



Temperature studies on allopolar isomerism
by Carol Linn Enwall

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry
Montana State University
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Abstract:

Known allopolar and meropolar dyes were synthesized. Solutions of the two allopolar dyes were prepared in various solvent systems. Visible absorption spectra were taken at four different temperatures. The extinction coefficients of the meropolar and holopolar forms of the allopolar dyes were determined, Entropy and enthalpy values for the equilibrium constants of the allopolar dyes were calculated.

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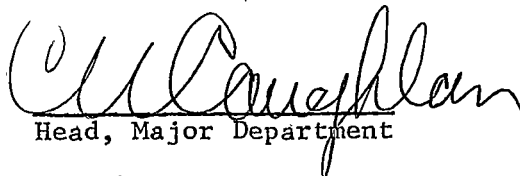
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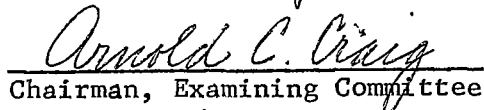
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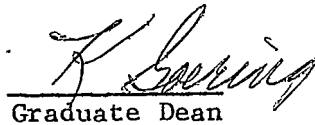
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ABSTRACT

Known allopolar and meropolar dyes were synthesized. Solutions of the two allopolar dyes were prepared in various solvent systems. Visible absorption spectra were taken at four different temperatures. The extinction coefficients of the meropolar and holopolar forms of the allopolar dyes were determined. Entropy and enthalpy values for the equilibrium constants of the allopolar dyes were calculated.

INTRODUCTION

Cyanine dyes can hardly be identified as a new class of heterocyclic compounds since their beginnings date back to 1856.¹ Quinoline was one of the first heterocyclic compounds to be isolated from natural sources, and because it was readily available, dyes containing quinoline nuclei were the type most commonly studied until the 1920's. In the 1920's the rediscovery of Hoffman's work with benzothiazole bases led to a new field of cyanine dye chemistry.²

Organic dye molecules having the ability to absorb visible light contain what is called a chromophoric system. The systems of greatest importance to this paper are the amidinium ion and the amide moiety. The two hetero atoms contained in these systems are nitrogen and oxygen. Each is capable of existing in two adjacent states of covalency. The charge-sharing ability between the hetero atoms is due to a vinylene residue (-C=C-) taken n times, where n is any positive integer. An example of an amidinium ion system is the following generalized thiacyanine:

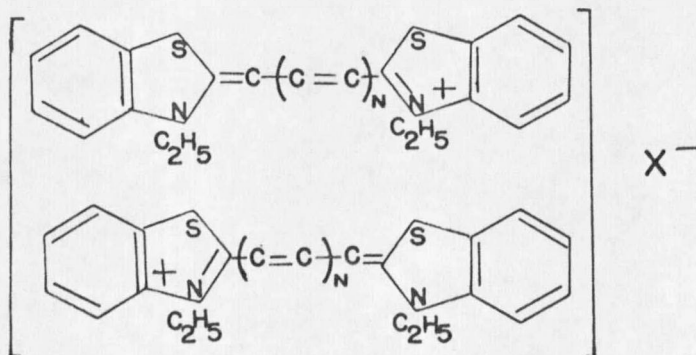


Fig. 1. AMIDINIUM ION SYSTEM of a THIACYANINE

The cation of the symmetrical cyanine dye in figure 1 is shown in two identical structures; the only difference is in the arrangement of the electrons. As mentioned earlier, the nitrogen atom is capable of existing in two states of covalency. Therefore, the nitrogen atom may exchange its two roles by acting as either an electron donor or basic nitrogen, or as an electron acceptor or acidic nitrogen.

A second classification of dye compounds containing two different nuclei is identified as the merocyanines.³ The typical structure of a merocyanine dye is shown in figure 2. Rather than containing two basic nuclei as does a cyanine, figure 1, a merocyanine is derived from one basic nucleus and one acidic nucleus. Merocyanines also differ from cyanine dyes in the fact that they are un-ionized. One distinguishing characteristic of merocyanine dyes is the sensitivity of their absorptions toward changes of solvent. The direction and the amount of change are dependent upon the degree of basicity and acidity of the nuclei.

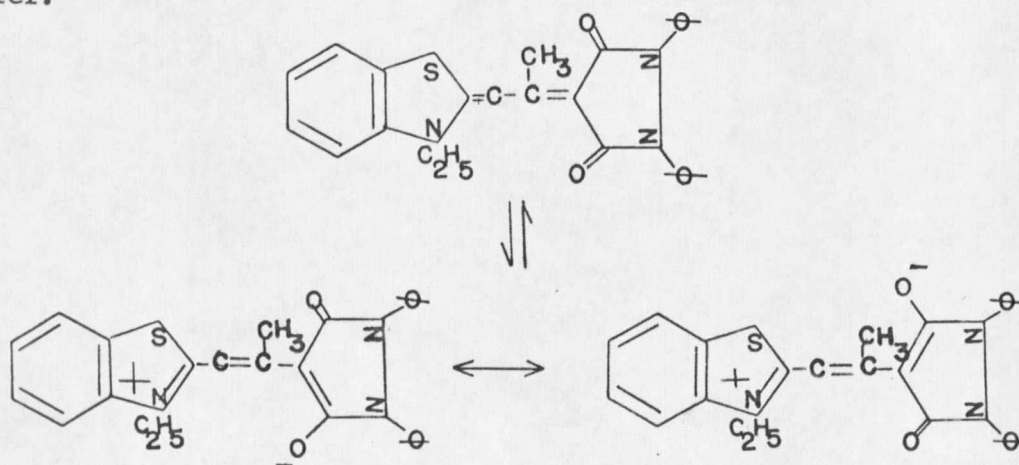


Fig. 2. EQUILIBRIUM and RESONANCE STRUCTURE of a MEROCYANINE DYE

Allopolare cyanine dyes are trinuclear dyes which contain two basic nuclei bonded to an acidic nucleus.⁴ A model of an allopolare cyanine dye (Fig. 3,A) clearly indicates that the overlapping of the Van der Waals' radii makes it impossible for all three nuclei to remain coplanar simultaneously. So that partial resonance may be preserved, two of the three nuclei may be coplanar, requiring that the third nucleus is in a plane perpendicular or nearly perpendicular to the other two (Fig. 3,B,C). An alternative suggestion is that all three nuclei are slightly turned out of the plane, decreasing the resonance interaction between the rings.

It is known that the chain methyl merocyanine dye, 4-(3-ethyl-2-benzothiazolinylidene)-isopropylidene-1,2-diphenyl-3,5-pyrazolidinedione, (Fig. 2), absorbs at 475 m μ and the 3,3'-diethyl-thiacarbocyanine iodide (Fig. 1) absorbs at 550 m μ .

The ultraviolet absorption spectrum of the trinuclear dye, 4- [1,3-Bis(3-ethyl-2-benzothiazolinylidene)-isopropylidene] -1,2-diphenyl-3,5-pyrazolidinedione, exhibits absorption maxima at 475 m μ and 550 m μ . These absorption maxima may be attributed either to two different types of transition or to a single type of transition in two different conformers of the molecule.

