of mathematical work but has deprived them at the same time of a type of analysis which forms in fact a necessary mode of presentation of the underlying concepts of differential geometry itself. For these reasons the reviewer does not consider this text desirable for graduate instruction in any American university.

The binding and printing are excellent, and the University of Chicago Press is to be congratulated for its part of the work.

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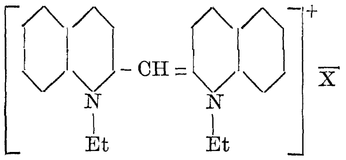
SPECIAL ARTICLES

THE STRUCTURE OF THE MESOMORPHIC PHASE OF CERTAIN CYANINE DYES

BASED partly on extensive work to be presented by the writer and colleagues, a structure is proposed for the aggregated phase of *di-ethyl-ψ-cyanine* and related dyes which give a remarkable new absorption (and fluorescence) band. Discovered by E. E. Jelley[1] and independently by G. Scheibe,[2] it is convenient to term it a Z-band, and the corresponding aggregation of the dye, a Z-state.

On silver halides[3] the dye cations are adsorbed edge-on at the ionizable hydrophile (ventral) aspect of the planar molecule. The counter-ion is furnished by the silver halide lattice. At high adsorption densities the dye cations form packets of parallel ordered molecules, like card-packs, but with an interval of ca 3.7 Å between adjacent cations. These "card-packs," but with an important modification, are regarded as constituting the separately sensitizing dye "aggregates" of Leermakers, Carroll and Staud[4] and the "nematic" filaments discovered by Jelley in aqueous suspension. From optical observations Jelley showed that the new absorption band corresponds to a light vibration *parallel* to the axis of the filament, and in the z-axis of the resultant crystal. In our model thus far presented this means a light-vibration perpendicular to the planes of the units of the card-packs. Conclusions similar in essentials were reached by Scheibe,[5] but from adsorption experiments on mica he considered that alternate parallel molecules are staggered. He has suggested that the forces orienting and holding the units in parallel apposition are inductive forces of the p-electrons of the (heterocyclic and aromatic) nuclei and of the chain joining these. The structure proposed here postulates a very different type of linkage, *viz., water molecules,* coordinated intermolecularly between *opposite* terminal nitrogen atoms of the parallel resonance chains. A reversible effect of moisture on the production and disappearance of the Z-band for ψ-cyanine adsorbed to silver bromide was observed by Leermakers, Carroll and Staud,[4] and confirmed by Sheppard, Lambert and Walker;[3] the fundamental importance of water for the Z-state of unadsorbed dye has been shown by Jelley[6] and equally recognized by Scheibe.[5]

The ψ-cyanine has the formula:



where $\overline{X}$ is a univalent anion, and the large cation derives its positive charge from the resonance hybrid between states having each N-atom alternately in the quaternary state. We will symbolize such a molecule as $N_p \sim N_p$, where the subscript represents the nuclear portion (and *its electromeric effect*) and is changed accordingly. Thus for a non-symmetrical cyanine we may write $N_{p'} \sim N_q$, where p' denotes the same nucleus as p, but changed because joined with q. In the Z-state we supposed these cations arranged in parallel, and between each successive opposite pair of molecules at least one water molecule—H_2O—coordinated between each pair of opposite N-atoms. Any adjacent pair of dye molecules form a cell or doublet; in the extended filament $(N_p \sim N_p)n$, where n is the number of cells, if there are just two H_2O molecules per cell, the ratio of H_2O/dye molecules will vary from 1:1 for $n=1$ to 2:1 for $n=\infty$ and similarly for other basic H_2O values per cell. These interstitial "hydrate" molecules furnish the mobile electrons permitting (in the ground state) inter-molecular or cross-resonance between the N-atoms of adjacent molecules, which evidently must be coupled, or in phase relationship, with the intramoleculer resonance of the component dye molecules. Hence, a condition of alternation or pulsation will obtain between successive adjacent cells, which is important as permitting undamped transfer of excited states throughout a filament. *These intermolecular resonance linkages through "hydrate" water molecules are supposed to furnish the characteristic*

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[1] E. E. Jelley, *Nature,* 138: 1009, 1936; *ibid.,* 139: 631, 1937.

[2] G. Scheibe, *Angew. Chem.,* 50: 51, 1937.

[3] S. E. Sheppard, *Atti. X. Congress Internat. Chim.* (Rome, 1938, V. I. pp. 235–283; S. E. Sheppard, R. H. Lambert and R. D. Walker, *Jour. Chem. Phys.,* 7: 265, 1939.

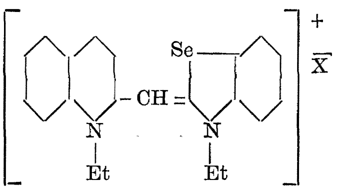
[4] J. A. Leermakers, B. H. Carroll and C. J. Staud, *Jour. Chem. Phys.,* 5: 878, 1937.

[5] G. Scheibe, *Koll. Zeitschr.,* 82: 1, 1938; *Angew. Chem.,* 52: 631, 1938.

[6] Unpublished work, these laboratories.

Z-band on excitation by light. The particular electron distribution in water molecules[7] is believed to lend itself to this and other participation of "hydrate" water in light absorption.

From the necessary alternation of "inactive" and "active" cells, the band intensity will grow with length of filament, but the characteristic frequency or wavelength will not change. Thus the structure behaves like the *meta*-bonded rather than the *para*-bonded polyphenyl.[8] Symbolizing such a cross-resonance by $N_p \times N_q$ the frequency, intensity and purity (sharpness) of the Z-band will depend upon p and q, hence on the actual structure of the component molecules, because the *basicity* of the related N-atoms is determinative.[9] For example, the dye *di-ethyl-ψ-selena-cyanine* was found by Scheibe[5] to give a Z-band. But



compared with that of the *symmetrical* ψ-cyanine it was relatively weak and diffuse and at shorter wavelength. This is predicated on the structure proposed. The non-symmetrical ψ-cyanine, when ordered in a Z-state, can give, according to the apposition of the molecules in the cells, *three* intermolecular bands, *viz.*, $N_{p'} \times N_q$, $N_{p'} \times N_{p'}$, and $N_q \times N_q$. Hence the observed band is relatively broad and weak. Lower intensity can be predicated also with asymmetric dyes because parallel paired identical intermolecular transitions are not possible. This condition, as shown by R. S. Mulliken[10] in molecular spectra (*e.g.*, H_2 molecule) makes for great intensification. On the structure proposed, a mixture of two dissimilar but pairable dyes can give, in addition to their own iso-molecular cells or doublets, hybrid doublets and two new related Z-bands, *e.g.*, with ψ-cyanine and the ψ-selena-cyanine, $N_p \times N_{p'}$ and $N_p \times N_q$. This is the interpretation of Scheibe's important observation with these two dyes; he found with mixtures a series of intermediate bands which could not be compounded by simple superposition of the 100 per cent. bands. Actually, his data show definite breaks in the neighborhood of 1 : 1 molecular composition, but such breaks might occur at other proportions, depending upon the degree of hybrid doublet formation in the filaments.

Scheibe has objected to Jelley's "nematic phase" from evidence that the Z-state occurs independently of the anion. However, not only has Jelley[6] obtained definite evidence of anion influence, but our conductivity data indicate disappearance of anions in the Z-state. The structure now proposed indicates a new type of nematic phase, constituted of plurimolecular filaments instead of elongated molecules. Similar mesomorphic phases may occur with other dyes than the cyanines, *e.g.*, with the porphyrins and phthalocyanines. With these, however, intermolecular hydrogen bridges bonding key atoms seem more probable, with different conditions for intermolecular resonance.

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[7] J. D. Bernal and R. H. Fowler, *Jour. Chem. Phys.*, I: 515, 1933.

[8] *Cf.* A. E. Gillam and D. H. Hey, *Jour. Chem. Soc.*, p. 1170, 1939.

[9] L. G. S. Brooker, R. H. Sprague, C. P. Smyth and G. L. Lewis, *Jour. Am. Chem. Soc.*, 62: 1116, 1940.

[10] R. S. Mulliken, *Jour. Chem. Phys.*, 7: 32, 1939.

ASSOCIATION OF PHOSPHATASE WITH A MATERIAL IN KIDNEY SEDIMENTABLE AT HIGH SPEED AND ITS LIBERATION BY AUTOLYSIS[1]

EXTRACTS of many normal and tumor tissues have been shown to contain large amounts of material which can be sedimented in the ultracentrifuge at 27,000 r.p.m. for one hour. The viruses of fowl leukosis and sarcoma[2,3] substances showing cytochrome oxidase and succinic dehydrogenase[4] activity, the heterogenetic, tissue and organ specific antigens,[5,6] have been shown to be associated with this fraction.

The effect of autolysis on tissue extracts was studied in an attempt to obtain information on the relation of the heavy fraction to biologically active constituents of tissues which are of much lower molecular size. Kidney phosphatase was selected because it is usually prepared from autolyzed tissues and is extremely stable in solution.

Kidneys from ten mice were divided into two equal parts. One part (A) was allowed to autolyze at room temperature for a week with 20 volumes of distilled water and a small amount of toluene. The other part (B) was kept frozen at −60° until the first half was autolyzed. It was then ground with sand and 20 volumes of distilled water and toluene. Sodium chloride was added to both solutions to make a final concentration of 0.9 per cent., and the material was centrifuged in the cold and at 8,000 r.p.m. for 15 minutes. These crude extracts were centrifuged at 27,000 r.p.m. during one hour, the supernatants decanted, and the sediments resuspended in the original volume of saline.

These fractions from autolyzed and non-autolyzed

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[1] This investigation was supported by grants from the Anna Fuller Fund and the Jane Coffin Childs Memorial Fund for Medical Research.

[2] E. A. Kabat and J. Furth, *Jour. Exp. Med.*, 71: 55, 1940.

[3] A. Claude, SCIENCE, 90: 213 ,1939; 91: 77, 1940.

[4] K. G. Stern, Cold Spring Harbor Symposia on Quantitative Biology, 7: 312, 1939.

[5] J. Furth and E. A. Kabat, SCIENCE, 91: 483, 1940.

[6] W. Henle and L. A. Chambers, SCIENCE, 92: 313, 1940.