



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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Ann Marie Bowler

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.

November 3 1986
Date

Arnold C. Craig
Chairperson, Graduate Committee

Approved for the Major Department

Nov 3, 1986
Date

Edwin H. Abbott
Head, Major Department

Approved for the College of Graduate Studies

November 20, 1986
Date

Henry L. Parsons
Graduate Dean

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TABLE OF CONTENTS

	PAGE
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	ix
INTRODUCTION.....	1
METHODS AND RESULTS.....	8
CONCLUSIONS.....	53
LITERATURE CITED.....	56
APPENDICES.....	58
APPENDIX A - MOLECULAR MECHANICS 2.....	59
APPENDIX B - GAUSSIAN 80	73

LIST OF TABLES

TABLE	PAGE
I. Gaussian 80 Test Results.....	11
II. Final Energies from MINDO/3, MNDO and AM1 Geometry Optimizations.....	12
III. Gaussian 80 Results for Hydrogen Substituted Dioxole Models.....	14
IV. MNDO and Gaussian 80 Results for Hydrogen and Methyl Substituted Dioxole Isomers.....	16
V. MNDO and Gaussian 80 Results for Diazoline Models.....	20
VI. Net Atomic Charges for Dioxole and Diazoline Models.....	23
VII. MNDO Results for Thiazoline Models.....	26
VIII. MNDO Results for Alkyl Substituted Dye Skeleton.....	28
IX. Computational Statistics for Alkyl Substituted Dye Skeleton.....	29
X. Z-Matrix Parameters for Methanol.....	65

LIST OF FIGURES

FIGURE	PAGE
1. Chromophoric System of a Dipolar Amidic Merocyanine System.....	1
2. Conformational Equilibrium of a Trinuclear Cyanine Dye.....	3
3. Conformational Equilibrium of a Merocyanine Dye.....	5
4. Conformational Equilibria of Sterically Crowded Merocyanines.....	6
5. Merocyanine Dye Skeleton Studied Using MM2.....	9
6. Torsional Angle Marked for Optimization by MNDO.....	17
7. Conformation of (11m) Before and After MNDO Torsional Angle Optimization.....	18
8. Proposed Hydrogen Bonding Effect in (13h).....	21
9. Proposed Resonance Structures for (13h).....	24
10. Dye Skeleton Studied Using MNDO.....	27
11. Final Geometry of Meropolar Hydrogen Isomer.....	36
12. Final Geometry of Holopolar Hydrogen Isomer.....	37
13. Net Atomic Charges for Hydrogen Isomers.....	38
14. Highly Crowded Conformation of Hydrogen Isomer.....	39
15. Final Geometry of Meropolar Methyl Isomer.....	40
16. Final Geometry of Holopolar Methyl Isomer.....	41
17. Net Atomic Charges for Methyl Isomers.....	42

LIST OF FIGURES--continued

FIGURE	PAGE
18. Final Geometry of Meropolar Ethyl Isomer.....	43
19. Final Geometry of Holopolar Ethyl Isomer.....	44
20. Net Atomic Charges for Ethyl Isomers.....	45
21. Final Geometry of Meropolar Propyl Isomer.....	46
22. Final Geometry of Holopolar Propyl Isomer.....	47
23. Net Atomic Charges for Propyl Isomers.....	48
24. Final Geometry for Meropolar Isopropyl Isomer.....	49
25. Final Geometry for Holopolar Isopropyl Isomer.....	50
26. Net Atomic Charges for Isopropyl Isomers.....	51
27. Relative Stabilities of Alkyl Substituted Dye Skeleton.....	52
28. N1-N2-N3-N4 Torsional Angle Convention.....	62
29. Example of Index Definition.....	63
30. Orientation of Methanol Molecule.....	66
31. Data File AMM.INP for Converting from Z-Matrix to Cartesian Coordinates Using Program CARTCOORD.....	67
32. Command File to Run Program CARTCOORD.....	67
33. Output File AMM.C00 from Program CARTCOORD.....	68
34. Breakdown of a Molecular Mechanics Data File.....	69
35. Complete Data File for a Molecular Mechanics Run.....	70
36. Command File to Run the Molecular Mechanics Program MM2NEW.....	71
37. Command File to Run MM2NEW as a Batchjob.....	72

LIST OF FIGURES--continued

FIGURE	PAGE
38. Data File for a Gaussian 80 Run.....	76
39. Breakdown of a Gaussian 80 Data File.....	77
40. Command File to Run Gaussian 80 as a Batchjob.....	78

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.

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.

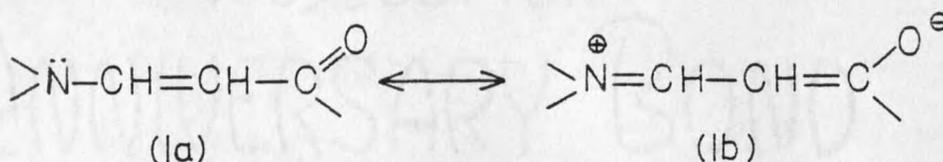


Figure 1. Chromophoric System of a Dipolar Amidic Merocyanine System.

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.

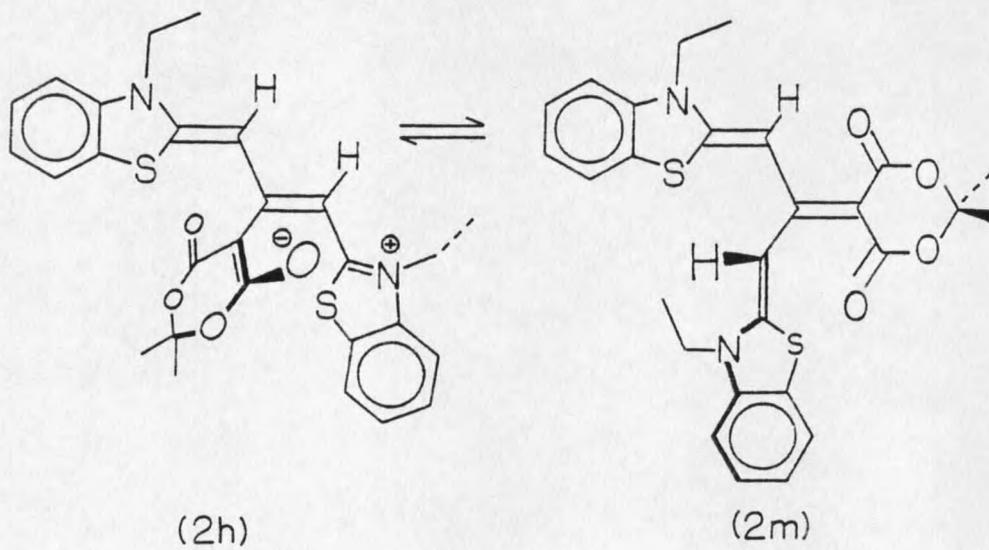
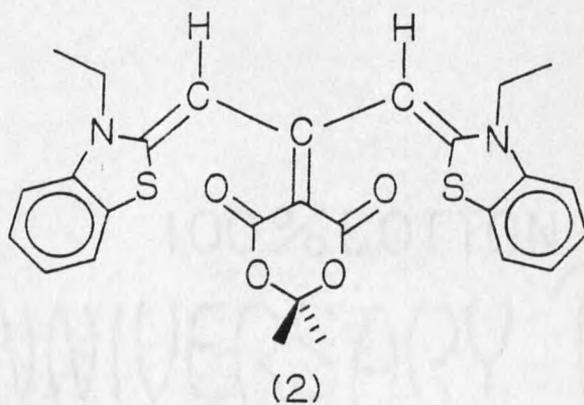


Figure 2. Conformational Equilibrium of a Trinuclear Cyanine Dye.

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 allopolarm 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 allopolarm 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 allopolarm isomerism in a simple merocyanine dye.

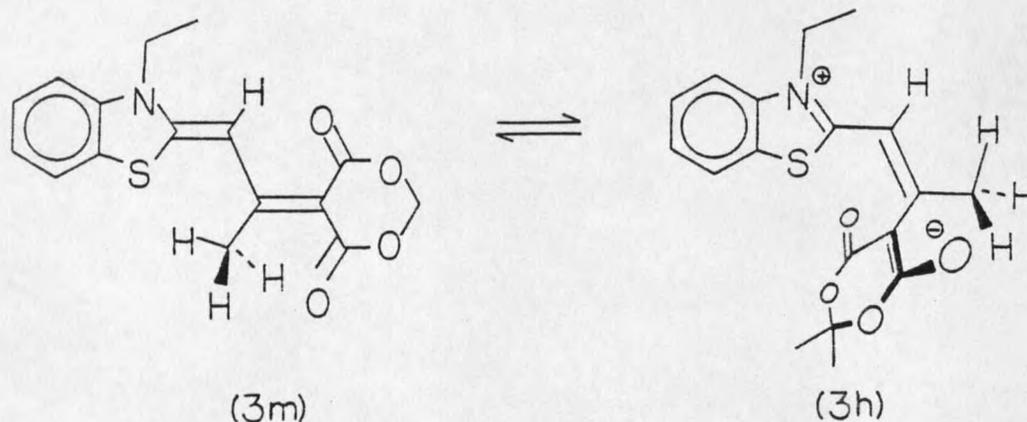


Figure 3. Conformational Equilibrium of a Merocyanine Dye.

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.

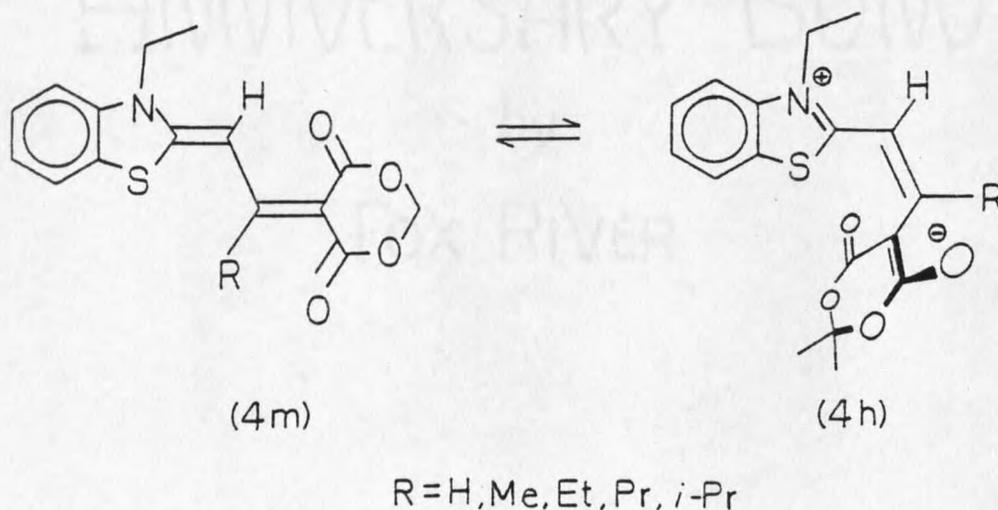


Figure 4. Conformational Equilibria of Sterically Crowded Merocyanines.

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

