupling with atomic vibrations occurs. But with other cyanine dyes J bands are found with much greater half-width than with dye V, and for reasons which will appear shortly.

An Alternative Hypothesis

The combination of relatively weak bonding by van der Waals forces with direct electronic interchanges or transitions between the thus bonded molecules seems somewhat surprising. The orbitals of the p electrons of aromatic nuclei extend perpendicularly to the plane of the molecule, and quantum mechanics may find some kind of "tunnel" effect permitting the transition. But it is at least noteworthy that in graphite there is practically metallic conductance in the layer planes of fused benzene nuclei, but insulation in the direction perpendicular to these planes, separated as they are by an interval of some 3.4A. In the case of silver erythrosin we suggested that the new long wave band, which is produced only in the solid state of aggregation, is made possible by the intercalation of silver ions between the alternative key oxygen atoms of the erythrosinate ions (vide infra). The silver atom ion is able to act under these conditions as an oscillatory acceptor-donor of electrons transferred from the erythrosin anion, completing a new or rather extended resonance system. For an analogue to this in the case of the mesophases of cyanine dyes, we must look for a comparable intercalation of an electron donor-acceptor between the key nitrogen atoms of the polymethine cations. The first possibility would be the anion X^- of the dye molecule and some support to this is lent by the evidence that anions are apparently taken up in the formation of the mesophase. On the other hand, while there is evidence of anion influence on the mesophase formation, it is relatively slight compared with the differences between the electronegativities of the anions. According to Mulliken (39) the absolute value for this should be the average of the first ionization energy and the electron affinity of the atom. This gives relatively: F 4, Cl 3, Br 2.8, and I 2.5. Without dismissing this possibility entirely, there is

another important experimental datum to weigh in. This is the evidence that water molecules are essential for the production of the J band and the mesophase of cyanine dyes. This was demonstrated by Leermakers, Carroll, and Staud (31) for the production of the J band of dye V on silver bromide. They showed that the effect was reversible by dehydrating and rehumidifying. Sheppard, Lambert, and Walker confirmed this (17) and also showed that the dye in the mesophase on silver bromide could be desorbed by alcohol, resorbed out of alcoholic solution to a sparse monomeric layer, and this again converted, in part at least, to the mesophase by hydrating with water or water vapor. Jelley had first prepared the mesophase of dye V by precipitation from solution in a polar solvent by a miscible non-polar liquid, but observed later (40) that the presence of a small amount of water⁸ was essential. Independent evidence for a reversible "hydration" effect was furnished by Scheibe (41), who added important corollaries. The Jband did not appear from solutions of the dye in such solvents as H₂S and HCN, having configurations similar to that of H_2O . But it was produced in deuterium oxide (D₂O) and with a shift of wave-length of the order of 50A. It appears difficult to fit this in with the hypothesis of direct electronic interchange between the aromatic nuclei of parallel dye cations. So far as we know, Scheibe has not suggested an explanation of the hydration effect, beyond a vague reference to hydrogen bridges.

In order to take this into account, as well as the other principal phenomena, Sheppard suggested (42) a specific intermediary role of water molecules. In the phenomenon of dimerization in solution we have suggested that a water molecule coordination between two dye cations plays an important part in maintaining their union. In the more highly organized mesophase, or "giant polymer," which separates as a new phase from water, but a hydrated phase, he suggested that two water molecules are intercalated between the nitrogen atoms—henceforth termed N atoms—of each pair of opposite planar cations, or rather, somewhat deformed (contracted) negatively charged portions of the H₂O

⁸ This could be afforded by condensation.



FIG. 30. Model of mesophase filament. H_2O molecules cross linking cyanine nitrogens. \bar{X} anions aligned along filament axis, each between two water molecules.

molecules. This portion, in accordance with the tetrahedral model for H_2O proposed by Bernal and Fowler (43), is located on the opposite pole of the oxygen atom from the hydrogens, and at right angles to the axis between the two hydrogen atoms. The hydrogens tend to remain in a plane parallel to that of the dye cations, and equidistant from them. With their positive charge excess (43) they can serve to hold anions at a position central to that of the four N atoms, but in a lower plane. By this the influence of the anion on the hydrate water molecules may be observed as an anion influence on the J band. Dye V has the formula



with a resonance between identical structures. We will symbolize such a symmetrical moleculeion as $N_p \sim N_p$, where the subscript refers to the nucleus proper to the N atoms, likewise to its electromeric capabilities, and is changed to indicate this. Thus for a non-symmetrical dye we may write $N_{p'} \sim N_{q'}$ where p' denotes the same nucleus as p but N_p is effectively changed because joined with N_q . In the mesophase we suppose these cations arranged in parallel, as previously discussed, and between each successive pair of dye cations a H₂O molecule coordinated between each pair of opposite N atoms. These interstitial hydration molecules furnish the mobile replaceable electrons permitting resonance between the two extreme square configurations, thus:

$$\begin{array}{c} N \sim \stackrel{\top}{N} \stackrel{\top}{\longrightarrow} \stackrel{\top}{H_{2O}} \stackrel{\top}{OH_{2}} \stackrel{\top}{\leftrightarrow} H_{2O} \stackrel{\top}{OH_{2}} \\ N \sim N \qquad N \sim \stackrel{\top}{N} \stackrel{\top}{\rightarrow} N \\ \stackrel{\top}{\rightarrow} \stackrel{\cdot}{\rightarrow} N \qquad N \sim \stackrel{\top}{N} \\ \end{array}$$

For a symmetrical dye $N_p \sim N_p$, the alternate structures will be identical and of equal energy, but this will not be so for unsymmetrical dyes, as $N_{p'} \sim N_q$. In any case, the corresponding electronic transition on absorption of light would be of longer wave-length than that proper to the dye cation itself, as observed with the silvererythrosin system.

If two cells are built up in this way, by adding on another dye cation in parallel, with two further interstitial water molecules, it appears that only one of the two cells can be excited at a time, from exclusion principles. And this will be true for an extended filament of n molecules or cells. But this alternation of active and passive cells would not impede the very rapid and complete propagation of excitation or energy quanta through the system, since active and passive cells have fundamentally identical structures. Nor would the characteristic frequency change with length of filament, i.e., number of cells, since it is determined by the structure of the unit cells themselves. It would seem to be requisite for the interstitial atoms or molecules in such a system that there be, if any a preference to give rather than to receive electrons-where dye cations are concerned. And, as pointed out, the differences in electronegativity of the actual anions seem excessive in relation to the "anion influence" on the J band. It has been pointed out by R. Robinson (44), one of the chief British chemists founding the theory of mesomerism, that the water molecule, nominally neutral, is effectively anionoid. The role suggested here for water molecules is, therefore, not repugnant to its chemical character. The possibility of a limited lateral, parallel shift of and

the dye cations, as required by the depolarization in the randomly oriented mesophase, is easily allowed for by rotation of the interstitial water molecules around axes parallel to the plane of the dye cations (cf. Fig. 30). Finally, not only does this function of water molecules agree best with the "hydration" factor in *J*-band production, in general, but particularly so for this phenomenon with the adsorbed mesophase, e.g., on silver halides.

Hetero-Polymerization in the Mesophase

The conceptions advanced appear to account for a further very important observation by



Scheibe (45). He found a limited degree of isomorphic mixture of cyanine dyes in mesophase formation, as exemplified in the *J*-band spectrum. Where each of two such dyes alone formed a mesophase with a different characteristic J band, with mixtures in different proportions there did not appear an absorption showing a variable ratio of the intensities of the two bands, but a series of intermediately placed bands. These bands could not be compounded by any superposition of the 100 percent single J bands. This was adduced as further evidence for electronic co-consciousness in the common giant molecule. In specific example, the two dyes



both give J bands at sufficient concentration and, in mixtures of variable proportions, a series of intermediately placed bands (cf. Fig. 31).

On analyzing the data, we may note that no explanation is given of the notable difference in character of the two J bands. We would not say that this is entirely incompatible with the hypothesis of direct electronic interchange. But it seems to us to accord quite well with the model proposed here. The ψ -cyanine—dye V—is a symmetrical cyanine. The doublet or cell may be represented as follows:



where the essential electronic transition more or less perpendicular to the plane of the molecule may be symbolized by $N_p \times N_p$. There will be a unique single band, and possibly, as in the case of the H₂ molecule elucidated by Mulliken (46), very high intensity because of parallel paired transitions. On the other hand, writing the asymmetric selena-cyanine as $N_{p'} \sim N_q$, the con-



FIG. 31. Absorption curves for hetero-polymer. (From G. Scheibe, Kolloid Zeits. 82, 1-14 (1938).)



FIG. 32. Schematic absorption curves for hetero-polymer of dyes A and B.

struction shows that the respective head-to-head and head-to-tail appositions of the molecules in the cells could give three intermolecular J bands, actually overlapping to give one relatively broad and weak band as observed for the mesophase of this dye, and at higher frequency than for the symmetrical dye.

For the hybrid doublet $N_p \sim N_p$ in apposition



These showed less complete isomorphism, there being evidence of a "break" at about 20 moles A to 80 moles B. Whether the 1 A to 4 B ratio is fortuitous or denotes a preferred periodicity of inclusion of the A molecules cannot be stated, but the question is well worthy of further study.

Mesophase of Cyanines and Proteins

We have observed (47) an interesting case of formation of a mesophase (J band) when certain

to $N_{p'} \sim N_{q'}$ we have a new double band given by the combination of the transitions $N_p \times N_{p'}$ and $N_p \times N_q$, a band which will be intermediate between that of the pure ψ -cyanine and the pure ψ -selena-cyanine. The three fundamental bands, one of which is simple, the intermediate dual, and the third a triplet, are shown in Fig. 32. By superpositions of these in various proportions, according to the averaged composition of the mesophase from the mixed dyes, all the intermediate stages observed by Scheibe can be compounded. In fact, Scheibe's data (cf. Fig. 33) do not show the complete continuity of band characteristics which is claimed, but rather a notable "break" in the region of 50:50, i.e., equimolecular proportions of the two dyes. One should, in fact, speak of two sets of quasicontinuous variations, viz., as between



as would be expected on the multiple doublet model. Other cases of this hetero-polymerization have been observed, as between dye V and the corresponding aza-cyanine, where = N - replaces the methine = CH -. Quantitatively the only other data at present available are given by Ecker (41) for mixtures of:



cyanine dyes in very dilute solution were mixed with dilute solutions of two proteins, viz., gelatin and protamine (salmine). The development of the J band for a particular dye (see below) and its disappearance as a function of the concentration of gelatin are shown in Fig. 34. The dye in water—in which its solubility is quite low—shows marked tendency to "dimerization," as indicated by the strong relative intensity of its β -band. In solutions of increasing gelatin content there was at first a rapid development of a long wave band at 6530A, which was identified with the J band given by this dye on salting out or on adsorption. Beyond a certain gelatin concentration, however, it is clear that the intensity of the J band falls rapidly, to practical disappearance.

While full interpretation of this behavior must await more experiments, the main outline can be presented. Gelatin in water solution at 20°-25°C is probably present in aggregated micelles rather than in completely molecular chains. The dye is adsorbed to these, probably elongated, micelles, at special points along the chain molecule structure at about 3.5 to 4.0A apart. The side-chain spacing in most proteins appears to be about 3.3 to 3.5A (48), but in gelatin either at 2.8A-or at 4.0A, according as three amino-acid residues are assumed for a fundamental interval of 8A in a twisted chain, or two amino-acid residues in the same interval. The latter would seem more compatible with the fixation of the mesophase of the dye. An interesting point is that fixation of dye molecules to something in the side chain would point apparently to a staggered parallel array similar to that proposed by Scheibe for adsorbed dye V on muscovite. Another feature is that while dye Ib

Dye Ib



(3,4-3',4'-dibenzothiacarbocyanine bromide)

Dye XIIIb





FIG. 33. Data on hetero-polymer (Scheibe).

gave the strongest mesophase formation, and next its isomer dye XIIIb no other cyanine dyes were found so far to give a mesophase (J band) with gelatin, except such as had at least one benzo-group in the 3,4 or 5,6 position on the benzothiazole nucleus, and these less strongly than the two above.

The resolution of the mesophase with excess of gelatin is to be attributed to formation of monomers in the interior of micelles of gelatin. This is shown by the increased strength of the α -band. The phenomenon has been paralleled with cetyl pyridinium chloride solutions (49). With protamine no resolution in excess was found, but the protamine-dye compound precipitated. The resemblance of the behavior to the combination of thymo-nucleic acid with protamine (50) deserves comment.

Adsorbents

The wave-length of the J band of a cyanine mesophase developed on an adsorbent appears to depend to some extent upon the adsorbent or substrate. Thus with dye IV the data of Table IV may be noted (51).

The lattice interval between the anions has a more definite significance for the silver and copper (cuprous) salts than for the mercurous halides, and indicates that the most favorable interval between the dye cations is about 4A.



Fig. 34. Development of mesophase of dye Ib in gelatin sol.

Symbol	Percent gelatin	Symbol	Percent gelatin
×	0.00000		0.00100
Õ	0.00005	\odot	0.002
Ă	0.00010	Ð	0.005
	0.00025	Ť	0.010
Ð	0.00050	÷	0.02
Ā	0.00100	¥	0.01

On the Structure of Cyanines Giving a Mesophase

We have too few observations available to venture to assert that such and such a cyanine can or cannot form a mesophase. With many of them it is probably easier to detect such a formation by their optical sensitizing. Valuable data in this connection have been given by G. Schwarz in an important memoir "Sur la répartition spectrale de la sensibilité des emulsions photographiques sensibilisées par les cyanines (52)." He deduces the existence of two definitely different types of optical (color) sensitizing by cyanine dyes. "The principal sensitizing maximum of the first kind corresponds to a wave-length about 25 to 50 m μ greater than the absorption maximum of the dye in alcoholic solution. For thirteen out of fifteen carbocyanines considered, the sensitizing maximum of the second kind corresponds to a wave-length 70 to 115 m μ greater than this maximum of absorption in alcohol. Another characteristic of sensitizing

of the second kind is the extremely abrupt decline of the spectral sensitizing curve on the long wave side immediately beyond the maximum. This specific aspect of the curve permits characterization of the second kind of sensitizing even when other evidence is lacking." The characteristics indicated by Schwarz are confirmed by the reflection spectra of the adsorbed dyes.

With reservations imposed by poverty of data, some tentative conclusions may be presented:

(i) Cyanine dyes whose molecules have a nonplanar structure do not form a mesophase. This is indicated by the apocyanines (16) which have no -CH = bond between the nuclei, by certain isocyanines, and by certain cyanines derived from phenanthridine (16).

(ii) No example has been instanced of an isocyanine giving a mesophase.

(iii) The symmetrical 1,1' dialkyl cyanines readily form a mesophase.

(iv) Certain asymmetrical 1 : 1' dialkyl cyanines (e.g., diethyl- ψ -selena-cyanine) form mesophases. Other data as to the effect of asymmetry are lacking.

(v) The simple symmetrical carbocyanine pinacyanol does not readily, if at all, form a mesophase.

(vi) Symmetrical thia- and oxacarbocyanines with a medial alkyl (9-alkyl) give mesophases. It is evident that there is here much to learn. It can be stated with certainty that the constitution of the cyanine molecule determines the position of the J band if a mesophase is formed,

TABLE IV. Wave-length of J band and lattice constant.

Substance	e Crystal type	Lattice constant angstroms	Lattice interval between anions	Wave- length of J band angstroms
AgCl AgBr AgI AgCN CuCl CuBr CuI	Cubic (NaCl) Cubic (NaCl) Hexagonal (ZnO) Hexagonal Cubic (ZnS) Cubic (ZnS) Cubic (ZnS)	5.54A 5.75 4.59 4.60 5.40 5.68 6.04	3.92A 4.06 <i>ca.</i> 4.60 <i>ca.</i> 4.60 3.82 4.02 4.27	6240 6250 Doubtful 6350 6250 6240 ca. 6200
$\begin{array}{c} Hg_2Cl_2\\ Hg_2Br_2\\ Hg_2I_2\\ \hline CdS \end{array}$	Tetragonal Tetragonal Tetragonal Hexagonal (ZnO)	3.30 3.40 3.55 4.14	$ \begin{array}{r} 3.30 \\ 3.40 \\ 3.55 \\ \hline ca. 4.14 \end{array} $	6120 Doubtful 6440 None

but, apart from planarity, not much is known as to the influence of constitution on mesophase formation.

The Heat of Mesophase Formation

From the data presented graphically in Fig. 26 for the effect of temperature on the formation of mesophase dye V, it is possible to deduce values of the heat of formation of the mesophase. The graph of values of log c^* as function of $1/T_{abs}$ approaches sufficiently to two straight lines inclined at a large angle that we can use for each sector the Van't Hoff isochore equation log $c^* = (\Delta H/RT) + \text{constant}$. Then eliminating the constant, we have

$$\Delta H = Rn[(\log c^{*}_{1} - \log c^{*}_{2})]/(1/T_{1} - 1/T_{2}),$$

where *n* refers to the number of constituent molecules involved (for example, for the heat of solution of AgBr crystal, n=2, Ag⁺ and Br⁻). The values calculated were :

Range	$\Delta H_n = 1$
6° to 38°C	11.4 kcal./mole dye
48° to 48°C	21.8 kcal./mole dye.

There are two possibilities in respect of the two-branched graph shown in Fig. 27. (i) It consists of two intersecting straight lines; (ii) it is really a continuous curve, of hyperbolic form, asymptotic to two straight lines. In the first case we are concerned with two different processes, and the intersection temperature represents a transition point. This is the interpretation placed upon similar graphs for the heats of hydration of certain inorganic salts by Carpenter and Jette (53). In dealing with a two-phase system, e.g., salt hydrate-water vapor, or, solid—solution, any abrupt transition must be assigned to the condensed phase rather than to a vapor phase (e.g., water) or to a solution of presumably continuously varying composition. In the present case of the mesophase of dye V, there appears at first no reason to assume a transition temperature, a discontinuity of state, because the selected criterion, viz., the J-band wave-length is unchanged. However, there could be changes of state of a mesophase not affecting this. Thus, the macromolecular nematoid filaments stable above the apparent transition temperature might unite below that temperature to form smectoid sheets by lateral condensation via integration of another water molecule per cell, or another anion. Such lateral condensation to smectoid aggregates has been deduced in certain cases by E. E. Jelley (54). This hypothesis admits of a heat of condensation of the same order of magnitude as the heat of nematoid filament formation itself. And it will be observed that the ΔH value for the upper temperature range is very nearly twice that for the lower. This may be fortuitous, as also the fact that the heats of hydration for a number of hydrated inorganic salts (53) are of the same order as our lower temperature range "heat of mesophase formation." Thus:

Salt	CuCO ₄ ·4 H ₂ O	$CdSO_4 \cdot 8/3 H_2O$
Heat of hydration per mole H ₂ O	13.26 kcal.	11.20 kcal.
Salt	$MgSO_4 \cdot 7 H_2O$	CoCO ₄ ·7 H ₂ O
Heat of hydration per mole H ₂ O	14.03 kcal.	12.80 kcal.

In the second case, we assume no abrupt transition in the solution phase in equilibrium with the (condensed) mesophase, but only a secondary process in continuous mobile equilibrium with this.

One possibility might be the "dimerization" already discussed. Rabinowitch and Epstein (14) obtained a value H_d for thionine = 6.8 kcal./mole dye, Scheibe obtained for pinacyanol (dye VIIa) $H_d = 7 \pm 2$ kcal./mole dye, and we have recently obtained for dye Va, $H_d = 6.4$ kcal./mole dye. If we assume the fixation of one molecule of water (H₂O) per dimer, i.e., per two moles dye, then the H_d values referred to one mole H₂O should be doubled. The values, of the order 12-13 kcal./ mole H_2O , are sufficiently near the difference between H_m (high) and H_m (low) to make the hypothesis plausible. According to this the mesophase is formed by the condensation of dimers and water molecules. The heat effects in question are definitely of the order of hydrate formation, i.e., of coordination of a water molecule, but from the vapor.

In conclusion, it appears feasible that the hydrous mesophases of the cyanine dyes may exist both in fibrillar and in sheet form, which we may term nematoid and smectoid, to differentiate from anhydrous liquid crystals. Whether the new spectral bands (cooperative spectra) are due to direct intermolecular interchange of electrons, or occur by way of interstitial water molecules or anion, the evidence is that the optical features (wave-length, half-width, and structure of the band) are essentially determined by the unit cells or doublets of parallel dye molecules, by an extension of the resonance system of the molecules. The donation and acceptance of electrons must be regarded as controlled by the chemical constitution and resonance systems of the cooperating molecules to precisely the same degree whether the transfer is direct or indirect. The direct interchange hypothesis does not account for the hydration and anion effects.

SECTION IV. LIQUID AND CRYSTALLINE STATE OF DYES

(with H. R. Brigham and P. T. Newsome)

So far as we know, observations on the spectra of liquid dyes are like the snakes of Irelandthere are none. However, this blissful state need not continue. We have observed definite fusion without decomposition of certain of the dyes previously mentioned-e.g., merocyanine XXIII melting at 185°-190°C and merocyanine XXXI at 150°C. It will be necessary to use extremely thin layers, of the order of 1 to 5 μ , to measure the absorption, but this is possible, and the results should be interesting. There are possibilities of mesomorphic phases with corresponding optical manifestations. The transition temperatures of any true anhydrous smectic or nematic phases must lie in the neighborhood of the melting point. Any such anhydrous phases would be quite unstable at room temperatures, when the hydrous mesophase is observed, and it is likely that they would not disclose the spectral features of the latter.

Actual information on the spectra of crystallized dyes is at present very meager. The experimental difficulties in the way of obtaining significant data are considerable. Owing to the

very high absorptions involved, it is necessary that very thin layers, again of the order of microns, be used. And this invokes a further difficulty for the interpretation, viz., that such layers should be slices of a single crystal, of known orientation to the axes of the crystal. One of the chief experimentalists in this field, E. E. Jelley (55) remarks: "Observations of the principal absorptions of strongly colored crystals are usually qualitative and are confined to the study of dichroism or trichroism. This is understandable, as a great many strongly absorbing organic compounds form monoclinic or triclinic crystals which often have extreme dispersions of the axes of the optical ellipsoid, so that the optical properties of the crystal are not easy to interpret." The philosopher Bergson has remarked somewhere, "La matière est ballastée de géometrie," and the mere chemist is often inclined to feel that nature has been inordinately liberal with that ballast in the case of solids. It is not, perhaps, surprising that, as Dr. Jelley has pointed out to us, even physicists (qua spectroscopists) have as it were by-passed, though indirectly utilizing, this barrier, in their studies of the spectroscopy of the solid state, since a large part of these has been concerned with the spectroscopy of "impurity" molecules or atoms confined within a crystal cage which could be utilized to ensure certain specific orientations for the impurity.

As basis for a thorough examination of the spectra of crystalline dyes, there are needed rather complete crystallographic and x-ray diffraction analyses, and these are still little available. Of the polymethine dyes, a crystallographic examination of "Pinaverdol" was made by Wherry and Adams (56) in 1919. Pinaverdol is an isocyanine, then termed 1,1',6'-trimethylisocyanine iodide-it would differ little, as to cation, from Orthochrome T (bromide). Orientation of the crystals was effected by taking advantage of the strong reflection pleochroism. Of two prominent zones of faces lying at right angles to each other, "all forms in one reflect brass-yellow light, while the dominant forms in the other-beetle green." The former zone was taken as the prismatic, and the latter held right and left. The crystal system was found to be monoclinic, though since the base lies only 1° 40'

away from the pole of the prism zone, it is decidedly close to the rhombic.

Concerning the pleochroism it is pointed out that "in any biaxial crystal there are three directions at right angles to each other in which properties connected with light are exhibited. In the rhombic system these directions coincide with the optic axes; in the monoclinic, one coincides with axis b, while the other two are limited to the plane of symmetry but do not, in general, coincide with either of the crystallographic axes lying in that plane. In the present, with a near rhombic form, marked deviations of the optical directions from the axes a and c are not likely. Faces lying perpendicular to axis cor nearly, show a deep bronze-violet reflection." By transmission (small crystallites) these crystals absorbed strongly between about 470 m μ in the blue to about 600 m μ in the red. Since the absorption band in sensitizing (adsorbed) has a maximum at 585 m μ , and an auxiliary β -band at 535 m μ , it is probable that this absorption corresponds to vibrations in planes of molecules perpendicular to the c axis. The directions in the crystals giving brown or greenish-brown reflectance behaved differently, in that the red end of the spectrum was considerably absorbed, also the blue violet, with slight though distinct transmission in the yellow-green. This study does indicate that the planar molecular absorption is preserved for planes perpendicular, or nearly, to the *c* axis. The nature of the apparently almost complementary absorption for the other directions is not explained. Considerably more light on the disposition of certain dye molecules in the crystal is obtainable from the valuable "X-ray examination of methylene blue" by W. H. Taylor (57), and some outstanding results may be noted. The crystals, elongated platelets, give a similar pleochroism (dichroism) to that of the cyanines-bright blue for vibration direction parallel to the needle axis, and purple brown for the vibration direction at right angles thereto. Twinning, however, prevented any accurate specification of the spectral (and optical) properties.

From the x-ray data the unit cell (for the S chloride) is monoclinic with angle β -97° and with axial lengths a=9.5A, b=31.3A, c=6.9A. Here the c axis is the needle axis, and the b axis

is normal to the plate face. From the density and cell dimensions, the best molecular weight is for $C_{16}H_{18}N_3S$: $Cl \cdot 4H_2O$. (The bromide indicated $5H_2O$, the iodide—I $3H_2O$, and the iodide —II, $1H_2O$). "The habit . . . and the optical properties point to an arrangement of lathshaped molecules, . . . lengths parallel approximately to the *b* axis, and their flat faces perpendicular to the *c* axis." The *b* axis might be parallel to the plate face of the crystal, or normal thereto, but "it is still the case that light vibrations parallel to the *b* axis are much more strongly absorbed than those parallel to the *c* axis."

The distance between one lath-shaped cation and the next above it or below it is then $\sim 3.5A$ and there is just sufficient clearance between the ends of the cations lying (end to end) in the same plane. Probably the plane of the cation is tilted slightly.

In a proposed structure of the iodide, allowing also for the anions and the water molecules, the cations (-C-N-C- chains) are supposed plane and the one lies directly above another in projection parallel to the *c* axis which is not far from normal to the plane (001)—the distance between is *ca.* 3.45A. "Adjacent stacks of cations are separated by layers containing halide ions and water molecules. All the halide ions have similar environments, with CH₃ groups as nearest neighbors."

The fine structure of methylene blue is probably in essentials that of the cyanines, though no doubt with specific variations.

This general pattern is again apparentmutatis mutandis—with the long-chain paraffins, and, more to the point, with the poly-p-phenyls, the polyenes, and the linear benzenes-naphthalene, anthracene (58), naphthacene, and pentacene. The arrangement with chrysene (59) is similar to that in naphthalene and anthracene. From the parallelism of the flat molecules with each other, at, e.g., in methylene blue, an interval of about 3.45A (although inclined to an axis through their centers), one might expect to observe definite indications of dimerization (in respect of the ratio of β - and α -bands) in accordance with the views of Rabinowitch. Unfortunately, not only do the crystal optic conditions already mentioned minimize the



FIG. 35. Transmission measurements of naphthacene. X—sublimed on glass and O—in α -brom-naphthalene.

probability of definite detection of such intermolecular and cooperative spectra, but there is the already mentioned obscuration by reason of incessant interpenetrative twinning.

Now that the question is posed, one may hope that the difficulties may be overcome, and a definite conclusion reached as to the existence of cooperative spectral manifestations in the crystals of such dyes. In the meantime, we return to the special case of naphthacene:



It is the next homologue of anthracene. G. Scheibe has stated that this hydrocarbon, in the solid crystalline state, shows a specific band at $\lambda = 525 \text{ m}\mu$ (38) in thin crystals for light polarized in the plane of the face while "light polarized perpendicularly thereto is only absorbed in the solution bands at 475, 445, etc." The disposition and orientation of the naphthacene crystal were not very specifically described and further investigation is necessary.

This "extra" long wave band in crystalline naphthacene is confirmed. A very pure sample dissolved in α -brom-naphthalene gave no absorption at that wave-length (see Fig. 35), the absorption bands agreeing with those found by other observers (38). A reflectance spectrum of a microcrystalline deposit showed definite bands at 434, 462, 495 and a shoulder of less intensity at 526 m μ . This was confirmed by transmission measurements of a film sublimed on to glass, shown in Fig. 35 with corresponding measurements of the absorption in α -brom-naphthalene.

It is probable that the absorption spectrum in solution is repeated in the crystal, with a displacement to longer wave-lengths, of 230 to 280A, such a displacement being indicated in the case of other lin-benzenes, of polyenes, and of dyes (see later). But there is no doubt of the existence of a new band at about 530 m μ . Such "film" spectra can say nothing definite as to the orientation of the absorbing system. Dr. E. E. Jelley kindly made a preliminary examination of the dichroism of this naphthacene sample which he recrystallized from α -brom-naphthalene. He reports as follows: "The crystal planes are so oriented that the normal to the surface has vibration planes corresponding to n_{β} and to a vibration in the XZ plane corresponding to a

refractive index between n_{β} and n_{α} . The following absorption bands were measured: Y vibration direction = n_{β} : $\lambda = 502 \text{ m}\mu$, 471 m μ , and 445 m μ . Vibration in XZ plane: $\lambda = 527$, 509, 478, and 445 m μ .

"A spectrographic analysis of the convergent polarized light absorption figure shows that the 527-m μ band becomes somewhat stronger in the direction which more nearly approaches n_{α} . The 527 and 509 maxima represent two peaks in a continuous absorption band which extends over that range. There was evidence that the direction of the XZ plane varied with wave-length, but the variation is not sufficient to affect the results given above."

It would appear from this that the 527-m μ band is a member of the system deriving from vibrations in the plane of the molecule, rather than from any system in which the transitions are perpendicular to the plane of the molecule. In this connection, it may be well to recall the appearance of a weak but definite "extra" long wave band (beyond the principal maximum) with merocyanine XXIII in vacuum and in non-polar solvents, which was completely suppressed in polar solvents (cf. Section I).

The question of the existence or not of specific J bands in anhydrous crystals of aromatic compounds is not decided yet. It is very important for the hypothesis that the J band of cyanine mesophases occurs by direct electron interchange perpendicular to the planes of parallel molecules.

The crystal structure of naphthacene has been determined by Hertel and Bergk (60). They found it to be very similar to that of naphthalene and anthracene, but the monoclinic symmetry of their lattice is not preserved, the crystals becoming triclinic.

Film Spectra of Dyes

A number of absorption spectra of "solid" films of dyes have been measured, of indigo, merocyanine XXIII, V (diethyl- ψ -cyanine), and various other cyanines and carbocyanines. There are three disturbing factors:

(i) There may be an oriented adsorbed layer formed on glass. But this should be too thin to contribute much.

(ii) The crystallites will have very uncertain

orientations. Improvement may be made in some cases by gentle brushing (Jelley).

(iii) Superficial mesophase formation may occur, depending upon the humidity. Thus, a J band may be imputed incorrectly to the crystal, and this, Dr. Jelley tells us, is apparently the case in the "ageing" of the mesophase of dve V. Contrary to his earlier findings, there appears to be no J band given by the dry crystals. Our "film" spectrum is in agreement. Generally, the spectra of the solid state show displacement of the gas and solution spectra to longer waves. They may show evidence of "dimerization," but this requires study in relation to the humidity. Evidence for extra "J" bands, and for "extra" bands in the short wave region is also inconclusive. It is hoped to reduce these and other pertinent data to a clearer picture later. (See Fig. 36.)

The remarkable optical and other properties of the mesophases of cyanine dyes suggest



FIG. 36. Transmission measurement of film. I—merocyanine XXIII; II—1,4-diaminoanthraquinone; III indigo; 1. vapor, 2. solid.

certain possible biological contacts. The propagation of energy in the threads may perhaps have some affinity with that of nervous impulses in nerve fibers. Again, there are the questions of mechanism in vision and in photosynthesis.

In conclusion, thanks are due to Mr. E. Richardson of the Physics Department of these Laboratories for reflectance measurements, to Dr. E. E. Jellev and other confrères for helpful discussions.

BIBLIOGRAPHY

- N. Q. Chako, J. Chem. Phys. 2, 644 (1934); cf. R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics* (1941), Vol. 8, p. 234-6.
 N. W. A. Start, Phys. Rep. Tran. Chim. 50
- (2) J. P. W. A. van B. Houckgeest, Rec. Trav. Chim. 59, 560 (1940).
- L. G. S. Brooker, R. H. Sprague, C. P. Smyth, and G. L. Lewis, J. Am. Chem. Soc. 62, 1116 (1940).
 (4) A. Reis and V. Schneider, Zeits. f. Krist. 68, 543
- (1928).
- F. Arndt, Ber. 72, 860 (1939)
- (6) J. Van Alphen, Rec. Trav. Chim. **60**, 138 (1931).
 (7) C. F. H. Allen, C. V. Wilson, and G. F. Frame, J. Org. Chem. **7**, 169 (1942).
 (8) In paper with P. T. Newsome awaiting publication.
 (9) G. N. Lewis and M. Calvin, Chem. Rev. **25**, 273
- (1939)
- (10) S. E. Sheppard, Proc. Roy. Soc. A82, 256 (1909); Phot. J. 48, 300 (1908).
- G. Kortüm, Zeits. f. physik. Chemie 34, 255 (1936).
 G. Scheibe, Kolloid Zeits. 82, 1 (1938).
- (13) A. A. Smith and J. C. Elgin, J. Phys. Chem. 39, 1149 1935).
- (14) E. Rabinowitch and L. F. Epstein, J. Am. Chem. Soc. 63, 69 (1941).
- (15) C. Robinson and H. A. T. Mills, Proc. Roy. Soc. A131, 576 (1931); S. E. Sheppard, Atti del X Con-gresso Internazionale di Chimica (Roma, 1938), Vol.
- (16) S. E. Sheppard, R. H. Lambert, and R. D. Walker, J. Chem. Phys. 7, 256 (1939).
 (17) S. E. Sheppard, R. H. Lambert, and R. D. Walker, *ibid.*, 9, 96 (1941).
 (18) L. G. S. Brooker and G. H. Keyes, J. Am. Chem. Soc. 56 (1036)
- 58, 659 (1936).
- (19) J. S. Anderson, E. F. Bradbrook, A. H. Cook, and R. P. Linstead, J. Chem. Soc., Part 2, p. 1151 (1938).
 (20) Cf. K. W. Hausser, Zeits. f. tech. Physik. 15, 10
- (1934)
- (1954).
 (21) S. E. Sheppard, Atti del X Congresso Internazionale di Chimica (Roma, 1938), Vol. 1, p. 234.
 (22) S. E. Sheppard and H. Crouch, J. Phys. Chem. 32, 751 (1928); K. Fajans, J. App. Phys. 12, 306 (1941).
 (23) R. Hilsch and R. W. Pohl, Zeits. f. Physik 77, 421
- (1932).

- (24) K. Feigl, Zeits. f. anal. Chemie 74, 380 (1928).
 (25) S. E. Sheppard and H. R. Brigham, J. Am. Chem. Soc. 58, 1046 (1936).
- (26) C. Liebermann and St. v. Kostanecki, Lieb. Ann. 240, 245 (1887)
- 245 (1887).
 A. Werner, Ber. **61**, 1062 (1908).
 (27) J. W. McBain, Nature, **145**, 702 (1940).
 (28) J. J. Trillat, J. chim. Phys. **33**, 742 (1936).
 (29) K. Blodgett, J. Am. Chem. Soc. **57**, 1007 (1935).
 I. Langmuir, Science **87**, 493 (1938).
 (30) L. Pauling, Phys. Rev. **34**, 954 (1929).
 (31) J. A. Leermakers, B. H. Carroll, and C. J. Staud, J. Chem. Phys. **5**, 875 (1937).
 (32) F. Lellev. Nature **138**, 1009 (1036).

- (32) E. E. Jelley, Nature 138, 1009 (1936).
 (33) G. Scheibe, L. Kandler, and H. Ecker, Naturwiss. (33) G. Scheibe, E. Rahder, and H. Zeker, recent reserve and the second secon

- (30) G. Friedel, Ann. de Finsk 18, 213 (1922), Cr. also D. Vorländer, *Chem. Krystallog. d. Flüssigkeiten*, (Akad. Verlag, Leipzig, 1924); K. Herrmann, Zeits. f. Krist. 92, 49 (1935).
 (37) G. Scheibe, A. Schöntag, and F. Katheder, Naturwiss.
- 27, 499 (1939)
- G. Scheibe and L. Kandler, Naturwiss. 26, 412 (1938). (38)
- (39) R. S. Mulliken, J. Chem. Phys. 2, 782 (1934); ibid., 3, 573 (1935).
- (40) E. E. Jelley (private communication).
 (41) Cf. H. Ecker, Kolloid Zeits. 92, 53 (1940); also G. Scheibe (reference 35).
- (42) S. E. Sheppard, Science 93, 42 (1941).
 (43) J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).
- (44) R. Robinson, Rapports 4me Conseil de Chem. Inst. *Solvay*, Bruxelles (Paris, 1931), p. 500. (45) G. Scheibe, Kolloid Zeits. **82**, 1 (1938).
- (46) R. S. Mulliken, J. Chem. Phys. 7, 32 (1939). (We are indebted to Dr. G. Kornfeld for drawing our attention to this.)
- (47)Unpublished work with R. H. Lambert.
- (48) W. T. Astbury, Trans. Faraday Soc. 29, 193 (1933). (49) Unpublished work with A. L. Geddes.
- (50) K. Linderstrom-Lang, Trans. Faraday Soc. 31, 324 (1935)
- (51) Unpublished work with R. D. Walker.
- (52) G. Schwarz, Sci. et Ind. Photo 8, 97 (1937).
- (53) C. D. Carpenter and E. R. Jette, J. Am. Chem. Soc. **45**, 578 (1923).
- (54) Private communication of unpublished observations. (55) E. E. Jelley, Ind. Eng. Chem. Anal. Ed. **13**, 196 (1941).
- (56) E. T. Wherry and E. Q. Adams, J. Wash. Acad. Sci.
- (50) D. 1. White y and D. 2. Transport of the second sec
- (58) J. M. Robertson, Proc. Roy. Soc. A142, 674 (1933); 140, 79 (1933).
- (59) K. S. Krishnan and P. K. Seshan, Proc. Ind. Acad. Sci. A18, 487 (1938).
 (60) E. Hertel and H. W. Bergk, Zeits. f. physik. Chemie
- B33, 319 (1936).

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FIG. 30. Model of mesophase filament. H₂O molecules cross linking cyanine nitrogens. $\overline{\mathbf{X}}$ anions aligned along filament axis, each between two water molecules.