



The synthesis and characterization of organic materials for non-linear optic studies
by David F Duncan

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Cyanines, merocyanines, allopolar and related dyes have been known for more than a century and have been utilized extensively in the photographic industry. However, in the last twenty years these compounds have become important in the field of nonlinear optics (NLO). As a result new synthetic methodologies are needed to prepare authentic and novel cyanines, merocyanines, allopolar and related dyes, as well as, some insight to their physical properties.

The synthesis of optically active merocyanines has been accomplished using chiral benzothiazolium salts which are then converted into dyes using traditional dye chemistry. Chiral acetamides can undergo a ring closure with chloroacetone to form optically active thiazolium salts which can be reacted with Dains intermediates to form novel thiazole derived merocyanines.

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Chain methyl merocyanines and 3-ethyl-2-bisanilo-isopropylidenebenzothiazoline have been used to prepare several intermediates (i.e.

3-ethyl-5-[2-(3-ethyl-2-benzothiazolinylydene)-(2-anilomethylethylidene)]-rhodanine) which have been utilized in the formation of both neocyanine and allopolar dyes. These dyes are trinuclear dyes which have two or more possible conformations that are in equilibrium with one another. Each conformer has a different type of chromophore which is represented by either a holopolar form (cyanine-like) or a meropolar form (merocyanine-like). These dyes have not been tested for NLO properties, but have the same properties as their straight chain cyanines and merocyanines counterparts which make them excellent candidates for NLO studies.

This thesis discusses the synthesis and characterization of several authentic straight chain merocyanines, as well as the synthesis and characterization of approximately five different types of new dyes. This thesis also discusses the crystal structure and the theoretical aspects of the individual dyes that have been prepared.

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David F. Duncan

A thesis submitted in partial fulfillment
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of

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in

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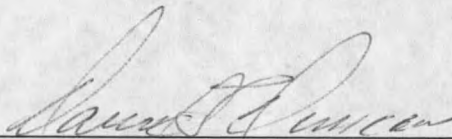
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ABSTRACT

Cyanines, merocyanines, allopolars and related dyes have been known for more than a century and have been utilized extensively in the photographic industry. However, in the last twenty years these compounds have become important in the field of nonlinear optics (NLO). As a result new synthetic methodologies are needed to prepare authentic and novel cyanines, merocyanines, allopolars and related dyes, as well as, some insight to their physical properties.

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This thesis discusses the synthesis and characterization of several authentic straight chain merocyanines, as well as the synthesis and characterization of approximately five different types of new dyes. This thesis also discusses the crystal structure and the theoretical aspects of the individual dyes that have been prepared.

INTRODUCTION

Historical Background (1850-1920)

Cyanines and related dyes have been known for more than a century. The first seventy years involved the actual discovery and structural elucidation of several different dyes. The first cyanine (figure 1) was discovered by Williams in 1856 while

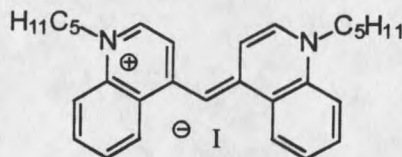


Figure 1. Williams' Cyanine (1856).

working with amyl-iodides of quinoline (shown later to be a mixture of quinoline and lepidine).¹ The importance of cyanines and related dyes was not apparent until 1873 when Vogel found that photographic plates treated with cyanine dyes, initially used to prevent halation, were sensitized to light outside the blue and ultraviolet region of the spectrum.² The discovery aroused considerable interest, even though other researchers contradicted and even ridiculed Vogel's finding. Vogel's work was confirmed in 1874 by Becquerel,³ who found that chlorophyll sensitized photographic plates to red light. It was further substantiated in 1875 by Waterhouse,⁴ who found that eosin sensitized

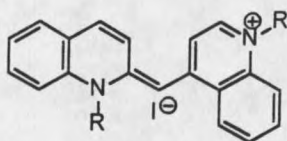


Figure 2. Isocyanine (1902).

plates to yellow and green light. Not all dyes of this type sensitized photographic plates; some dyes were desensitizers, and many dyes that did sensitize had side effects which rendered the plates useless. Even the best sensitizing dyes were unsuccessful eighty percent of the time.⁵ However, in 1902 an important advance was made by Miethe and Traube, who synthesized a series of dyes they called the isocyanines (figure 2). These dyes were by far the most effective sensitizing dyes for the green and yellow regions of the spectrum.⁶ By adding substituents to the parent nuclei of the dyes developed by Miethe and Traube, König extended the sensitizing range of the isocyanines into the near red region of the spectrum.⁵ König was also responsible for the synthesis of pinaverdol, orthochrome and pinachrome (figure 3).⁷ The sensitizing action of the isocyanines was extended into the red region when Homolka prepared

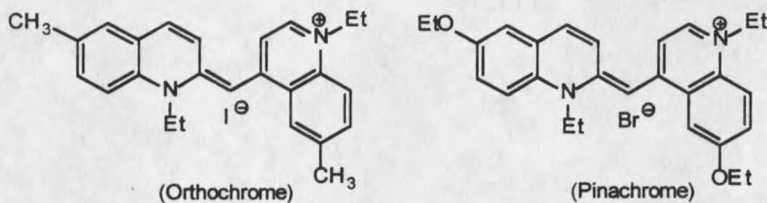


Figure 3. Cyanines prepared by König.

pinacyanol (figure 4).⁵ Dicyanine A was the first dye that sensitized into the infrared region, and was developed by Hoechst Dye Works in 1903.⁸ The isocyanines not only

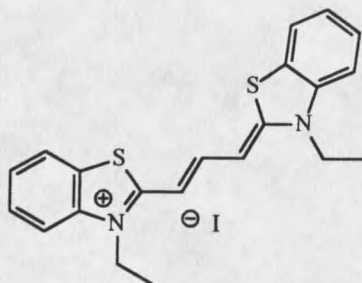
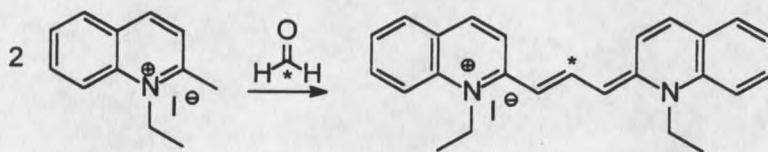


Figure 4. Pinacyanol.

had superior sensitization properties, but also had excellent results with respect to reproducibility.⁹ From this point on, cyanine dyes became the focus of research into optical sensitizers. In the years preceding 1914, sensitizing dyes were obtained primarily from Germany. When the supply was cut off by the outbreak of World War I, the problem of supplying photographic sensitizers was taken up by Pope and Mills at Cambridge University.^{5,10}

In 1920, the first in a series of papers by Mills was published, detailing the structure and synthesis of all the cyanines known at the time. Perhaps the single most important contribution made by Mills was the structure elucidation of pinacyanol. Mills and Hamer showed that formaldehyde was being incorporated into the dye, resulting in

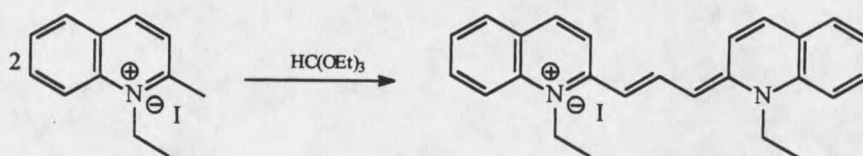


Scheme 1.

a three carbon methine bridge between the two quinoline nuclei (Scheme 1).¹⁰ This discovery provided insight into ways of developing new intermediates for the synthesis of new and old cyanines and related dyes.

Historical Background (1920-1950)

Since 1920, most of the research into cyanine and related dyes involved the development of several generalized synthetic procedures that provided new intermediates for the production of symmetrical and unsymmetrical dyes. Following Mills' elucidation of pinacyanol, Konig found that dyes of this type could be prepared more efficiently using ethyl orthoformate instead of formaldehyde to supply the central



Scheme 2.

carbon of the polymethine chain (Scheme 2).¹¹ Konig also developed the use of triethoxypropene to form longer chain cyanines, called pentamethine or dicarbocyanines.¹² In 1933, a dianilide prepared from dinitrophenylpyridinium chloride was used to make heptamethine or tricarbocyanines.¹³ It thus became possible to prepare a series of cyanines where the parent heterocyclic nuclei were the same, but the number of carbons making up the connecting bridge could be changed. Dyes related in

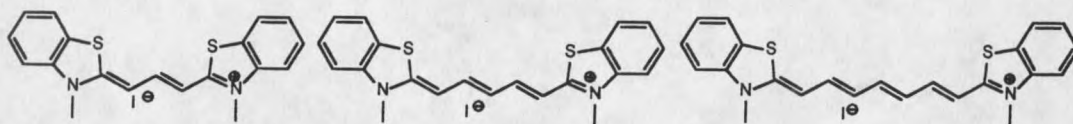
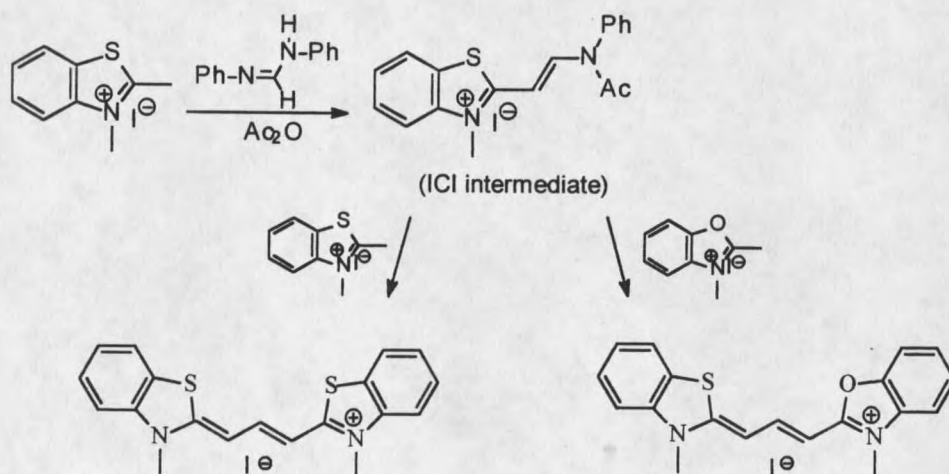


Figure 5. A Vinylogous Series of Dyes.

this way became known as a vinylogous series (figure 5). As the number of carbons making up the bridge increases, the absorption is shifted toward the longer wavelengths.⁵

A reaction of considerable importance was discovered by Piggot and Rodd in 1929 in which diphenylformamide was used instead of ethyl orthoformate to form carbocyanines.^{7,14} The importance of this reaction was that the anilino vinyl-intermediate could be isolated. These compounds were called ICI intermediates and were used in the preparation of both symmetrical and unsymmetrical carbocyanines (Scheme 3).^{14,15}



Scheme 3.

Soon after β -anilinoacraldehyde anil hydrochloride and glutaconic aldehyde dianilide hydrochloride were used to prepare pentamethine and heptamethine cyanine dyes respectively.¹⁶

The merocyanines, which are closely related to the cyanines but behaved quite differently, were discovered in 1933 by Kendal and Brooker. They later published several papers in which the preparation of several hundred different merocyanines were outlined.¹⁶

Historical Background (1950-1970)

By 1950 most of the synthetic methods needed to prepare cyanine and related dyes had been covered in the literature. From 1950 to the late 1970's there were no major advances in the general synthesis of cyanine and related dyes. However, the knowledge and application of cyanine and related dyes exploded. Most of this work appears in the patent literature as attempts to obtain photographic sensitizers of superior performance.

In addition to research related to photographic processes, application of dyes involving lasers became an important area of research. In 1964, Murray found that kryptocyanine and a benzothiazole pentamethinecyanine produced giant laser pulses in ruby lasers by the Q-switching technique.¹⁷ In 1966, Bartfeld demonstrated that pentimethinecyanine could be optically pumped by a Q-switch laser so that the dye is stimulated to emit fluorescent radiation. The final result was a solution that acted as a

new type of liquid laser.¹⁸ Cyanine and related dyes, especially merocyanines, could be used in chemical analysis as indicators for acid-base titrations,¹⁹ solvent polarity indicators,²⁰ and absorption indicators in argentometric titrations.²¹

Historical Background (1970 - present)

In the late 1970s to the present, organic materials with non-linear optic (NLO) properties have been the subject of intense investigation because of their potential use in a variety of areas including telecommunication,²² laser technology,²³ optical processing and storage,²⁴ and many other photonic based technologies.²⁵ The pioneering work into organic materials with NLO properties began with the work of Ducuing, who measured the non-linear susceptibilities of molecules having long conjugated chains, e.g. β -carotene.²⁶ In 1974 Ducuing measured the third harmonic generation (THG) of cyanine dyes dissolved in dimethylsulfoxide and reported that cyanine molecules exhibit exceptionally large third order hyperpolarizabilities, up to five orders of magnitude larger than molecules previously studied.²⁷

Early investigation into the NLO properties of merocyanines was reported in 1989 by Ikeda. Ikeda investigated the second order NLO properties of merocyanines derived from thiobarbituric acid, barbituric acid, thiohydantoin and rhodanine by the electric field induced second harmonic generation (EFISH) method.²⁸ From 1989 - 1991, Ikeda demonstrated that a number of merocyanines possess extremely high second order hyperpolarizabilities.²⁹

In 1991, Marder published a number of papers dealing with the theoretical and physical aspects of π -conjugated systems with NLO properties.³⁰ The biggest contribution from Marder and Perry came in 1994 when he introduced their unified description of linear and nonlinear polarization of organic polymethine dyes, which correlates the polarizabilities α , β and γ (from the Taylor series expansion-- $\mu_i = p = \alpha E + \beta E^2 + \gamma E^3 + \dots$ -- which represents the polarization in an electric field) with a single chemically relevant parameter, bond length alternation (BLA). From this work, Marder has shown that molecules such as cyanines and merocyanines can be "tuned" to optimize certain NLO properties, by changing the donor-acceptor strength of the end groups and/or by changing their environment.^{30d}

Cyanines and related dyes have been shown to possess NLO properties. Therefore an attempt to provide new synthetic methodologies, physical and structural insight as to why these molecules may or may not exhibit certain properties is a compelling reason for further studies.

TYPES OF CYANINES AND RELATED DYES

Molecules that are considered to be dyes are capable of absorbing some, but not all, of the radiation which comprises the visual spectrum. The radiation which is not absorbed reaches the eye, by transmission or reflection, and is interpreted as color. A dye is able to absorb light because it can exist in at least two states of energy, a ground

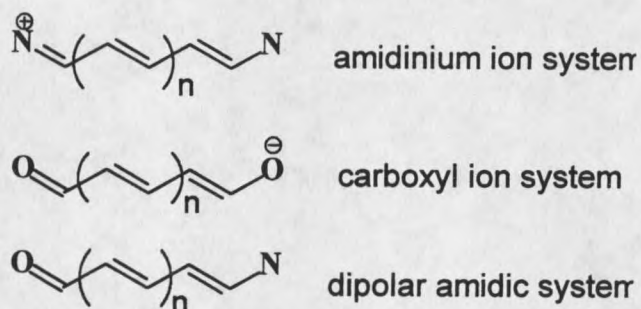


Figure 6. Three Types of Chromophores found in Cyanine and related Dyes.

state and an excited state. Molecules classified as dyes contain within their structure a chromophore or chromophoric system. The three chromophores that are significant to cyanines and related dyes are the amidinium ion, the carboxylic ion and the dipolar amidic systems (figure 6).³¹

Cyanine dyes

True cyanines are complex amidinium salts with two nitrogens contained within heterocyclic rings connected by a conjugated chain of carbon atoms in which a positive

charge is distributed between two nitrogen atoms (figure 7). All of the different types

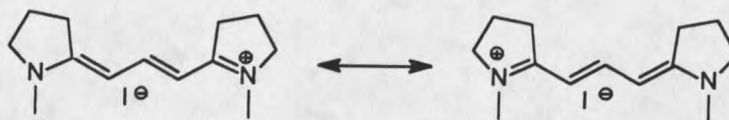


Figure 7. Resonance Structures for a Cyanine Dye.

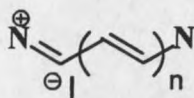


Figure 8. Amidinium Ion Chromophore.

of cyanines can be represented by a generalized polymethine structure (Figure 8) in which n is an odd positive integer and the number of π - electrons distributed over the polymethine chain is equal to $(2n + 4)$. The terminal atoms of the amidinium chromophore must be nitrogens . The counterion can be any number of different anions, i.e. iodide, bromide, perchlorate etc.³¹

Oxonols

Oxonols are similar to cyanines except the chromophore is based on the carboxyl ion system (Figure 9). A negative charge is distributed between two keto-methylene moieties which are separated by a conjugated carbon chain. Oxonols can be



Figure 9. Resonance Structures for a Oxonol Dye.

represented by the generalized polymethine structure (Figure 10) in which n is an odd positive integer and the number of π - electrons distributed over the polymethine chain is equal to $(2n + 4)$. The terminal atoms of a carboxylic ion system must be oxygens.³¹

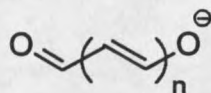


Figure 10. Oxonol Chromophore.

Merocyanines

Merocyanines can be regarded as a cross between a cyanine and an oxonol.

Merocyanines are molecules with donor-acceptor heterocyclic rings (one nitrogen and one oxygen bearing heterocycle) separated by a conjugated carbon methine chain.

Merocyanines have a dipolar amidic system with an even number of chain methine carbon atoms. Unlike cyanines and oxonols, merocyanines are unsymmetrical and neutral. Also unlike cyanines and oxonols, which have identical extreme resonance

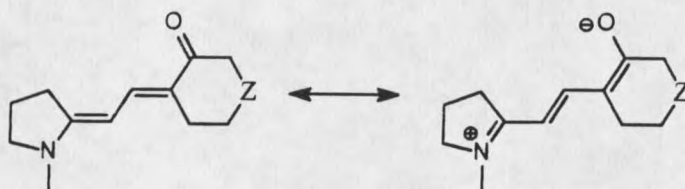


Figure 11. Resonance Structures for a Merocyanine Dye.

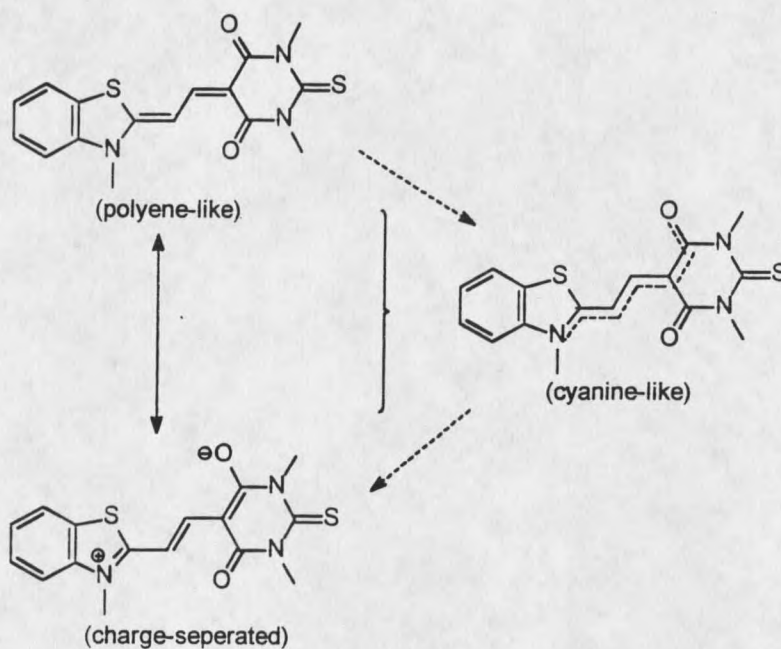


Figure 12. Contribution Between the Two Extreme Resonance Structures.

structures, merocyanines have two distinct resonance structures described as neutral and charge-separated (figure 11). The contribution between these two resonance structures depends on the strength of the donor-acceptor groups and/or solvent. By changing the donor-acceptor groups it is possible to “tune” a merocyanines to resemble

the neutral or charge-separated resonance forms and all the electron distributions in between (figure 12).^{30c-32}

Allopolar Dyes

Allopolar dyes are trinuclear dyes made up of a combination of merocyanine and cyanine components. There are two types of allopolar dyes that are relevant to this thesis (figure 13). The first type are dyes containing two basic, and one acidic

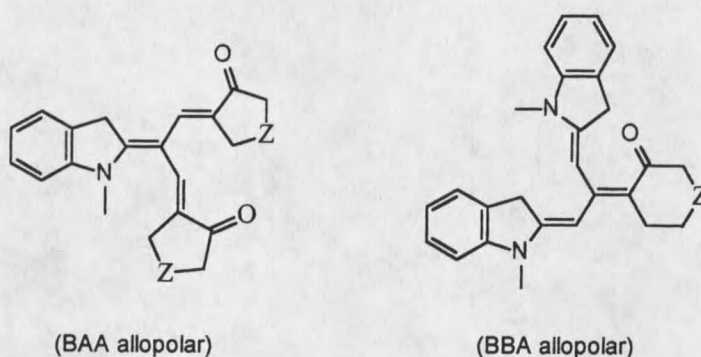


Figure 13. BAA and BBA Allopolar Dyes.

heterocyclic nuclei, and are referred to as BBA dyes. The second type consists of one basic heterocyclic nuclei and two acidic nuclei and are referred to as BAA dyes. A model of an allopolar dye clearly indicates that the overlapping of the Van der Waals' radii make it impossible for all three nuclei to remain coplanar simultaneously (figure 14).³³

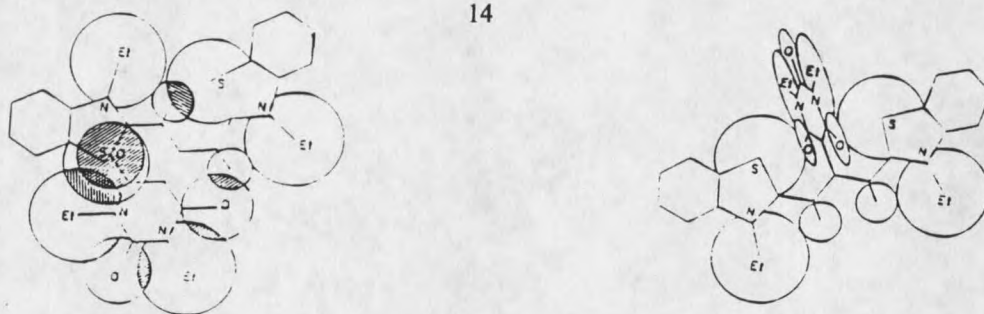


Figure 14. The Van der Waals' Overlap for an Allopolar Dye.

One suggestion is that partial resonance may be preserved if two of the three nuclei are coplanar, requiring that the third nucleus be twisted out of the plane of the other two. An alternate suggestion is that all three nuclei are slightly turned out of the plane, resembling a propeller-type conformation, which allows for the best compromise between resonance stabilization and steric interaction for the three nuclei. There is evidence that suggests BBA allopolar dyes have two nuclei that are coplanar and one twisted outside the plane of the other two. The evidence lies in the fact there are two different absorption bands in the UV/VIS spectrum. One to represent the merocyanine or meropolar form (dipolar amidic chromophore) and the other to represent the cyanine or halopolar form (amidinium ion chromophore). However the UV/VIS spectrum of BAA allopolar dyes suggest a propeller-type configuration which is supported by X-ray crystal data (page 49).

NONLINEAR OPTICS (NLO)

Organic materials with NLO properties have been the subject of intense investigation because of their potential use in a variety of areas including telecommunications,²² laser technology²³ optical processing and storage.²⁴ As a result, much research has been directed toward the synthesis of organic materials that have NLO properties. They possess several advantages over non-organic NLO materials, for example, the NLO responses of many organic materials are extremely rapid (femtoseconds) because the effects occur primarily through electronic polarizations. In contrast, NLO effects in most liquid crystal materials operate via reorientation of the whole molecule, and most inorganic materials operate primarily through lattice distortions. Other advantages deal with the stability, crystal growth, preparation and cost efficiency of organic NLO materials.³⁴ In spite of the potential advantages, useful organic NLO materials have not been developed because the physical requirements necessary for NLO response to generated has only recently begun to be understood.

In order to synthesize organic molecules with the desired NLO properties, an understanding of the structural and physical properties that promote the desired NLO effect is a prerequisite. Optical effects in matter result from the polarization of the electrons in a medium, in response to the electric field associated with light traveling through the medium. When an applied electric field (i.e., the electric field associated with light) polarizes the electrons in a material, an internal electric field is generated. This internal electric field modifies the applied field and the subsequent polarizations.

The result is a mixture of the fundamental frequency and harmonics that have two, three or four times the frequency of the fundamental. This response has a complex, "nonlinear" relation to the field strength. A general representation of the nonlinear polarization is that of the power series expansion in the electric field. This expansion is given by:

$$\mu_i = p = \alpha E + \beta E^2 + \gamma E^3 + \dots$$

where p and E are the polarization and electric field, the coefficients α , β , γ are its linear, second and third order polarizabilities, and μ is the induced dipole moment of the molecule.³⁵ Second-order nonlinear optical properties (β), which can be exploited as frequency doublers and electro-optic switches, arise in organic donor-acceptor substituted conjugated π -systems. Examples of compound classes whose members possess these structural characteristics include: azo dyes, stilbenes, polyenes, cyanines and merocyanines. In order to observe second-order NLO effects in the bulk material, it must have an electronic asymmetry (non-centrosymmetric), so that electrons are more likely to be polarized in one direction.³⁶ Otherwise, the oscillation of the electrons in one direction would cancel the oscillation of the electrons in the other, resulting in no NLO effect being generated.

AREAS OF INTEREST

Synthesis of Cyanine and Related Dyes

The object of this thesis concerns the synthesis and characterization of cyanine, merocyanine, allopolar and related dyes. These dyes have the potential to play an important role in the development of NLO materials. These dyes have the physical requirements that are necessary for NLO properties (properties discussed in NLO section of the thesis). A few cyanines and merocyanines have already been tested and the results have shown that these dyes possess large NLO properties for both 2nd and 3rd hyperpolarizabilities.²⁶⁻²⁸ NLO materials are basically organic molecules that can effectively shuttle electrons back and forth between two functional groups. In other words, materials that allow electrons to oscillate back and forth along the conjugated chain between donor and acceptor nuclei have the capability to produce a NLO response. Most studies of organic molecules have focused on donor-acceptor π -conjugated molecules containing aromatic groups, ie. 4-methoxy-4'-nitrostilbene.³⁷ This arrangement requires that the electrons oscillate through the aromatic ring system and disrupt the aromaticity of the molecule in order to make a complete oscillation

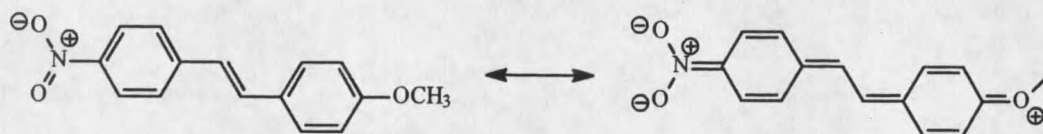


Figure 15. Resonance through Aromatic Rings (4-Methoxy-4'-nitrostilbene).

between the donor and acceptor groups (Figure 15). Cyanines and merocyanines are not conjugated through an aromatic ring system and therefore do not have to disrupt or pass through any aromatic systems between the donor and acceptor groups (Figure 16).

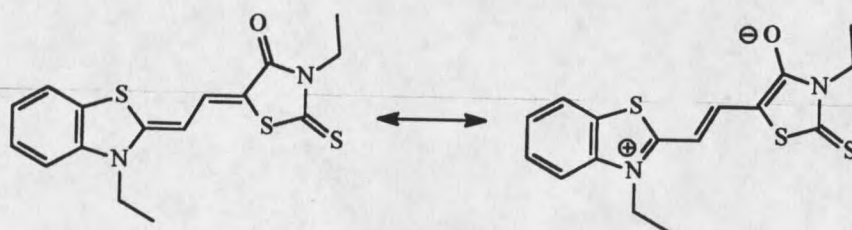


Figure 16. Resonance Through a Merocyanine Dye Chromophore.

The original goal was to improve and develop new and better methods to prepare several samples of authentic and novel merocyanines. Synthetically, these dyes are interesting because they can be “tuned” so that the BLA is altered, depending on the end groups used. An example of how the BLA changes as a result of substituting

DYE	N_1-C_1	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_{11}
BOXIND	1.343 (3)	1.375 (4)	1.382 (4)	1.385 (4)	1.451 (4)
BTHRHO	1.362 (4)	1.371 (5)	1.404 (5)	1.367 (5)	1.442 (5)
BTHIND	1.365 (3)	1.386 (3)	1.384 (3)	1.388 (3)	1.452 (3)

Table 1. Bond Distances of Dimethine Merocyanines.³⁸

* The structures for BOXIND, BTHRHO, and BTHIND are in Appendix B.

different groups is apparent by examining the change in bond distances of several dimethine merocyanines (table 1).³⁸ BLA is defined as the difference between the average length of carbon-carbon double and single bonds in a π -conjugated chain. This measurement has been important because BLA has been shown to be a useful parameter when considering structure-property relationships in other donor-acceptor molecules with NLO properties.^{30d} According to the literature weak donors-acceptor groups result in a positive BLA because the neutral resonance structure is the dominant contributor to the ground state. As the donor-acceptor strengths increase, the charge separated resonance structure contributes until both resonance forms contribute equally and the ground state BLA is zero. Increasing donor-acceptor strength further will result in a charge-separated ground state, which results in a negative BLA (figure 12).³⁰ In other words, it is possible to prepare merocyanines that resemble the neutral through polar or charge-separated resonance forms by changing the donor-acceptor groups. From this information, dyes could be prepared so that the BLA could be optimized for a particular NLO application. Therefore, the development of new or improved methods for the preparation of known and novel cyanine and merocyanines needs to be developed.

Optically Active Dyes

A physical requirement for second order NLO materials is that the molecule must be asymmetric and have a non-centrosymmetric center in the solid state structure.

Merocyanines tend to aggregate in solution in a head-to-tail fashion, which may result in the formation of a symmetric "system" with regards to the bulk material (Figure 17).^{22, 36}

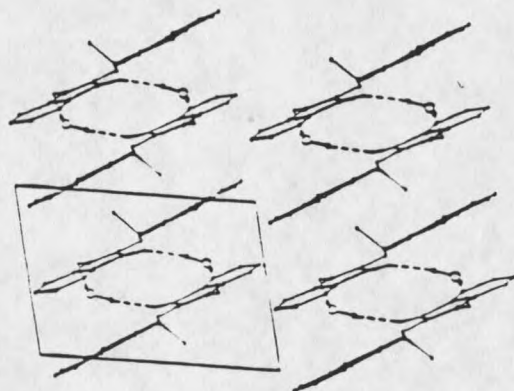


Figure 17. Packing Diagram for Merocyanine Dyes.

Therefore, these dyes could have limited or hindered NLO properties.

However, merocyanines in solution have been shown to possess large β s (second order NLO effects). A dye with an optically active center is guaranteed to possess a non-centrosymmetric center which could possibly enhance the NLO properties these dye already have. Therefore, the development of new or improved methods for the preparation of optically active dyes is an important objective.

Allopolar and Related Dyes

The development of new procedures to prepare allopolar dyes for conformational and possible NLO studies is another area of interest. These dyes

contain multiple chromophores (amidinium, carboxyl or dipolar amidic) and therefore could possibly have properties similar to the dominating chromophore or a combination of the chromophores as a whole. These dyes have characteristics that should make them interesting, at least from a theoretical standpoint. Both BAA and BBA dyes theoretically have a three way ground state conformational equilibrium which is dependent on the environment (figure 18). By changing the environment, such as the polarity of the solvent, the equilibrium ratio between the conformations can be pushed in one direction over the other. This should result in two or more separate absorptions in the UV/VIS spectrum (Figure 34).³⁹ Therefore, the development of new or improved methods for the preparation of known and novel allopolar dyes needs to be developed.

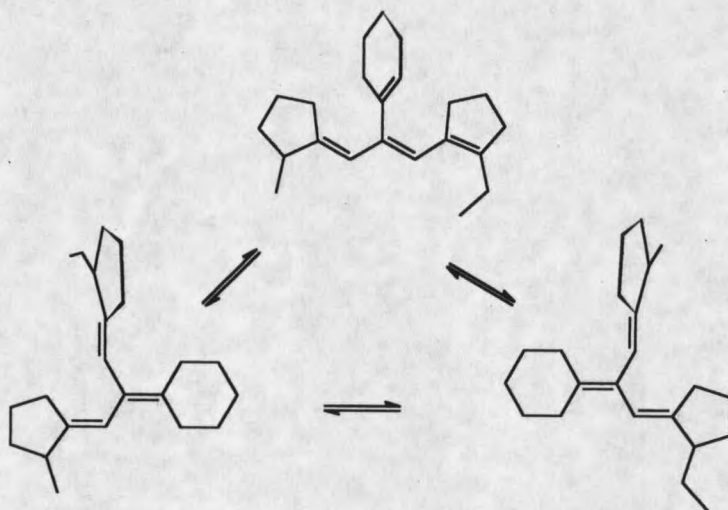


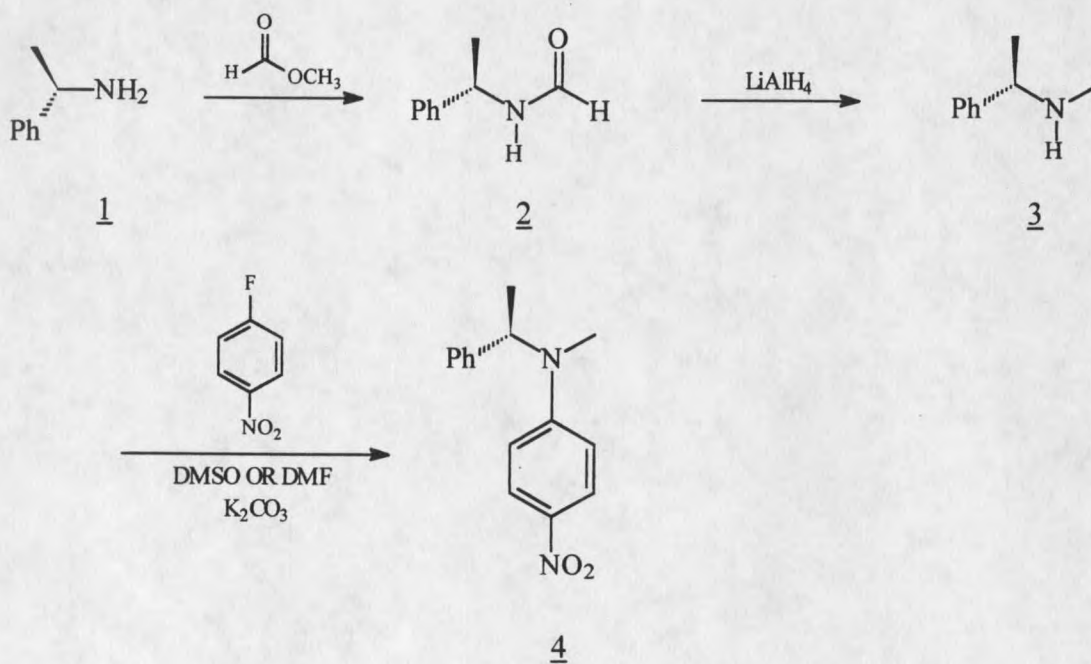
Figure 18. Three way Equilibrium of BBA Allopolar Dyes.

I would like to emphasize that the main goal of this research project and thesis is the development of new procedures for the preparation of new and old cyanines, merocyanines, allopolar and related dyes. The NLO, conformational and NMR studies, although important, are considered to be additional or secondary areas of study.

RESULTS AND DISCUSSION

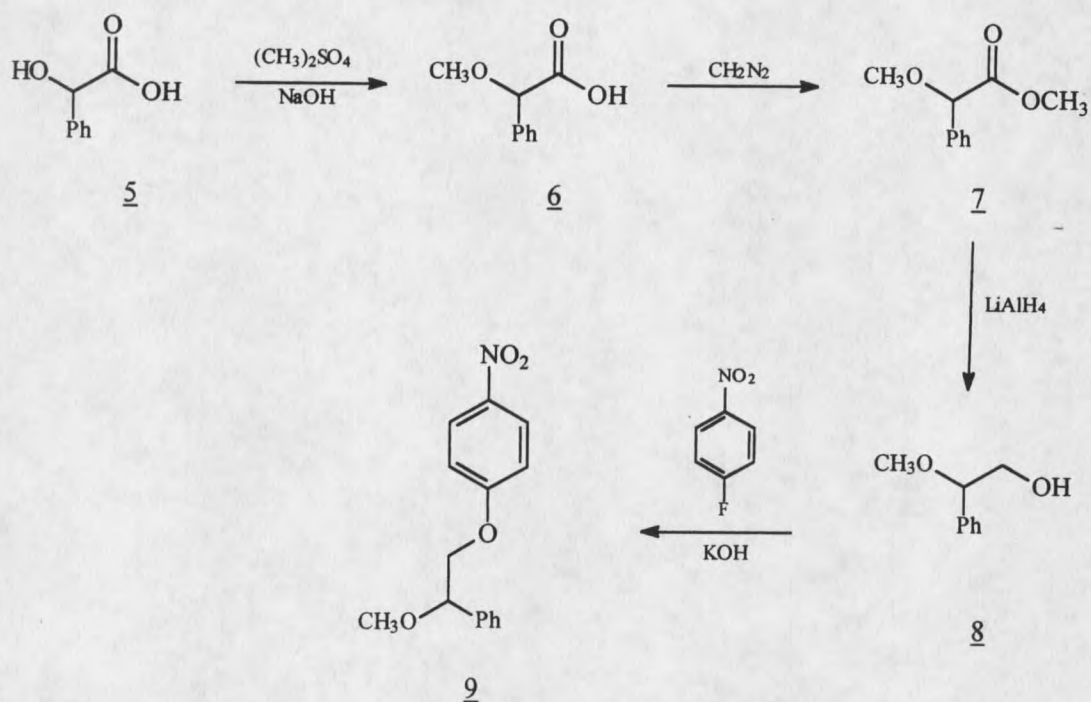
Synthetic Routes**Synthesis of Optically Active Aromatic Donor-Acceptor Compounds**

Optically active aromatic donor-acceptor compounds were prepared by the reaction of an optically active amine or alcohol and 4-fluoro-1-nitrobenzene in a polar solvent such as dimethylsulfoxide or dimethylformamide over solid potassium hydroxide or sodium carbonate (Scheme 4).⁴¹ The optically active amine 3 was prepared by condensing the primary amine 1 with methylformate and then reducing the resulting formamide 2 with LiAlH_4 . The primary 1 and secondary 2 amines were both utilized to prepare donor-acceptor nitroaniline compounds (Scheme 4).



Scheme 4.

The racemic nitro-phenolic ether 9 was prepared from mandelic acid 5. The first step was to methylate the alcohol functionality with dimethylsulfate to give 6.⁴² This compound was then converted into the methyl ester 7 with diazomethane and reduced with LiAlH_4 to give 2-methoxy-2-phenylethanol 8 (Scheme 5).

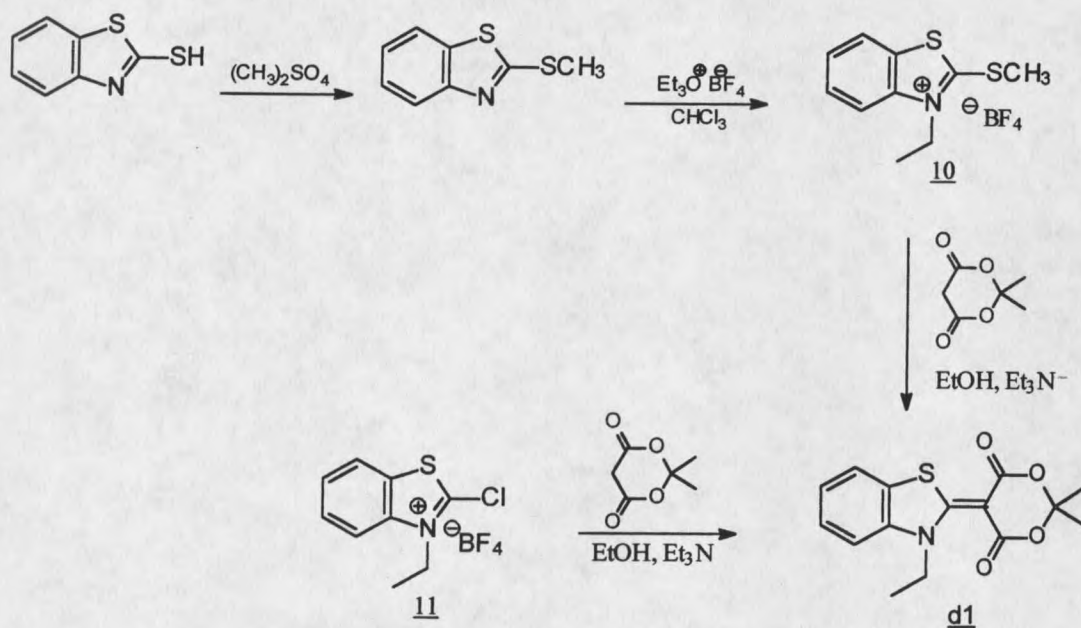


Scheme 5.

Synthesis of Merocyanines

The starting benzothiazole quaternary salts 10 and 11 were prepared by reacting 2-(methylthio)-benzothiazole or 2-chloro-benzothiazole with an appropriate alkylating agent, such as, diethylsulfate. The merocyanines d1 were prepared from a keto-

methylene compound, such as 2,2-dimethyl-1,3-dioxane-4,6-dione, with 2-(methylthio)-3-ethylbenzothiazolium tetrafluoroborate 10 or 2-chloro-3-ethylbenzothiazolium tetrafluoroborate 11 (Scheme 6).

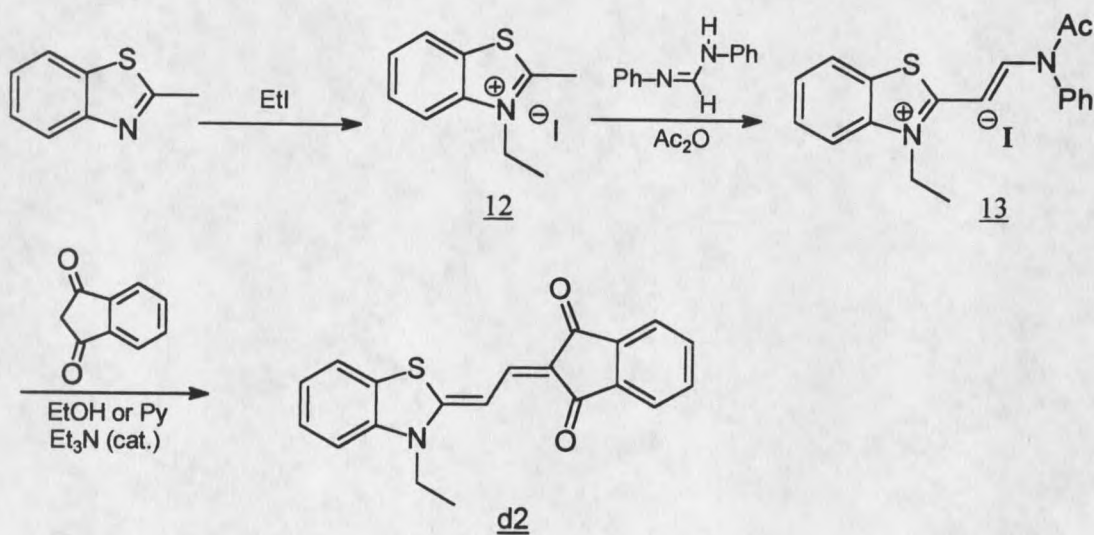


Scheme 6.

Synthesis of Dimethine Merocyanines

The synthesis of most merocyanines, besides simple merocyanines, starts with the alkylation of benzothiazole, which will eventually become the basic or donating heterocyclic portion of the dye. 2-methylbenzothiazole was converted into the ethyl quaternary salt 12 using a variety of reagents: ethyl iodide, diethylsulfate, ethyltrifluoromethanesulfonate and triethyloxonium tetrafluoroborate. Other alkyl (methyl, octyl, benzyl, etc.) quaternary salts can be formed by using the appropriate alkylating

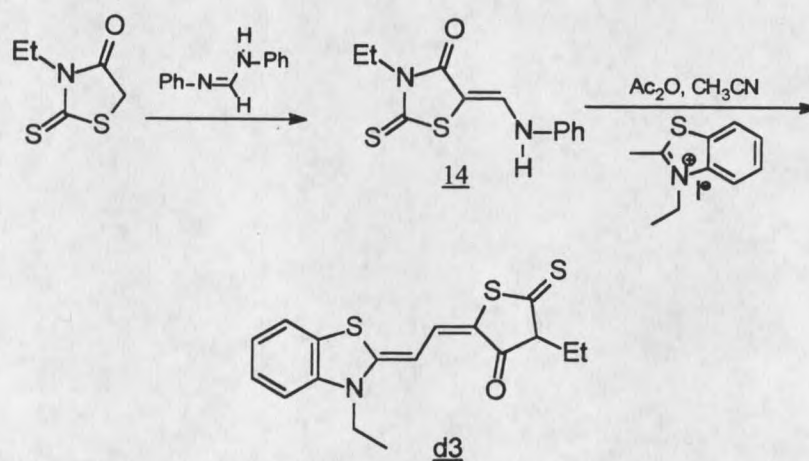
agent. The ethyl group was chosen over other alkyl groups because of the crystallographic data, collected by previous members of the group, on dyes made from the ethyl quaternary salts as well as favorable solubility characteristics.³⁸ In most cases ethyl iodide was the alkylating agent of choice because the reaction was simple and isolation of the product was accomplished by filtering the product from the reaction mixture then washing with acetone to give the quaternary salt in excellent yields (> 96 %). The next step in the synthesis of dimethine merocyanines d2 was the formation of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide an, ICI⁴³ intermediate) 13⁴⁴. 13 was prepared from condensation of diphenylformamidinium and the quaternary salt 12 in the presence of acetic anhydride. From the ICI intermediate several dimethine merocyanines could be prepared by condensing it with a number of keto-methylene compounds (Scheme 7).⁴⁵



Scheme 7.

The dyes were usually prepared using ethanol or pyridine as the solvent. Dyes prepared with ethanol as a solvent usually precipitated from the solution upon cooling. Dyes prepared with pyridine as the solvent could usually be precipitated from the reaction mixture by the addition of cold methanol. However, dyes that did not precipitate out of the solution could usually be isolated by running the crude reaction mixture through a plug of silica gel, concentrating and recrystallizing the crude product from ethanol.

Most of the keto-methylene compounds gave the desired dye in reasonable yields, except 3-ethylrhodanine d3. All attempts to prepare the rhodanine derived dye via way of the ICI intermediate method gave the dye in low yields (> 8 %). Therefore, the dye was prepared using an alternative synthetic route. 3-ethylrhodanine was fused together with diphenylformamide under rather harsh conditions to give 5-

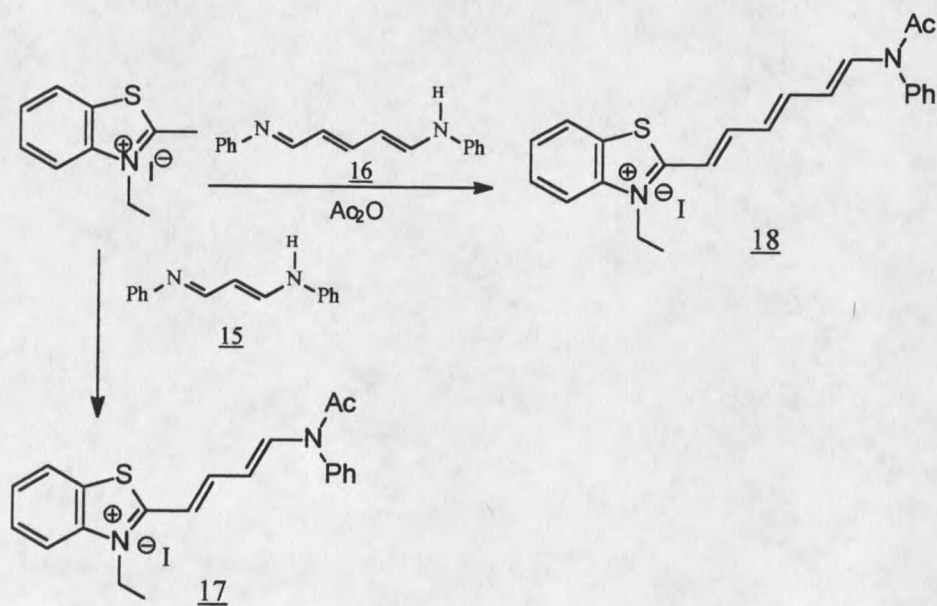


Scheme 8.

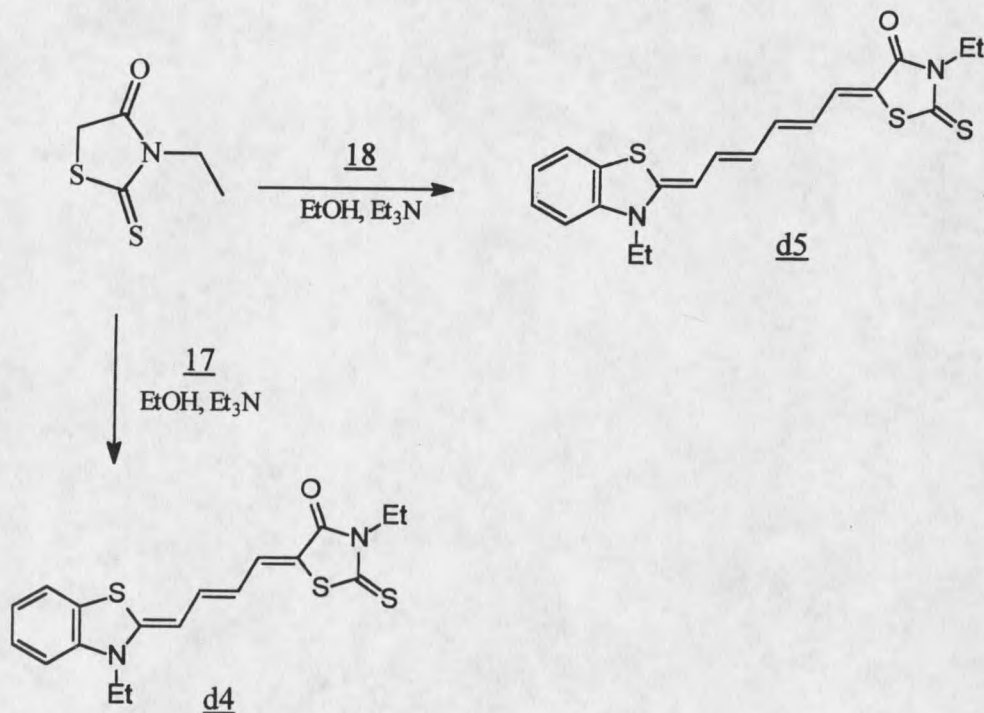
anilinomethylene-3-ethylrhodanine 14 (a Dains intermediate).⁴⁶ The Dains intermediate was then converted into a merocyanine d3 by condensing it with 3-ethyl-2-methylbenzothiazolium iodide 12 (Scheme 8).

Synthesis of Longer Straight Chain Merocyanines

The longer straight chain merocyanines, tetramethine d4 and hexamethine d5, were prepared from ICI intermediates derived from β -anilinoacraldehyde dianil hydrochloride 15 and glutaconaldehyde dianilide hydrochloride 16 (Scheme 9 and 10).⁴⁵ Unlike the ICI intermediates derived from diphenylformamidine the tetra 17 and hexa 18 ICI intermediates could be recrystallized without substantial loss of product.



Scheme 9.



Scheme 10.

The longer chain merocyanines were prepared in the same manner as the dimethine merocyanines. However purification proved to be more tedious because the impurities formed could not be removed by simply recrystallizing the crude product. The impurities would co-crystallize with the desired dye. Therefore several recrystallizations in which the dye was collected while the recrystallization solvent was still hot was required to obtain pure samples. The 3-ethylrhodanine hexamethine merocyanine **d5** required 4 recrystallizations from ethanol with loss of 40 % of the crude material which resulted in low yields of pure dye. The hexamethine derived from 1,3-diethylthiobarbituric acid was recrystallized from 50 % pyridine/ethanol with a loss of 53 % of the total amount of crude material collected. The overall yield could be

increased if the molar concentration of the keto-methylene were increased. This method reduced the amount of impurities and increased yields.

Synthesis of Optically Active Merocyanines

Merocyanines can be essentially divided into three parts: the two heterocyclic end groups and the carbon methine chain (figure 19). In order to prepare optically

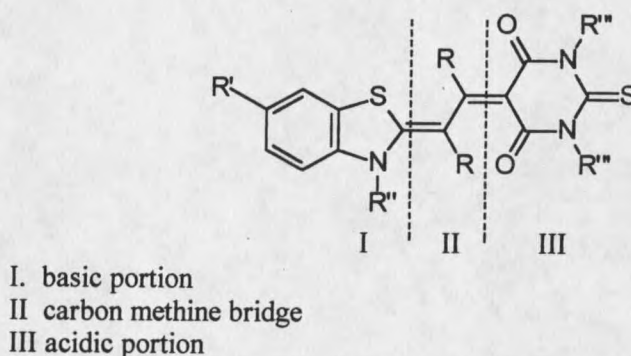
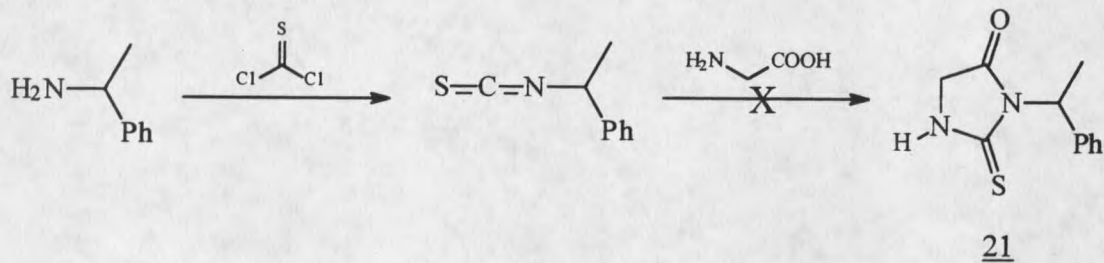
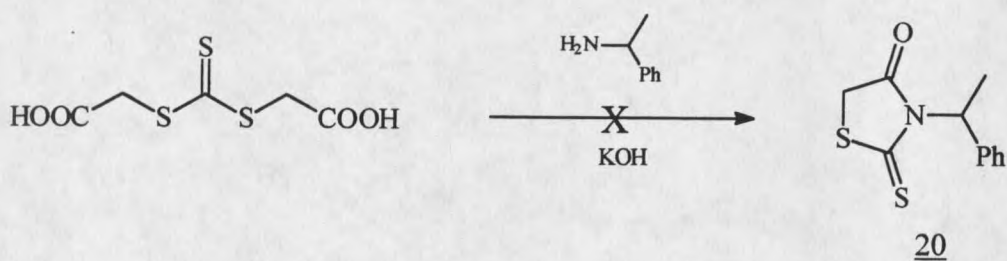
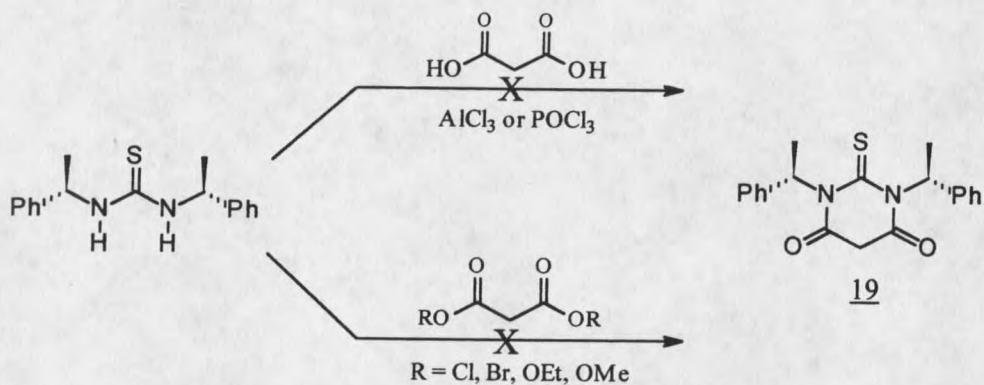


Figure 19. Merocyanines can be Divided into Three Different Parts I, II and III.

active merocyanine a chiral group needed to be incorporated onto one of the three different parts of the dye. The original plan was to incorporate the chiral group onto the acidic heterocyclic portion of the dye. However, the synthesis of an optically active acidic heterocycle was reconsidered after several unsuccessful attempts to synthesize an optically active thiobarbituric acid 19, rhodanine 20 and hydantoin 21 derivatives (Scheme 11).^{47,48}

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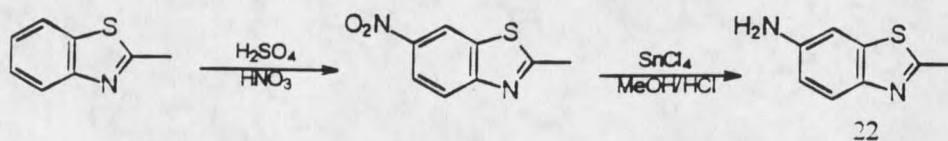


Scheme 11.

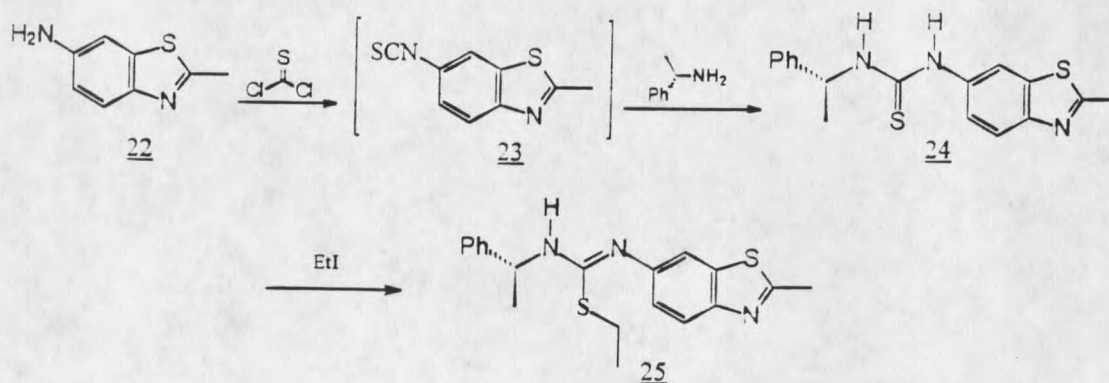
An alternative procedure was to incorporate the chiral group onto the basic heterocyclic portion of the dye. This option proved to be more eventful because the optically active group could be accomplished by two different synthetic routes. The

first procedure involved adding a functional group in order to provide a handle onto which a chiral moiety could be attached. The functional group addition was accomplished by nitrating the sixth position of 2-methylbenzothiazole which was then reduced with tin chloride to give 2-methyl-6-aminobenzothiazole 20 (Scheme 12).⁴⁹

Originally the procedure required forming an isocyanine intermediate 23 using

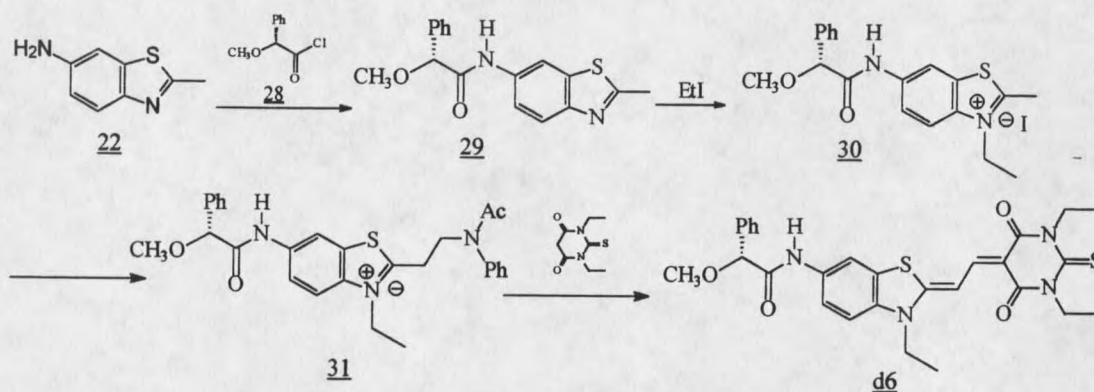


thiophosgene which is eventually converted into the thiourea by reacting 23 with α -methylbenzylamine to give the unsymmetrical thiourea derivative 24 (Scheme 13).⁴⁸ The synthesis then stalled here because the sulfur associated with the thiourea was alkylated before the nitrogen of the benzothiazole ring. This resulted in the formation of compound 25 which presented solubility and conformation problems.



Scheme 13

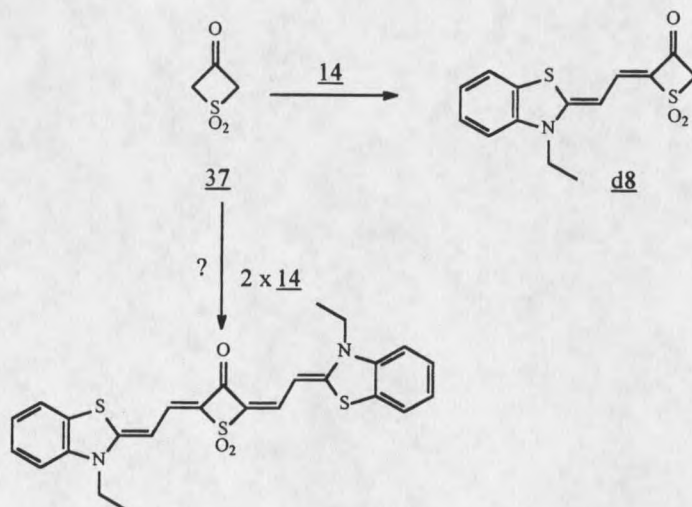
In an alternative approach, the amino derivative 22 was converted into a chiral amide by the action of (-)-(R)-2-methoxy-2-phenylacetyl chloride 28⁴² to give an optically active benzothiazole 29. The benzothiazole was then converted into an ICI intermediate 31 and subsequently into a number of optically active merocyanines d6 using the procedures discussed earlier (Scheme 14).



Scheme 14.

The second procedure involved introducing the chirality in the group attached to the nitrogen atom of a thiazole ring. 3- α -Methylbenzyl-2,4-dimethylthiazolium perchlorate 34 was prepared by first converting the α -methylbenzylacetamide 32 into the thioacetamide 33⁵⁰ and cyclizing to the quaternary salt 34.⁵¹ All attempts to prepare an ICI intermediate from the quaternary perchlorate salt were unsuccessful. However, the desired merocyanines (d7) could be prepared from the quaternary perchlorate salt 34 and a Dains intermediate 14⁴⁶ (Scheme 15).

thietanone-1,1-dioxide had to be prepared from bromoacetaldehyde 39 which is converted into a ketene acetal 40.⁵³ The ketene acetal 40 then undergoes a 2+2 cycloaddition with the sulfene compound 41b derived from methanesulphonyl chloride 41a to form 3,3-diethoxy-thietanone-1,1-dioxide 42.⁵⁴ Deprotection of the 3,3-diethoxy-thietanone was accomplished by dissolving 42 in cold concentrated HCl and the 3-thietanone-1,1-dioxide 37 slowly crystallizes out of solution (Scheme 16).⁵⁵ Mono-merocyanines (d8) could be prepared by reacting 3-thietanone-1,1-dioxide 37 with one equivalent of an ICI intermediate 14 (scheme 19), however, even with very dilute concentrations of both reagents the mono-substituted merocyanine d7 was the minor product formed. The bis-merocyanine presumably could be prepared by adding 2 equivalence of the ICI intermediate 14 and heating the reaction at reflux temperatures overnight (scheme 17).



Scheme 17.

