

## LETTERS TO THE EDITORS

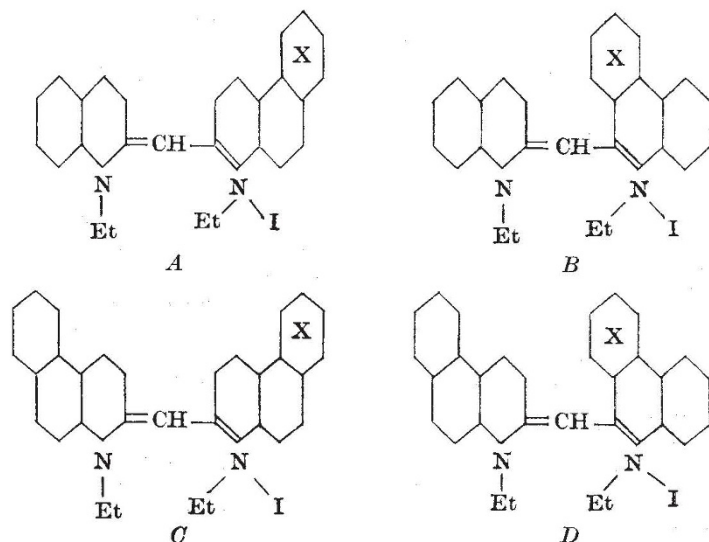
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IN THE PRESENT CIRCUMSTANCES, PROOFS OF "LETTERS" WILL NOT BE SUBMITTED TO CORRESPONDENTS OUTSIDE GREAT BRITAIN.

NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 391. CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

## Steric Influence in Optically Sensitizing Dyes

In a paper by L. G. S. Brooker and C. H. Keyes<sup>1</sup>, the preparation is described of certain isomeric cyanine dyes having the following formulæ :



Brooker and Keyes noted that dyes *A* and *C* were strong sensitizers, while *B* and *D* did not sensitize. These substances were investigated later by J. A. Leermakers, B. H. Carroll and C. J. Staud<sup>2</sup>, who confirmed the sensitizing results. But in addition they observed strong adsorption to gelatino-silver bromide grams of *all* the isomers, and "pronounced absorption maxima (by reflection)".

In recent work on these compounds we have observed, first, that the *rate* of adsorption to silver bromide from aqueous gelatin solution of dyes *B* and *D* is very much lower than for dyes *A* and *C*, although much the same adsorption densities (in molecules per unit area) were ultimately obtained. While this might account to some extent for lack of sensitizing (because of insufficient time of treatment), it does not appear an entirely sufficient explanation. A further complication was encountered in the form of a strong tendency of isomers *B* and *D* to bleach or fade, even in alcoholic solutions, probably by autoxidation.

On constructing the formulæ for these isomers, using correct bond angles and interatomic distances, it can be seen that complete coplanarity of the molecule is not possible in case *B* without bringing the 3,4-benzo-radicle within a distance of *ca.* 1.7 Å. of the opposite quinoline group, and in case *D*, of

the opposite  $\beta$ -naphtho-quinoline. This condition is not improved by 180° rotation of a nuclear group about a =CH-CH< linkage to an alternate coplanar stereoisomer. The same condition obtains for 1,1'-diethyl-3',4'-dibenzo-2,2'-carbo-cyanine iodide (having three methines between two phenanthridine nuclei), which was found also not to sensitize, but does not for 1,1'-diethyl-5,6,5',6'-dibenzo-2,2'-carbo-cyanine iodide (having three methines between two  $\beta$ -naphtho-quinoline nuclei), which sensitizes strongly, and also not for 1,1'-diethyl-3,4,5',6'-dibenzo-2,2'-carbo-cyanine iodide (having three methine groups between one  $\beta$ -naphtho-quinoline and one phenanthridine nucleus), and which definitely sensitizes.

On examining the absorption spectra (in alcoholic solution) of the non-coplanar isomers, it was observed that the half-width of the absorption band of maximum wave-length was much greater for the non-coplanar isomers than for their isomers, and the molecular extinction coefficients at  $\lambda_{\max}$  were much less. There is also evidence that the yields are considerably lower than in synthesis of similar dyes which can readily assume a coplanar form of the fully extended (*trans-trans*) molecule.

It was suggested by Leermakers, Carroll and Staud<sup>2</sup> that "the phenyl group (*X*) in dyes *B* and *D* interferes with the proper exchange of energy between dye and silver halide, because of some steric effect in the molecule". The steric effect we believe to be the inhibition of coplanarity (cf. for analogous cases C. J. B. Clewes and K. Lonsdale<sup>3</sup>, also J. M. Robertson<sup>4</sup>) of the dye molecule, and consequent interference with its resonance. In a fuller account the relation of coplanarity to adsorption (cf. Sheppard, Lambert and Walker<sup>5</sup>) will be discussed, as well as the temperature influence. The steric factor here indicated is of far-reaching importance in regard to the effects of substituents in the polymethine dyes.

S. E. SHEPPARD.

R. H. LAMBERT.

R. D. WALKER.

Research Laboratories,  
Eastman Kodak Company,  
Rochester, N.Y.

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<sup>1</sup> *J. Amer. Chem. Soc.*, **58**, 659 (1936).

<sup>2</sup> *J. Chem. Phys.*, **5**, 878 (1937).

<sup>3</sup> *Proc. Roy. Soc., A*, **161**, 493 (1937).

<sup>4</sup> *J. Chem. Soc.*, 232 (February 1939).

<sup>5</sup> *J. Chem. Phys.*, **7**, 256 (1939).