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-benzothiazolinylidene)-(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 (merocyanne-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.
THE SYNTHESIS AND CHARACTERIZATION OF ORGANIC MATERIALS FOR NON-LINEAR OPTIC STUDIES

by

David F. Duncan

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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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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-isopropylidenebenzothiazolines have been used to prepare several intermediates (i.e. 3-ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylene)]-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.
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 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
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. 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. By adding substituents to the parent nuclei of the dyes developed by Miethe and Traube, Konig extended the sensitizing range of the isocyanines into the near red region of the spectrum. Konig was also responsible for the synthesis of pinaverdol, orthochrome and pinachrome (figure 3). The sensitizing action of the isocyanines was extended into the red region when Homolka prepared pinacyanol (figure 4). Dicyanine A was the first dye that sensitized into the infrared region, and was developed by Hoechst Dye Works in 1903. The isocyanines not only
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.](image)
a three carbon methine bridge between the two quinoline nuclei (Scheme 1). 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 carbon of the polymethine chain (Scheme 2). Konig also developed the use of triethoxypropene to form longer chain cyanines, called pentamethine or dicarbocyanines. In 1933, a dianilide prepared from dinitrophenylpyridinium chloride was used to make heptamethine or tricarbocyanines. 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 diphenylformamidine was used instead of ethyl orthoformate to form-
carbocyanines.7–14 The importance of this reaction was that the anilinovinyl-
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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{18} Cyanine and related dyes, especially merocyanines, could be used in chemical analysis as indicators for acid-base titrations,\textsuperscript{19} solvent polarity indicators,\textsuperscript{20} and absorption indicators in argentometric titrations.\textsuperscript{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,\textsuperscript{22} laser technology,\textsuperscript{23} optical processing and storage,\textsuperscript{24} and many other photonic based technologies.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{28} From 1989 - 1991, Ikeda demonstrated that a number of merocyanines possess extremely high second order hyperpolarizabilities.\textsuperscript{29}
In 1991, Marder published a number of papers dealing with the theoretical and physical aspects of $\pi$-conjugated systems with NLO properties. 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 $\alpha$, $\beta$ and $\gamma$ (from the Taylor series expansion $\mu_i = p = \alpha E + \beta E^2 + \gamma E^3 + \ldots$ 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.

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 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).\textsuperscript{31}

\begin{figure}[h]
    \centering
    \includegraphics[width=0.8\textwidth]{chromophores.png}
    \caption{Three Types of Chromophores found in Cyanine and related Dyes.}
\end{figure}

\textbf{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

\[
\begin{align*}
\text{Figure 7. Resonance Structures for a Cyanine Dye.}
\end{align*}
\]

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 \( \pi \) - 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 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
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).\textsuperscript{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 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).\textsuperscript{33}

![BAA and BBA Allopolar Dyes](image)

*Figure 13. BAA and BBA Allopolar Dyes.*
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 place of the other two. The evidence lies in the fact there are two different absorption is 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, laser technology, optical processing and storage. 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. 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 time 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:

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

where $p$ and $E$ are the polarization and electric field, the coefficients $\alpha$, $\beta$, $\gamma$ are its linear, second and third order polarizabilities, and $\mu$ is the induced dipole moment of the molecule.\textsuperscript{35} Second-order nonlinear optical properties ($\beta$), which can be exploited as frequency doublers and electro-optic switches, arise in organic donor-acceptor substituted conjugated $\pi$-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.\textsuperscript{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. 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 \( \pi \)-conjugated molecules containing aromatic groups, ie. 4-methoxy-4'-nitrostilbene. 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).](image-url)
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.](image)

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

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<th>N1-C1</th>
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<th>C2-C3</th>
<th>C3-C4</th>
<th>C4-C11</th>
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<td>1.343 (3)</td>
<td>1.375 (4)</td>
<td>1.382 (4)</td>
<td>1.385 (4)</td>
<td>1.451 (4)</td>
</tr>
<tr>
<td>BTHRHO</td>
<td>1.362 (4)</td>
<td>1.371 (5)</td>
<td>1.404 (5)</td>
<td>1.367 (5)</td>
<td>1.442 (5)</td>
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<tr>
<td>BTHIND</td>
<td>1.365 (3)</td>
<td>1.386 (3)</td>
<td>1.384 (3)</td>
<td>1.388 (3)</td>
<td>1.452 (3)</td>
</tr>
</tbody>
</table>

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 I). 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. 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).
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).\textsuperscript{22,36}

![Packing Diagram for Merocyanine Dyes.](image)

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 $\beta$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).\textsuperscript{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). The optically active amine 3 was prepared by condensing the primary amine 1 with methylformate and then reducing the resulting formamide 2 with LiAlH₄. The primary 1 and secondary 2 amines were both utilized to prepare donor-acceptor nitroaniline compounds (Scheme 4).

\[
\text{Ph} - \text{NH}_2 \xrightarrow{\text{HCOOCH}_3} \text{Ph} - \text{N} = \text{C} \xrightarrow{\text{LiAlH}_4} \text{Ph} - \text{NH}
\]

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. This compound was then converted into the methyl ester 7 with diazomethane and reduced with LiAlH₄ 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 11 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 triethylxonium tetrafluoroborate. Other alkyl (methyl, octyl, benzyl, etc.) quaternary salts can be formed by using the appropriate alkylation
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. 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, ICI intermediate. 13 was prepared from condensation of diphenylformamidine 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).
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-
anilinomethylene-3-ethylrhodanine 14 (a Dains intermediate). The Dains intermediate was then converted into a merocyanine 3 by condensing it with 3-ethyl-2-methylbenzothiazolium iodide 12 (Scheme 8).

**Synthesis of Longer Straight Chain Merocyanines**

The longer straight chain merocyanines, tetramethine 4 and hexamethine 5, were prepared from ICI intermediates derived from β-anilinoacraldehyde dianil hydrochloride 15 and glutaconaldehyde dianilide hydrochloride 16 (Scheme 9 and 10). Unlike the ICI intermediates derived from diphenlyformamidine the tetra 7 and hexa 8 ICI intermediates could be recrystallized without substantial loss of product.

![Scheme 9](image-url)

Scheme 9.
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 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
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).

Originally the procedure required forming an isocyanine intermediate 23 using

![Image]

thiophosgene which is eventually converted into the thiourea by reacting 23 with α-methylbenzylamine to give the unsymmetrical thiourea derivative 24 (Scheme 13). 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.
In an alternative approach, the amino derivative 22 was converted into a chiral amide by the action of (-)-(R)-2-methoxy-2-phenylacetyl chloride 28 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).

![Chemical structure diagram]

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 33 and cyclizing to the quaternary salt 34. 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 14 (Scheme 15).
Synthesis of Trinuclear Merocyanines

The synthesis of trinuclear merocyanines in which two donating heterocycles are attached to one accepting heterocycle was accomplished using keto-methylene compounds in which there are two reactive methylene sites. 3-Thietanone-1,1-dioxide 37 and 2,5-dihydroxy-1,4-quinone 38 were used to prepare mono- and possibly bis-merocyanines. 2,5-dihydroxy-1,4-quinone could be ordered, but the 3-
thietanone-1,1-dioxide had to be prepared from bromoacetylaldehyde 39 which is converted into a ketene acetal 40. 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. 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).

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).
The synthesis of unsymmetrical bismcerocyanines has not been accomplished using d7 or any other mono substituted dye and ICI intermediate (Scheme 18). The reasoning for this is still under investigation.

**Scheme 18.**

**Synthesis of Chain Methyl Merocyanines**

Chain methyl merocyanines with benzothiazole or napthothiazole as the basic heterocycle needed to be prepared because they are precursors to more complicated allopolar dyes that will be discussed below. Chain methyl merocyanines d9 were prepared from benzothiazolium or napthothiazolium salts 44 and a keto-methylene compound in the presence of strong base in excess acetic anhydride (Scheme 19).56
Synthesis of BBA (basic, basic, acidic) Allopolar Dyes

There are two types of neutral allopolar dyes (figure 20). The synthesis of BBA allopolar dyes can be divided into two separate syntheses. The first being the synthesis of BBA allopolar dyes with strong acceptor groups d10 and the second being dyes with weak acceptor groups d11. The dyes look very similar, but are prepared by different procedures. BBA allopolar dyes d10 with strong acceptors can be prepared by reacting a chain methyl merocyanine d9 and a 3-ethylbenzthiazolium salt 10 with a leaving group at the 2-position (Scheme 20).
The synthesis of BBA dyes (d11) with weak accepting heterocycles was accomplished by condensing 3-ethylrhodanine with an unsymmetrical merocaptothiacarbocyanine iodide 48. The carbocyanine intermediate 48 was prepared from the following sequence of reactions. The methylene base dimer 45 was exposed to a large excess of carbon disulfide to form the thiocarboxylic acid derivative 46 which was methylated with dimethylsulfate to give the dimethylthio compound 47 (Scheme 21). Next, 2-methyl-3-ethyl-β-napthothiazolium iodide was condensed with one of the methylthio groups of the 47 to give the merocaptothiacarbocyanine iodide 48. When 3-ethylrhodanine was treated with 48 the desired BBA allopolar dye d11 was formed (Scheme 22). The desired product was obtained but, was contaminated with the straight chain cyanine shown in scheme 22.

Purification of the allopolar dye by multiple recrystallization usually resulted in small amounts of pure allopolar dye. Attempted purification by silica gel or size exclusion chromatography usually resulted in a dyed column and no purified product.
When 48 was treated with strongly acidic heterocycles no allopolar dyes were isolated, instead, the unsymmetrical thioketone 49 was formed (Scheme 22).

However, 49 could be converted into a chlorothiacarbocyanine by treating it with thiony chloride. The carbocyanine 49 was never isolated but, was used without purification. Crude 49 could be reacted with a keto-methylene compound to form the desired BBA allopolar dyes d10 (Scheme 23).
Synthesis of BAA (basic, acidic, acidic) Allopolar Dyes

The synthesis of BAA allopolar dyes starts with the formation of bis-aniloisopropylidenebenzthiazoline 54 by the action of zinc chloride and ethylisoforinanililde 52 on the dimer of benzothiazole methylene base 51 to give the zinc complex 53. Treatment of 53 with KOH allowed the free bis-anilo compound 54 to be isolated (Scheme 24). From the dianilo-compound 54 Hamer prepared several neocyanines, as well as several allopolar dyes with two identical heterocyclic end groups (Scheme 25). By using comparatively mild conditions, the reaction could
be stopped when the dianilo-intermediate had condensed with only one keto-methylene compound resulting in a monosubstituted dye intermediate (i.e. 5-(3-ethylrhodanine) \[2-(3-ethylbenzthiazoline)\]-\(\beta\)-anilomethyldimethinemerocyanine 55. From 55 a number of unsymmetrical BAA dyes could be prepared (Scheme 26).

However, this reaction had some limitations. When 5-(3-ethylrhodanine)\[2-(3-ethylbenzthiazoline)\]-\(\beta\)-anilomethyldimethinemerocyanine 55 was reacted with strong acceptor heterocycles the isolated product was not the expected allopolar dye, but a simple straight chain merocyanine d3 (Scheme 27). This unexpected reaction
occurred whenever the acidic heterocycles accepting strengths were vastly different from one another. For example, when 1,3 diethylthiobarbituric acid, meldrum’s acid or 1,3-dimethylbarbituric acid was reacted with the 3-ethylrhodanine anilo compound 55 the isolated product was the dimethine rhodanine derived merocyanine. The proposed mechanism for the appearance of the straight chain dimethine merocyanine is diagrammed in scheme 27.
Scheme 27.
Synthesis of Neocyanine Dyes

The synthesis of charged allopolar or neocyanine dyes was accomplished by two different synthetic procedures. The first procedure involves treating aniloi-intermediate 55 with 3-α-methylbenzyl-2,4-dimethylthiazolium perchlorate 34 to give the neocyanine d15 (Scheme 28). This procedure produced the desired dye but, also a symmetric chain methyl carbocyanine side product (Scheme 29). The presence of the cyanine dye made purification very difficult and yields were usually in the low fifties.

Scheme 28.

Scheme 29.
The second procedure involved preparing a mono-anilo cyanine 56 from the dianilo-compound 54. The cyanine 56 was then condensed with a ketomethylene compound to give the desired neocyanine d15 (Scheme 30). This procedure produced the desired dye without the cyanine side product.

Scheme 30.

Synthesis of Long Chain Merocyanine Intermediates

Commercially available 1,4-dichloro-2-butyne\textsuperscript{66} 57 was exposed to a solution of methanol and sodium methoxide to form 1-methoxy-1-buten-3-yne 58.\textsuperscript{67} The grignard of 58 combined smoothly with N-methoxy-N-methylamide\textsuperscript{68} 60 to give 1-methoxy-1-pentene-3-ynone 59 (Scheme 31).\textsuperscript{69} The enynone was then converted into the

Scheme 31.
unsaturated ketone 62, via 61, by two successive two-carbon elongations using silyl aldime reagents (Scheme 32).\textsuperscript{70,71}

The yne portion of the molecule can then be selectively reduced using Pd/CaCC\textsubscript{b}\textsuperscript{c} catalyst with lead poison and the crude product can then condensed with piperidine and piperdinum perchlorate to give cyanine 63 as illustrated in scheme 32 (presumably the cis configuration is converted into the trans during this step).\textsuperscript{72,73} Cyanine 63 could then be converted into the aldehyde which could then be reacted with either a keto-methylene compound or quaternary salt to form a merocyanine or a cyanine dye (Scheme 33).
Scheme 33.
X-RAY CRYSTALLOGRAPHY

Structure determination of allopolar dyes and long chain merocyanine dyes by x-ray crystallography has been and continues to be problematic at best. Growing x-ray quality crystals has proven to be very tedious and frustrating. There have been minimal success growing crystals of BBA, BAA or long chain merocyanines by conventional methods such as: dissolving the material in one solvent and then allowing a solvent, in which it is insoluble, to diffuse into the mixture over an extended period of time; by dissolving the material in an excess of solvent that it is soluble in and allowing the solvent to slowly evaporate over an extended period of time; or by dissolving the material in a solvent at elevated temperatures and allowing the solvent to slowly cool to room temperature or less. Only one recrystallization resulted in an x-rayable crystal—[5-(3-Ethylrhodanine)][2-(3-ethyl-benzothiazoline)][β-methine-4'(-5'-(3-ethylrhodanine)]methinemerocyanine (Figure 21). These crystals were obtained by

Figure 21. [5-(3-Ethylrhodanine)][2-(3-ethyl-benzothiazoline)][β-methine-4'(-5'-(3-ethylrhodanine)]methinemerocyanine.
suspending the dye in a large test tube with hot petroleum ether and then adding carbon disulfide until the material was completely dissolved, at which point the amount of carbon disulfide was doubled. The test tube was sealed with tin foil and followed by parafilm. A needle was poked through the top and the carbon disulfide was allowed to slowly evaporate at room temperature. After four months small crystals started to form and two months after that the crystals were filtered of and washed with petroleum ether to give crystals that were large enough to obtain a crystal structure (figures 22-29).

Figure 22. Thermal Ellipsoid Plot of the Allopolar Dye.
Figure 23. Numbering Scheme for Allopolar Dye.
Figure 24. X-ray View Parallel with the Benzothiazole Heterocycle.
Figure 25. X-ray View Parallel with the S(2) Rhodanine.
Figure 26. X-ray View Parallel with the S(4) Rhodanine.
Figure 27. Torsion Angle between the Two Rhodanine Heterocycles.
Figure 28. Torsion Angle between the Rhodanine and the Benzothiazole.
Figure 29. Torsion Angle between the Rhodanine and the Benzothiazole.
The crystal structure of the allopolar dye has a geometry where three nuclei are arranged in such a way that all the nuclei are twisted out of the plane and no two are coplanar. The three nuclei are completely cooperative meaning that all of the nuclei are twisted out of the plane to form a propeller shaped molecule. The bond length from the crystal data suggested the molecule has an electron sink at C2 or a psuedo-charged separated component between C1 and C2 (figure 30).

Figure 30. BAA Allopolar Dye with Electron Sink or Psuedo-Charge Separation.

These results suggest that BAA dyes are quite different from BBA allopolar dyes which are proposed to be in an arrangement where two nuclei are coplanar while the remaining nuclei is twisted out of the plane. This arrangement has not been proven, for BBA dyes, by x-ray crystallography but, is supported by UV/VIS spectroscopy. If the acidic heterocycle of a BBA allopolar dye is twisted out of the plane of the basic rings the molecule is then basically a cyanine cation which is electronically neutralized by the attached acid heterocyclic end group. The dye then should absorb very much like an ordinary cyanine dye. The problem with this is that
the undissociated dye would be in a form where there was a complete separation of charges, a positive charge in the cyanine plane and a negative charge in the acid heterocyclic end group that is out of the plane of the two basic heterocycles. This type of molecule is referred to as a holopolar conformation. Complete charge separation is a source of instability and is strongly favored in polar solvents such as aqueous solvents and alcohols. However, in nonstabilizing solvents such as lutidine, the dye will absorb at much shorter wavelength. An isomerization has occurred, the acidic heterocycle is now in the plane of one of the basic heterocycles and the second basic heterocycle is now out of the plane. The dye is now basically a merocyanine with a heterocyclic group attached to the carbon methine chain. Therefore these dyes can exist in two stereo isomeric structures which differ in their polarity. The holopolar isomer is stable in strongly polar solvents and the partly polar or meropolar isomer in nonpolar solvents. This situation would result in two UV/VIS absorptions (Figure 31). The crystal structure of the BAA dye is supported by the fact the there is only one UV/VIS absorption in all of the BAA allopolar dyes whereas the BBA dyes have two absorptions.
Figure 31. UV/VIS Spectra of an allopolar dye.
An additional area of interest involves the preparation of stable, uniform and reliable materials to be used in NLO-polymer applications. There are several avenues that would open up if merocyanines and allopolar dye intermediates could be covalently attached to polymer films (figure 33-34). The BAA and BBA intermediates described below are ideal materials for NLO related applications because they have the desired NLO properties, are relatively easy to prepare and are stable to high temperatures. If
these dyes could be attached to a polymer, they could outperform conventional devices.\textsuperscript{74}

Figure 33. Allopolar Polymer.
EXPERIMENTAL

Physical Data: $^1$H NMR and $^{13}$C-NMR were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. $^1$H NMR chemical shifts are reported as δ values in ppm relative to the residual protons of CDCl$_3$ (7.24), (CD$_3$)$_2$CO, C$_3$D$_2$N or CD$_3$CN. $^{13}$C-NMR chemical shifts are reported as δ values in ppm relative to CDCl$_3$ (77.0), (CD$_3$)$_2$CO (2.04), C$_3$D$_2$N (8.71), or CD$_3$CN (1.93). $^1$H NMR coupling constants are reported in Hz and refer to real or apparent multiplicities which are indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); br (broad); m (multiplet); dd (doublet of doublets); etc.

High-resolution mass spectra were measured on a VG Analytical 7070E spectrometer by Dr. L. J. Sears. X-ray data was collected and on a Siemens P4 upgrade of Nicolet R3m four cycle diffractometer and solved by Ray Larsen using Siemens SHELXTL plus. Infrared spectra were recorded with a Perkin-Elmer 1600 FTIR. Melting points were determined with a Mel-Temp II melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter.

Thin layer chromatography was performed on plates supplied by Alltech Associates (k42-G). Visualization of plates was accomplished by one or more of the following: a) UV illumination; b) exposure to I$_2$ vapor; c) KMNO$_4$ oxidation; d) anisaldehyde derivatization. All chromatography was performed according to Still on
E. Merck 230 - 400 ASTM mesh, 0.040 - 0.063 nm particle size, silica gel 60. Solvent systems used for elution are reported in % (volume/volume).

**Materials:** Tetrahydrofuran (THF), heptane and hexane were distilled from K. Diethylether (Et$_2$O) was distilled from Na-benzophenone. DMF (DMF) was distilled from CaH$_2$ at 20 mm. Dichloromethane (CH$_2$Cl$_2$), acetonitrile (CH$_3$CN) were distilled from CaH$_2$ at atmospheric pressure under an inert atmosphere of argon or nitrogen. Pyridine and Et$_3$N were distilled from KOH at atmospheric pressure under an inert atmosphere of argon or nitrogen. Dimethyl sulfoxide was distilled from CaH$_2$ under reduced pressure. Absolute ethanol was used unless noted otherwise.

All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried vessels. Concentrations were performed under reduced pressure with a Buchi rotary evaporator and "drying" of an organic solution was accomplished with anhydrous Na$_2$SO$_4$ or MgSO$_4$.

(+)-(R)-N-Methyl-N-(a-methylbenzyl)amine (3).

(+)-(R)-Methylbenzylformamide (5 g, .034 mol) (which was prepared from the condensation of (+)-(R)-methylbenzylamine with methylformate) is added to a suspension of LiAlH$_4$ (1.9 g, .051 mol) and THF (30 mL). The reaction mixture is heated at reflux for 12 h., cooled to 0°C and quenched with 5 % HCl (30 mL). Ether (30 mL) is added and the organic layer is separated and the aqueous layer was extracted with ether (3 x 20 mL). The organic layers were combined, washed with
water (3 x 10 mL), brine (10 mL) and dried (MgSO₄) and the solvents were removed under reduced pressure. The resulting residue was purified by distillation to yield a clear, colorless liquid (4.11 g, 85.6 %).

\[
[\alpha]_D + 43^\circ (CH_2Cl_2) \quad \text{^1H-NMR (300MHz, CDCl}_3) : \quad \delta \ 1.34 \text{ (d, 3H, J = Hz, -CHCH}_3), \ 2.31 \text{ (s, 3H, -NCH}_3), \ 3.62 \text{ (q, 1H, J = Hz, -NCHCH}_3), \ 7.21 - 7.35 \text{ (m, 5H, Ar-H); ^13C-NMR (75.4 MHz, CDCl}_3): \quad \delta \ 23.82, 34.47, 60.23, 126.55, 126.81, 128.34, 145.50
\]

(+)-(R)-4-Nitro-1-N-methyl-N-(x-methylbenzyl)aniline (4).

Fluoro-4-nitrobenzene (.1 g, .071 mmol) and (+)-(R)-N-Methyl-N-(x-methylbenzyl)amine (.096 g, .071 mmol) were dissolved in DMSO (10 mL) with Na₂CO₃ (1 g). The mixture is heated to 100°C for 12 h. The reaction mixture is poured into ice water (10 mL) and extracted with ether (3 x 15 mL). The organic extracts were combined, washed with 5 % HCl, dried (MgSO₄) and concentrated under reduced pressure. The crude material was recrystallized from ethanol to afford large yellow crystals (.155 g, 85.2 %). mp. 163-164 °C; [\alpha]_D +123 (CH_2Cl_2); \lambda_{\text{max}} (CHCl_3) = 388 nm \varepsilon = 7.2 \times 10^4.

\[
\text{^1H-NMR (300MHz, CDCl}_3) : \quad \delta \ 2.38 \text{ (d, 3H, J = 6.9 Hz, -CHCH}_3), \ 3.58 \text{ (s, 3H, -NCH}_3), \ 6.00 \text{ (q, 1H, J = 6.9 Hz, -NCHCH}_3), \ 7.47 \text{ (d, 2H, J = 3.5 Hz, Ar-H), 7.98 - 8.14 \text{ (m, 2H, Ar-H), 8.87 (d, 1H, J = 10.8 Hz, Ar-H); ^13C-NMR (75.4 MHz, CDCl}_3):}
\]
(±)-2-methoxy-2-phenylethanol (8).

α-Methoxyphenylacetic acid (.1 g, .6 mmol) is added to a suspension of LiAlH₄ (.25 g, .66 mmol) and THF (10 mL). The reaction mixture is heated at reflux temperatures for 12 h., cooled to 0°C and quenched with 5 % HCl (10 mL). Ether (20 mL) is added and the organic layer is separated and the aqueous layer was extracted with ether (3 x 10 mL). The organic layers were combined, washed with brine (10 mL), dried (MgSO₄) and concentrated under reduced pressure. The resulting residue was purified by bulb-to-bulb distillation to yield a colorless oil (.084 g, 91.3 %).

¹H-NMR (300MHz, CDCl₃): δ 2.46 (br, 1H, -OH), 3.29 (s, 3H, -OCH₃), 3.62 (m, 2H, -O-CH₂CH₂-), 4.28 (dd, 1H, J = 4.2, 8.3 Hz, O-CH₂CH₂), 7.31 (m, 5H, Ar-H);

¹³C-NMR (75.4 MHz, CDCl₃): δ 56.87, 67.34, 84.66, 126.86, 128.11, 128.52, 138.35
(+/-)-4-Nitro-1-O-(2-methoxy-2-phenylethyl)]-phenol ether (9).

Nitrofluorobenzene (.1g, .07 mmol) and 2 -methoxy-2-phenylethanol (.1 g, .07 mmol) were dissolved in DMSO (10 mL) with KOH (2 g). The mixture was heated at 100°C for 12 h. The reaction mixture is poured into ice water (10 mL) and extracted with ether (3 x 15 mL). The organic extracts were combined, washed with 5 % HCl, dried (MgSO₄) and ether was evaporated under reduced pressure. The resulting pale yellow oil was purified by flash chromatography on silica gel (30 % EtOAc / hexane) to give viscous yellow oil (.012 g, 64 %).

λ<sub>max</sub> (CHCl₃) = 390 nm; ε = 5.3 x 10⁴

¹H-NMR (300MHz, CDCl₃): δ 3.19 (s, 3H, -OCH₃), 3.91 (dd, 1H, J = Hz, -O-CH-CH₂), 4.08 (dd, 1H, J = Hz, -O-HCH-CH₂), 4.47 (dd, 1H, J = Hz, -OCH-CH₂), 6.78 (d, 2H, J = Hz, Ar-₉), 7.25 (m, 4H, Ar-H), 8.01 (d, 2H, J = Hz, Ar-₉); ¹³C-NMR (75.4 MHz, CDCl₃): δ 57.19, 72.85, 81.99, 114.72, 125.82, 126.23, 126.99, 128.58, 128.76, 137.83, 141.79, 163.79
3-Ethyl-5-(3-ethyl-2-benzothiazolinylidene)-rhodanine (d1).

![Chemical structure of 3-Ethyl-5-(3-ethyl-2-benzothiazolinylidene)-rhodanine (d1).](image)

2-(Methylthio)-3-benzothiazolium tetrafluoroborate (.05 g, .161 mmol) and 3-ethyl-rhodanine (.026 g, .161 mmol) were dissolved in ethanol (15 mL) with triethylamine (5 dps) and heated to a reflux for 1 h. The reaction mixture was chilled overnight and the precipitate is collected by vacuum filtration. The crude material is recrystallized from absolute ethanol to afford clear, yellow crystals (.046 g, 89 %).

mp. 246° - 247° \( \lambda_{\text{max (EtOH)}} = 426 \text{ nm} \) \( \varepsilon = 2.87 \times 10^5 \)

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta \ 1.29 \ (t, \ 3\ H, \ d = 7.0 \ Hz, \ -NCH\_2CH\_3), \ 1.51 \ (t, \ 3\ H, \ d \) = 7.30 Hz, -N'CH\_2CH\_3), \ 4.19 \ (q, \ 2\ H, \ d = 7.0 \ Hz, \ -N\_CH\_2CH\_3), \ 4.31 \ (q, \ 2\ H, \ d = 7.30, \ -N'CH\_2CH\_3), \ 7.19-7.29 \ (m, \ 2\ H, \ Ar-H), \ 7.41 \ (t, \ 1\ H, \ d = 1.1 \ Hz, \ Ar-H), \ 7.62 \ (d, \ 1\ H, \ d = 0.75 \ Hz, \ Ar-H); \(^{13}\)C-NMR (75.4 MHz, CDCl\(_3\)): \( \delta \ 12.02, \ 14.36, \ 39.95, \ 42.40, \)
83.85, 110.51, 122.27, 124.09, 126.80, 127.10, 139.45, 153.24, 165.92, 187.95

1,3-Diethyl-5-(3-ethyl-2-benzothiazolinylidene)-thiobarbituric acid

The reaction of 1,3-diethyl-2-thiobarbituric acid (.032 g, .161 mmol) and 2-(methylthio)-3-benzothiazolium tetrafluoroborate (.05 g, .161 mmol) was carried out in the same manner as the 3-ethyl rhodanine analogue (d1) to afford small orange crystals (.041 g, 70.6 %).
mp. 222 - 233° dec.; $\lambda_{\text{max}}$ (EtOH) = 352 nm  $\epsilon = 4.72 \times 10^4$

$^1$H-NMR (300 MHz, CDCl$_3$):  $\delta$ 1.31 - 1.36 (m (3 triplet on top of each other), 9H, --NCH$_2$CH$_3$), 4.58-4.67 (m (3 quartets on top of each other), 6H, -NCH$_2$CH$_3$), 7.41 (t, 1H, J = 7.13 Hz, Ar- H), 7.49 - 7.59 (m, 2H, Ar- H), 7.80 (d, 1H, J = 7.84 Hz, Ar-H);

$^{13}$C-NMR (75.4 MHz, CDCl$_3$):  $\delta$ 12.30, 12.38, 12.58, 42.91, 43.10, 114.04, 122.48, 125.17, 127.89, 128.38, 137.75, 160.16, 161.64, 167.73, 177.56

2-(3-Ethyl-2-benzothiazolinylidene)-1,3-indandione

The reaction of 1,3-indandione (.024 g, .161 mmol) and 2-(methylthio)-3-benzothiazolium tetrafluoroborate (.05, .1161 mmol) was carried out in the same manner as the 3-ethyl rhodanine analogue (d1) to afford small orange crystals (.021 g, 40.4 %).

mp. 313 - 314° dec.; $\lambda_{\text{max}}$ (EtOH) = 374 nm  $\epsilon > 8.57 \times 10^4$

$^1$H-NMR (300 MHz, CDCl$_3$):  $\delta$ 1.51 (t, 3H, J = 7.11 Hz, -NCH$_2$CH$_3$), 5.14 (q, 2H, J = 7.11 Hz, -NCH$_2$CH$_3$), 7.32 - 7.74 (m, 8H, Ar-H);  $^{13}$C-NMR (75.4 MHz, CDCl$_3$):

$\delta$ 14.40, 45.88, 112.73, 121.23, 122.60, 124.77, 127.13, 128.57, 129.65, 139.28, 139.46, 162.94, 188.62
2-(2-Acetanilidovinyl)-3-ethyl-benzthiazolium iodide (13).

3-Ethyl-2-methylbenzothiazolium iodide (5 g, 0.016 mol) and diphenylformamidine (3.14 g, 0.016 mol) are heated at reflux temperatures in excess acetic anhydride for 1 h. The reaction mixture was cooled to RT and the product was collect by vacuum filtration (5.93 g, 96.7 % crude). No further purification attempted.

2-(2-Acetanilidovinyl)-3-ethyl-benzoxazolium iodide

3-Ethyl-2-methylbenzoxazolium iodide (4.6 g, 0.016 mol) and diphenylformamidine (3.14 g, 0.016 mol) are heated at reflux temperatures in excess acetic anhydride for 1 h. The reaction mixture was cooled to RT and the product was collect by vacuum filtration (4.13 g, 59.4 % crude). No further purification attempted.

2-(2-Acetanilidovinyl)-3-methyl-benzthiazolium iodide

3-Methyl-2-methylbenzothiazolium iodide (2.3 g, 0.008 mol), and diphenylformamidine (1.6 g, 0.008 mol) are heated in excess acetic anhydride for 1 h. The reaction mixture was cooled to RT and the product was collect by vacuum filtration (3.17 g, 90.8 % crude). No further purification attempted.
2-(4-Acetanilido-1,3-butadienyl)-3-ethyl-benzothiazolium iodide (17)

3-Methyl-2-methylbenzthiazolium iodide (1 g, 3.3 mmol), and β-anilinoacraldehyde anil (.75 g, 3.3 mmol) are heated in excess acetic anhydride for 1 h. The reaction mixture was cooled to RT and the product was collect by vacuum filtration (1.37 g, 87.8 % crude). No further purification attempted

2-(6-Acetanilido-1,3,5-hexatrienyl)-3-ethyl-benzothiazolium Iodide (18).

Glutaconaldehyde dianilide hydrochloride (.933 g, 3.3 mmol) and 3-ethyl-2-methylbenzothiazolium iodide (1 g, 3.3 mmol) are refluxed in excess acetic anhydride for 15 min.. The reaction mixture was chilled to 0°C for 1 h. and the resulting precipitate was collected by vacuum filtration. The crude material was recrystallization from acetic acid (3x) to afforded reddish-brown crystals (1.54 g, 93.7%).

mp. 203°-206°C dec
2-[2-(3-Ethyl-2-benzthiazolinylidene)-ethylidene]-1,3-indandione (d2).

![Chemical structure](image)

2-(2-Acetanilidovinyl)-3-ethyl-benzthiazolium iodide (.135 g, .36 mmol) and 1,3-indandione (.055 g, .38 mmol) were dissolved in absolute ethanol (10 mL) with a catalytic amount of triethylamine (5 dps) and heated to a reflux for 45 min. The reaction was chilled overnight and the precipitate was collect by vacuum filtration. The crude material was recrystallized from absolute ethanol to afford a purple crystalline solid (.05 g, 42 %).

mp. 255°-257° dec.; \( \lambda_{\text{max}}(\text{EtOH}) = 504 \text{ nm} \); \( \varepsilon_{504} = 1.23 \times 10^5 \)

\(^1\)H-NMR (300MHz, CDCl\(_3\) ): \( \delta \) 1.49 (t, 3H, J = 7.21 Hz, -NCH\(_2\)CH\(_3\)), 4.25 (2H, q, J = 7.21 Hz, -NCH\(_2\)CH\(_3\)), 7.21 (m, 9H, (8 Ar-H and 1 chain proton =CH-CH=)), 7.85 (d, 1H, J = 13.34 Hz, =CH-CH=); \(^{13}\)C -NMR (75.4 MHz, CDCl\(_3\) ): \( \delta \) 12.28, 41.49, 94.79, 111.45, 115.24, 120.89, 121.57, 122.43, 124.51, 125.63, 127.52, 32.89, 133.04, 140.32, 141.06, 141.70, 166.69, 191.07, 192.5
2,2-Dimethyl-5-[2-(3-ethyl-2-benzothiazolinyldene)-ethyldene]-1,3-dioxane-4,6-dione.

Acetanilidovinyl-3-ethyl-benzthiazolium iodide (.1 g, .22 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (.034 g, .24 mmol) were dissolved in pyridine (10 mL) with a catalytic amount of triethylamine and heated to a reflux for 1 h. Methanol was added and the reaction mixture was chilled in the refrigerator overnight. The resulting precipitate was collect by vacuum filtration and recrystallized with pyridine/ethanol solution (50%) to afford small, yellow crystals (.047 g, 64%).

mp. = 225°-226° dec.; $\lambda_{\text{max}}$(EtOH) = 456 nm, $\varepsilon_{456} = 1.66 \times 10^4$

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 1.48 (t, 3H, J = 7.3 Hz, -NCH$_2$C$_3$S), 1.69 (s, 6H, C(CH$_3$)$_2$), 4.28 (q, 2H, J = 7.3 Hz, -NC$_2$H$_5$CH$_3$), 7.29 (m, 2H, J = 5.3 Hz, Ar-H$_2$), 7.41-7.46 (m, 2H, J = 5.4 Hz, Ar-H$_2$), 7.43 (d, 1H, J = 13.74 Hz, =CH-CH=), 8.33 (d, 1H, J = 13.74 Hz, =CSCH=); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 12.39, 27.11, 41.79, 93.78, 96.58, 103.16, 112.03, 122.59, 125.09, 125.73, 127.77, 140.87, 150.65, 163.72, 165.22, 168.69

1,3-Diethyl-5-[2-(3-ethyl-2-benzothiazolinyldene)-ethyldene]-2-thiobarbituric acid.

2-(2-Acetanilidovinyl)-3-ethyl-benzthiazolium iodide (.135 g, .36 mmol) and 1,3-diethyl-2-thiobarbituric acid (.072 g, .36 mmol) were dissolved in absolute ethanol (10 mL) with triethylamine (5 dps) and heated to a reflux for 45 min. The reaction was
chilled overnight and the precipitate was collected by vacuum filtration. The crude product was purified by dissolving it in hot pyridine and precipitating the product out of solution with cold ethanol (.095 g, 68%).

mp. = 318°-321° dec.; λ_{max} (EtOH) = 495 nm ε_{495} = 1.20 \times 10^5

\^H-NMR (300 MHz, CDCl\textsubscript{3}): δ 1.3 (t, 6H, J = 6.8 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 1.51 (t, 3H, J = 7.27 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 4.35 (q, 2H, J = 7.27 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 4.56 (q, 4H, J = 6.8 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 7.35 (m(d & dd overlapping, 2H, Ar-H), 7.5 (dd, 1H, J = 7.59 Hz, Ar-H), 7.67 (d, 1H, J = 7.85 Hz, Ar-H), 7.83 (d, 1H, J = 14 Hz, =CH-CH=), 8.38 (d, 1H, J = 14 Hz, =CH-CH=); \^C-NMR (75.4 MHz, CDCl\textsubscript{3}): δ 12.5, 12.65, 42.15, 42.57, 43.23, 98.71, 101.13, 112.35, 122.67, 125.53, 126.08, 127.96, 140.81, 150.17, 161.34, 161.82, 169.83, 169.83, 178.33

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-ethylidene]-rhodanine (d3).

Method A:

5-Anilinomethylene-3-ethylrhodanine (.1 g, .36 mmol) and acetic anhydride were dissolved in acetonitrile (10 mL) and heated at reflux temperatures for 30 min. 3-Ethyl-2-methylbenzthiazolium iodide (.11 g, .36 mmol) in acetonitrile was added and heated to a reflux for 1 h. Acetonitrile is removed under reduced pressure and hot ethanol is added to the remaining residue. The reaction mixture was chilled in the
refrigerator overnight. The crystalline product was collect by vacuum filtration and recrystallized from absolute ethanol to yield dark purple crystals (.087 g, 69.6 %).

METHOD B:

2-(2-Acetanilidovinyl)-3-ethyl-benzthiazolium iodide (.28 g, .6 mmol) and 3-rhodanine (.1 g, .6 mmol) were dissolved in absolute ethanol (10 mL) with triethylamine (5 dps) and heated to a reflux for 45 min. The reaction was chilled overnight and precipitate was collect by vacuum filtration and recrystallized from absolute ethanol to afford a dark, crystalline powder (.008 g, 8.2 %).

mp. 262°-263° dec.; $\lambda_{\text{max}}$ (EtOH) = 527 nm $\epsilon_{527} = 8.76 \times 10^4$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.25 (t, 3H, $J = 7.12$ Hz, -NCH$_2$CH$_3$), 1.38 (t, 3H, $J = 7.25$ Hz, -NCH$_2$CH$_3$), 4.00 (q, 2H, $J = 7.25$, -NCH$_2$CH$_3$), 4.15 (q, 2H, 7.12 Hz, -NCH$_2$CH$_3$), 5.27 (d, 1H, $J = 12.71$ Hz, =CH-CH=), 7.03 (d, 1H, $J = 8.14$ Hz, Ar-$H$), 7.15 (dd, 1H, $J = 2.62$ Hz, Ar-$H$), 7.33 (dd, 1H, $J = 2.62$ Hz, Ar-$H$), 7.46 (d, 1H, $J = 8.14$ Hz, Ar-$H$), 7.56 (d, 1H, $J = 12.44$ Hz, =CH-CH=); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 11.76, 12.28, 39.57, 40.48, 89.43, 109.76, 110.25, 122.14, 123.44, 127.15, 132.29, 159.26, 166.46
2,2-dimethyl-5-[4-(3-ethyl-2-benzothiazolylidene-2-butenylidene)]-1,3-dioxane-4,6-dione

![Chemical Structure](attachment:image.png)

2-(4-Acetanilido-1,3-butadienyl)-3-ethyl-benzothiazolium iodide (.125 g, .3 mmol), and 2,2-dimethyl-1,3-dioxane-4,6-dione (.05 g, .3 mmol) were dissolved in ethanol (10 mL) with a catalytic amount of triethylamine (5 dps) and heated at reflux temperatures for 1 h. The reaction mixture was chilled in the refrigerator overnight and the resulting precipitate was collected by vacuum filtration. The crude dye was purified by recrystallized from absolute ethanol (5x) to afford a green crystalline solid (.054 g, 32.7%).

mp. 215° - 216° dec. \( \lambda_{\text{max}} (\text{EtOH}) = 554 \text{ nm} \quad \varepsilon = 4.28 \times 10^5 \)

\(^1\text{H}-\text{NMR} (300 \text{ MHz}, \text{CDCl}_3): \delta 1.41 (t, 3H, J = 7.3 \text{ Hz}, -\text{NCH}_2\text{CH}_3), 1.68 (s, 6H, -C(\text{CH}_3)_2), 4.11 (q, 2H, J = 7.3 \text{ Hz}, -\text{NCH}_2\text{CH}_3), 6.05 (d, 1H, J = 11.7 \text{ Hz}, -\text{CH=CH}-), 7.16 (d, 1H, J = 8.2 \text{ Hz}, \text{Ar-H}), 7.25 (m (d covered by \text{CHCl}_3), 1H, -\text{CH=CH}-), 7.41 (m (dd-\text{Ar-H, d-Ar-H, d-CH=CH-}), 3H, 2 x \text{Ar-H}, -\text{CH=CH}-), 7.58 (d, 1H, J = 7.8 \text{ Hz}, \text{Ar-H}), 7.97 (d, 1H, J = 12.3 \text{ Hz}, -\text{CH=CH-})
1,3-Diethyl-5-[4-(3-ethyl-2-benzothiazolinyldene-2-butenylidene)]-2-thiobarbituric acid.

The reaction of 1,3-diethyl-2-thiobarbituric acid (.123 g, .25 mmol) and 2-(4-acetanilido-1,3-butadienyl)-3-ethyl-benzothiazolium iodide (.05 g, .25 mmol) was carried out in the same manner as the 2,2-dimethyl-1,3-dioxane-4,6-dione analogue. The crude product was recrystallized from 50 % pyridine/ethanol to afford a green crystalline solid (.026 g, 25.2 %).

mp. 234° - 236° dec.; $\lambda_{\text{max}}$ (EtOH) = 594 nm  $\varepsilon > 6.62 \times 10^4$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.25 (t, 6H, J = 6.8 Hz, -NCH$_2$CH$_3$), 1.47 (t, 3H, J = 7.3 Hz, -NCH$_2$CH$_3$), 4.13 (q, 2H, J = 7.3 Hz, -NC(CH$_3$)$_2$CH$_3$), 4.56 (q, 4H, J = 6.9 Hz, -NCSCH$_3$), 6.16 (d, 1H, J = 12.9 Hz, =CH-CH=C), 7.2 - 7.31 (m, 3H, =CH-CH= and Ar-H), 7.43 (t, 1H, J = 7.6 Hz, Ar-H), 7.55 (d, 1H, J = 12.5 Hz, =CH-CH=), 7.58 (d, 1H, J = 7.8 Hz, Ar-H), 7.76 - 7.91 (m, 2H, J = Hz, =CH-CH= and Ar-H)

3-Ethyl-5-[4-(3-ethyl-2-benzothiazolinyldene-2-butenylidene)]-rhodanine (d4)

The reaction of 3-ethyl-rhodanine (.05 g, .3 mmol) and 2-(4-acetanilido-1,3-butadienyl)-3-ethyl-benzothiazolium iodide (.15 g, .3 mmol) was carried out in the same manner as the 2,2-dimethyl-1,3-dioxane-4,6-dione analogue. The crude product was recrystallized from ethanol to afford a green crystalline solid (.03 g, 26.7 %).

mp. 223° - 224° dec.; $\lambda_{\text{max}}$ (EtOH) = 598 nm  $\varepsilon > 1.49 \times 10^4$
$^1$H-NMR (300MHz, CDCl$_3$):  δ 1.22 (t, 3H, J = 7.2 Hz, -NCH$_2$CH$_3$), 1.34 (t, 3H, J = 7.0 Hz, -NCH$_2$CH$_3$), 3.91 (q, 2H, J = 7.2 Hz, -NCH$_2$CH$_3$), 4.14 (q, 2H, J = 7.0 Hz, -NCH$_2$CH$_3$), 5.66 (d, 1H, J = 11.9 Hz, =CH-CH=), 5.93 (t, 1H, J = 12.8 Hz, =CH=C), 6.98 (m (one d and one t), 2H, =CH-CH=, Ar-H), 7.05 (t, 1H, J = 7.4 Hz, Ar-H), 7.28 (m (one d and one t), 2H, =CH-CH=, Ar-H), 7.39 (m, (one d and one t), 2H, =CH-CH=, Ar-H)

1,3-Diethyl-5-[6-(3-ethyl-2-benzothiazolinylidene-2,4-hexadienylidene)]-2-thiobarbituric acid.

2-(6-Acetanilido-1,3,5-hexatrienyl)-3-ethyl-benzothiazolium iodide (.1 g, .199 mmol.), and 1,3-diethyl-2-thiobarbituric acid (.132 g, .66 mmol) were dissolved in ethanol (10 mL) with a catalytic amount of triethylamine (5 dps) was heated at reflux temperatures for 1h. The reaction mixture was chilled in the refrigerator overnight and the resulting precipitate was collected by vacuum filtration. The crude dye was purified by recrystallization from absolute ethanol (3x) to afford a green crystalline solid (.032 g, 37%).

mp. 172° -174°C dec.; $\lambda_{max}$ (EtOH) = 696 nm $\varepsilon > 5.12 \times 10^5$
$^1$H-NMR (300MHz, CDCl$_3$):  δ 1.23 (t, 6H, J = 7.1 Hz, -NCH$_2$CH$_3$), 1.45 (t, 3H, J = 7.2 Hz, -NCH$_2$CH$_3$), 4.09 (q, 2H, J = 7.1 Hz, -NC$H_2$CH$_3$), 4.56 (q, 4H, J = 7.2 Hz, -NC$H_2$CH$_3$), 5.90 (d, 1H, J = 12.5 Hz, =CH=CH-), 6.38 (dd, 1H, J = 12.7 Hz, =CH=CH-), 7.13 (d, 1H, J = 8.2 Hz, Ar-$H$), 7.23 - 7.54 (m, 3H, J = Hz, Ar-$H$ and =CH-C=H$-$), 7.98 (d, 1H, J = 13.4 Hz, =CH-C=H$-$)

3-Ethyl-5-[6-(3-ethyl-2-benzothiazolinylidene-2,4-hexadienylidene)]rhodamine (d5).

The reaction of 3-ethylrhodanine (.032 g, .2 mmol) and 2-(6-acetanilido-1,3,5-hexatrienyl)-3-ethyl-benzothiazolium iodide (.1 g, .2 mmol) was carried out in the same manner as the 1,3-diethyl-3-thiobarbituric acid analogue. The crude dye was recrystallized from 85 % ethanol/pyridine solution to afford a green crystalline solid (47% crude product was collected from several reactions and recrystallized together).

mp. 216° - 217°C dec.; $\lambda_{\text{max}}$(EtOH) = 622 nm  ε >> 7.21 x 10$^3$

$^1$H-NMR (300MHz, CDCl$_3$):  δ 1.22 (t, 3H, J = 7.1 Hz, -NCH$_2$CH$_3$), 1.32 (t, 3H, J = 7.2 Hz, -NCH$_2$CH$_3$), 3.86 (q, 2H, J = 7.2 Hz, -NC$H_2$CH$_3$), 4.14 (q, 2H, J = 7.1 Hz, -NC$H_2$CH$_3$), 5.58 (d, 1H, J = 11.6 Hz, =CH-C=H$-$) 6.01 (dd, 1H, J = 12.8 Hz, =CH-C=H$-$), 6.19 (dd, 1H, J = 12.2 Hz, =CH-C=H$-$), 6.70 (dd, 1H, J = 13.3 Hz, =CH-C=H$-$), 6.9(d (on top of a dd), 1H, Ar-$H$), 6.86 (dd (on top of a d), 1H, =CH-C=H$-$),
6.98 (dd, 1H, J = 7.5 Hz, Ar-H), 7.20 (d (partially covered by -CHCl₃), 1H, J = 10.6 Hz, Ar-H), 7.33 (d (on top of a d), 1H, Ar-H), 7.36 (d (on top of a d), 1H, =CH-CH=); High resolution DIP EIMS calcd. for C₂₀H₂₀N₂O₃S₄ 400.0737 Found 400.0762

2,2-dimethyl-5-[6-(3-ethyl-2-benzothiazolylidene-2,4-hexadienyldene)]-1,3-dioxane-4,6-dione

The reaction of 2,2-dimethyl-1,3-dioxane-4,6-dione (.032 g, .219 mmol) and 2-(6-acetanilido-1,3,5-hexatrienyl)-3-ethyl-benzothiazolium iodide (.1 g, .199 mmol) was carried out in the same manner as the 1,3-diethyl-3-thiobarbituric acid analogue. The crude dye recrystallized from absolute ethanol to yield a light blue crystalline solid (.059 g, 77.6 %).

mp. 156° - 157°C dec.; λₘₐₓ (EtOH) = 656 nm  ε = 2.48 x 10⁵

¹H-NMR (300MHz, CDCl₃):  δ 1.39 (t, 3H, J = 7.1 Hz, -NCH₂CH₃), 1.68 (s, 6H, C(CH₃)₂), 4.01 (q, 2H, J = 7.3 Hz, -NCH₂CH₃), 5.82 (d, 1H, J = 7.2 Hz, =CH-CH=), 6.31 (dd, 1H, J = Hz, =CH-CH=); ¹³C-NMR (75.4 MHz, CDCl₃): δ 12.04, 27.27, 40.52, 95.52, 101.20, 122.10, 122.31, 123.52, 125.12, 127.32, 141.37, 146.97, 156.68, 157.76, 158.84, 162.43, 164.74

6-Amino-2-methylbenzothiazole (22)

6-Nitrobenzothiazole (1 g, .005 mol) is dissolved in a mixture of methanol (10 mL), concentrated HCl (10 mL) and stannous chloride (5 g, .026 mol). The reaction is
heated to a reflux for 15 min. Methanol is removed under reduced pressure and the residue is dissolved in water (100 mL) and strongly basified with KOH. The solution is extracted with ether (3 x 50 mL) and concentrated under reduced pressure. The crude material is recrystallized from ethanol to afford long yellow crystals (.76 g, 89.4 %). mp. 82-85 °C

\[ ^1H-NMR \text{ (300MHz, CDCl}_3 \text{): } \delta \begin{align*} &2.71 \text{ (s, 3H, } -\text{CH}_3), \quad 3.75 \text{ (br, 2H, } -\text{NH}_2), \quad 6.74 \text{ (d, 1H, } J = 8.6, \ 2.1 \text{ Hz, Ar-}H, \quad 7.03 \text{ (s, 1H, } J = 2.1 \text{ Hz, Ar-}H), \quad 7.69 \text{ (d, 1H, } J = 8.6 \text{ Hz, Ar-}H) \end{align*} \]

\[ ^13\text{C-NMR (75.4 MHz, CDCl}_3 \text{): } \delta \begin{align*} &19.74, \ 105.82, \ 115.16, \ 122.75, \ 137.30, \ 144.03, \ 146.88, \ 162.50 \end{align*} \]

6-(2-Methoxy-2-phenylethylamido)-2-methylbenzothiazole (29)

![Chemical Structure](image)

6-Amino-2-methylbenzothiazole (1 g, 4.42 mmol) and pyridine (.384 g, 4.86 mmol) were dissolved in methylene chloride (30 mL) and cooled to -5°C. O-methylmandeloyl chloride (.72 g, 4.42 mmol) dissolved in methylene chloride (20 mL) was then added over a 30 min. period. After the addition was complete the reaction was allowed to warm to RT and stirred for an addition 2 h. The reaction was then quenched with 5 % HCl and the organic layer was separated. The aqueous layer was extracted with methylene chloride (3 x 25 mL), washed with sat. NaHCO\textsubscript{3}, brine, and dried (MgSO\textsubscript{4}).
The methylene chloride was removed under reduced pressure and the residue was recrystallized from ethanol to afford white crystalline solid (1.28 g, 93%).

mp. 114° - 115° C

^1^H-NMR (300MHz, CDCl$_3$):  δ 1.53 (s, 3H, -CH$_3$), 2.78 (s, 3H, -OCH$_3$), 4.76 (s, 1H, CH$_3$O-CH-), 7.31 - 7.47 (m, 7H, Ar-H), 7.85 (d, 1H, J = 8.7 Hz, Ar-H), 8.4 (s, 1H, Ar-H), 8.65 (s, 1H, O=CNH)

6-(2-Methoxy-2-phenylethlamido)-3-ethyl-2-methylbenzothiazolium iodide (30)

(.1 g, .32 mmol) was dissolved in excess ethyl iodide (30 mL) and heated to a reflux for 72 h. Upon cooling to RT a light yellow solid material precipitates from the reaction mixture. The precipitate is filtered by vacuum filtration, suspended in Et$_2$O and heated to a reflux for 12 h. The suspension is cooled to 0° and the precipitate is filtered off by vacuum filtration to afford a light yellow solid (.148 g, 99%).

mp. 183° C (blackens)

^1^H-NMR (300MHz, CD$_2$CN):  δ 1.43 (br(t), 3H, -NCH$_2$CH$_3$), 3.29 (s, 3H, -OCH$_3$), 4.71 (br(q), 2H, -NCH$_2$CH$_3$), 4.98 (s, 1H, CH$_3$OCCH$_3$), 7.40 (m, 3H, Ar-H), 7.57 (d, 2H, J = 8.0, 1.4 Hz, Ar-H), 8.05 (d, 1H, J = 9.2, 1.8 Hz, Ar-H), 8.31 (d, 1H, J = 9.1 Hz, Ar-H), 8.93 (s, 1H, O=CNH); ^13^C-NMR (75.4 MHz, CD$_3$CN):  δ 13.81, 16.39, 44.60, 83.20, 114.10, 116.69, 122.69, 126.97, 128.23, 136.40, 137.19, 138.06 169.42, 175.20
2-(2-Acetanilidovinyl)-6-(2-methoxy-2-phenyl-ethylamido)-3-ethylbenzothiazolium iodide (31)

The reaction of 6-(2-methoxy-2-phenyl-ethylamido)-3-ethyl-2-methylbenzothiazolium iodide (0.25 g, 0.53 mmol) and diphenylformamidine (0.105 g, 0.53 mmol) was carried out as described above for the preparation of 4. The precipitate was collected by vacuum filtration to afford dark purple crystals (0.241 g, 93.4% crude). No further purification attempted.

$^1$H-NMR (300MHz, CDCl$_3$):  $\delta$ 1.29 (t, 3H, J = 7.4 Hz, -NCH$_2$C$_3$H$_3$), 2.06 (s, 3H, O=CC$_3$H$_3$), 3.45 (s, 3H, -OCH$_3$), 4.53 (q, 2H, J = 7.4 Hz, -NCH$_2$C$_3$H$_3$), 4.90 (s, 1H, CH$_3$OCH$_3$), 5.60 (d, 1H, J = 14.1 Hz, -CH=CH-), 7.35 - 7.41 (m, 12H, Ar-H), 7.82 (d, 1H, Ar-H), 7.97 (d, 1H, Ar-H), 8.69 (s, 1H, J = 9.2 Hz, Ar-H), 8.9 (d, 1H, J = 13.9 Hz, -CH=CH-), 9.26 (s, 1H, O=CNH)

(+)-1,3-Diethyl-5-[2-(3-ethyl-6-(2S)-2-methoxy-2-phenylethylamide)benzothiazolinylidene]-2-thiobarbituric acid (d6).

2-(2-Acetanilidovinyl)-6-(2-methoxy-2-phenyl-ethylamido)-3-ethylbenzothiazolium iodide (0.05 g, 0.081 mmol) and 1,3-diethyl-2-thiobarbituric acid (0.05 g, 0.081 mmol) were dissolved in absolute ethanol (10 mL) with a catalytic amount of triethylamine (5 dps)
and heated at reflux temperatures for 45 min. the solvents were removed under reduced pressure and the residue was dissolved in ethyl acetate and run through a plug of silica gel (ethylacetate). The ethyl acetate was distilled off under reduced pressure and the residue was recrystallized from a minimal amount of ethanol to afford a dark orange powder (.015 g, 33 %).

mp. 243° - 244° C.; $\lambda_{\text{max}}$ (EtOH) = 506 nm $\varepsilon = 1.29 \times 10^5$ [\(\alpha\)]D + 147°(EtOH)

$^1$H-NMR (300MHz, CDCl₃): $\delta$ 1.27 (t, 6H, J = 6.8 Hz, -NCH₂C₃), 1.51 (t, 3H, J = 7.2 Hz, -NCH₂CH₃), 3.45 (s, 3H, -OCS), 4.3 (q, 2H, J = 7.2 Hz, -NCSCH₃), 4.56 (q, 4H, J = 6.8 Hz, -NCH₂CH₃), 4.76 (s, 1H, -OCH₃), 7.27 (d, 1H, Ar-()), 7.39 (m, 5H, Ar-()), 7.55 (dd, 1H, J = 5.3, 1.9 Hz, Ar-()), 7.85 (d, 1H, J = 13.8 Hz, =CH-CH=), 8.21 (s, 1H, Ar-()), 8.38 (d, 1H, J = 14.1 Hz, =CH-CH=), 8.75 (s, 1H, O=CNS; High resolution DIP EIMS calcd. for C₂₈H₃₀N₄O₄S₂ 550.1708 Found 550.0417

3-Ethyl-6-[2-(3-ethyl-5-(2-methoxy-2-phenylethlamido)benzothiazolinylidene)-ethylidene]-3-ethylrhodanine

The reaction of 2-(2-acetanildiovinyl)(6-(2-methoxy-2-phenylethlamido)-ethylbenzothiazolium iodide (.05 g, .081 mmol) and 3-ethylrhodanine (.013 g, .081 mmol) was carried out as described above for the preparation of d6. Upon cooling a precipitate was formed and was collected by vacuum filtration and recrystallized from ethanol to afford small yellow crystals (.001 g, 2.6 %)
mp. 196° - 197° C.; \( \lambda_{\text{max (EtOH)}} = 524 \text{ nm} \) \( \varepsilon > 5.52 \times 10^5 \)

\(^1\text{H-NMR (300MHz, CDCl}_3\)): \( \delta \) 1.42 (t, 3H, \( J = 7.3 \text{ Hz}, -\text{NCH}_2\text{CH}_3 \)), 1.69 (s, 6H, -C(CH\(_3\))\(_3\)), 3.44 (s, 3H, -OCH\(_3\)), 4.23 (q, 2H, \( J = 7.3 \text{ Hz}, -\text{NCH}_2\text{CH}_3 \)), 4.76 (s, 1H, -OC\(_2\text{H}_4\)), 7.18 (d, 1H, \( J = 8.9 \text{ Hz}, \text{Ar-H} \)), 7.39 (m, 5H, \( \text{Ar-H} \)), 7.57 (dd, 1H, \( J = 5.0, 2.0 \text{ Hz}, \text{Ar-H} \)), 8.13 (s, 1H, \( \text{Ar-H} \)), 8.23 (d, 1H, \( J = 13.8 \text{ Hz}, =\text{CH-CH=} \)), 8.71 (s, 1H, O=CNH); High resolution DIP EIMS calcd. for C\(_{25}\)H\(_{25}\)N\(_3\)O\(_3\)S\(_3\) 511.1058 Found 511.1101

2,2-Dimethyl-5-[2-(3-ethyl-5-(2-methoxy-2-phenylethylamido)benzothiazolinylidene)-ethylidene]-1,3 dioxane-4,6-dione

The reaction of 2-(2-acetanildiovinyl)(6-(2-methoxy-2phenylethlamido)-3-ethylbenzothiazolum iodide (.1 g, .16 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (.23 g, .16 mmol) was carried out as described above for the preparation of \( \text{d6} \). Upon cooling a precipitate was formed and was collected by vacuum filtration and recrystallized from ethanol to afford small yellow crystals (.023 g, 29 %)

mp. 210° C (darkens); \( \lambda_{\text{max (EtOH)}} = 468 \text{ nm} \) \( \varepsilon = 1.15 \times 10^5 \)

\(^1\text{H-NMR (300MHz, CDCl}_3\)): \( \delta \) 1.42 (t, 3H, \( J = 7.3 \text{ Hz}, -\text{NCH}_2\text{CH}_3 \)), 1.69 (s, 6H, -C(CH\(_3\))\(_2\)), 3.45 (s, 3H, -OCH\(_3\)), 4.23 (q, 2H, \( J = 7.3 \text{ Hz}, -\text{NCH}_2\text{CH}_3 \)), 4.76 (s, 1H, -OC\(_2\text{H}_4\)), 7.19 (d, 1H, \( J = 8.9 \text{ Hz}, \text{Ar-H} \)), 7.42 (m, 6H, \( \text{Ar-H} \)), 7.45 (dd, 1H, \( J = 8.3, 1.2 \text{ Hz}, \text{Ar-H} \)), 8.13 (s, 1H, \( \text{Ar-H} \)), 8.23 (d, 1H, \( J = 13.8 \text{ Hz}, \text{Ar-H} \)), 8.71 (s, 1H, -
O=CNH); High resolution DIP EIMS calcd. for C_{26}H_{26}N_{2}O_{6}S 494.1511 Found 494.0578

2-[2-(3-ethyl-6-(2-methoxy-2-phenylethlamido)benzothiazolylidene)-ethylidene]-1,3-indandione

The reaction of 2-(2-acetanildiovinyl)(6-(2-methoxy-2-phenylethlamido)-3-ethylbenzothiazolium iodide (.1 g, .16 mmol) 1,3-indandione (.2 g, .16 mmol) was carried out as described above for the preparation of d6. Upon cooling a precipitate was formed and was collected by vacuum filtration and recrystallized from ethanol to afford small yellow crystals (.027 g, 33.3 %)

mp. 239° - 240° C.; λ_{max} (EtOH) = 506 nm  ε = 2.35 x 10^5

^1H-NMR (300MHz, CDCl$_3$):  δ 1.44 (t, 3H, J = 7.2 Hz, -NCH$_2$CH$_3$),  3.45 (s, 3H, -OCH$_3$), 4.18 (q, 2H, J = 7.2 Hz, -NCCH$_2$CH$_3$),  4.75 (s, 1H, -OC=H),  7.11 (d, 1H, J = 9.0, Ar-H),  7.24 - 8.07 (m, 11H, Ar-H and =CH=CH=),  8.21 (s, 1H, Ar-H),  8.75 (s, 1H, O=CNH); High resolution DIP EIMS calcd. for C$_{29}$H$_{24}$N$_2$O$_4$S 496.1457 found 496.0770
(S)-(-)-3-α-Methylbenzyl-2,4-dimethylthiazolium perchlorate (34).

(S)-(-)-N-α-Methylbenzylacetamide (.1 g, .612 mmol) and Lawesson's reagent (.124 g, .306 mmol) were dissolved in toluene (10 mL) and heated to a reflux for 2 h. The reaction mixture was extracted with 5% HCl, 5% NaOH, brine and dried over MgSO₄ and the toluene is evaporated under reduced pressure. The crude yellow oil is taken up in THF (15 mL) and monochloroacetone (.0624 g, .674 mmol.) is added and heated at 50°C for 12 h. Water is added and THF is distilled off under reduced pressure. Activated charcoal is added and heated at 60°C for 15 min. and filtered. Concentrated NaClO₄ is added and heated at 60°C for 1 h. Water is evaporated under reduced pressure and acetone (50 mL) is added to precipitate NaCl, which is removed by vacuum filtration. Acetone is evaporated under reduced pressure to yield a white powder (.138 g). Recrystalization with absolute ethanol yielded white crystals (.132 g, 68%).

mp. 157°-158° dec.; [α]D -65°(acetone)

¹H-NMR (300 MHz, (CD₃)₂CO): δ 2.19 (d, 3H, J = 7.28 Hz, -CH₃), 2.45 (s, 3H, -CH₃), 3.1 (s, 3H, -CH₃), 6.52 (q, 1H, 7.28 Hz, N-CH), 7.3-7.5 (m, 5H, Ar-H), 7.91
(s, 1H, C=CH-S); $^{13}$C-NMR (75.4 MHz (CD$_3$)$_2$CO)): $\delta$ 15.54, 17.28, 17.64, 61.78, 120.13, 127.64, 129.73, 130.15, 137.13, 147.80, 173.82; IR (film) 3094, 3010, 2364, 1578, 1446, 13.86, 1302, 1231, 1099, 704, 614

5-Anilinomethylene-3-ethylrhodanine (14).

3-Ethyl-rhodanine (5 g, .031 mol) and diphenylformamidine (6.1 g, .031 mol) are heated at 120°C for 1 h. Methanol is added and the precipitate is collected by vacuum filtration and washed with methanol to afford yellow needle like crystals (5.41 g, 75.14%). Product was used without further purification. Analytically pure samples were obtained by recrystallization from acetic acid.

mp. 184°-186°C

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.14 (t, 3H, J = 7.0 Hz. -NCH$_2$CH$_3$), 4.00 (q, 2H, J = 7.0 Hz. -NCH$_2$CH$_3$), 7.2-7.4 (m, 5H, Ar-H), 8.13 (s, 1H, =CH-N), 10.39 (s, 1H, -NH); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 11.90, 38.68, 94.24, 116.72, 123.82, 129.49, 135.37, 139.97, 166.46, 190.70; IR (film) 2987, 1679, 1638, 1584, 1470, 1440, 1308, 1105, 702
5-Anilinomethylene-1,3-diethyl-2-thiobarbituric acid

1,3-Diethyl-2-thiobarbituric acid (.5 g, .0025 mol) and diphenylformamidine (.49 g, .0025 mol) was carried out in the same manner as the 3-ethyl-rhodanine analogue. The crude product was recrystallized from methanol to afford light yellow crystals (.69 g, 90.8 %).

mp. 184°-186°C

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.28 (t, 6H, $J = 7.0$ Hz, -CH$_3$), 4.53 (q, 4H, $J = 7.0$ Hz, -CH$_2$), 7.24-7.25 (m, 5H, Ar-H), 8.7 (d, 1H, $J = 13.9$ Hz, =C-H-N), 12.28 (d, 1H, $J = 13.0$ Hz, -NH); $^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 12.23, 12.37, 42.33, 43.01, 94.86, 118.15, 126.92, 130.09, 137.90, 152.87, 160.73, 163.09, 178.83

(S)-(−)-3-Ethyl-5-[2-(3-α-methylbenzyl-4-methyl-2-thiazolinylidene)-ethylidene]-rhodanine (d7).

(S)-(−)-3-α-Methylbenzyl-2,4-dimethylthiazolium perchlorate (.3 g, .944 mmol), 5-anilinovinyl-2-ethylrhodanine (.25 g, .994 mmol), acetic anhydride (.096 g, .944 mmol)
and triethylamine (.048 g, .473 mmol) are stirred in acetonitrile (10 mL) at RT for 24 h. Acetonitrile is evaporated under reduced pressure and methanol (20 mL) is added and chilled for 2 h. The crude product is filtered off and recrystallized with 10% pyridine/ethanol to yield a greenish-purple solid (.216 g, 58.9%).

mp. 162°-164°, \([\alpha]_D^\circ +1200^\circ (\text{CHCl}_3), \lambda_{\text{max}} (\text{EtOH}) = 542 \text{ nm (CHCl}_3), s = 8.6 \times 10^5;\)

\(^1^H\)-NMR (300MHz, CDCl\(_3\)): \(\delta 1.19 (t, 3\text{H, } J = 7.04 \text{ Hz, -NCH}_2\text{CH}_3), 1.87 (d, 3\text{H, } J = 7.10 \text{ Hz, -NCHCH}_3), 2.14 (s, 3\text{H, } =\text{CCH}_3), 4.09 (q, 2\text{H, } J = 7.04 \text{ Hz, -NCH}_2\text{CH}_3), 5.0 (d, 1\text{H, } J = 12.86 \text{ Hz, C=CH}), 5.55 (q, 1\text{H, } J = 7.10 \text{ Hz, NCH-Ph}), 6.05 (s, 1\text{H, } =\text{CH-S}), 7.19-7.54 (m, 6\text{H, Ar-H}); \(^{13}C\)-NMR (75.4 MHz, CDCl\(_3\)): \(\delta 12.23, 15.47, 15.86, 55.72, 92.40, 101.43, 105.78, 125.96, 128.38, 129.04, 129.31, 132.23, 137.58, 139.23, 163.153, 165.95, 190.18;\) \(\text{D} \text{IP} \text{EIMS}\))

for C\(_{19}\)H\(_{20}\)N\(_2\)O\(_3\) \(388.0737\) Found \(387.9962\)

\((S)-(-)-1,3-\text{Diethyl-5-[2-(3-\alpha-\text{methylbenzyl-4-methyl-2-thiazolinylidene})-ethylidene]-2-thiobarbituric acid}\)

\((S)-(-)-3-\alpha-\text{Methylbenzyl-2,4-dimethylthiazolium perchlorate (.1 g, .33 mmol, 5-}

\text{anilinovinyl-1,3-diethyl-2-thiobarbituric acid (.11 g, .33 mmol), acetic anhydride (.016}

g, .33 mmol) and triethylamine (3 dps) are stirred in acetonitrile (10 mL) at RT for 24 h. Acetonitrile is evaporated under reduced pressure to give a thick oil. the oil is taken up in ethyl acetate and washed with 10% HCl, 10% NaOH, brine and dried over
Mg$_2$SO$_4$. The solvent was removed under reduced pressure and purified by flash chromatography on silica gel (30% EtOAc/Hex followed by 5% MeOH/CH$_2$Cl$_2$) to afford an orange-red powder (.048 g, 34%).

mp. 174° -175° C, [α]$_D$ +1100° (CHCl$_3$), $\lambda_{max}$ (EtOH) = 486 $\varepsilon = 8.74 \times 10^4$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.26 (t, 3H, $J=7.0$ Hz, -NCH$_2$CH$_3$), 1.97 (d (on top of a singlet), 3H, $J=7.2$ Hz, -NCHCH$_3$), 1.99 (s, 3H, -C-CH$_3$), 4.55 (q (br), 4H, -NCH$_2$CH$_3$), 6.03 (s, 1H, $J=7.0$ Hz, -NCH-Ph), 6.53 (s, 1H, -SC=), 7.16 - 7.41 (m, 5H, Ar-$H$), 7.92 (d, 1H, $J=14.3$ Hz, -CH=C), 8.27 (d, 1H, $J=14.2$ Hz, -C=CH); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 12.61, 15.89, 17.15, 42.85, 57.70, 98.81, 100.49, 108.67, 126.24, 128.73, 129.31, 136.59, 141.88, 147.39, 173.52, 178.03; High resolution DIP EIMS calcd. for C$_{22}$H$_{25}$N$_3$O$_2$S$_2$ 427.1388 Found 427.1573

Ketene diethylacetal (40)

Followed the procedure given in Organic Synthesis Collective Volume 3, page 506.

3, 3-Diethyl acetal cyclobutane sulfone (42).
A solution of methansulfonyl chloride (6.9 g, .06 mol) in ether (30 mL) was added dropwise to a solution of ketene diethylacetal (7.0 g, .06 mol) and triethylamine (6.1 g, .06 mol) in ether (30 mL). After the addition, the reaction mixture was stirred for an additional 45 min at RT. The triethylamine hydrochloride was filtered and the ether removed under reduced pressure to afford the product as a clear liquid which solidified upon standing at RT (6.25 g, 53.5 %).

\[ \text{mp. } 47 - 49 ^\circ \text{C} \]

\[ ^1\text{H-NMR (300MHz, CDCl}_3 \text{): } \delta 1.18 (t, 6H, J = 7.2 \text{ Hz, } -\text{OCH}_2\text{CH}_3), 3.43 (q, 4H, J = 7.0 \text{ Hz, } -\text{OCH}_2\text{CH}_3), 4.14 (s, 4H, S-\text{CH}_2\text{C}=\text{O}); \]

\[ ^{13}\text{C-NMR (75.4 MHz, CDCl}_3 \text{): } \delta 14.16, 55.79, 63.35, \text{ IR (neat) } 730.1, 1102.6, 1196.0, 1452.1, 1676.0, 1734.5, 2344.9, 2940.7, 3441.6, 3598.8 \]

3-Thietanone-1,1-dioxide (43).

3,3-Diethyl-cyclobutane-3-sulfone-acetal (3 g, .015 mol) was dissolved in cold conc. hydrochloric acid (30 mL) at 25°C and the product precipitates as a white crystalline solid after 15 min. (2.8 g). More of the product was obtained by concentrating the solution under reduced pressure (2.1 g, .017 mol). Recrystallization from absolute ethanol gave clear crystals (1.56 g, 84 %).
mp. 223°-225°C

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 5.32 (s, 4H, -CH$_2$-)

$\text{2-[2-(3-Ethyl-2-benthiazolinylidene)ethyldene]-3-thietanone-1,1-dioxide (d8).}$

3-Thietanone-1,1-dioxide (.027 g, .22 mmol), 2-acetanolidovinyl-3-ethylbenzothiazolium iodide (.1 g, .22 mmol) and triethylamine (.031 mmol, .22 mmol) were stirred at RT for 12 h and chilled overnight in the refrigerator. The resulting precipitate was collected by vacuum filtration to afford a purple colored material. This material was taken up in a minimal amount of ethyl acetate and purified by flash chromatography (40 % EtOAc/Hex) which results in a dark orange compound. This product was recrystallized from absolute ethanol to afford a dark orange solid (.0084 g, 12 %)

mp. 198°C (darkens); $\lambda_{\text{max}}$ (EtOH) = 474 nm $\varepsilon > 4.14 \times 10^4$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.45 (t, 3H, J = 7.3 Hz, -NCH$_2$CH$_3$), 4.26 (q, 2H, J = 7.3 Hz, -NCH$_2$CH$_3$), 4.44 (s, 2H, -S-$\text{CH}_2$-$\text{C}=\text{O}$), 6.04 (d, 1H, J = 13.9 Hz, =CH-$\text{CH}=$), 6.89 (d, 1H, J = 13.7 Hz, =CH-$\text{CH}=$), 7.36 - 7.46 (m, 2H, Ar-$\text{H}$), 7.54 (dd, 1H,
$J = 7.9 \text{ Hz, Ar-H}, 7.71 \text{ (d, } 1\text{H, } J = 7.9 \text{ Hz, Ar-H})$; High resolution DIP EIMS calcd. for $C_{14}H_{13}NO_3S_2$ 307.0336 Found 307.0325

1,3-Diethyl-5-[2-(3-ethyl-2-\beta-napothiazolinylidene)-1-methyl-ethyldiene]-2-thiobarbituric acid (d9)

1,3-Diethyl-2-thiobarbituric acid (.3 g, .0015 mol) and 3-ethyl-2-methyl-\beta-napthothiazolium iodide (.5 g, .0015 mol) and 1,4-diazabicyclo[2.2.2]octane (.52 g, .0044 mol) are stirred with acetic anhydride (10 mL) at RT for 48 h. The crude product was filtered from the reaction mixture and washed with cold methanol. The crude product was recrystallized twice with absolute ethanol to afford an orange solid (.12 g, 18%).

mp. 272° -273°C; $\lambda_{\text{max}}^{(\text{EtOH})} = 508 \text{ nm}$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.32 (t, 6H, $J = 6.81 \text{ Hz, -NCH}_2\text{CH}_3$), 1.96 (t, 3H, $J = 6.89 \text{ Hz, -NCH}_2\text{CH}_3$), 2.81 (s, 3H, =C-CH$_3$), 4.63 (q, 4H, $J = 6.81 \text{ Hz, -NCH}_2\text{CH}_3$), 4.94 (q(br), 2H, -NC$\^{\text{=}}$CH$_3$), 7.66-8.07 (m, 4H, Ar-H), 8.07 (d, 1H, AR-H), 8.41 (d, 1H, Ar-H), 8.95 (s (br), 1H, =CH-); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 12.78, 13.89, 30.81, 47.18, 118.66, 121.02, 122.11, 127.14, 127.66, 128.38, 130.56, 134.17, 177.18, 206.56
1,3-Diethyl-5-[2-(3-ethyl-2-benzothiazolinyldene)-1-methyl-ethylidene]-2-thiobarbituric acid.

1,3-Diethyl-2-thiobarbituric acid (.066 g, .33 mmol) and 3-ethyl-2-methyl-benzothiazolium iodide (.1 g, .293 mmol) and 1,4-diazabicyclo[2.2.2]octane (.77 g, .66 mmol) are stirred with acetic anhydride (10 mL) at RT for 48 h. The crude product was filtered from the reaction mixture and washed with cold methanol. The crude product was recrystallized twice with absolute ethanol to afford an orange solid (.031 g, 25%).

mp. 213° - 215° C; λmax(EtOH) = 508 nm

1H-NMR (300MHz, CDCl3) : δ 1.28 (t, 6H, J = 7.0 Hz, -NCH2CH3), 2.78 (s, 3H, J = Hz, =C-CS), 3.92 (s, 3H, -N CS), 4.57 (q, 4H, J = 7.0 Hz, -NCSCH3), 7.38 (m, 2H, Ar-H), 7.60 (d, 1H, J = 8.4 Hz, Ar-H), 7.75 (d, 1H, J = 7.8 Hz, Ar-H), 8.87 (br (s), 1H, =CH=)

1,3-Diethyl-5-[2-(3-methyl-2-benzothiazolinyldene)-1-methyl-ethylidene]-2-thiobarbituric acid

The reaction of 1,3-diethyl-2-thiobarbituric acid (.5 g, 2.5 mmol) and 3-methyl-2-methylbenzothiazolium iodide (.73 g, 2.5 mmol) were carried out in a similar manner as the 3-ethyl-2-methyl-β-naphthothiazolium analogue (d9) to afford small orange crystals (.31 g, 32 %).
mp. 281° - 282 °C dec.; $\lambda_{\text{max}}(\text{EtOH}) = 492$ nm

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.30 (t, 3H, J = 7.0 Hz, -NCH$_2$CH$_3$), 2.78 (s, 3H, -C(CH$_3$)=), 3.92 (s, 3H, -NCH$_3$), 4.59 (q, 2H, J = 7.0 Hz, -NCH$_2$CH$_3$), 7.43 (m, 2H, Ar-$H$), 7.57 (dd, 1H, J = 7.6 Hz, Ar-$H$), 7.75 (d, 1H, J = 7.8 Hz, Ar-$H$), 8.87 (s (br), 1H, =CH-C-)

2-[3-Ethyl-2-benzthiazolinylidene]-dithioacetic acid (46).

3-Ethyl-2-methylenebenzthiazoline (.1 g) and carbon disulfide (20 mL) was stirred in ethanol (50 mL) at RT for 48 h. Reaction mixture chilled in the refrigerator for 12 h. and the resulting precipitate is collected by vacuum filtration and used without further purification.

mp. 231° - 233 °C

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.31 (t, 3H J = 7.3 Hz, -NCH$_2$CH$_3$), 4.26 (q, 2H, J = 7.3 Hz, -NCH$_2$CH$_3$), 7.31 (m, 2H, Ar-$H$), 7.43 (dd, 1H, J = 7.5 Hz, Ar-$H$), 7.64 (s, 1H, =CH-$H$), 7.70 (d, 1H, J = 7.6 Hz, Ar-$H$)
2-(2,2-Dimethylmercaptopenyl)-3-ethylbenzothiazolium iodide (47)

\[
\begin{align*}
\text{MeS} & \quad \text{SMe} \\
\end{align*}
\]

2-[3-Ethyl-2-benzthiazolinylidene]-dithioacetic acid (.2 g, .51 mmol) was heated with excess dimethyl sulfate (50 mL) at 50° for 24 h. The reaction mixture is poured into aqueous KI and the dimethylated product precipitates out of solution. The product was collected by vacuum filtration to afford a yellow solid (.288 g, 89%).

mp. 231° - 233 °C

\[ ^1\text{H-NMR (300MHz, CDCl}_3 \text{): } \delta 1.60 (\text{t (covered by water peak), 3H, } -\text{NCH}_2\text{CH}_3), 2.87 (\text{s, 3H, } -\text{SCH}_3), 3.11 (\text{s, 3H, } -\text{SCH}_3), 5.24 (\text{q, 2H, } J = 7.3 \text{ Hz, } -\text{NCH}_2\text{CH}_3), 7.12 (\text{s, 1H, } -\text{CH}=_), 7.61 (\text{dd, 1H, } J = 7.1 \text{ Hz, Ar-}H), 7.72 (\text{dd, 1H, } J = 7.5 \text{ Hz, Ar-}H), 7.83 (\text{dd, 1H, } J = 8.2 \text{ Hz, Ar-}H), 7.99 (\text{d, 1H, } J = 8.0 \text{ Hz, Ar-}H)\]

2-[3-[1-Ethyl-2-β-naphthothiazolinylidene]-2-methylthio-1-propenyl]-3-ethylbenzothiazolium iodide (48)

\[
\begin{align*}
\end{align*}
\]

2-(2,2-Dimethylmercaptopenyl)-3-ethylbenzothiazolium iodide (.1 g, .24 mmol) and 3-ethyl-2-methyl-β-napthothiazole (.083 g, .24 mmol) were refluxed in ethanol (15 mL)
with triethylamine (1 mL) for 1 h. and cooled to RT. Aqueous KI was added and stirred for 30 min. The resulting precipitate was collected by vacuum filtration. The crude product was recrystallized from methanol to afford a dark green solid (.049 g, 33%).

mp. 205 - 206 °C dec.

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.50 (t, 3H, $J = 7.1$ Hz, -NCH$_2$CH$_3$), 1.91 (t, 3H, $J = 7.0$ Hz, -NCH$_2$CH$_3$), 4.62 (q, 2H, $J = 7.0$ Hz, -NCH$_2$CH$_3$), 5.16 (q, 3H, $J = 7.1$ Hz, -NCSCH$_3$), 7.23 (m, 2H, Ar-S), 7.36 - 7.75 (m, 6H, Ar-S), 7.76 (s, 1H, -CH=), 7.79 (s, 1H, =CH), 7.86 (d, 1H, $J = 8.2$ Hz, Ar-H), 8.37 (d, 1H, $J = 8.8$ Hz, Ar-H).

1,3-Diethyl-5-[1-(3-ethyl-2-benzothiazolylidene)(1-ethyl-2-β-naphthothiazolylidene) isopropylidene]-2-thiobarbituric acid (d10).

1,3-Diethyl-5-[2-(3-ethyl-2-β-napthothiazolylidene)-1-methyl-ethylidene]-2-thiobarbituric acid (d8) (.13 g, .22 mmol) and 3-ethyl-2-chlorobenzothiazolium tetrafluoroborate (.1 g, .22 mmol) are dissolved in pyridine (2 mL) with triethylamine (5 dps) and heated to a reflux for 20 min. Methanol is added and cooled in the
refrigerator for 24 h. The precipitate was filtered by vacuum filtration and recrystallized from pyridine to afford a green crystalline solid (.05 g, 39.5 %).

mp. 327-329°C.; $\lambda_{\text{max}}$ (EtOH) = 528, 564 nm $\varepsilon > 6.28 \times 10^4$

$^1$H-NMR (300MHz, CDCl$_3$):

δ 1.23 (t, 6H, J = 6.8 Hz, -NCH$_2$CH$_3$), 1.45 (t, 3H, J = 7.3 Hz, -NCH$_2$CH$_3$), 1.87 (t, 3H, J = 7.1 Hz, -NCH$_2$CH$_3$), 4.19 (q, 2H, J = 7.2 Hz, -NCH$_2$CH$_3$), 4.73 (m, 6H, -NC$H_2$CH$_3$), 6.45 (s, 1H, =CH-C=), 6.60 (s, 1H, =CH-C=), 7.16 (dd, 1H, J = 8.2 Hz, Ar-H), 7.19 (dd, 1H, J = 7.6 Hz, Ar-H), 7.34 (dd, 1H, J = 7.6 Hz, Ar-H), 7.50 - 7.63 (m, 4H, J = Hz, Ar-H), 7.71 (d, 1H, J = 8.6 Hz, Ar-H), 7.96 (d, 1H, J = 7.6 Hz, Ar-H), 8.25 (d, 1H, J = 8.5 Hz, Ar-H); High resolution DIP EIMS calcd. for C$_{34}$H$_{36}$N$_4$O$_3$S$_2$ 612.2228 Found 612.0683

1,3-Diethyl-5-[1-(3-ethyl-2-benzothiazolinylidene)(1-methyl-2-β-naphthothiazolylidene) isopropylidene]-2-thiobarbituric acid

1,3-Diethyl-5-[2-(3-methyl-2-β-naphthothiazolinylidene)-1-methyl-ethylidene]-2-thiobarbituric acid (d8) (.099 g, .22 mmol) and 3-ethyl-2-methylbenzothiazolium tetrafluoroborate (.067 g, .22 mmol) are dissolved in pyridine (1 mL) with triethylamine
(5 dps) and heated to a reflux for 20 min. Methanol is added and cooled in the refrigerator for 24 h. The precipitate was filtered by vacuum filtration and recrystallized from pyridine to afford a green crystalline solid (.083 g, 67.5 %).

mp. 342 - 344° C; $\lambda_{\text{max}}(\text{EtOH}) = 544, 582$ nm $\varepsilon > 2.5 \times 10^5$

$^1$H-NMR (300 MHz): $\delta$ 1.18 (t, 6H, $J = 7.9$ Hz, -NCH$_2$CH$_3$), 1.45 (t, 3H, $J = 7.2$ Hz, -NCH$_2$CH$_3$), 3.69 (s, 3H, -NC$_2$H$_5$), 4.21 (q, 2H, $J = 7.3$ Hz, -NCH$_2$CH$_3$), 4.78 (m, 4H, -NCH$_2$CH$_3$), 6.48 (s, 1H, =CH-C=), 6.49 (s, 1H, =CH-C=), 7.13-7.22 (m, 4H, Ar-H), 7.32-7.39 (m, 3H, Ar-H), 7.52 (t, 2H, $J = Hz$, Ar-H), 8.63 (dd, 1H, $J = Hz$, Ar-H);

$^{13}$C-NMR (75.4 MHz): $\delta$ 12.57, 13.04, 33.18, 41.71, 42.84, 100.72, 103.12, 103.36, 110.95, 119.06, 122.29, 122.44, 124.58, 127.32, 127.41, 127.95, 128.37, 136.99, 139.43, 140.21, 148.80, 159.51, 161.02, 161.83, 162.00, 177.79; High resolution DIP EIMS calcd. for C$_{33}$H$_{34}$N$_4$O$_2$S$_3$ 614.1843 Found 614.00

3-ethyl-[1-(3-ethyl-2-benzothiazolinylidene)(1-ethyl-2-ß-naphthothiazolylidene) isopropylidene] rhodanine (d11)
2-[3-[1-Ethyl-2-β-naphthothiazolinylidene]-2-methylthio-1-propenyl]-3-ethylbenzothiazolium iodide (.1 g, .17 mmol) and 5-ethylrhodanine (.027 g, 17 mmol) are dissolved in pyridine (2 mL) and a catalytic amount of triethylamine are heated at reflux temperatures for 20 min. The reaction mixture is cooled to 0° and water is added and stirred for 10 and chilled. The precipitate was collected by vacuum filtration and recrystallized from 50 % methanol/pyridine (2x) to yield dark green solid (.006g, 6 %).

mp 277 - 279°C; \( \lambda_{\text{max (EtOH)}} = 554 \text{ nm} \quad \varepsilon > 3.67 \times 10^4 
\]

High resolution DIP EIMS calcd. for C\(_{31}\)H\(_{31}\)N\(_3\)OS\(_4\) 589.1350 Found 589.1295

**Ethylisoformanilide (52)**

![Ethylisoformanilide](image)

Ethyl orthoformate (63.7 g, .43 mol) and aniline (20 g, .215 mol) were heated at 120°C for 4 h. in a round bottom flask with a distillation setup to collect the ethanol produced during the reaction. The reaction mixture was cooled to RT. and diphenylformamidine was filtered off. The remaining filtrate was fractionally distilled under reduced pressure. Excess ethyl orthoformate was collected during the forerun, between b.p. 90°-100°/~20 mm (aspirator) and ethylisoformanilide was collected at 140°-160°/~20 mm Hg (aspirator) (21g, 65.4%).
$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.39 (t, 3H, J = 7.1 Hz, -NCH$_2$CH$_3$), 4.33 (q, 2H, J = 7.1 Hz, -OCH$_2$CH$_3$), 7.00 (d, 2H, J = 8.0 Hz, Ar-$H$), 7.14 (dd, 1H, J = 7.0 Hz, Ar-$H$), 7.32 (dd, 2H, J = 7.8 Hz, Ar-$H$), 7.71 (s, 1H, N=C=O); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 13.98, 62.06, 121.22, 124.01, 128.85, 147.99, 154.81; IR (neat) 2975.0, 1643.9, 1596.1, 1488.4, 1446.5, 1386.7, 1261.0, 1189.2, 1009.7, 758.5, 698.6

Dimer of 3-Ethyl-2-methylenebenzthiazoline (51)

2-Methyl-3-ethylbenzothiazolium $\rho$-toluenesulphonate (5g) was dissolved in water (10 mL) and stirred vigorously. The solution was cooled to 0°C and a cold solution of sodium hydroxide (1 g / 5 mL H$_2$O) was dripped into the reaction over a 30 min. period. The white precipitate was collected by vacuum filtration and washed with cold water (the product may form large clumps that will eventually breakup with stirring). Water was removed under high vacuum to yield a white, pinkish powder (78%)

mp. 126° -128 °C

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.11 (t, 3H, J = 7.1 Hz, -NCH$_2$CH$_3$), 1.29 (t, 3H, J = 7.3 Hz, -NCH$_2$CH$_3$), 1.80 (s, 3H, -CH$_3$), 3.19 (m, 2H, J = 7.3, -NC$_2$CH$_3$), 3.79 (q, 2H, J = 7.1 Hz, -NCH$_2$CH$_3$), 4.58 (s, 1H, -CCH$_3$), 6.37 (d, 1H, J = 7.8 Hz, Ar-$H$),
6.65 (dd, 1H, J = 7.4 Hz, Ar-\(H\)), 6.79 (dd, 1H, J = 8.1 Hz, Ar-\(H\)), 6.84 (dd, 1H, J = 7.4, Ar-\(H\)), 6.99 (dd, 1H, J = 7.7 Hz, Ar-\(H\)), 7.07 (m, 2 dd on top of each other) 2H, Ar-\(H\)), 7.19 (d, 1H, J = 7.7 Hz, Ar-\(H\)); \(^{13}\)C-NMR (75.4 MHz, CDCl\(_3\)): \(\delta\) 10.89, 13.34, 32.55, 37.35, 39.22, 80.94, 87.23, 107.23, 107.35, 117.53, 119.77, 121.06, 121.31, 124.98, 125.37, 125.68, 127.07, 141.50, 145.17, 148.78; IR (KBr)

3-Ethyl-2-bisaniloiso-propylidenebenzothiazoline (54)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) -- (0.5,0.5) -- (1,0);
\draw[thick] (0.5,0) -- (0.5,0.5);
\draw[thick] (1,0) -- (1,0.5);
\draw[thick] (0.5,0.5) -- (1.5,0.5);
\draw[thick] (1.5,0.5) -- (2,0);
\draw[thick] (2,0) -- (2,0.5);
\draw[thick] (2,0.5) -- (2.5,0.5);
\draw[thick] (2.5,0.5) -- (3,0);
\draw[thick] (3,0) -- (3,0.5);
\draw[thick] (3,0.5) -- (3.5,0.5);
\draw[thick] (3.5,0.5) -- (4,0);
\draw[thick] (4,0) -- (4,0.5);
\draw[thick] (4,0.5) -- (4.5,0.5);
\draw[thick] (4.5,0.5) -- (5,0);
\draw[thick] (5,0) -- (5,0.5);
\draw[thick] (5,0.5) -- (5.5,0.5);
\draw[thick] (5.5,0.5) -- (6,0);
\draw[thick] (6,0) -- (6,0.5);
\draw[thick] (6,0.5) -- (6.5,0.5);
\draw[thick] (6.5,0.5) -- (7,0);
\draw[thick] (7,0) -- (7,0.5);
\draw[thick] (7,0.5) -- (7.5,0.5);
\draw[thick] (7.5,0.5) -- (8,0);
\draw[thick] (8,0) -- (8,0.5);
\draw[thick] (8,0.5) -- (8.5,0.5);
\draw[thick] (8.5,0.5) -- (9,0);
\draw[thick] (9,0) -- (9,0.5);
\draw[thick] (9,0.5) -- (9.5,0.5);
\draw[thick] (9.5,0.5) -- (10,0);
\end{tikzpicture}}
\]

3-ethyl-2-methylenebenzthiazoline (8.3 g, .022 mol), zinc chloride (19.13 g, .14 mol), and ethylisofomalilide (69.25 g, .47 mol) were heated together at 175°-180°C with vigorous stirring for 2 h. The reaction was cooled to RT and acetone added and heated until all the lumps had been broken up. After cooling the zinc chloride complex is filtered off and washed with acetone, water and twice with hot methanol. The complex is converted into the base by dissolving the complex in 40% aqueous sodium hydroxide (10 mL/g) and extracting with acetone (3x). Acetone was evaporated under reduced pressure and the crude product was recrystallized from methanol to afford yellow needle-like crystals. (51%).

mp. = 125°-126°
1H-NMR (300MHz, CDCl3): δ 1.54 (t, 3H, J = 7.1Hz, -NCH2CH3), 4.44 (q, 2H, J = 7.1 Hz, -NCH2CH3), 7.11-7.44 (m, 14 H, Ar-H), 7.66 (d, 1H, J = 7.6 Hz, Ar-H), 8.83 (s, 2H, =C-CH=N); 13C-NMR (75.4 MHz, CDCl3): δ 14.37, 46.61, 103.31, 111.57, 121.00, 122.12, 123.49, 124.42, 126.49, 129.07, 129.31, 140.98, 152.63, 156.73, 160.58; IR (KBr) 3441, 2344, 1560, 1493, 1446, 1199

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylethylidene)]-rhodanine (55)

3-Ethyl-2-bisanioloisopropylidenebenthiazoline dimer (.5 g, 1.3 mmol), 3-ethyl-rhodanine (.21 g, 1.3 mmol), and pyridine (5 mL) were stirred together at 50° for 30 min. The product was precipitated from the reaction mixture by the addition of ether and collected by vacuum filtration. The crude product was recrystallized from 50% methanol/pyridine to yield small red crystals (.48 g, 81.1 %).

mp.175° C (blacken)

1H-NMR (300MHz, CDCl3): δ 1.29 (t, 3H, J = 7.1 Hz, -NCH2CH3), 1.74 (t, 3H, J = 7.2 Hz, -NCH2CH3), 4.69 (q, 2H, 7.2 Hz, -NCH2CH3), 4.38 (q, 2H, 7.1 Hz, -NCH2CH3) 7.15 - 7.24 (m, 3H, Ar-H), 7.32 - 7.52 (m, 5H, Ar-H), 7.68 (d, 1H, J = 7.8 Hz, Ar-H), 7.98 (s, 1H, =C-CH=N), 8.53 (s, 1H, =C-CH=C-S); 13C-NMR (75.4 MHz,
CDCl₃): δ 12.28, 15.10, 39.72, 47.24, 100.92, 109.72, 112.57, 120.84, 122.38, 124.77, 125.24, 127.34, 129.09, 129.29, 132.48, 140.99, 150.83, 153.83, 163.32, 167.77, 192.51

1H-NMR (300MHz, CDCl₃): δ 1.61 (t, 3H, J = 7.4 Hz, -NCH₂C₂H₅), 4.58 (q, 2H, J = 7.4 Hz, -NCSCH₃), 7.23 (m, 4H, Ar-H), 7.45 (t, 1H, J = 7.5 Hz, Ar-H), 7.55 (m, 3H, Ar-H), 7.74 (m, 1H, Ar-H), 7.89 (d, 1H, J = 13.3 Hz, Ar-H)

13C-NMR (75.4 MHz, CDCl₃): 14.05, 46.41, 115.20, 120.96, 123.43, 124.97, 126.75, 128.24, 129.16, 132.45, 141.98, 151.65, 160.17

2-[2-(3-Ethyl-2-benzothiazolylidene)-(2-(methylamino)ethylidene)]-1,3-indandione

The reaction of 3-ethyl-2-bisaniloisopropylidenebenthiazoline dimer (.5 g, 1.3 mmol), 1,3-indandione (.191 g, 1.3 mmol) was carried out in the same manner as the rhodanine analogue (30). The crude product was recrystallized from absolute alcohol to yield an orange powder (.48 g, 81%).

mp. 194 - 195°C

1H-NMR (300MHz, CDCl₃): δ 1.61 (t, 3H, J = 7.4 Hz, -NCH₂C₂H₅), 4.58 (q, 2H, J = 7.4 Hz, -NCSCH₃), 7.23 (m, 4H, Ar-H), 7.45 (t, 1H, J = 7.5 Hz, Ar-H), 7.55 (m, 3H, Ar-H), 7.74 (m, 1H, Ar-H), 7.89 (d, 1H, J = 13.3 Hz, Ar-H)

13C-NMR (75.4 MHz, CDCl₃): 14.05, 46.41, 115.20, 120.96, 123.43, 124.97, 126.75, 128.24, 129.16, 132.45, 141.98, 151.65, 160.17

1,3-Diethyl-5-[2-(3-ethyl-2-benzothiazolylidene)-(2-methylaminoethylidene)]-2-thiobarbituric acid

The reaction of 3-ethyl-2-bisaniloisopropylidenebenthiazoline dimer (.5 g, 1.31 mmol), 1,3-diethyl-2-thiobarbituric acid (.26 g, 1.31 mmol) was carried out in the same manner.
as the rhodanine analogue (30). The crude product was recrystallized with 50% pyridine/methanol to yield an orange powder (.59 g, 91%).

mp. 148 - 149°C

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.14 (t, 6H, J = 6.7 Hz, -NCH$_2$CH$_3$), (t, 3H, J = 7.1 Hz, -NCH$_2$CH$_3$), 4.48 (br (q), 4H, -NCH$_2$CH$_3$), 4.51 (q, 2H, J = 7.2 Hz, -NCSCH$_3$), 7.03 (d, 2H, J = 7.8 Hz, Ar-$(H)$), 7.13 (dd, 2H, J = 7.4 Hz, Ar-$(H)$), 7.30 (dd, 2H, J = 7.8 Hz, Ar-$(H)$), 7.64 (dd, 1H, J = 7.7 Hz, Ar-$(H)$), 7.79 (dd, 1H, J = 8.1 Hz, Ar-$(H)$), 7.86 (d, 1H, J = 8.4 Hz, Ar-$(H)$), 7.98 (d, 1H, J = 8.0 Hz, Ar-$(H)$), 8.14 (s, 1H, =C-CH=N), 8.36 (s, 1H, =C-CH=C-S); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 12.48, 13.04, 42.73, 46.04, 96.11, 107.74, 115.77, 120.66, 123.41, 125.22, 127.34, 128.54, 129.07, 130.69, 139.69, 149.49, 151.39, 160.92, 161.23, 176.62, 177.92

2,2-Dimethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-methylaniloethylidene)]-1,3-dioxane-4,6-dione.

The reaction of 3-ethyl-2-bisaniloisopropylidenebenthiazoline dimer (.5 g, 1.31 mmol), of 2,2-dimethyl-1,3-dioxane-4,6-dione (1.31 mmol) was carried out in the same manner as the rhodanine analogue (30). The crude product was recrystallized with 50% pyridine/methanol to yield an yellow powder (.4 g, 54%).

mp. 167 - 168°C
\( ^1H \text{-NMR (300MHz, CDCl}_3 \text{):} \quad \delta 1.55 \text{ (t, 3H, } J = 7.4 \text{ Hz, } -\text{NCH}_2\text{CH}_3), 1.63 \text{ (s, 6H, C(CH}_3)_2), 4.61 \text{ (q, 2H, } J = 7.4 \text{ Hz, } -\text{NCH}_2\text{CH}_3), 6.97 \text{ (d, 2H, } J = 7.6 \text{ Hz, Ar- } H), 7.13 \text{ (dd, 1H, } J = 7.3 \text{ Hz, Ar- } H), 7.28 \text{ (dd, 1H, } J = 7.8 \text{ Hz, Ar- } H), 7.60 \text{ (dd, 1H, } J = 7.8 \text{ Hz, Ar- } H), 7.7 \text{ (dd, 1H, } J = 8.3 \text{ Hz, Ar- } H), 7.83 \text{ (d, 1H, } J = 8.1 \text{ Hz, Ar- } H), 7.96 \text{ (d, 1H, } J = 8\text{ Hz, } =\text{C-CH=H-N), 8.29 \text{ (s, 1H, } =\text{C-CH=H-C-S); } ^13\text{C-NMR (75.4 MHz, CDCl}_3 \text{):} \quad \delta 13.08, 26.73, 27.04, 102.23, 104.56, 116.03, 120.65, 123.67, 127.47, 128.59, 129.12, 130.81, 140.08, 150.15, 161.05 \)

5-[2-(3-ethyl-2-benzothiazolinylidene-2-(2-thio-4-oxo-3-ethylthiazolin-5-ylidene-methyl) ethylidene]-3-ethylrhodanine (d14).

![Chemical structure](image_url)

Method A:

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylethylidene)]-rhodanine (.143 g, .886 mmol), sodium acetate (2.42 g, 2.65 mmol) and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride and ether (.22 g, 96.5 %).
Method B:

3-Ethyl-2-bisaniloisopropylidenebenthiazoline (.443 mmol), 3-ethylrhodanine (.286 g, 1.77 mmol), sodium acetate (2.42 g, 2.65 mmol), and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride and ether (.11 g, 86.6 %).

mp. 228° - 230° C;

\[ \text{'H-NMR (300MHz, CDCl}_3 \text{' : } \delta 1.27 \text{ (t, 3H, } J = 7.3 \text{ Hz, } -\text{NCH}_2\text{CS}_3), 1.51 \text{ (t, 3H, } J = 7.5 \text{ Hz, } -\text{NCH}_2\text{CH}_3), 4.14 \text{ (q, 2H, } J = 7.3 \text{ Hz, } -\text{NCH}_2\text{CH}_3), 4.29 \text{ (q, 2H, } J = 7.3 \text{ Hz, } -\text{NCH}_2\text{CH}_3), 7.45 \text{ (m, 2H, Ar-H), 7.54 \text{ (s, 2H, } =\text{C-CH}=), 7.55 \text{ (m (covered by s), 1H, Ar-H), 7.73 (d, 1H, } J = 9.1 \text{ Hz, Ar-H)}; \text{ High resolution DIP EIMS calcd. for} \]

\[ \text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2\text{S}_5 \text{ 519.0237 Found 518.9011} \]

3-phenyl-4-[2-(3-ethyl-2-benzothiazolinylidene-2-(2-thio-4-oxo-3-ethylthiazolinylidene-methyl)ethylidene]-5-isoxazolone

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylethylidene)]-rhodanine (.1 g, .221 mmol), 3-phenyl-5-isoxazolone (.107 g, .663 mmol), sodium acetate(.113
g, 1.33 mmol) and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride and ether. Flash chromatography on silica gel (50/50 ethyl acetate/hexane) afforded the product as a light red powder (.038 g, 32%). Recrystallization of the chromatographed material afforded a fine red crystalline powder (.026 g, 22%)

mp. 283°-285°C dec.; λ_{max} (EtOH) = 512 nm ε > 6.37 x 10^4

^1^H-NMR (300MHz, CDCl₃): δ 1.25 (t, 3H, J = 7.1 Hz, -NCH₂CH₃), 1.53 (t, 3H, J = 7.2 Hz, -NCH₂CH₃), 4.10 (q, 2H, J = 7.0 Hz, -NCH₂CH₃), 4.49 (q, 2H, J = 7.1 Hz, -NCH₂CH₃), 7.33 (s, 1H, =C-C=), 7.55 (m, 4H, Ar-H), 7.58 (s, 1H, =C-C=), 7.7 (dd, 1H, J = 7.4 Hz, Ar-H), 7.82 (dd, 1H, J = 7.3 Hz, Ar-H), 7.97 (d, 1H, J = 8.3 Hz, Ar-H), 8.11 (d, 1H, J = 8.0 Hz, Ar-H); ^1^C-NMR (75.4 MHz, CDCl₃): δ 12.12, 12.27, 39.90, 46.27, 96.22, 98.74, 108.74, 116.69, 124.39, 128.63, 128.98, 129.90, 131.47, 136.32, 140.18, 145.80, 164.05, 167.19, 190.67; High resolution DIP EIMS calcd. for C₂₇H₂₅N₃O₃S₃ 535.1058 Found 535.2143
2-[2-(3-ethyl-2-benzothiazolylidene)-2-(2-thio-4-oxo-3-ethylthiazolylidene-ethyl)ethylidene]-1,3-indandione (d14)

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolylidene)-(2-anilomethylthiazolylidene)]-rhodanine (.22 g, .487 mmol), 1,3-indandione (.214 g, 1.46 mmol), sodium acetate (.24 g) and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride and ether. Dissolve in ethanol and filter hot. Cool and collect the precipitate (.021 g). Recrystallization from absolute ethanol/pyridine (50/50) yielded a red powder (.016 g, 64%).

mp. 278 - 279 °C dec.; \(\lambda_{max} (EtOH) = 494 \text{ nm} \quad \epsilon > 1.16 \times 10^5 \)

\(^1\)H-NMR (300MHz, CDCl3): \(\delta\) 1.19 (t, 3H, J = 7.2 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 1.48 (t, 3H, J = 7.1 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 4.09 (q, 2H, J = 7.1 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 4.46 (q, 2H, J = 7.2 Hz, -NCH\textsubscript{2}CH\textsubscript{3}), 7.35-7.51 (m, 3H, Ar-\(H\)), 7.69-7.94 (m, 4H, Ar-\(H\)), 7.72 (s, 1H, =C-CH\textsubscript{3}=), 7.85 (s, 1H, =C-CH\textsubscript{3}=), 8.11 (d, 1H J = 6.8 Hz, Ar-\(H\)); \(^{13}\)C-NMR (75.4 MHz, CDCl\textsubscript{3}): \(\delta\) 12.13, 12.76, 39.91, 46.29, ~96.00, 98.71, 101.39, ~105.00, 111.63, 116.69, 124.79, 128.63, 128.72, 128.99, 129.77, 129.90, ~132.00, 136.33, ~141.00,
145.82, (4 peaks between 164 - 175), 190.68; High resolution DIP EIMS calcd. for C_{26}H_{20}N_{2}O_{3}S_{3} 504.0636. Found 504.0935

2,2-dimethyl-5-[2-(3-ethyl-2-benzothiazolylidene-2-(1,3-indandione-ylidene-methyl)ethylidene)]-1,3-dioxane-4,6-dione

[Chemical structure image]

2-[2-(3-Ethyl-2-benzthiazolylidene)-(2-(methylamino)ethylidene)]-1,3-indandione (.099 g, .69 mmol), sodium acetate (.113 g, 1.38 mmol) and acetic anhydride (5 mL) were heated together at 110\(^{\circ}\) for 15 min. and cool to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride and ether. The crude material was recrystallized (3x) from 85 % ethanol/pyridine to yield a brown powder (.021 g, 18.1 %).

mp. 215-216 \(^{\circ}\)C dec.; \(\lambda_{max}(\text{EtOH}) = 549 \text{ nm } \epsilon > 3.83 \times 10^{4}\)

\(^{1}\)H-NMR (300MHz, CDCl\textsubscript{3}): \(\delta 1.48 (t, 3H, J = 7.4 \text{ Hz}, -NCH\textsubscript{2}CH_{3}), 1.63 (s, 6H - C(CH\textsubscript{3})_{2}), 4.47 (q, 2H, J = 7.3 \text{ Hz}, -NCH\textsubscript{2}CH\textsubscript{3}), 7.43 (dd, 1H, J = 7.2 \text{ Hz}, Ar-H), 7.51 (dd, 1H, J = 8.0 \text{ Hz}, Ar-H), 7.61 (dd, 1H, J = 7.0 \text{ Hz}, Ar-H), 7.69 - 7.92 (m, 4H, Ar-H), 7.88 (s, 1H, =C-CH=), 8.03 (d, 1H, J = 7.9 \text{ Hz}, Ar-H), 8.47 (s, 1H, =C-CH=);

\(^{13}\)C-NMR (75.4 MHz, CDCl\textsubscript{3}): \(\delta 12.46, 27.01, 45.79, 98.55, 101.70, 102.85, 116.39,\)
121.71, 122.19, 124.08, 127.74, 128.95, 131.34, 133.59, 139.74, 140.63, 141.44,
148.95, 157.69, 189.63;  High resolution DIP EIMS calcd. for C_{28}H_{25}NO_{6}S  503.1402
Found 503.1475

3-phenyl-4-[2-(3-ethyl-2-benzothiazolylidene-2-(1,3-indandionylidene- methy1)ethylidene)]-5-isoxazolone

\[ \text{Ph} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{O} \]

2-[2-(3-Ethyl-2-benzthiazolylidene)-(2-(methylanilo)ethylidene)]-1,3-indandione (.1 g, .23 mmol), 3-phenyl-5-isoxazolone (.11 g, .69 mmol), sodium acetate (.113 g, 1.38 mmol) and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride and ether. Crude material was recrystallized from absolute alcohol to yield a deep, clear, red crystals (.098 g, 82 %).

mp. 234-236°C dec.; \( \lambda_{\text{max}} = 506 \text{ nm} \) \( \epsilon > 4.83 \times 10^4 \)

\( ^1\text{H-NMR (300MHz, CDCl}_3 \): \( \delta \) 1.51 (t, 3H, J = 7.3 Hz, -NCH\text{CH}_3), 4.46 (q, 2H, J = 7.3 Hz, -NCH\text{CH}_2\text{CH}_3), 7.43 - 7.62 (m, two singlets from chain protons and eight
aromatic protons) 10H, Ar-H and =C-CH=), 7.75 - 7.87 (m, 3H, Ar-H), 7.97 (d, 1H, J = 8.5 Hz, Ar-H), 8.09 (d, 1H, J = 7.8 Hz, Ar-H); 13C-NMR (75.4 MHz, CDCl3): δ
12.73, 45.80, 100.10, 102.14, 115.83, 116.55, 121.65, 122.04, 124.17, 127.87, 128.71, 129.08, 129.21, 130.13, 132.01, 133.58, 139.74, 140.85, 141.36, 146.58, 150.86, 164.37, 189.52, 191.07; High resolution DIP EIMS calcd. for C$_{30}$H$_{20}$N$_{2}$O$_{4}$S 504.1143 Found 504.1186

1,3-dimethyl-5-[2-(3-ethyl-2-benzothiazolylidene-2-(1,3-indandionylidene-methyl)ethylidene)]barbituric acid.

2-[2-(3-Ethyl-2-benzthiazolylidene)-(2-(methylanilo)ethylidene)]-1,3-indandione (.1 g, .23 mmol), 1,3-dimethylbarbituric acid (.11 g, .687 mmol), sodium acetate (.11 g, 1.37 mmol) and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water, acetic anhydride, ether and ethanol. Crude material can be recrystallized several times (5x) in absolute alcohol to yield a fine, red, crystalline powder (.068 g, 57 %). Better results were obtained when the crude material was chromatographed on silica (50% ethyl acetate/hexane) followed
by a single recrystallization from absolute ethanol to yield a red crystalline powder (.096 g, 81%).

mp. 284 - 285 °C dec.; $\lambda_{\text{max}}(\text{EtOH}) = 486$ nm $\varepsilon > 1.15 \times 10^5$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 1.45 (t, 3H, $J = 7.4$ Hz, -NCH$_2$CH$_3$), 2.94 (s, 3H, -NCH$_3$), 3.34 (s, 3H, -NCH$_3$), 4.39 (q, 2H, $J = 7.4$ Hz, -NCH$_2$CH$_3$), 7.43 (m (3 dd on top of each other), Ar-$H$), 7.70 - 7.92 (m, 4H, Ar-$H$), 7.95 (s, 1H, =C-CH=), 8.04 (d, 1H, $J = 7.9$ Hz, Ar-$H$), 8.55 (s, 1H, =C-CH=); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$

12.43, 45.54, 100.59, 102.15, 116.19, 121.67, 122.06, 123.88, 127.49, 128.79, 131.52, 133.51, 139.71, 140.50, 141.54, 149.83, 156.95, 178.22, 190.10, 190.96;

High resolution DIP EIMS calcd. for C$_{27}$H$_{21}$N$_3$O$_5$S 499.1201 Found 499.1619

1,3-diethyl-5-[2-(3-ethyl-2-benzothiazolinylidene-2-(1,3-indandionylidene-methyl)ethylidene)]-2-thiobarbituric acid

2-[2-(3-Ethyl-2-benzothiazolinylidene)-(2-(methylanilo)ethylidene)]-1,3-indandione (.1 g, .23 mmol), 1,3-indandione (.14 g, 69 mmol), sodium acetate (.113 g, 1.38 mmol) and acetic anhydride (5 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum
filtration and washed with water, acetic anhydride, ether and recrystallized from absolute ethanol (3x) to afford a light red powder (.027 g, 21%)

mp. 253 -254 °C dec.; $\lambda_{\text{max}}$(EtOH) = 508 nm $\varepsilon > 7.71 \times 10^4$

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ .96 (br, 3H, -NCH$_2$C$_2$H$_5$), 1.27 (br, 3H, -NCH$_2$CH$_3$), 1.46 (t, 3H, J = 7.2 Hz, -NCH$_2$CH$_3$), 4.19 (br, 2H, -NC$_2$H$_2$CH$_3$), 4.37 (q, 2H, J = 7.3 Hz, -NCH$_2$CH$_3$), 4.52 (br, 2H, J = Hz, -NCH$_2$CH$_3$), 7.44 - 7.62 (m, 3H, Ar-$H$), 7.72 - 7.89 (m, 4H, Ar-$H$), 8.04 (d, 1H, J = 7.9 Hz, Ar-$H$), 8.52 (s, 1H, =CH-CH=).

$^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ High resolution DIP EIMS calcd. for C$_{29}$H$_{25}$N$_3$O$_4$S$_2$ 543.1286 Found 543.1552

1,3-diethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-2-(1,3-dimethyl-1,3-pyrimidine-2,4,6-trione-5-yldene-methyl)ethylidene]-2-thiobarbituric acid

[Chemical Structure Image]

1,3-Diethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-methylaniloethylidene)]-2-thiobarbituric acid (.314 g, .64 mmol), 1,3-dimethylbarbituric acid (.1 g, .64 mmol), sodium acetate (.157 g, 1.9 mmol) and acetic anhydride (25 mL) were heated together at 110° for 15 min. and cooled to RT. Ether was added to precipitate the crude product which was collected by vacuum filtration and washed with water and ether.
Column chromatography (18-6-1 toluene/EtOAc/EtOH) afforded a dull red powder (.067 g, 19%).

mp. 278 - 279 °C dec.; λmax = 498 nm

1H-NMR (300 MHz, CDCl3): δ .92 (br, 3H, -NCH2CH3 of the thiobarbituric acid), 1.27 (br, 3H, -NCH2CH3 of the thiobarbituric acid), 1.48 (t, 3H, J = 7.3 Hz, -NCH2CH3), 2.94 (s, 3H, -NCH2CH3), 3.34 (s, 3H, -NCH2CH3), 4.13 (br, 2H, -NCH2CH3), 4.32 (q, 2H, J = 7.3 Hz, -NCH2CH3), 4.53 (br, 2H, -NCH2CH3), 7.67 (dd, 1H, J = 5.2 Hz, Ar-H), 7.79 (dd, 2H, J = 7.2 Hz, Ar-H), 7.97 (d, 1H, J = 8.1 Hz, Ar-H), 8.52 (s, 1H, =C-CH=), 8.53 (s, 1H, =C-CH=); High resolution DIP EIMS calcd. for C26H27N5O5S2 553.1454. Found 553.1118

2-[3-(3-Ethyl-2-benzothiazolinylidene)-3-(anilomethyl)-1-propenyl]-3-methylbenzothiazolium iodide (56)

3-Ethyl-2-bisaniloisopropylidenebenzothiazoline (.01 g, .03 mmol) and 2,3-dimethylbenzothiazolium iodide (8.3 mg, .03 mmol) were dissolved in pyridine (1 mL) and stirred at RT for 12 h. Ether was added and the precipitate was collected by
vacuum filtration. The crude material was washed with hot ethanol and dried to give a brown solid (.012 g, 70.6%).

mp. 148-150°  \( \lambda_{\text{max}} (\text{EtOH}) = 434, \ 546 \text{nm} \  \varepsilon = 2.76 \times 10^5 \)

\(^1\text{H}-\text{NMR} (300 \text{ MHz, CDCl}_3): \ \delta \ 1.66 (t, 3H, J = 7.1 \text{ Hz, } -\text{NCH}_2\text{C}_3\text{H}_3), \ 3.91 (s, 3H, \ -\text{NCH}_2\text{C}_3\text{H}_3), \ 4.94 (q, 2H, J = 7.1 \text{ Hz, } -\text{NCH}_2\text{C}_3\text{H}_3), \ 6.50 (\text{br} \ (d), 1H, \ -\text{CH} = \text{C}_3\text{H}_2\text{)}, \ 7.15 (d, 2H, J = 6.8 \text{ Hz, } \text{Ar-H}), \ 7.27-7.34 (m, 5H \ \text{Ar-H}), \ 7.40 (d, 1H, J = 7.9 \text{ Hz, } \text{Ar-H}), \ 7.61 (dd, 3H, J = 7.4 \text{ Hz, } \text{Ar-H}) \ 7.77 (dd, 2H, J = 7.6 \text{ Hz, } \text{Ar-H}), \ 8.16 (d, 2H, J = 8.3 \text{ Hz, } \text{Ar-H}), \ 8.46 (s, 1H, =\text{C-CH}=) \)

\[2-[3-(3\text{-Ethyl}\text{-2-benzothiazolinylidene})\text{-3-(2-thio-4-oxo-3-ethylthiazolin-5-ylidene-methyl)}\text{-1-propenyl]}\text{-3-methylbezothiazolium iodide (d16).} \]

Method A:

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylidene)]-rhodanine (.1 g, .2 mmol), 2,3-dimethylbenzothiazolium iodide (.058 g, .2 mmol) and triethylamine (5 dps) are dissolved in acetic anhydride (3 mL) and heated at reflux for 15 min. Ether is added and the precipitate was collected by vacuum filtration and washed with water and ether several times. The crude product was boiled in methanol
and cooled to RT. The product was collected by vacuum filtration to afford a purple solid (.061 g, 47.0 %).

Method B:
2-[3-(3-Ethyl-2-benzothiazolinylidene)-3-(anilomethyl)-1-propenyl]-3-methylbenzothiazolium iodide (.1 g, .17 mmol), 3-ethylrhodanine (.028 g, .17 mmol) and triethylamine (5 dps) are dissolved in acetic anhydride (1 mL) and heated at reflux for 15 min. Ether is added and the precipitate was collected by vacuum filtration and washed with water and ether several times. The crude product was boiled in methanol and cooled to RT. The product was collected by vacuum filtration to afford a purple solid (.049 g, 44.5 %).

mp. 236 - 238° C \( \lambda_{\text{max}}(\text{EtOH}) = 576 \) \( \varepsilon = 8.46 \times 10^5 \)

\(^1\)H-NMR (300MHz, CDCl\(_3\)) :  \delta 1.24 (t, 3H, J = 7.0 Hz, -NCH\(_2\)CH\(_3\)), 1.60 (t, 3H, J = 7.3 Hz, -NCH\(_2\)CH\(_3\)), 3.99 (s, 3H, -NCH\(_3\)), 4.14 (q, 2H, J = 7.2 Hz, -NCH\(_2\)CH\(_3\)), 4.82 (q, 2H, J = 7.3 Hz, -NCH\(_3\)), 6.51 (d, 1H, J = 13.8 Hz, -CH=CH-), 7.28 (d, 1H, J = 7.8 Hz, Ar-H), 7.35 (dd, 1H, J = Hz, Ar-H), 7.48 (dd, 1H, J = Hz, Ar-H), 7.60 (d, 1H, J = Hz, Ar-H), 7.64 (s, 1H, =C-CH=), 7.69 (dd, 1H, J = Hz, Ar-H), 7.78 (dd, 1H, J = Hz, Ar-H), 7.87 (dd, 1H, J = Hz, Ar-H), 8.15 (d, 1H, J = 8.5 Hz, Ar-H), 8.29 (d, 1H, J = 8.2 Hz, Ar-H)
2-[3-(3-Ethyl-2-benzothiazolinylidene)-3-(2-thio-4-oxo-3-ethylthiazolin-5-ylidene-methyl)-1-propenyl]- 3-α-methylbenzyl-4-methylthiazolium iodide (d15).

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylene)]-rhodanine (.1 g, .2 mmol), 3-α-Methylbenzyl-2,4-dimethylthiazolium perchlorate (.068 g, .2 mmol) and triethylamine (5 dps) are dissolved in acetic anhydride and heated at reflux for 5 min. 30% KI in water is added and stirred overnight at RT. Water is decanted and ether was added and reflux for 2 h. The reaction mixture was cooled to RT and the precipitate was collected by vacuum filtration. The crude product is washed with hot methanol and benzene afford a purple solid which is then washed with hot benzene to afford a dark purple solid (.085 g, 60.3 %).

mp. 146 - 148° λ_{max} (EtOH) = 580 nm ε > 3.24 x 10^4

^1^H-NMR (300MHz, CDCl3): δ 1.24 (t, 3H, J = 7.0 Hz, -NCH₂CH₃), 1.47 (t, 3H, J = 7.1 Hz, -NCH₂CH₃), 2.01 (d, 3H, J = 7.1 Hz, -NCHCH₃), 2.40 (s, 3H, =CCH₃), 4.10 (q, 2H, J = 7.1Hz, -NCH₂CH₃), 4.42 (br, 2H, -NCHCH₂CH₃), 5.79 (d, 1H, J = 13.8 Hz, CH=CH-), 5.89 (q, 1H, J = 7.1 Hz, -NCHCH₃), 7.12 - 7.34 (m (several aromatic and 1 chain proton), 7.39 (s, 1H, =C-CH=), 7.56 (dd, 1H, J = 7.3 Hz, Ar-H), 7.73 (m, 2H, Ar-H), 7.99 (d, 1H, J = 8.1, Ar-H)
2-[3-(3-Ethyl-2-benzothiazolinylidene)-3-(2-thio-4-oxo-3-ethylthiazolin-5-ylidene-methyl)-1-propenyl]-3,3-dimethyl-1-ethylindolinium iodide

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-(2-anilomethylethylidene)]-rhodanine (.1 g, .2 mmol), 1-ethyl, 3,3-dimethylindolium iodide (.066 g, .2 mmol) and triethylamine (5 dps) are dissolved in acetic anhydride (3 mL) and heated at reflux for 15 min. Ether is added and the precipitate was collected by vacuum filtration and washed with water and ether several times. The crude material is then heated in 1 % sodium hydroxide and filtered (hot) to afford a purple solid (.093 g, 67.4 %).

mp. 154 - 156° \( \lambda_{\text{max}}(\text{EtOH}) = 562 \text{ nm} \quad \varepsilon > 5.03 \times 10^4 \)

\(^1\text{H-NMR (300MHz, CDCl}_3\text{):} \quad \delta 1.22 (m (2-t), 6H, -NCH}_2CH_3), 1.58 (t, 3H, J = 7.3 Hz, -NCH}_3), 1.71 (s, 6H, -C(CH}_3)_2), 4.14 (m (2-d), 4H, -NCH}_2CH_3), 4.75 (q, 2H, J = 7.3 Hz, -NCH}_2CH_3), 6.01 (d, 1H, J = 14.1 Hz, -CH=CH-), 7.00 (d, 1H, J = 7.9 Hz, Ar-\( \text{H}\)), 7.19 (dd, 1H, J = 7.6 Hz, Ar-\( \text{H}\)), 7.36 (m-2t, 2H, Ar-\( \text{H}\)), 7.69 (s, 1H, =C=CH=), 7.78 (dd, 1H, J = 7.6 Hz, Ar-\( \text{H}\)), 7.90 (dd, 1H, J = 7.8 Hz, Ar-\( \text{H}\)), 8.00 (d, 1H, J = 14.1, -CH=CH-), 8.19 (d, 1H, J = 8.4 Hz, Ar-\( \text{H}\)), 8.43 (d, 1H, J = 8.1 Hz, Ar-\( \text{H}\));
120

13C-NMR (75.4 MHz, CDCl₃): δ 12.18, 12.62, 14.49, 28.23, 40.04, 40.28, 47.62, 49.28, 95.85, 103.56, 110.31, 117.81, 122.14, 124.97, 125.12, 128.68, 129.10, 130.45, 131.36, 140.92, 141.10, 141.74, 148.1, 167.20, 170.22, 172.57, 184.53, 190.24

2-[3-(3-Ethyl-2-benzothiazolylidene)-3-(2-thio-4-oxo-3-ethylthiazolin -5-ylidene- methyl)-1-propenyl]-1-ethylquinolium iodide

3-Ethyl-5-[2-(3-ethyl-2-benzothiazolylidene)-(2-anilomethylene)-ethyl]-rhodanine (.01 g, .02 mmol), 1-ethyl, 3-ethylquinolium iodide (.006 g, .02 mmol) and triethylamine (2 dps) are dissolved in acetic anhydride (1 mL) and heated at reflux for 15 min. Ether is added and the precipitate was collected by vacuum filtration and washed with water and ether several times. The product was recrystallized from ethanol to afford green solid (.009 g, 68.2 %).

mp. 234 - 236° λ_max(EtOH) = 606 nm ε > 5.98 x 10⁵

¹H-NMR (300MHz, CDCl₃): δ 1.28 (t, 3H, J = 7.1, -NCH₂CH₃), 1.57 (m, 6H, -NCH₂CH₃), 4.17 (q, 2H, J = 6.9 Hz, -NCH₃CH₃), 4.65 (q, 2H, J = 7.1 Hz, -
NC\textsubscript{3}H\textsubscript{3}), 4.79 (q, 2H, J = 7.2 Hz, -NC\textsubscript{3}H\textsubscript{3}), 6.36 (d, 1H, J = 13.8 Hz, -CH=CH-), 7.48 (dd, 1H, J = 6.9, Ar-H), 7.69 (dd, 1H, J = 7.8 Hz, Ar-H), 7.75 (m, 5H), 7.91 (d, 1H, J = 8.2 Hz, Ar-H), 8.12 (2-d, 2H, J = 8.0 Hz, Ar-H), 8.31(d, 1H, J = 13.7 Hz, -CH=CH-), 8.43 (d, 1H, J = 9.1 Hz, Ar-H)

1-Methoxybutene-3-yne (58)

1,4-Dichloro-2-butyne (11.9 mL) was slowly dripped into a solution of methanol (100 mL) and sodium methoxide (6 g) after a 1 h. period. After the addition is complete the reaction is heated to a reflux for 1 h. The reaction is cooled to room temperature and the reaction mixture is filtered through a sintered glass filter into water (500 mL). Stored in water until needed and purified according to the procedure below.

Purification of 1-methoxybut-1-en-3-yne for use as a reagent

A 25 mL portion of 1-methoxybut-1-ene-3-yne in water was extracted with 35 % (v/v) ether-pentane (3 x 25 mL). The combined organic layers were washed with water (2 x 10 mL) and dried over anhydrous calcium chloride (1 g) and calcium carbonate (0.5 g) at 4°C overnight. The dark yellowish-orange solution was filtered, calcium carbonate (0.5 g) was added and the solvents were distilled at atmospheric pressure under argon (distillate 34-36°C). The remaining oil was distilled at 102 mm of mercury (aspirator pressure with an argon bleed), with the fraction coming off at 67 - 69°C being
collected. The colorless liquid was transferred by cannula to a dry bottle. The bottle was protected from light and used immediately or stored at -78°C.

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 3.03 (dt, 1H, $J = 1.2$ Hz, $-H$), 3.74 (s, 3H, $-OCH_2$), 4.46 (dt, 1H, $J = 1.2$, 6.9 Hz, $-CH=CH-$), 6.31 (d, 1H, $J = 7.0$ Hz, $O=CH=CH$); $^{13}$C-NMR (75.4 MHz, CDCl$_3$): $\delta$ 60.60, 78.17, 80.44, 84.25, 157.85

N-Methoxy-N-methylacetamide (60)

N-methoxy-N-methylamine (.2 g, 2 mmol) and pyridine (.35 g, 4.5 mmol) was dissolved in dry methylene chloride (20 mL) and cooled to 0°C. Acetyl chloride (2 mmol) in methylene chloride (5 mL) was slowly added to the reaction mixture over a 1h period. After the addition was complete the reaction was stirred at 0°C for 2 h. and then warmed to RT. and stirred for an additional 30 min. The reaction was then quenched with cold 10 % HCl (5 mL) and the organic layer was separated. The aqueous layer was extracted with methylene chloride (2 x 5 mL). The organic layers were combined and washed with 10 % Na$_2$CO$_3$, brine and dried (MgSO$_4$). The solvents were removed under reduced pressure and crude product was used without further purification (.193 g, 93.7 %).

$^1$H-NMR (300MHz, CDCl$_3$): $\delta$ 2.08 (s, 3H, O=CH$_3$), 3.17 (s, 3H, $-OCH_3$), 3.69 (s, 3H, $-NCH_3$)
1-Methyl-5-methoxy-4-pentene-2-ynone (59)

1-Methoxybut-1-en-3-yne (.5 g, 6.1 mmol) is dissolved in THF (5 mL) and cooled to 0°C. 3 M ethylmagnesium bromide (2.0 mL, 6.1 mmol) was slowly added to the reaction mixture, heated to 50°C and stirred for 10 min. The reaction mixture was then cooled to 0°C and N-methoxy-N-methylacetamide (.63 g, 6.1 mmol), dissolved in THF, and was added to the reaction and slowly heated to 50°C for 1 hr. The reaction is cooled to 0°C and quenched with 5 % HCl and extracted with ethyl acetate (3 x 10 mL). The organic layer was combined and washed with brine and dried (MgSO4). The ethyl acetate was removed by distillation under reduced pressure and the crude material was purified by bulb to bulb distillation 54 - 59°C at ~.25 mm of mercury (.641 g, 84.7 %).

$^1$H-NMR (300MHz, CDCl$\text{3}$): δ 3.97 (s, 3H, O=C-CH$\text{3}$), 4.46 (s, 3H, -OCH$\text{3}$), 6.22 (d, 1H, J = 6.3 Hz, =CH-C), 8.21 (d, 1H, J = 6.3 Hz, -O-CH=); $^{13}$C-NMR (75.4 MHz, CDCl$\text{3}$): δ 32.16, 61.05, 82.33, 86.87, 92.56, 161.96, 183.98

Ethylidene-\text{-}t\text{-}butyl amine
A round bottom flask was charged with t-butylamine (13.9 g, .19 mol) and cooled to 0° C. Acetylaldehyde (8.38 g, .19 mol) was added gradually over a period of 2 h. The reaction mixture was stirred 30 min and then KOH flakes (3 g) were added and allowed to stand until the reaction mixture separated into two layers (about 15 min.). The organic layer was removed and allowed to stand over crushed KOH in the refrigerator overnight (12 h.) The dried material is decanted from the liquefied KOH and distilled from fresh KOH. The product was collected between 86 - 92°C as a clear liquid.

\[ \text{H-NMR (300MHz, CDCl}_3\text{): } \delta 1.08 \text{ (m, 9H, } -\text{C(CH}_3\text{)}_3\text{), 1.89 (m, 3H, } =\text{CH-C}_3\text{), 7.61 (m, 1H, } =\text{C}_3\text{-CH}_3\text{);} \]

\[ \text{C-NMR (75.4 MHz, CDCl}_3\text{): } \delta 22.70, 29.55, 32.47, 154.58 \]

Silylation of ethylidene-t-butyl amine

\[
\text{Si} \quad \equiv \quad =\text{N} \quad \equiv
\]

To a stirred solution of lithium diisopropylamide (.066 mmol) in 25 mL of THF was added ethylidene-t-butyl amine (6.33 g, .064 mol.) at 0° under argon. The solution was treated with a solution of trimethylchlorosilane (8.12 mL, .064 mol) in THF with stirring at 0°. The reaction mixture was warmed to 0° over 3 h. period and poured into water (50 mL) and extracted with ether. The combined organic extracts were washed
with brine, dried (MgSO₄) and concentrated. The residual liquid was distilled at 157 - 163° to afford (8.97 g, 82.1 %) of clear colorless product.

\[^1\text{H}\text{-NMR (300MHz, CDCl}_3\text{)}: \delta 0.05 (s, 9H, -\text{Si(CH}_3)_3), 1.09 (s, 9H, -\text{C(CH}_3)_3), 1.81 (d, 2H, J = 6.4 Hz, -\text{Si-CH}_2\text{CH=}), 7.60 (t, 1H, J = 6.4 Hz, -\text{Si-CH}_2\text{CH=}); \]
\[^13\text{C-NMR (75.4 MHz, CDCl}_3\text{): } -1.52, 1.43, 28.47, 29.23, 156.56\]

3-Methyl-7-methoxyhepta-2,6-dien-4-ynal (61).

Trimethylylethylidene-\(t\)-butyl amine (6.85 g, .04 mol) was added to a solution of lithium diisopropylamide (.04 mol—prepared from of diisopropylamine (4.05 g) and 2.54 M BuLi in hexane (15.75 mL)) in THF (50 mL) at 0°C over a 10 min. period. The reaction mixture was stirred for 15 min. and cooled to -78°C and treated with ketone 59 (5 g, .04 mol). The resulting mixture was warmed to -20°C over a 3 h period and then quenched with water (5 mL). Solid oxalic acid was added to bring the pH to 4.5 and stirring was continued for 30 min. The reaction was poured into brine and (10 mL) and extracted with ether (20 mL). The organic extracts were washed with sodium bicarbonate solution, dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (20 %)
EtOAc/hexane) to give a clear oil which was used immediately in the (the next two-carbon elongation). The crude yield was approximately 4.56 g, 76%.

5-Methyl-9-methoxyna9na-2,4,8-trien-6-ynal

Trimethylsilyl ethylidene-3-butyl amine (1.15 g, 6.66 mmol) was added to a solution of lithium diisopropylamide (6.66 mmol—prepared from diisopropylamine (0.68 g) and 2.54 M BuLi in hexane (2.62 mL)) in THF (30 mL) at 0°C over a 10 min. period. The reaction mixture was stirred for 15 min. and cooled to -78°C and treated with 3-methyl-7-Methoxyhepta-2,6-dien-4-ynal (1.0 g, 6.66 mmol). The resulting mixture was warmed to -20°C over a 3 h period and then quenched with water (5 mL). Solid oxalic acid was added to bring the pH to 4.5 and stirring was continued for 30 min. The reaction was poured into brine and (10 mL) and extracted with ether (3x20 mL). The organic extracts were washed with sodium bicarbonate solution, dried (MgSO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (20 % EtOAc/hexane) to give a yellow oil (containing several spots on the TLC that were too close to separate) that darkened rapidly at
room temperature even when under vacuum, in the dark and under argon (0.89 g 71 %).

$^1$H-NMR (300MHz, CDCl$_3$): δ The nmr was not very clean probably due to rate at which the compound decomposed and because of the number of conformational isomers that could have been present. There was some evidence for the presence of the desired product. 1.94 (s, 3H, =CH$_3$), 4.41 (s, 3H, -OCH$_3$), 6.69 (dd, 1H, J = 14.7, 8.2 Hz, methylene next to the aldehyde), 9.37 (d, 1H, J = 8.1 Hz, O=CH).
REFERENCES
REFERENCES


43. ICI are the initials for Imperial Chemical Industries.


APPENDIX A

X-RAY DATA
X-ray Structure Determination of C_{22}H_{21}N_{3}O_{2}S_{5}.

Crystal data: triclinic, space group P1 (#2), a = 6.996(2) Å, b = 12.532(1) Å, c = 13.591(1) Å, α = 64.600(6)°, β = 88.930(7)°, γ = 79.820(7)°, V = 1208.3(3) Å³, z = 2, T = 26°C, radiation MoKα (λ = 0.71073 Å), F(000) = 540, μ(MoKα) = 5.05 cm⁻¹, d_{calc} = 1.43 gcm⁻³, R = 0.050, wR = 0.037, S = 1.51, 289 parameters. A parallelepiped magenta crystal (~0.04 x 0.5 x 0.6 mm) was mounted on a glass fiber. Intensity data were taken as omega scans on an automated four-circle diffractometer (Siemens P4 upgrade of Nicolet R3m) for 10234 unique reflections in the range 3° < 2θ < 70°, of which 2344 with I > 3σ(I) were used for structure solution and refinement. The data were corrected for Lorentz and polarization effects, and absorption corrections were calculated from measured dimensions between indexed crystal faces (transmission factor range 0.82 to 0.98). No extinction corrections were needed.

The structure was solved by direct methods. Non-hydrogen atoms were refined by full-matrix least-squares with anisotropic thermal parameters, using statistical weighting. Calculated hydrogen positions were used with isotropic thermal parameters fixed at 1.2 times the carbon thermal parameters. The atom labeling scheme is shown in figure 23. Positional coordinates, bond distances and angles and anisotropic thermal parameters are given in tables 2-7. The largest peak on the final difference map was 0.35 eÅ⁻³ at 0.07Å from s(2).
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The anisotropic displacement exponent takes the form:

$$-2\pi^2 \left( h^2a^2U_{11} + \cdots + 2hka^bU_{12} \right)$$
Table 5. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\AA^2 \times 10^3$)

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Table 6: Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^2x10^3)

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* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.*
B. THERMAL ELLIPSOID PLOTS

BTHIND

BOXIND

BTHPHO