Determination of the relative steric sizes of alkyl groups using a calculational approach
by Ann Marie Bowler

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University
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Abstract:
Allopolar isomerism in merocyanine dye models was studied using molecular mechanics, semi-empirical, and ab initio techniques. The relative steric sizes of alkyl groups were determined by comparing the energy differences between meropolar and holopolar conformations of a model system. The results indicate that methyl, ethyl, and propyl groups have approximately the same amount of steric bulk when they are in a 1,3 sandwiched configuration and, also, that an isopropyl group has significantly more steric bulk than the straight chain alkyl groups.

MNDO calculations also showed a significant amount of charge separation in the holopolar isomers of the model system. Because these results agree with experimental data and with predictions made on the basis of resonance theory, it is suggested that MNDO calculations may provide a useful means for predicting the charge distribution in other delocalized systems.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Signature _Ann Marie Bowler_

Date _November 3, 1986_

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES--continued

LIST OF FIGURES--continued

ABSTRACT

Allopolar isomerism in merocyanine dye models was studied using molecular mechanics, semi-empirical, and ab initio techniques. The relative steric sizes of alkyl groups were determined by comparing the energy differences between meropolar and holopolar conformations of a model system. The results indicate that methyl, ethyl, and propyl groups have approximately the same amount of steric bulk when they are in a 1,3 sandwiched configuration and, also, that an isopropyl group has significantly more steric bulk than the straight chain alkyl groups.

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INTRODUCTION

Since their discovery in the 1930's, members of the subclass of cyanine dyes known as merocyanines have found wide use as photographic sensitizers and as intermediates for the synthesis of larger dyes. (See Reference 1.) Merocyanines, which are derived from an acidic heterocyclic nucleus and a basic heterocyclic nucleus, contain the primary chromophore shown in Figure 1. The merocyanines are best represented as a hybrid of two resonance forms. One of these resonance species, (1a), is neutral; and the other, (1b), has permanent charge separation brought about by conjugation of the two nuclei through a methine linkage.

$$\ce{>\overset{..}{N}-CH=CH-C{<}^{O}} \longleftrightarrow \ce{>\overset{\oplus}{N}=CH-CH=C{<}^{O^{\ominus}}}$$

(1a)   (1b)
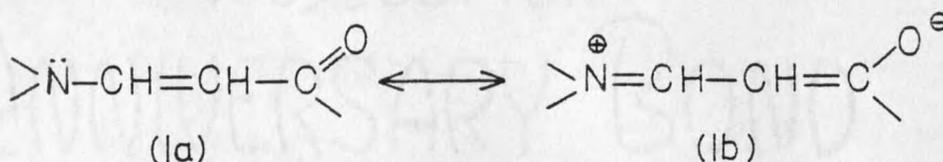
Figure 1. Chromophoric System of a Dipolar
Amidic Merocyanine System.

Allopolar cyanine dyes are composed of three heterocyclic nuclei. Two of the nuclei contain heteroatoms that can act as electron donors, or bases; and the third contains a heteroatom that can act as an electron acceptor, or acid. Because each of the nuclei can exist in two distinct valence states, the cyanines are also best described as resonance hybrids.

Some of the cyanines have been the subject of considerable investigation because they have been found to exist in two distinct conformations. The trinuclear dye (2) is sterically crowded; and it is impossible for all three nuclei to be simultaneously coplanar. However, if two nuclei remain coplanar and the third resides in a plane perpendicular to the other two, resonance stabilization is partially preserved; and steric crowding is significantly reduced. This situation gives rise to two possible conformations.

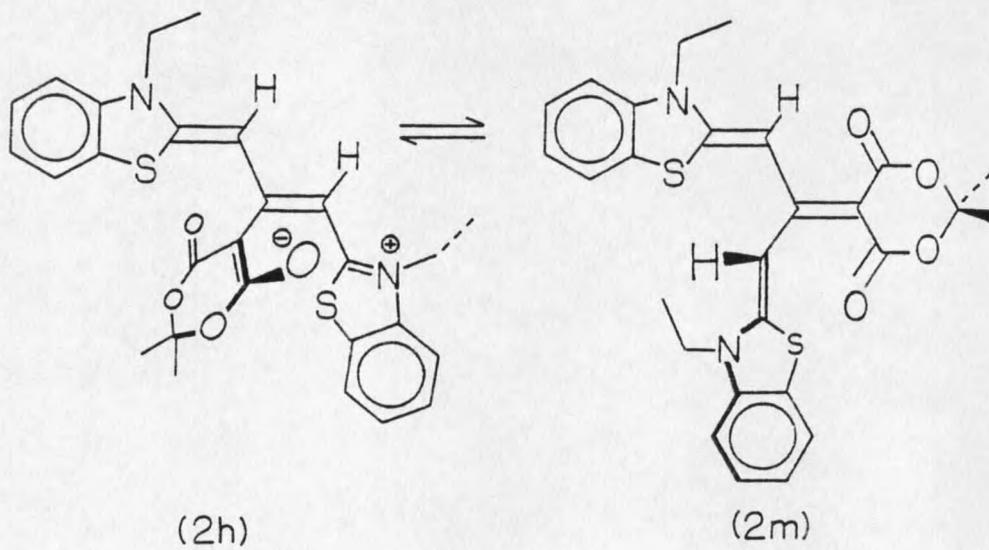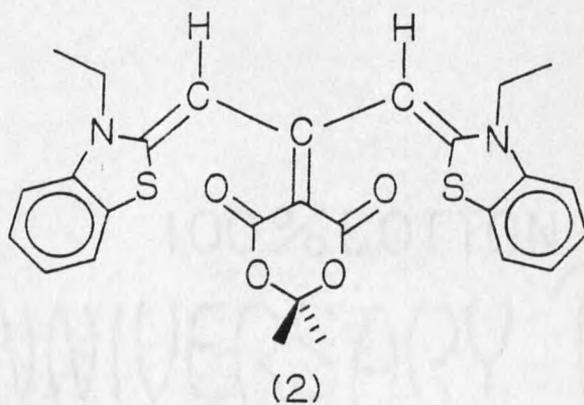Figure 2. Conformational Equilibrium of a
Trinuclear Cyanine Dye.

The so-called holopolar isomer, (2h), has permanent charge separation; and, although it is polar, the meropolar isomer, (2m), exists as an uncharged species. Since the system is resonance stabilized, interconversion between the two isomers requires rotation around three bonds having total bond orders between 1.0 and 2.0. It has been demonstrated that the equilibrium in Figure 2 is highly solvent sensitive, with the holopolar isomer predominating in polar solvents. (See Reference 2.) The term allopolar isomerism is used to describe solvent-sensitive, ground state conformational equilibria such as this.

Interest in the present investigation stems from the discovery that the methyl substituted merocyanine, (3m), exhibits what appears to be allopolar isomerism. As solvent polarity is increased, the typical merocyanine absorption at about 460 nm becomes less intense; and absorptions in the ultraviolet region, which are presumably due to the propenylbenzothiazolium salts and diketodioxane anion, increase. An equilibrium such as the one shown in Figure 3 would be consistent with this observation and would represent the first reported incidence of allopolar isomerism in a simple merocyanine dye.
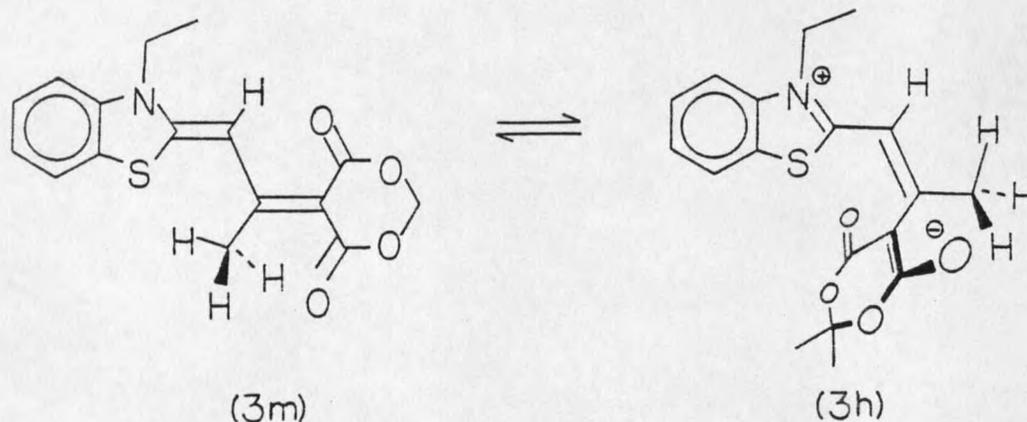
Figure 3. Conformational Equilibrium of a
Merocyanine Dye.

Substituents that increase the steric hindrance of a
dye can alter several of its properties including absorption
wavelength, photographic sensitization, and crystallization
and aggregation patterns. Therefore, the effects of steric
crowding on dye properties have been of considerable
historical importance. Deviations from planarity induced by
steric crowding in pyrrole dyes were demonstrated
spectrophotometrically as early as 1947. (See Reference 3.)
More recently, x-ray crystallographic studies of highly
overcrowded cyanines have shown angles of as much as 60
degrees between the planes defined by heterocyclic rings.
(See Reference 4.) It is anticipated that the equilibrium
between (3h) and (3m) will not only be solvent sensitive but
also highly "bulk" sensitive.

As the R group in (4m) is changed from hydrogen to methyl to ethyl to propyl, and finally, to isopropyl, the equilibrium should systematically shift toward the holopolar isomer, (4h).   Because the 1,3 sandwiched configuration of (4m) doesn't allow steric crowding to be reduced by rotation of the alkyl groups, the position of the equilibrium should provide a measure of the relative steric sizes of these groups.

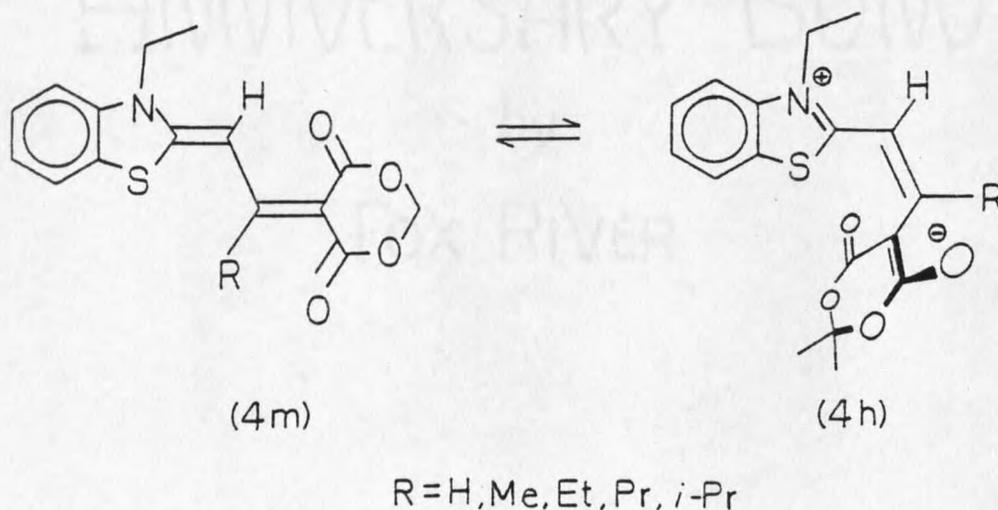(4m)   (4h)

R = H, Me, Et, Pr, i-Pr

Figure 4. Conformational Equilibria of Sterically
Crowded Merocyanines.

The recent "birth" of theoretical calculations as powerful tools in structural chemistry seems to lend itself to this situation. Darden, et. al., were able to successfully calculate the minimum energy conformations of highly conjugated diethylstilbestrol isomers using molecular mechanics, semi-empirical, and ab initio techniques. (See Reference 5.) Because the basic structure of the merocyanines is similar to these compounds, it was thought that the effect of steric crowding on the equilibrium between (4m) and (4h) could be studied using a calculational approach.

The primary purposes of this investigation were: (1) to determine the level of sophistication at which calculations could be performed on model dye systems; (2) to test the ability of computational methods to mimic experimental observations; and (3) to determine the relative steric sizes of alkyl groups by calculating the energies of the meropolar and holopolar conformations of merocyanine models.

METHODS AND RESULTS

Molecular mechanics, semi-empirical, and ab initio methods were employed in the present study. These methods are discussed in detail in Reference 6. Semi-empirical calculations were done primarily at the MNDO level; and the ab initio methods were mainly confined to single point, closed shell, restricted Hartree-Fock calculations on small model systems. All calculations were performed using a DIGITAL VAX/11 780 system with the Molecular Mechanics 2, Molecular Orbital Package, and Gaussian 80 programs made available through the Quantum Chemistry Program Exchange. Some additional information about using the Molecular Mechanics 2 and Gaussian 80 programs is provided in the Appendices.

Initial attempts to study the merocyanine dye skeleton shown in Figure 5 using the Molecular Mechanics 2 program were, for the most part, unsuccessful because the program is not parameterized to treat conjugated pi systems. The program gave "realistic" results for compound (5a); but when R was changed to methyl and then ethyl, it produced minimum energy conformations that were "bent" in the plane, rather than twisted out of the plane. This result should have been anticipated because the torsional energy terms that the