Temperature studies on allopolar isomerism
by Carol Linn Enwall

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry
Montana State University
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Abstract:
Known allopolar and meropolar dyes were synthesized. Solutions of the two allopolar dyes were prepared in various solvent systems. Visible abatirption specera were taken at four different temperatures. The extinction coefficients of the meropolar and holopolar forms of the allopolar dyes were determined, Entropy and enthalpy values for the equilibrium constants of the allopolar dyes were calculated.

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Approved:

Head, Major Department

Chairman, Examining Committee

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
INTRODUCTION	1
DISCUSSION	8
EXPERIMENTAL	
1-Ethyl-2-methylbenzothiazolium iodide	38
1,2-Diphenyl-3,5-pyrazolidinedione	38
4-Isopropylidene-1,2-diphenyl-3,5-pyrazolidinedione	38
5-[1,3-Bis-(3-ethyl-2-benzothiazolinylidene)-isopropylidene]-2-dimethyl-1,3-dioxane-4,6-dione	39
1,2-Diethoxycarbonyl-3,5-pyrazolidinedione	39
5-(3-Ethyl-2-benzothiazolinylidene)-isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione	39
5-Isopropylidene-2,2-dimethyl-1,3-dioxane	40
4-[1,3-Bis-(3-ethyl-2-benzothiazolinylidene)-isopropylidene]-1,2-diphenyl-3,5-pyrazolidinedione	40
1-Ethyl-2-methylthiobenzothiazolium ethylsulfate	41
4-(3-Ethyl-2-benzothiazolinylidene)-isopropylidene-1,2-diphenyl-3,5-pyrazolidenedione	41
2,2-Dimethyl-1,3-dioxane-4,6-dione	41
3,3'-Diethyl-9-methylthiacarbocyanine iodide	41

Page

SUMMARY 46

LITERATURE CITED 47

LIST OF TABLES

		Page
I.	Least Squares Data from Plot of d_h/d_m Vs $1/d_m$	26
II.	Thermodynamic Values of Allopolar Dye (V) for Equilibrium Constants K_h	32
	Constants K_m	33
	Constants $K_{\frac{h+m}{2}}$	34
	Thermodynamic Values of Allopolar Dye (IX) for Equilibrium Constants K_h	35
	Constants K_m	36
	Constants $K_{\frac{h+m}{2}}$	37
III.	Nuclear Magnetic Resonance Data	45

LIST OF FIGURES

		Page
1.	Amidinium Ion System of a Thiacyanine	1
2.	Equilibrium and Resonance Structure of a Merocyanine	2
3.	Stereo Projections of an Allopolar Dye	4
4.	Equilibrium and Resonance Structure of a Trinuclear Dye	5
5.	Solvent Dependence of a Trinuclear Dye	7
6.	Visible Absorbance of Allopolar Dye (V) at 6 C	16
7.	Visible Absorbance of Allopolar Dye (V) at 25 C	17
8.	Visible Absorbance of Allopolar Dye (V) at 35 C	18
9.	Visible Absorbance of Allopolar Dye (V) at 45 C	19
10.	Visible Absorbance of Allopolar Dye (IX) at 6 C	20
11.	Visible Absorbance of Allopolar Dye (IX) at 25 C	21
12.	Visible Absorbance of Allopolar Dye (IX) at 35 C	22
13.	Visible Absorbance of Allopolar Dye (IX) at 45 C	23
14.	Plot of Equilibrium Constant VS 1/T for Allopolar Dye (IX) Sample E	30
15.	Plot of Equilibrium Constant VS 1/T for Allopolar Dye (V) Sample H	31
16.	Infrared Spectrum of 2,2-Dimethyl-1,3-Dioxane-4,6-Dione	43
17.	Infrared Spectrum of 1,2-Dicarbethoxy-3,5-Pyrazolidinedione	43
18.	Infrared Spectrum of 1,2-Diphenyl-3,5 Pyrazolidinedione	44

ABSTRACT

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

INTRODUCTION

Cyanine dyes can hardly be identified as a new class of heterocyclic compounds since their beginnings date back to 1856.[1] Quinoline was one of the first heterocyclic compounds to be isolated from natural sources, and because it was readily available, dyes containing quinoline nuclei were the type most commonly studied until the 1920's. In the 1920's the rediscovery of Hoffman's work with benzothiazole bases led to a new field of cyanine dye chemistry.[2]

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

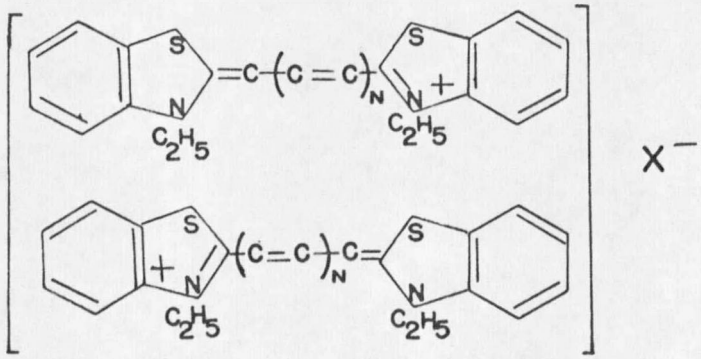


Fig. 1. AMIDINIUM ION SYSTEM of a THIACYANINE

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

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

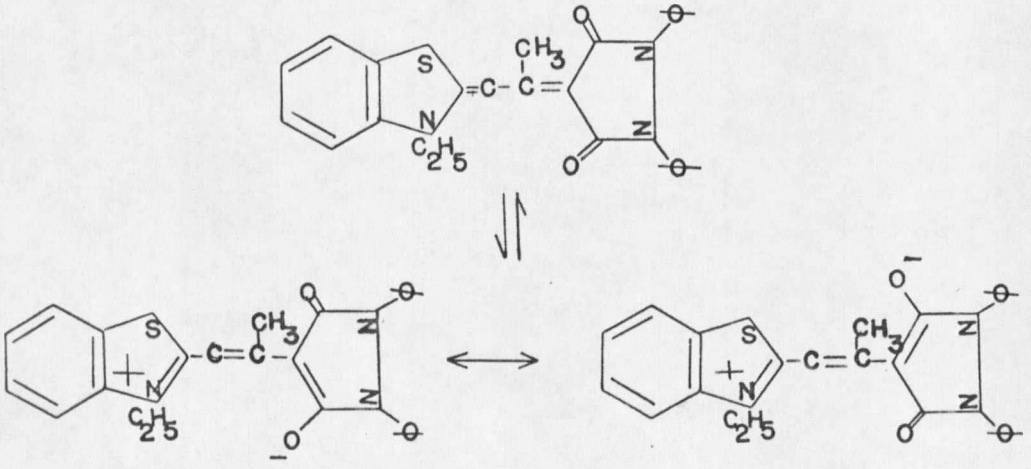
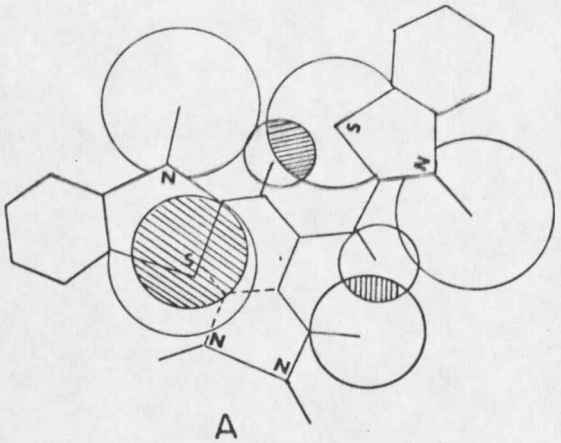


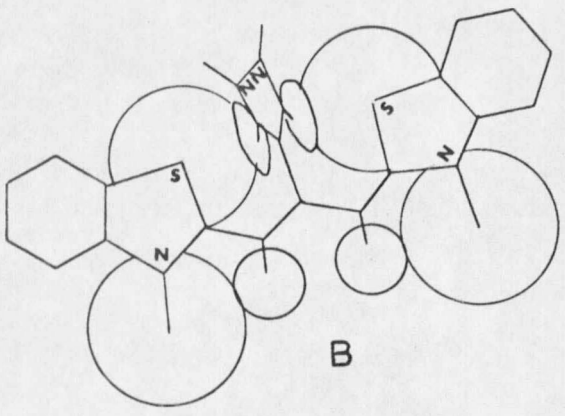
Fig. 2. EQUILIBRIUM and RESONANCE STRUCTURE of a MEROCYANINE DYE

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

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

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





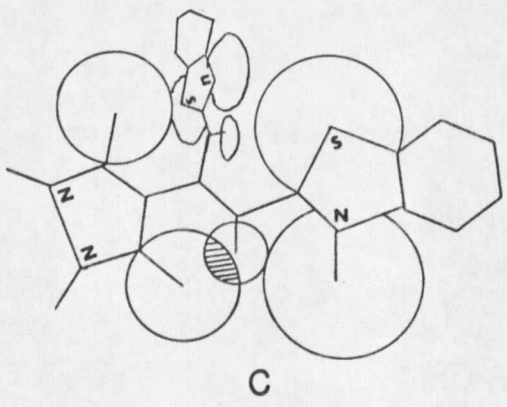


Fig. 3. STEREO PROJECTIONS of an ALLOPOLAR DYE

The trinuclear dye may be shown to exist in two possible conformers (Fig. 4).

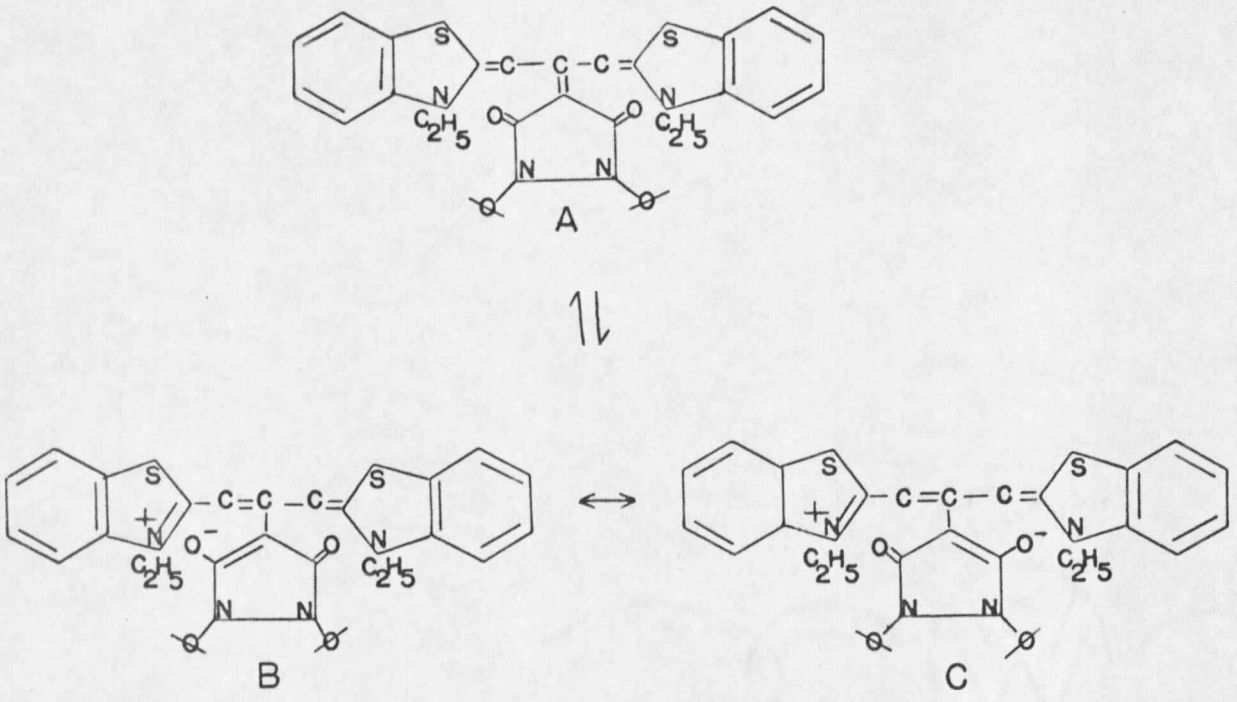


Fig. 4. EQUILIBRIUM and RESONANCE STRUCTURE of a TRINUCLEAR DYE

In the uncharged conformation of the trinuclear dye (Fig. 4,A), the meropolar form, the acidic nucleus is in the plane of one of the benzothiazole nuclei, and the second benzothiazole nucleus is twisted out of the plane. This is the same conformation as that of the chain methyl merocyanine dye (Fig. 2) and corresponds to stereo projection C, Fig. 3. In the complete charge-separated conformation of the trinuclear dye (Fig. 4,B,C,), the holopolar form, the pyrazolone nucleus is twisted out of the plane of the benzothiazole rings, giving the same conformation as

that of the 3,3'-diethylthiacarbocyanine iodide dye (Fig. 1, n=1), and corresponds to stero projection B, Fig. 3. Therefore, it was on the basis of the similiarity in the absorption maxima of the trinuclear dye to the carbocyanine dye and the chain methyl merocyanine dye that the two bands of the trinuclear dye were assigned to the holopolar and meropolar conformers.

Allopolar dyes are solvent sensitive. The ratio of holopolar to meropolar forms may be changed by varying the polarity of the solvent. In a strongly polar solvent such as methanol or water the trinuclear dye has a major absorption maximum at 550 mμ (Fig. 5,A). As a relatively nonpolar solvent such as lutidene is added to the dye-methanol solution, the absorption band at 475 mμ begins to increase (Fig. 5,B). This evidence indicates that an isomerization has occurred.

The dynamic equilibrium between two stereoisomeric dye structures which is polarity dependent has been given the term "allopolar isomerism".

It was the purpose of this project to investigate the temperature dependence of the existing holopolar-meropolar equilibrium for some known allopolar dyes.

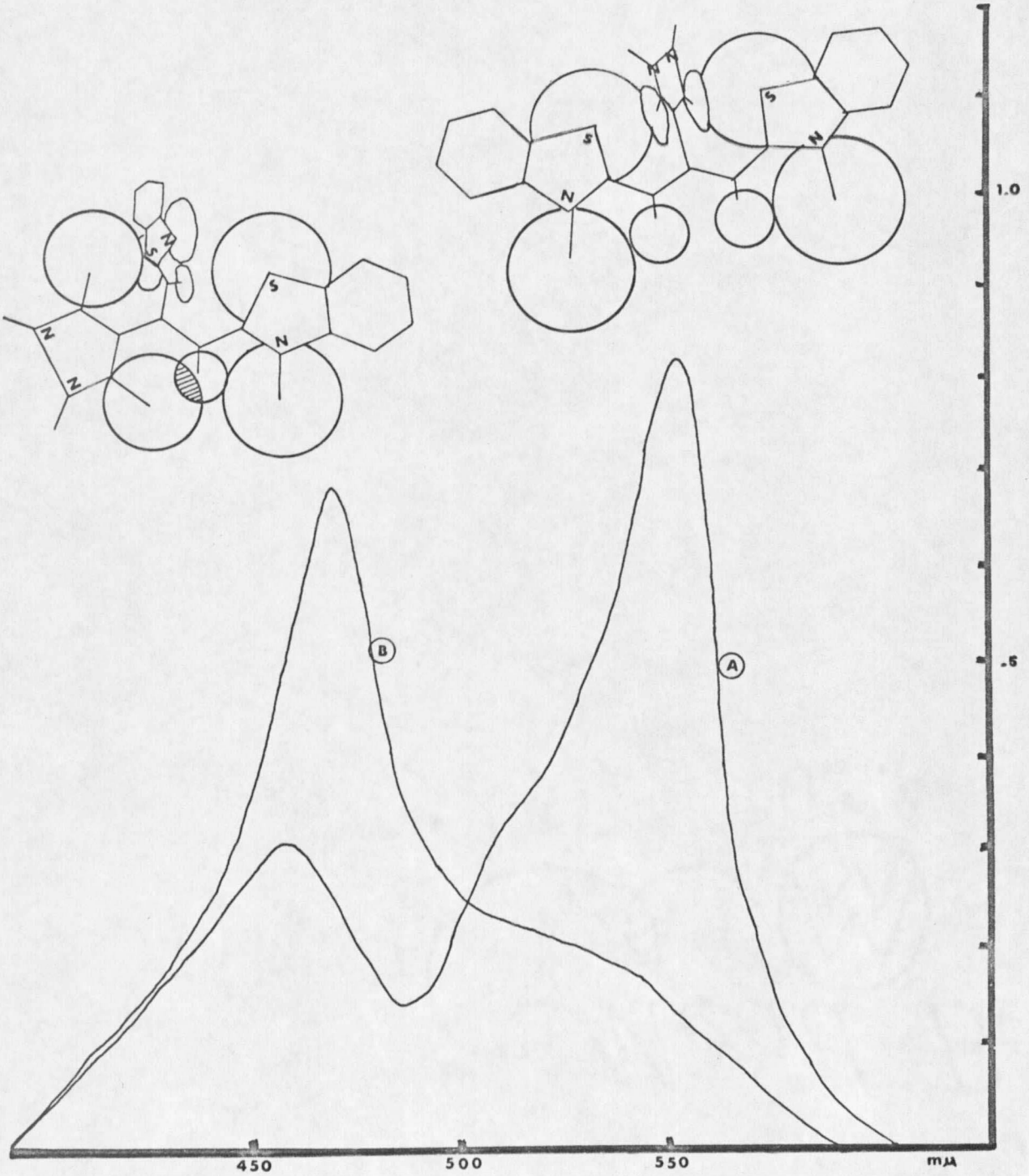
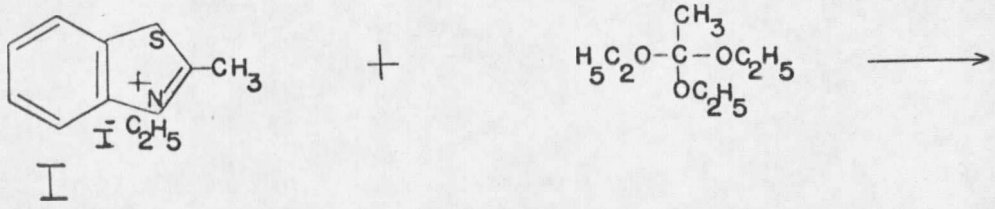


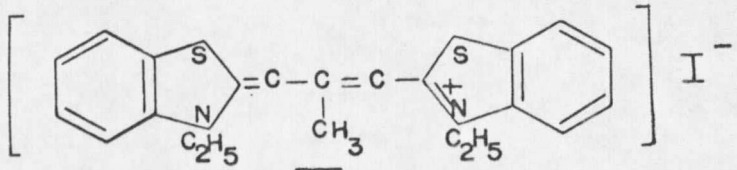
Fig. 5. SOLVENT DEPENDENCE of a TRINUCLEAR DYE

DISCUSSION

The carbocyanine dye, 3,3'-diethyl-9-methylcarbocyanine iodide (II), was the first of the dyes to be prepared. It was made by the reaction of two portions of 3-ethyl-2-methylthiobenzothizaolium iodide (I) with one portion of methyl orthoacetate.[5] Attempts to obtain a single crystal of the carbocyanine dye for x-ray structural determination were unsuccessful. Recrystallization of the purple colored powder from methanol gave only twinned crystals.

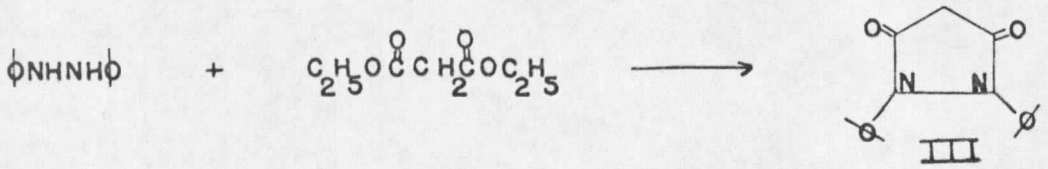


I



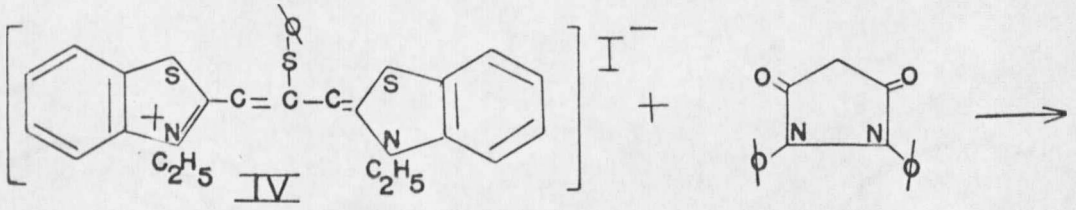
II

Four electron-attracting or acidic nuclei were synthesized to be used later for the synthesis of the allopolar dyes. 1,2-diphenylhydrazine and diethyl malonate were cyclized in the presence of sodium ethoxide to give 1,2-diphenyl-3,5-pyrazolidinedione (III). The infrared and the nuclear magnetic resonance spectra gave no indication of any enol form (Fig. 18 and Table III).

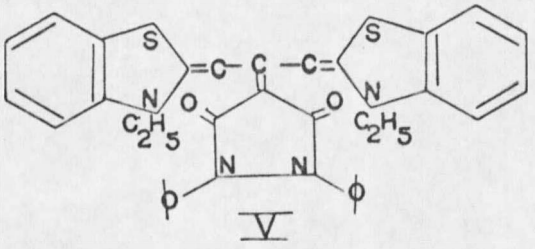


III

The allopolar dye, 4-[1,3-Bis-(3-ethyl-2-benzothiazolinylidene)-isopropylidene]-1,2-diphenyl-3,5-pyrazolidinedione (V), was prepared by heating 3,3'-diethyl-9-phenylthiothiacarbocyanine iodide (IV) with 1,2-diphenyl-3,5-pyrazolidinedione in the presence of triethylamine with pyridine.

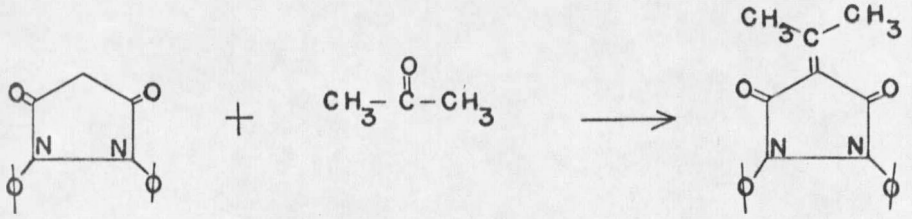


IV

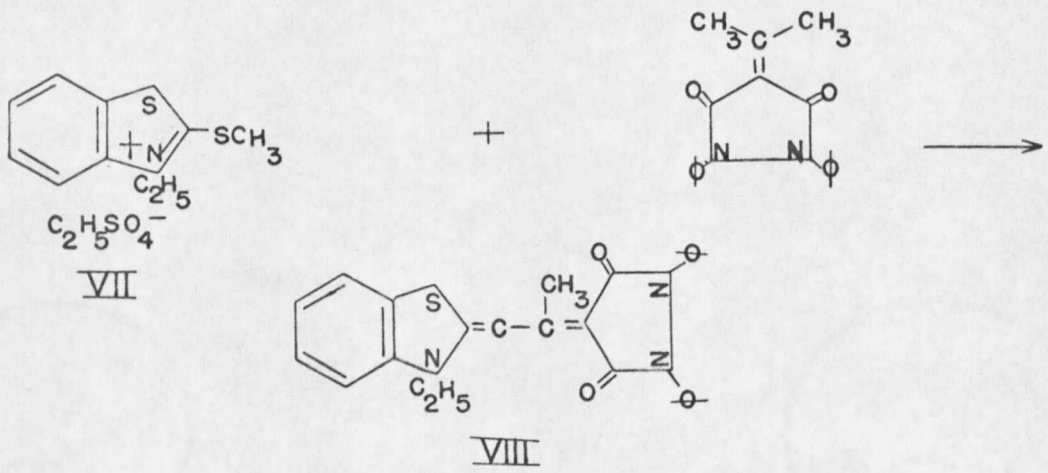


V

Before the corresponding merocyanine could be prepared, it was necessary to condense 1,2-diphenyl-3,5-pyrazolidinedione with acetone in the presence of anhydrous zinc chloride. The two reactive methyl groups provided sites for further condensations.

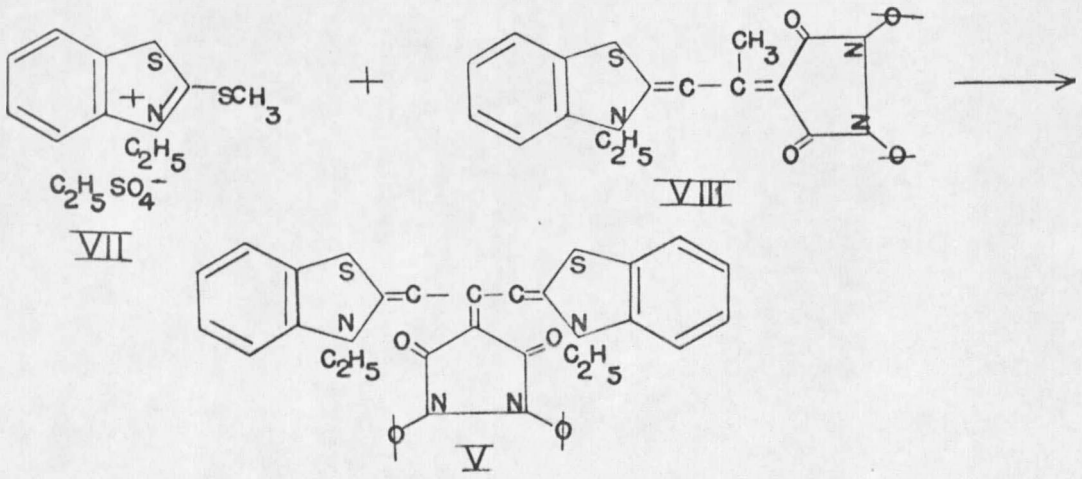


The reaction of one mole of 1-ethyl-2-methylthiobenzothiazolium ethylsulfate (VII) with one mole of 1,2-diphenyl-4-isopropylidene-3,5-pyrazolidinedione gave the corresponding chain methyl merocyanine dye, 4-(3-ethyl-2-benzothiazolinylidene)-isopropylidene-1,2-diphenyl-3,5-pyrazolidinedione (VIII).



VII VIII

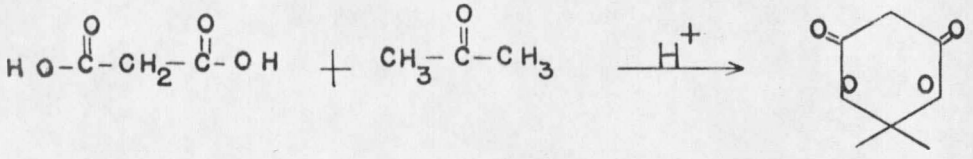
This now provided an alternative method for the synthesis of the allopolar dye (V). One mole of the isolated chain methyl merocyanine dye (VIII) and one mole of quaternary salt (VII) reacted in the presence of triethylamine and pyridine to yield the desired allopolar dye (V).



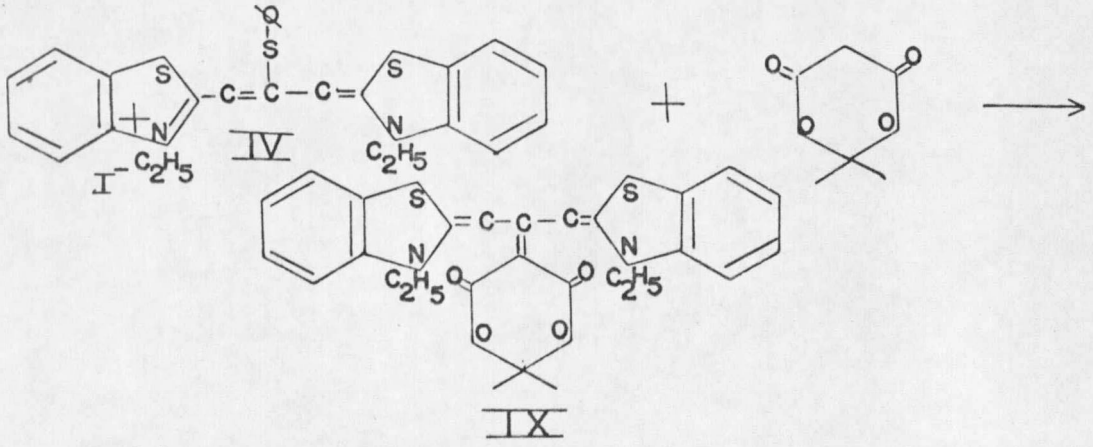
VII VIII V

The allopolar dye (V) may also be prepared by the reaction of two moles of quaternary salt (VII) with 4-isopropylidene-1,2-diphenyl-3,5-pyrazolidinedione.

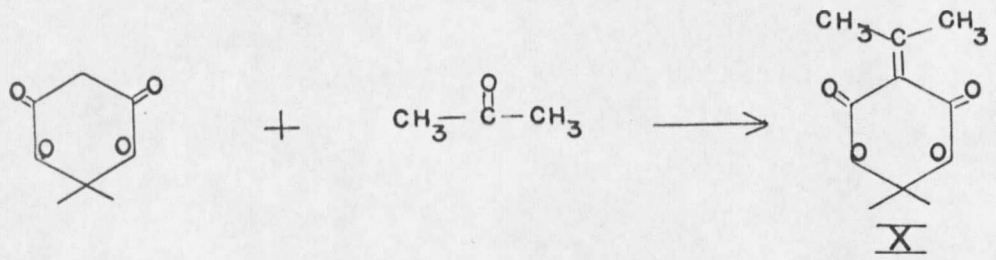
It was thought that because of additional crowding, the introduction of a six membered ring would favor one of the isomeric forms of the allopolar dye. The ring system chosen was 2,2-dimethyl-1,3-dioxane-4,6-dione. This diketo dioxane, known as Meldrum's lactone, was easily prepared by the reaction of malonic acid with acetone. The infrared and nuclear magnetic spectra indicated only the keto structure (Fig. 16 and Table III).



The allopolar dye, 5-[1,3-Bis(3-ethyl-2-benzothiazolinylidene)-isopropylidene] -2,2-dimethyl-1,3-dioxane-4,6-dione, (IX), was formed by heating 2,2-dimethyl-1,3-dioxane-4,6-dione and the quaternary salt (IV) with triethylamine and diethylformamide. The green crystals of the allopolar dye (IX) separated out of the chilled dimethylformamide solution.

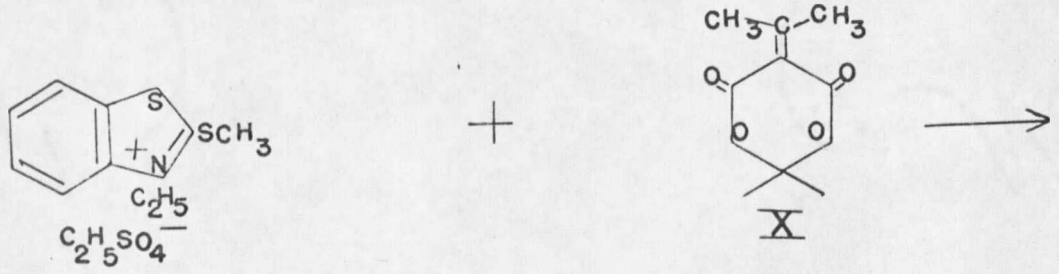


The acetone condensation product, 5-isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione, (X), was necessary for the preparation of the corresponding chain methyl merocyanine dye (XI). 2,2-dimethyl-1,3-dioxane-4,6-dione and acetone were mixed with piperidine and glacial acetic acid.



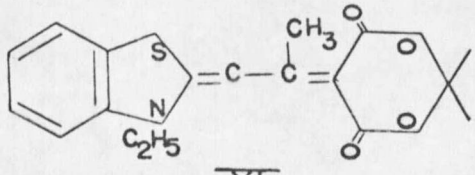
X

Triethylamine and dimethylformamide were added to a mixture of 5-isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione, (X), and the quarternary salt (VII).



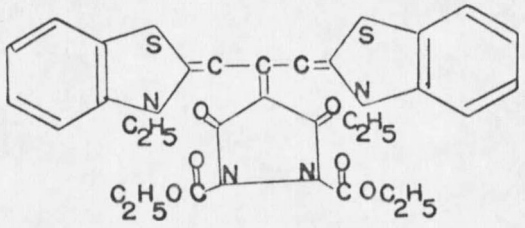
VII

X



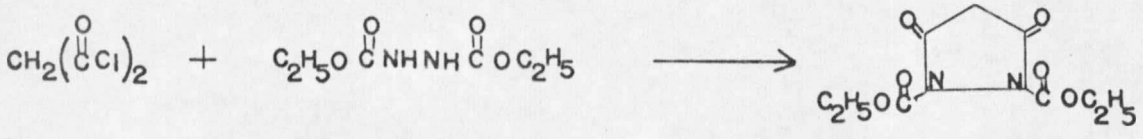
XI

Attempts were made to synthesis the allopolar dye, 4- [1,3-Bis-(3-ethyl-2-benzothiazolinylidene)-isopropylidene] -1,2-dicarbethoxy-3,5-pyrazolidinedione (XII).



XII

It was necessary to use malonyl chloride with 1,2-dicarbethoxy-hydrazine to form the acidic nucleus. This procedure gave the desired product, 1,2-dicarbethoxy-3,5-pyrazolidinedione. A keto structure was indicated by the infrared and nuclear magnetic resonance spectra (Fig. 17 and Table III).



It was impossible to ever obtain more than trace amounts of the allopolar dye (XII). The alternative procedure for preparing the desired allopolar dye (XII), required the condensation product of acetone and 1,2-dicarbethoxy-3,5-pyrazolidinedione. However, the only identifiable

product obtained was 1,2-dicarbethoxyhydrazine.

Attempts at preparing 1,2-dimethyl-3,5-pyrazolidinedione as an acidic nucleus were likewise a failure. The real problem was freeing 1,2-dimethylhydrazine from its di-hydrogen chloride salt.

The spectrophotometric data for the allopolar dyes were taken with a Beckman DK-2 spectrophotometer. A Beckman constant temperature cell holder was used in obtaining data at the four different temperatures. The cell holder consisted of metal block through which water from a constant temperature bath circulated. Because of the cell holder apparatus the range of temperatures was somewhat limited. Data were taken at six degrees, twenty-five degrees, thirty-five degrees and forty-five degrees, centigrade.

The solvents chosen for the allopolar isomerism study were methanol and 2,6-lutidine. A stock solution containing 5 mg. of allopolar dye in one hundred milliliters of lutidine was prepared. Ten samples, all containing the same amount of stock solution, were diluted with methanol and lutidine in the following manner:

Sample	Stock	Lutidine	Methanol
A	1 ml	9 ml	
B	1 ml	8 ml	1 ml
C	1 ml	7 ml	2 ml
D	1 ml	6 ml	3 ml
E	1 ml	5 ml	4 ml
F	1 ml	4 ml	5 ml
G	1 ml	3 ml	6 ml
H	1 ml	2 ml	7 ml
I	1 ml	1 ml	8 ml
J	1 ml		9 ml

The recorded absorption curves are given in Figs. 6-13.

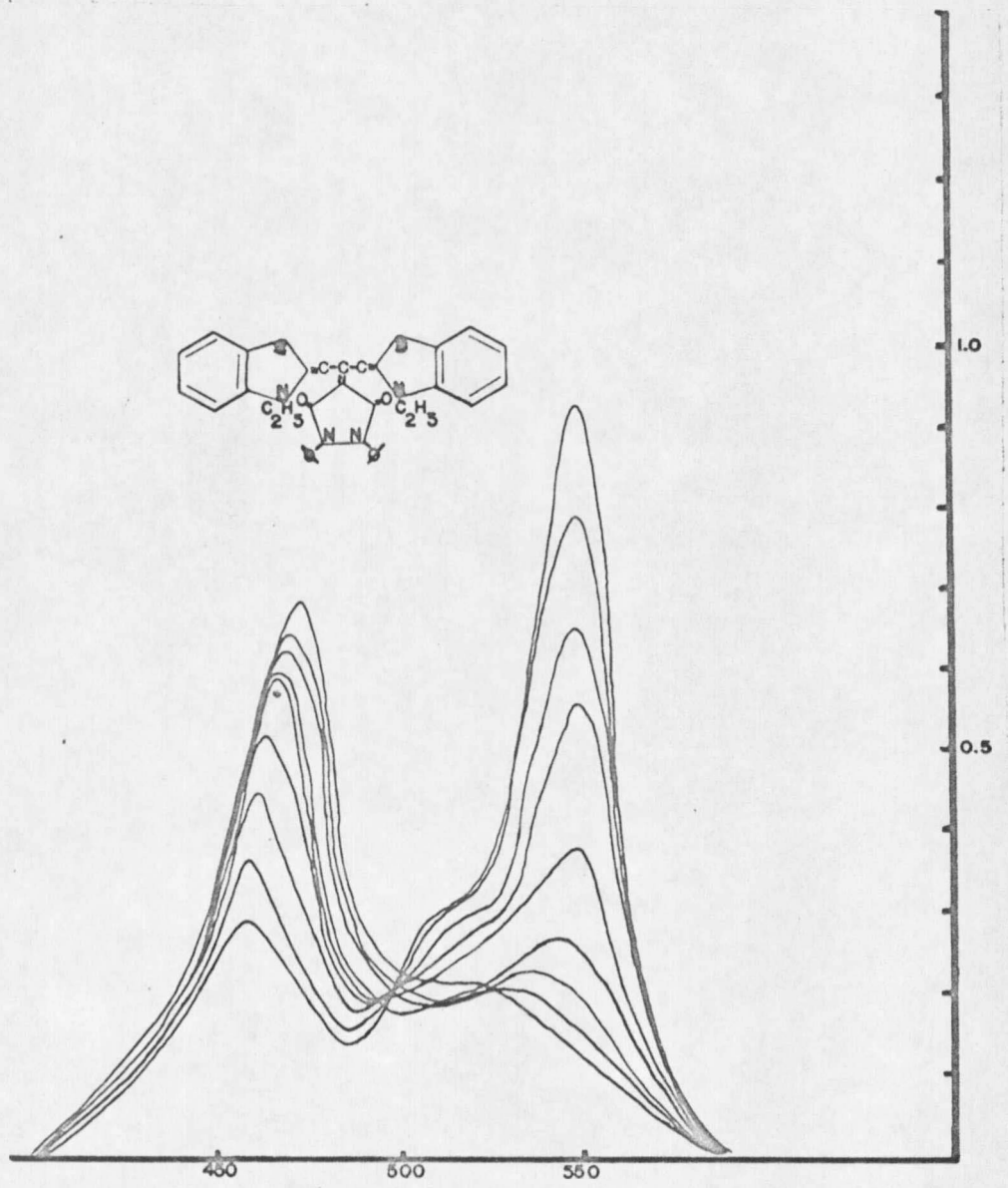


FIG. 6. VISIBLE ABSORBANCE OF ALLOPOLAR DYE(V) AT 6° C

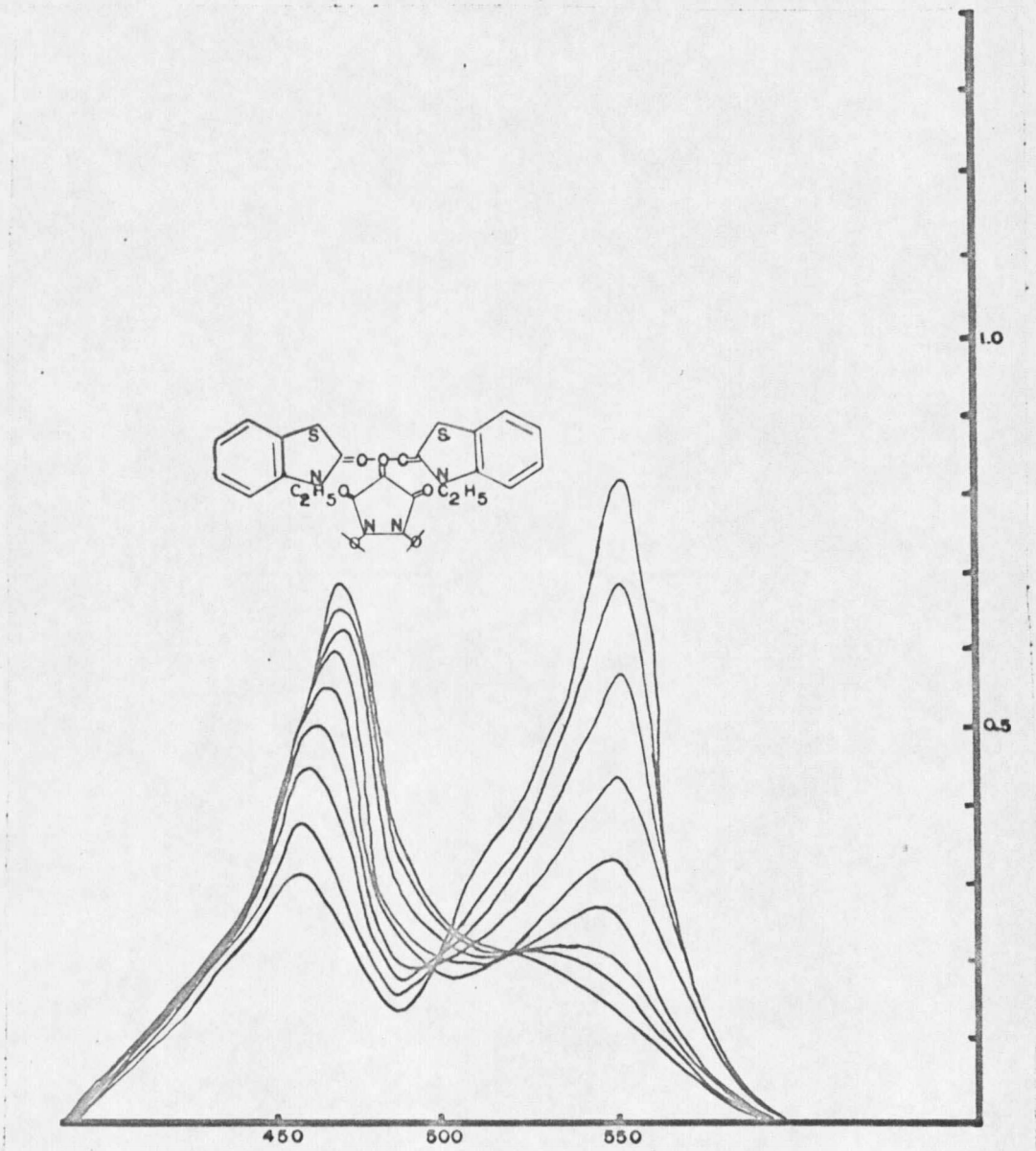


FIG.7. VISIBILE ABSORBANCE OF ALLOPOLAR DYE(V) AT 25°C

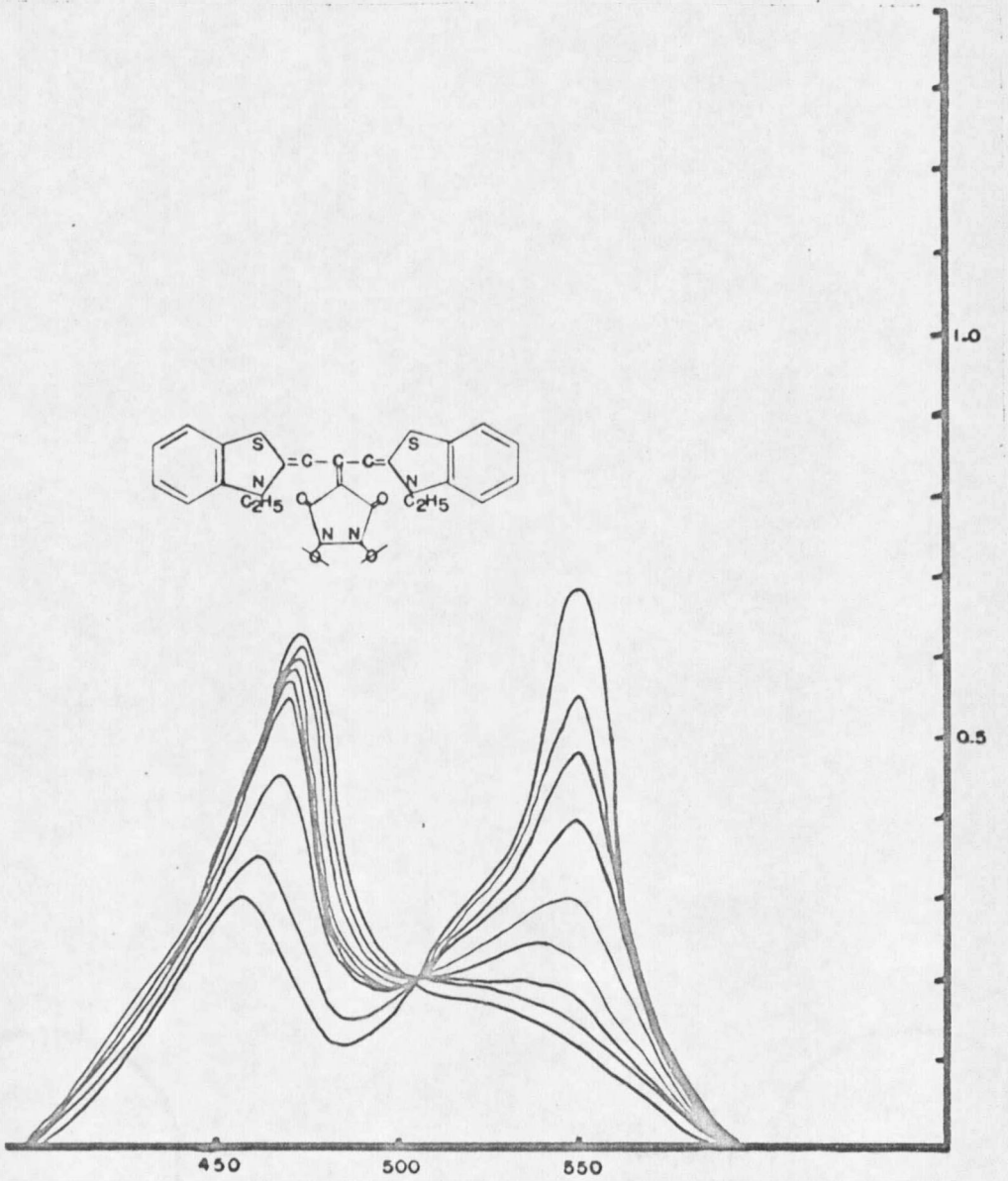


FIG. 8. VISIBLE ABSORBANCE OF ALLOPOLAR DYE(V) AT 35°C

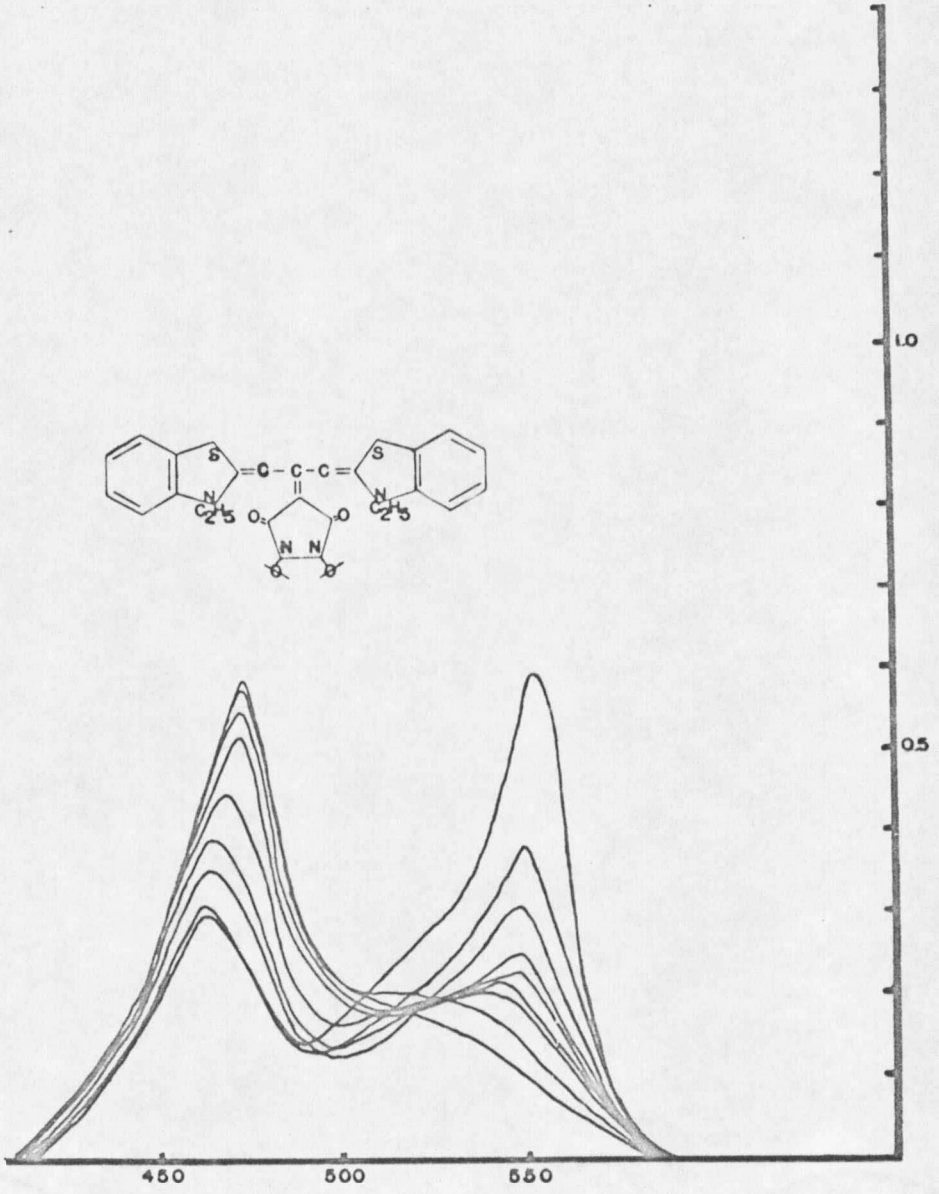


FIG. 9. VISIBLE ABSORBANCE OF ALLOPOLAR DYE (V) AT 45°C

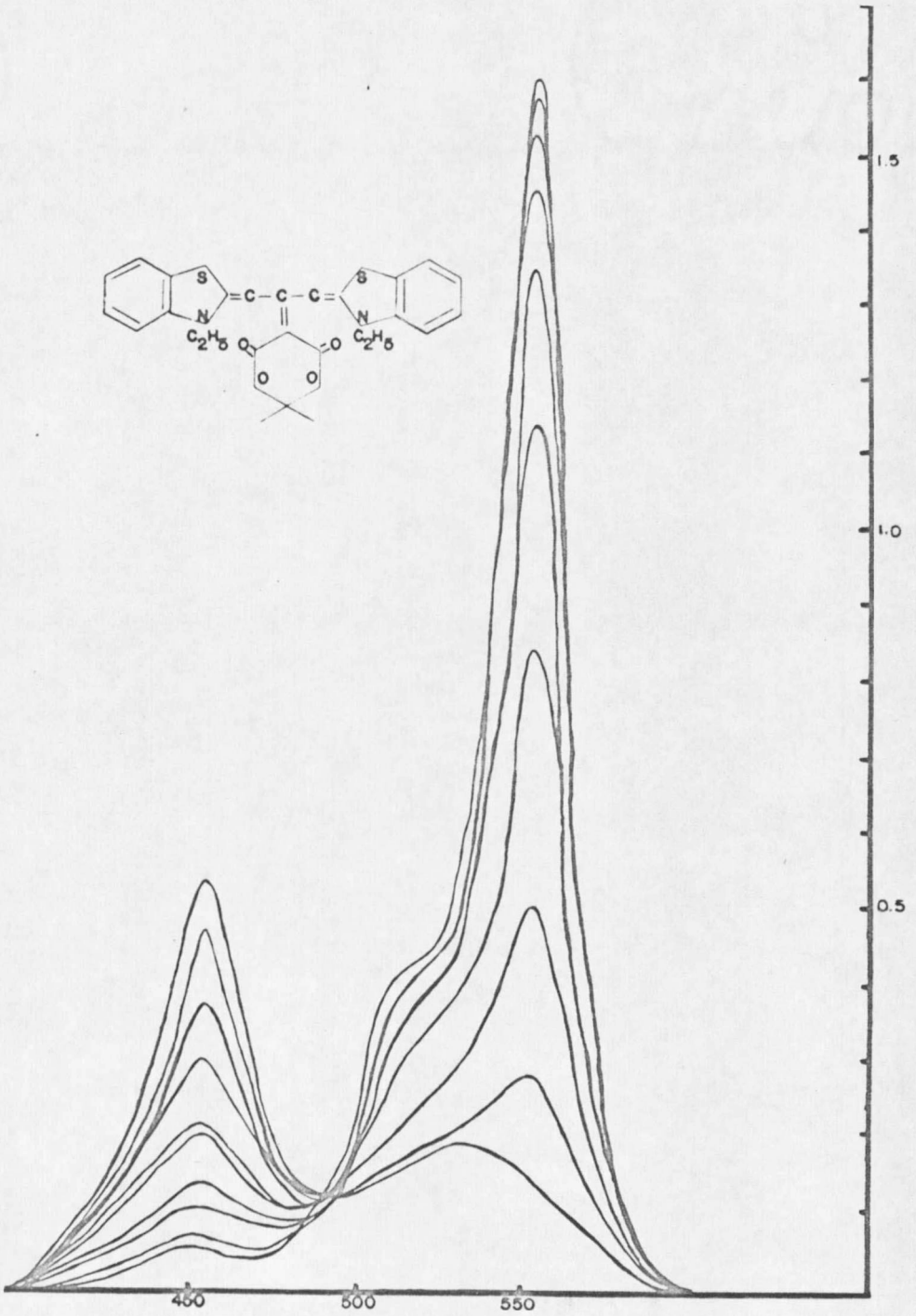


FIG. 10. VISIBLE ABSORBANCE OF ALLOPOLAR DYE (IX) AT 6°C

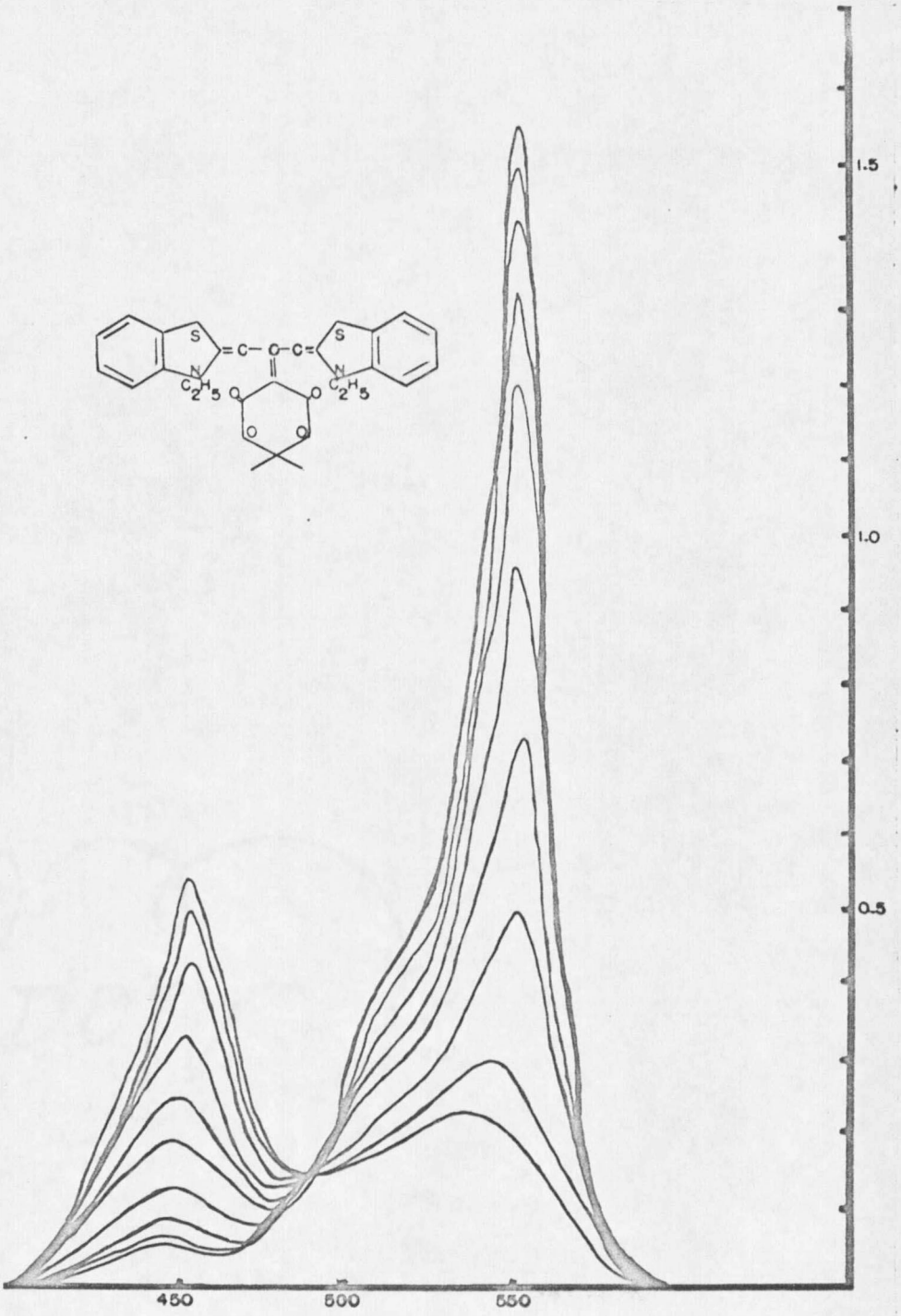


FIG. II. VISIBLE ABSORBANCE OF ALLOPOLAR DYE(IX) AT 25° C

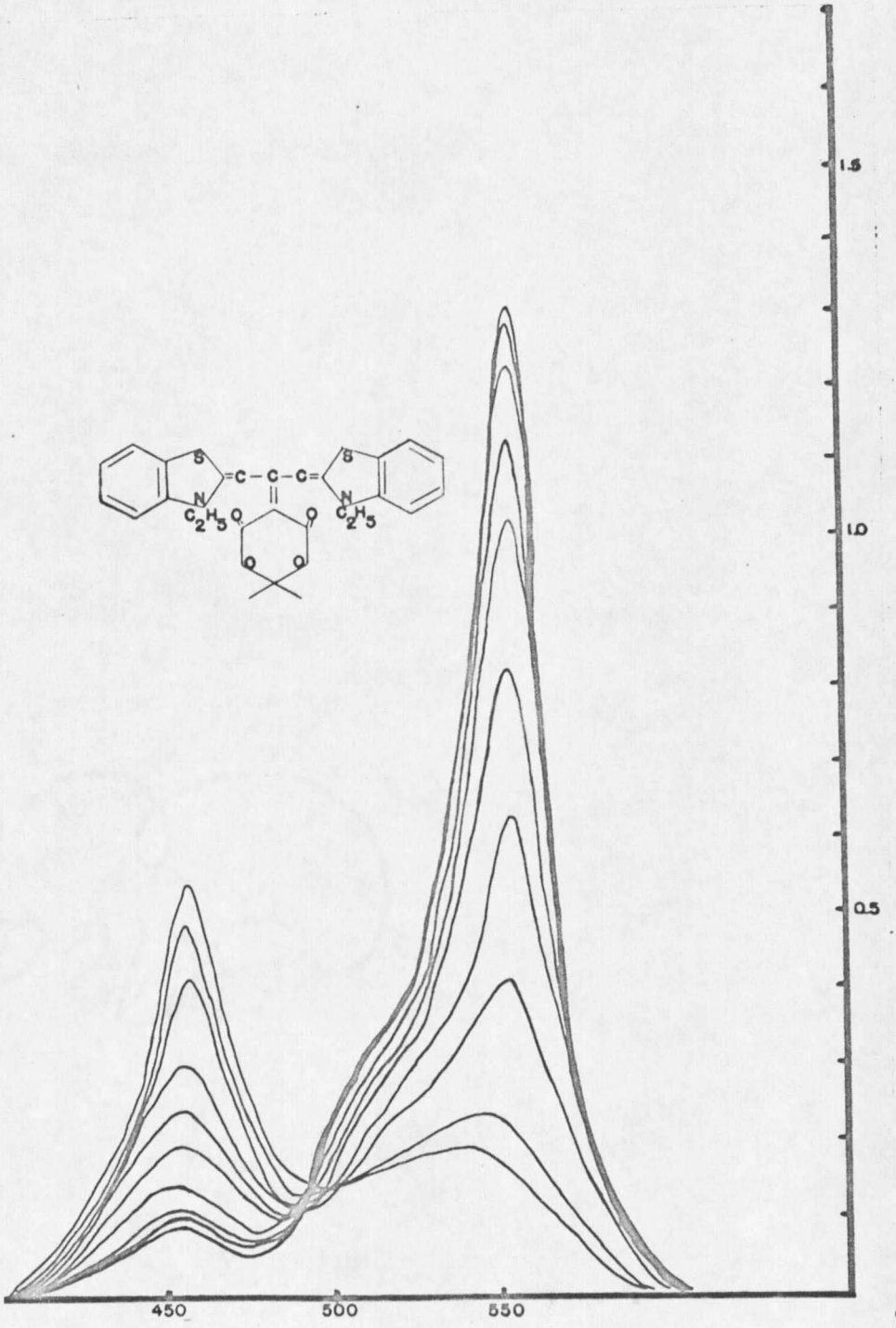


FIG. 12. VISIBLE ABSORBANCE OF ALLOPOLAR DYE (X) AT 35°C

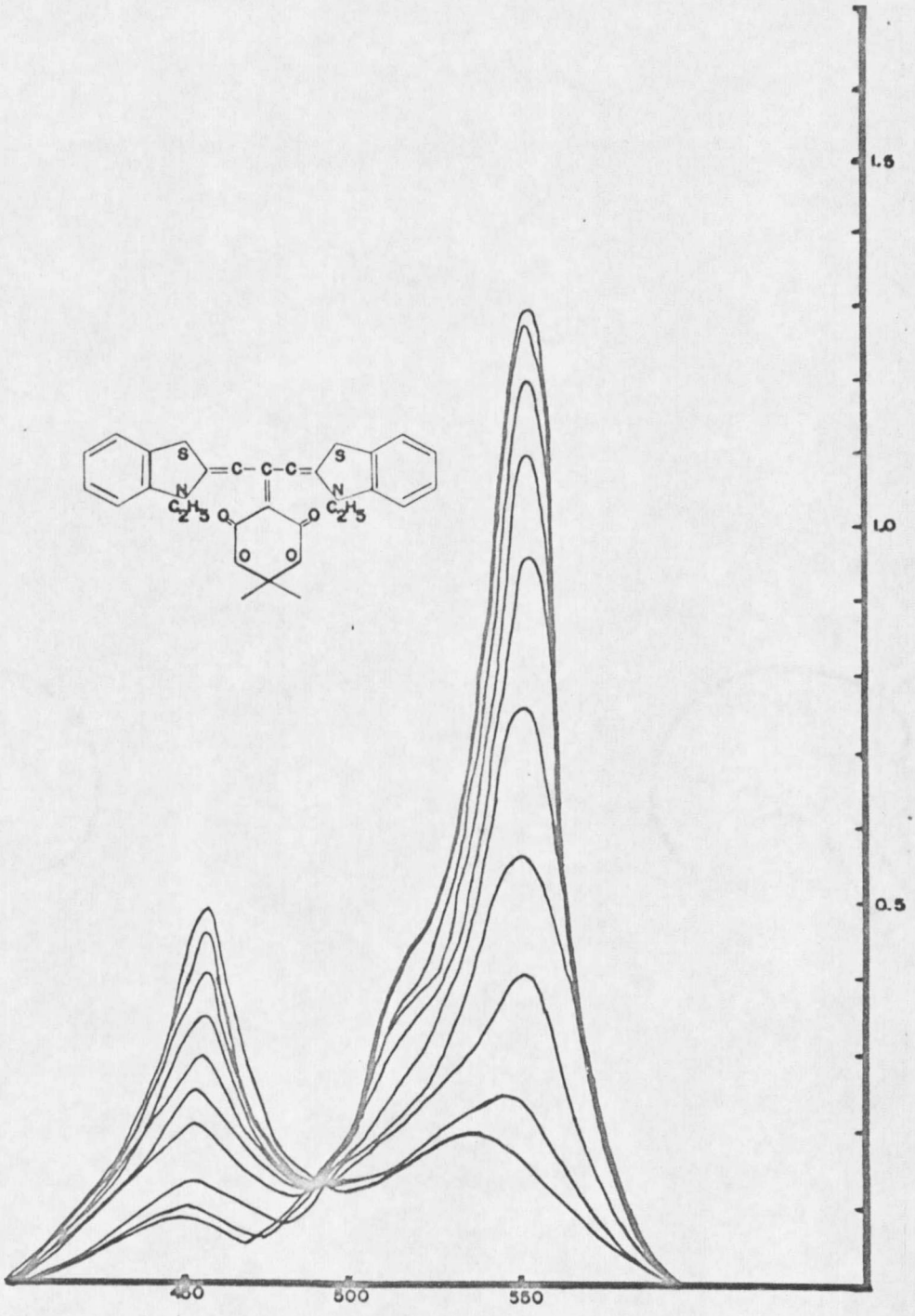


FIG. 13. VISIBLE ABSORBANCE OF ALLOPOLAR DYE (IX) AT 45°C

The calculations for determining the extinction coefficient and the equilibrium constants for the allopolar dyes involve the following equations.

Internal Solvent Series Method[7]

Absorption spectra are often characterized in terms of absorbency A where

$$A = \log I_o/I \tag{1}$$

I is the intensity of light transmitted by the sample and I_o is the intensity of light incident on the sample. For the purposes of the following calculations, the quantity, $\log (I_o/I)$ will be defined as the optical density.

The optical density of the solution in a one-cm. cell is related to the concentration (c) of the absorbing molecules by the Beer-Lambert law,

$$d = \epsilon c \tag{2}$$

where the proportionality constant ϵ is called the extinction or absorptivity coefficient. The concentration (c) is expressed in moles per liter.

Therefore, rearranging the Beer-Lambert law gives the relation,

$$\epsilon = d\ MW/C \tag{3}$$

ϵ is the molar extinction coefficient

d is the optical density of the solution in a one-cm. cell

MW is the molecular weight of the allopolar dye

C is now the concentration of absorbing molecules expressed as grams per liter

Using the subscript h to represent the holopolar form and m to represent the meropolar form, one may write equation (3) as:

$$\not{\epsilon}_h = d_h \, MW_h / C_h \tag{4}$$

$$\not{\epsilon}_m = d_m \, MW_m / C_m \tag{5}$$

However,

$$MW_h = MW_m \tag{6}$$

and

$$C_h + C_m = C \tag{7}$$

Combining equations (4) and (5) with equations (6) and (7) one obtains

$$C / MW = d_h / \not{\epsilon}_h + d_m / \not{\epsilon}_m \tag{8}$$

Equation (8) may be now rearranged into the form of a straight line $y = mx + b$

$$d_h / d_m = (\not{\epsilon}_h C / MW) \; (1/d_m) - \not{\epsilon}_h / \not{\epsilon}_m \tag{9}$$

Therefore, from the spectral data for a given dye in several solvent mixtures one may obtain a plot of d_h/d_m vs $1/d_m$ and determine the best fit by the method of least squares; $\not{\epsilon}_h$ may be evaluated from the slope and $\not{\epsilon}_m$ may be calculated from the intercept.

A best value for the linear plots was determined by the 1620 computer. The program entitled "Regression Coefficients" for the method of least squares was taken from the MSU computer library files. The resulting data were compiled in the following table.

TABLE I

DYE	TEMP	$\overline{X}$	$\overline{Y}$	p	b	R
V	6	2.03	1.07	1.55	2.08	.99
V	25	2.01	9.26	1.42	1.93	.99
V	35	2.34	1.17	1.23	1.73	.99
V	45	2.32	1.03	1.24	1.83	.99
IX	6	6.44	8.81	1.81	2.84	.99
IX	25	5.97	7.26	1.65	2.58	.99
IX	35	5.77	6.09	1.52	2.69	.99
IX	45	4.65	4.67	1.56	2.61	.99

Using the values obtained from the slope and intercept, the calculated $\not{\epsilon}_h$ and $\not{\epsilon}_m$ for the allopolar dye (V) and (IX) are:

ALLOPOLAR DYE V M.W. 646	45° C	35° C	25° C	6° C
$\not{\epsilon}_h$	16.0×10^4	15.9×10^4	18.5×10^4	20.0×10^4
$\not{\epsilon}_m$	8.7×10^4	9.3×10^4	9.4×10^4	9.6×10^4

ALLOPOLAR DYE IX M.W. 538	45° C	35° C	25° C	6° C
$\not{\epsilon}_h$	16.5×10^4	16.4×10^4	17.8×10^4	19.6×10^4
$\not{\epsilon}_m$	6.1×10^4	6.1×10^4	7.0×10^4	6.9×10^4

Assuming that there are only two species present, the equilibrium for the allopolar compounds is

$$\text{Meropolar} \rightleftharpoons \text{Holopolar}$$

Since the fraction of meropolar molecules is equal to 1 - the fraction of holopolar molecules, the equilibrium constant may be written as

$$K = F_h/1-F_h \tag{10}$$

The fraction of holopolar molecules F_h may be determined as follows

$$F_h = \frac{\epsilon_{h(app.)}}{\epsilon_{h(calc.)}} \tag{11}$$

ϵ_h (app.) is the apparent extinction coefficient of the holopolar dye

ϵ_h (calc.) is the calculated extinction coefficient of the holopolar dye

Substituting the appropriate equations into expression (11) one may obtain

$$F_h = d_{h(app.)}^{MW/C_o} \epsilon_{h(calc.)}$$

The fraction of meropolar molecules F_m may be calculated in an identical manner as a check on the relation $F_h = 1-F_m$.

In order to determine the thermodynamic parameters, the following expressions are employed.

$$\Delta G^\circ = -RT\ln K \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

where ΔG° is the change in standard free energy.

Substituting equation (14) into equation (13), one may obtain

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \qquad (15)$$

Equation (15) is then a function which is linear between variables K and 1/T. The entropy and enthalpy may be determined from the intercept and slope respectively.

To obtain the best values for the entropy and enthalpy, three equilibrium constants, K_h, K_m, and $K_{\frac{h+m}{2}}$ for each of the samples of the two allopolar dyes (V) and (IX) were obtained. All values reported were determined by the method of least squares. The theromodynamic values may be found in Table II pages 32-37. Two sample plots of Log. K vs 1/T are shown in Figs. 14 and 15.

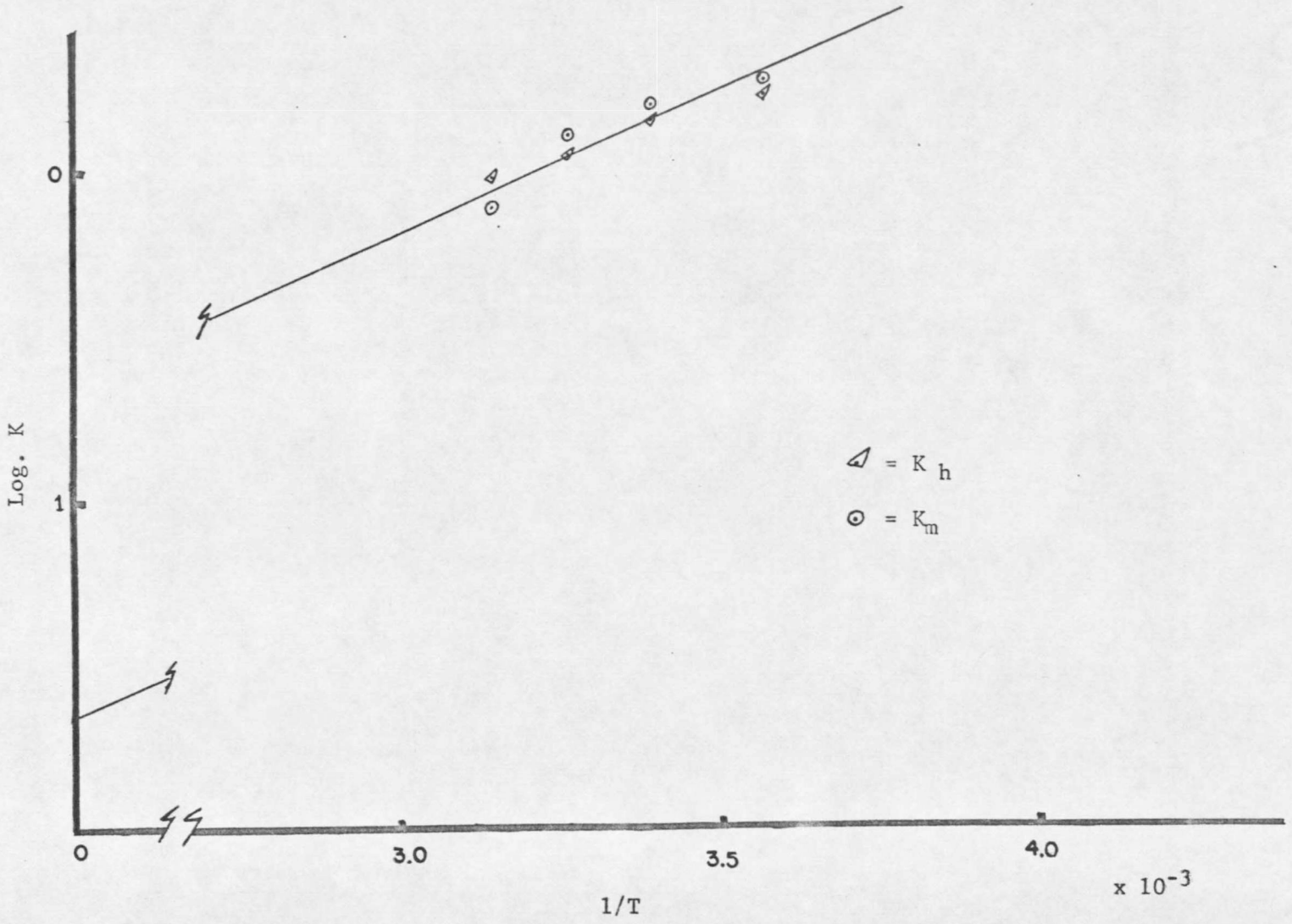


Fig. 14. PLOT of EQUILIBRIUM CONSTANT VS 1/T for ALLOPOLAR DYE (IX) SAMPLE E

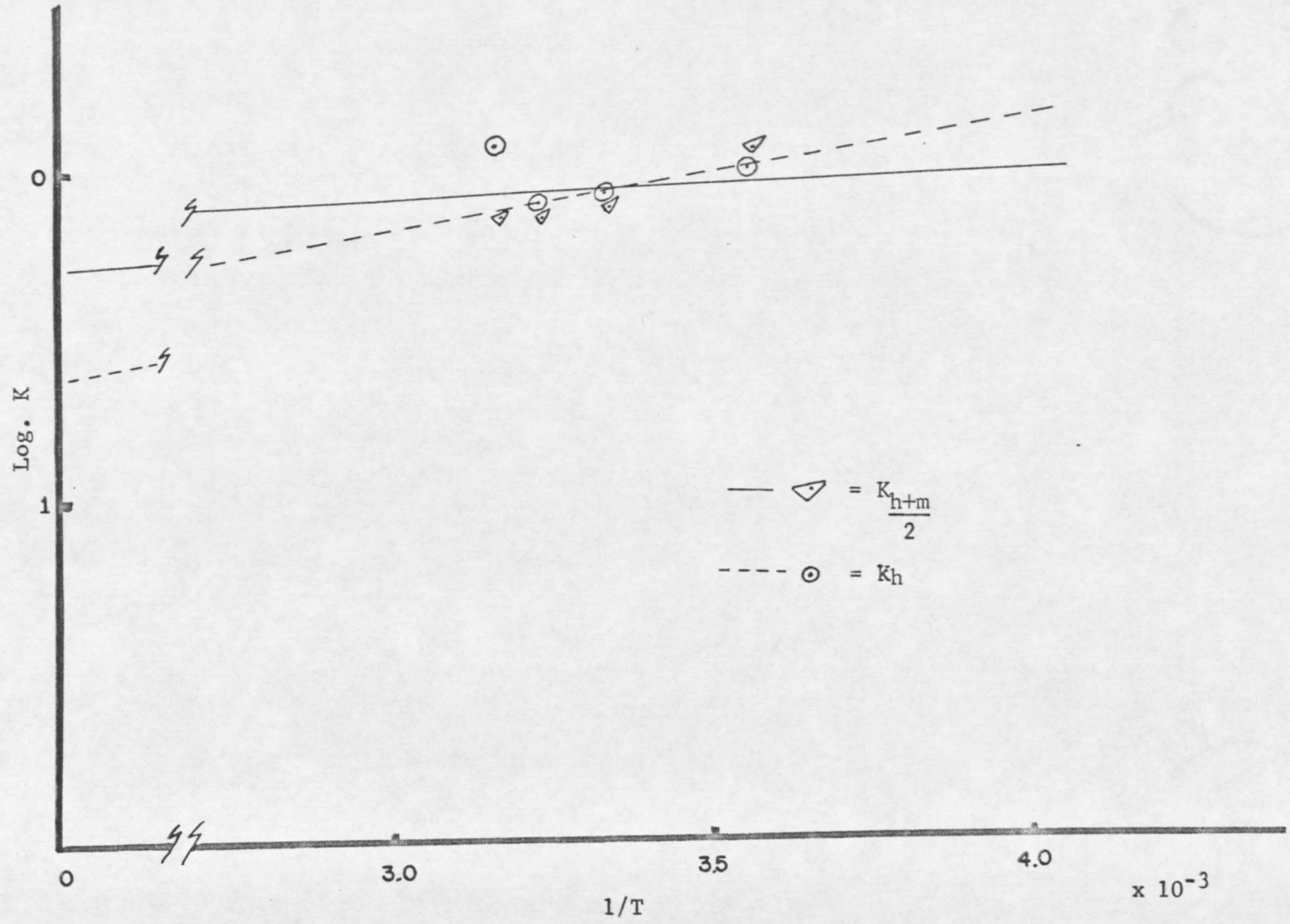


Fig. 15. PLOT of EQUILIBRIUM CONSTANT VS 1/T for ALLOPOLAR DYE (V) SAMPLE H

TABLE II

ALLOPOLAR DYE (V)

EQUILIBRIUM CONSTANTS K_h

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	.05	-4.33
B	.94	- .96
C	.51	-1.81
D	.10	-2.65
E	- .06	-2.43
F	- .68	-3.74
G	- .58	-2.69
H	- .64	-2.14
I	- .95	-2.50

EQUILIBRIUM CONSTANTS K_h *

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	.84	-1.76
B	1.73	1.64
C	1.33	.89
D	.96	.16
E	.87	.62
F	.37	- .30
G	.59	1.16
H	.73	2.31
I	.69	2.86

* determined by reversing the values of d_m and d_h in equation 9

TABLE II

ALLOPOLAR DYE (V)

EQUILIBRIUM CONSTANTS K_m

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	-1.25	- 8.65
B	-2.14	-11.20
C	.15	- 2.81
D	.05	- 2.60
E	.67	- .10
F	1.11	2.17
G	- .70	- 3.15
H	- .58	- 2.00
I	-1.32	- 3.76

EQUILIBRIUM CONSTANTS K_m *

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	1.88	1.64
B	- .17	- 4.79
C	1.81	2.58
D	1.35	1.62
E	1.86	3.76
F	1.99	5.03
G	- .07	- 1.11
H	- .10	- .44
I	- .92	- 2.47

* determined by reversing the values of d_m and d_h in equation 9

TABLE II

ALLOPOLAR DYE (V)

EQUILIBRIUM CONSTANTS $K_{\frac{h+m}{2}}$

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	- .61	-6.50
B	- .70	-6.39
C	.32	-2.34
D	.07	-2.63
E	.29	-1.31
F	.17	- .91
G	- .63	-2.88
H	- .61	-2.07
I	-1.14	-3.13

EQUILIBRIUM CONSTANTS $K_{\frac{h+m}{2}}^{*}$

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	1.38	.03
B	.80	-1.51
C	1.56	1.69
D	1.15	.85
E	1.40	2.29
F	1.22	2.48
G	.24	- .03
H	.33	.98
I	- .08	.31

* determined by reversing the values of d_m and d_h in equation 9

TABLE II

ALLOPOLAR DYE (IX)

EQUILIBRIUM CONSTANTS K_h

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	.64	-1.99
B	.00	-3.29
C	- .44	-3.29
D	-1.71	-6.28
E	-2.24	-6.91
F	-2.36	-6.24
G	-2.21	-4.96
H	-2.49	-5.32
I	-2.01	-3.08
J	-2.20	-3.42

EQUILIBRIUM CONSTANTS K_h^*

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	.47	-2.60
B	- .19	-3.91
C	- .64	-3.99
D	-1.93	-7.04
E	-2.49	-7.81
F	-2.66	-7.30
G	-2.55	-6.20
H	-2.94	-6.90
I	-2.48	-4.79
J	-2.70	-5.34

* determined by reversing the values of d_m and d_h in equation 9

TABLE II

ALLOPOLAR DYE (IX)

EQUILIBRIUM CONSTANTS K_m

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	- .19	-4.55
B	-1.66	-8.22
C	-1.71	-7.27
D	-1.39	-4.98
E	-2.38	-7.33
F	-1.28	-3.09
G	-2.66	-6.73
H	-1.35	-1.61
I	-2.22	-3.82
J	-2.47	-4.23

EQUILIBRIUM CONSTANTS K_m^*

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	1.68	1.23
B	-1.59	-8.34
C	-1.59	-7.10
D	-1.35	-5.01
E	-2.38	-7.47
F	-1.21	-2.97
G	-2.63	-6.74
H	-1.26	-1.42
I	-2.14	-3.61
J	-2.39	-4.03

* determined by reversing the values of d_m and d_h in equation 9

TABLE II

ALLOPOLAR DYE (IX)

EQUILIBRIUM CONSTANTS $K_{\frac{h+m}{2}}$

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	.33	-2.88
B	-1.02	-6.34
C	-1.14	-5.47
D	-1.54	-5.59
E	-2.31	-7.11
F	-1.90	-4.91
G	-2.40	-5.74
H	-1.96	-3.60
I	-2.11	-3.43
J	-2.35	-3.85

EQUILIBRIUM CONSTANTS $K_{\frac{h+m}{2}}$ *

SAMPLE	DELTA H (Kcal/mole)	DELTA S (cal/mole·degree)
A	1.13	- .51
B	- .82	-5.89
C	-1.10	-5.48
D	-1.65	-6.05
E	-2.44	-7.66
F	-1.81	-4.74
G	-2.60	-6.49
H	-2.03	-3.95
I	-2.36	-4.38
J	-2.61	-4.86

* determined by reversing the values of d_m and d_h in equation 9

EXPERIMENTAL

1-Ethyl-2-methylbenzothiazolium iodide. 2-Methylbenzothiazole (7.78 g., 0.10 mole) and ethyl iodide (20.5 g., 0.15 mole) were mixed and refluxed on a steam bath for six hours. The solid which began forming in about .5 hr. was collected by filtration and washed with acetone (3 x 10 ml), yielding 8.0 g. of white powder, m.p. 194-196°C.

1,2-Diphenyl-3,5-pyrazolidinedione.[8] Sodium (1.15 g., 0.15 g.-atom) was dissolved in absolute ethanol (25 ml) and 1,2-diphenylhydrazine (9.2 g., 0.05 mole) was added. Diethyl malonate (8 g., 0.05 mole) was next added and the mixture was heated to a temperature of 170-180 for 2 hr., during which time 20 ml of ethanol was removed by distillation. The cooled residue was partially dissolved in water (150 ml). The water layer was extracted with ether (3 x 10 ml). The crude product precipitated from the acidified (conc. HCl) water soln., and was recrystallized three times from absolute ethanol, giving 3.0 g. (25%) of a white powder, m.p. 170-172°C.

Anal. Calcd. for $C_{15}H_{12}N_2O_4$: C, 71.4; H, 4.80. Found: C, 71.1 H, 4.9.

4-Isopropylidene-1,2-diphenyl-3,5-pyrazolidinedione.[9] 1,2-Diphenyl-3,5-pyrazolidinedione (5 g., 0.02 mole) was dissolved in anhydrous benzene (80 ml). Anhydrous zinc chloride (about 1 g.,) and dropwise acetone (4 ml) were added to the refluxing benzene solution. The mixture was refluxed for 40 hr. in a system designed for the continuous removal of water. The cooled benzene solution was evaporated to dryness and the residue was recrystallized twice from anhydrous benzene-ligroin. The yield of yellow needles was 1.2 g. (21%), m.p. 112-113°C.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 74.0; H, 5.5; N, 9.6. Found: C, 74.3; H, 6.2; N, 9.5.

5- 1,3-Bis-(3-ethyl-2-benzothiazolinylidene-isopropylidene -2,2-dimethyl-1,3-dioxane-4,6-dione (IX). A mixture of 1-ethyl-2-methylthiobenzothiazolium ethyl sulfate (0.08 g., 0.0005 mole), 5-(3-ethyl-2-benzothiazolinylidene)-isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (XI) (0.08 g., 0.0005 mole), triethylamine (1 ml), and dimethylformamide (8 ml) was refluxed for 3 min. The addition of methanol (5 ml) and water (30 ml) were needed to separate the dye. The dye was recrystallized from pyridine-methanol to afford 0.045 g. (1.8%) of green crystals, m.p. 232-234° C. dec.

Anal. Calcd. for $C_{27}H_{26}N_2O_4S_2 \cdot 1$ mole CH_3OH: C, 62.6; H, 5.6; N. 5.2. Found: C, 62.6; H, 5.4; N, 5.3.

1,2-Diethoxycarbonyl-3,5-pyrazolidinedione (XII).[6] To a solution of 1,2-dicarbethoxyhydrazine (10.0 g., 0.057 mole) in anhydrous benzene (80 ml) was added portionwise malonyl chloride (8.2 g., 0.057 mole). The temperature of the solution was raised to 50 C during 1 hr., and was held at that temperature for 12 hr. Nitrogen was passed through the solution for 30 min. and the product separated after cooling. The dione was recrystallized four times from anhydrous benzene to yield 4 g. (29%) of colorless needles, m.p. 104-105°C.

5-(3-Ethyl-2-benzothiazolinylidene)-isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (XI). 5-Isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (0.267 g., 0.0014 mole), 1-ethyl-2-methylthiobenzothiazolium ethylsulfate (0.57 g., 0.0017 mole), triethylamine (1 ml) and dimethyl-

formamide (10 ml) were mixed and refluxed for 5 min. The dye separated from the solution with cooling, and was recrystallized from pyridine-methanol to yield 0.35 g. (70%) of orange crystals, m.p. 227-229°C. dec.

Anal. Calcd. for $C_{18}H_{19}NO_4S$: C, 62.4; H, 5.5; N, 4.1. Found: C, 62.5; H, 6.1; N, 3.9.

The dye absorbs in methanol with a λ_{max} 475 mu.

5-Isopropylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (X).[12] Piperidine (8 drops) and glacial acetic acid (1.5 drops) were added to a solution of 2,2-dimethyl-1,3-dioxane-4,6-dione. The solution was stirred continuously for 12 hr. The white oil which formed with addition of ice-water (50 ml) solidified on cooling. The white solid was recrystallized twice from methanol-water, to yield 3.0 g. (39%) of white felt-like needles, m.p. 74-75°C.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.8; H, 6.5. Found: C, 59.1; H, 6.2.

4- 1,3-Bis-(3-ethyl-2-benzothiazolinylidene)-isopropylidene -1,2-diphenyl-3,5-pyrazolidinedione (V). A mixture of 3,3'-diethyl-9-phenyl-thiocarbocyanine iodide (0.6 g., 0.001 mole), 1,2-diphenyl-3,5-pyrazolidinedione (0.3 g., 0.0012 mole), and trimethylamine (1 ml) in pyridine (8 ml) was heated under reflux for 19 min. The dye separated with the addition of methanol (40 ml). The dye was recrystallized twice from pyridine-methanol, to yield 0.1 g. (17%) of green crystals, m.p. 190-195°C. dec.

Anal. Calcd. for $C_{36}H_{30}N_4O_2S_2 \cdot 1\ CH_3OH$: C, 68.6; H, 5.3; N, 8.6. Found: C, 67.8; H, 4.8; N, 8.6.

The dye absorbs in methanol with a λ_{max} 550 mu.

1-Ethyl-2-methylthiobenzothiazolium ethylsulfate (VII). 2-Methylthiobenzothiazole (3.62 g., 0.02 mole) and diethyl sulfate (6 g., 0.04 mole) were heated under reflux for 5 min. The white solid which formed as the solution cooled was washed three times with acetone. The quaternary salt was used without further purification; yield 3.3 g. (49%), m.p. 178-181° C.

4-(3-Ethyl-2-benzothiazolinylidene)-isopropylidene-1,2-diphenyl-3,5-pyrazolidenedione.[11] A mixture of 1-ethyl-2-methyl-thiobenzothiazolium ethylsulfate (0.058 g., 0.0017 mole), 1,2-diphenyl-4-isopropylidene-3,5-pyrazolidinedione (0.05 g., 0.0017 mole), and triethylamine (1 ml) in pyridine (7 ml) was heated under reflux for 5 min. The dye separated after chilling and was recrystallized from pyridine-methanol. The yield was 0.055 g. (71%) of orange powder, m.p. 297-299° C. dec.

Anal. Calcd. for $C_{27}H_{23}N_3O_2S$: C, 71.6; H, 5.1; N, 9.3. Found: C, 71.9; H, 5.0; N, 9.1.

2,2-Dimethyl-1,3-dioxane-4,6-dione.[10] Concentrated HCl was added to a solution of malonic acid (5.2 g., 0.1 mole) in acetic anhydride (6 ml) with constant stirring. The solution was chilled to 20-25 C, and acetone (4 ml) was added. The reaction mixture remained in the refrigerator for 12 hr. and the resulting crystals were removed by suction filtration and washed with ice-water. The lactone was recrystallized from an acetone-water solution, yielding 2.8 g. (20%) of white needles, m.p. 92-93° C. dec.

3,3'-Diethyl-9-methylthiacarbocyanine iodide. 3-Ethyl-2-methyl-thiobenzothiazolium iodide (18.3 g., 0.06 mole) and methyl orthoacetate

(4.86 g., 0.03 mole) were heated with trimethylamine (3 ml) in pyridine (25 ml) under reflux for five min. The solution was added to methanol (50 ml) and the dye separated out to yield 13 g. (85%) of purple powder. A portion of the dye was recrystallized from methanol to give a m.p. of 176-179° C.

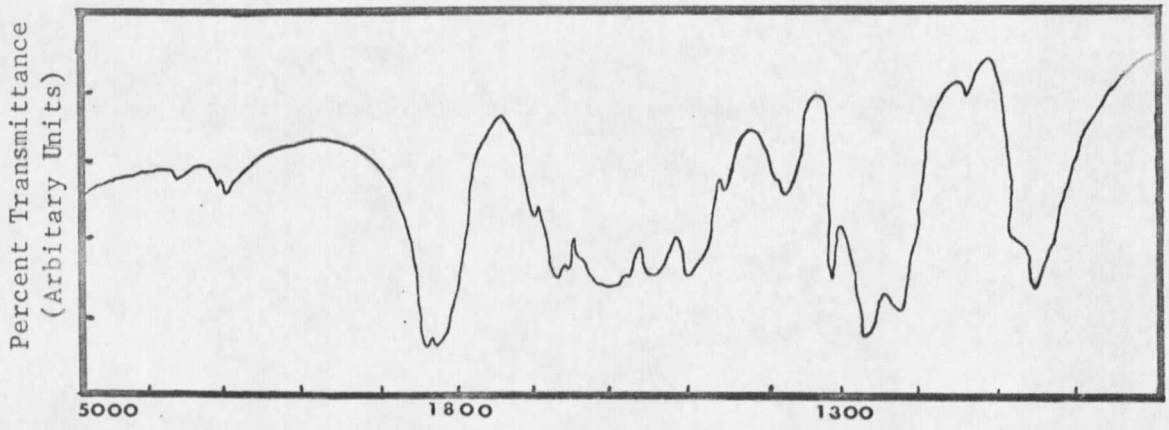


Fig. 16. Infrared Spectrum of 2,2-Dimethyl-1,3-dioxane-4,6-dione

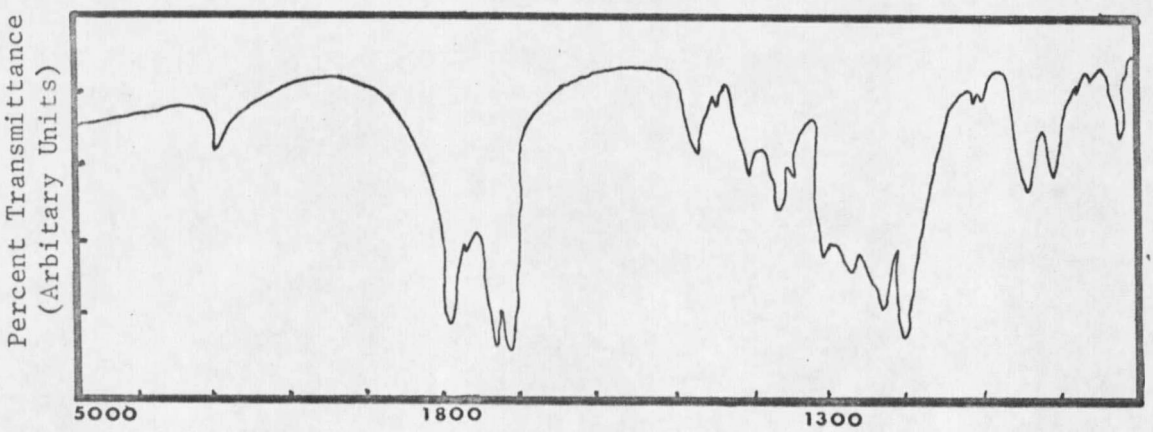


Fig. 17. Infrared Spectrum of 1,2-Dicarbethoxy-3,5-pyrazolidinedione

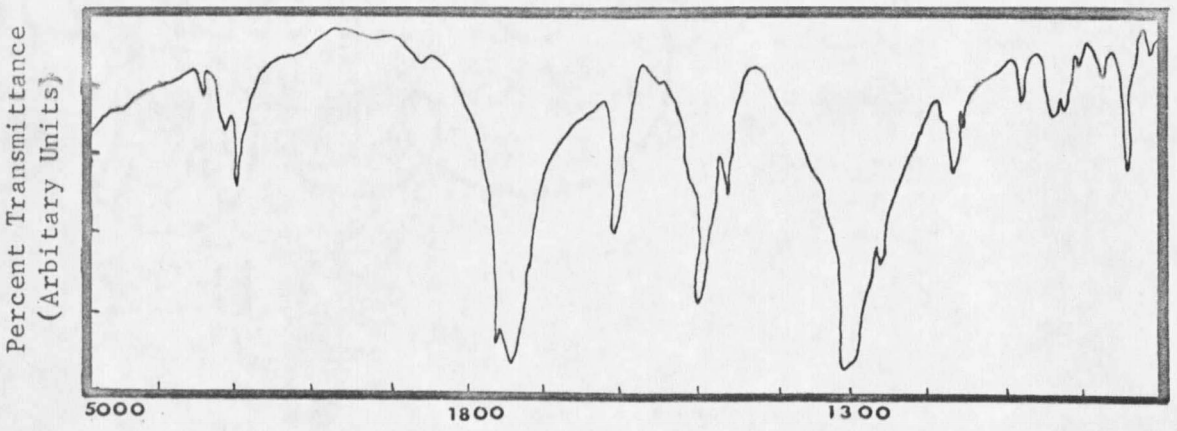
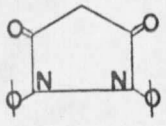
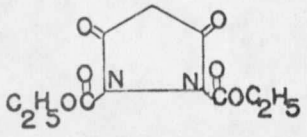
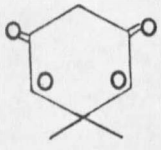


Fig. 18. Infrared Spectrum of 1,2-Diphenyl-3,5-pyrazolidinedione

TABLE III

NUCLEAR MAGNETIC RESONANCE

COMPOUND	PROTON TYPE	CHEMICAL SHIFT * (ppm δ, ref. TMS)
	methylene $-CH_2-$	3.58
	phenyl	7.40
1,2-DIPHENYL-3,5-PYRAZOLIDINEDIONE		
	methylene $-CH_2-$	3.49
	methylene $-CH_2-O-$	4.38
	methyl	1.35
1,2-DICARBETHOXY-3,5-PYRAZOLIDINEDIONE		
	methylene $-CH_2-$	3.67
	methyl	1.80
2,2-DIMETHYL-1,3-DIOXANE-4,6-DIONE		

* All samples were run in $CDCl_3$.

SUMMARY

The project indicated that the equilibrium process for allopolar isomerism was temperature dependent. However, the equilibrium process is still more dependent on solvent polarity.

Since solvent polarity was sufficient to cause a shift in equilibrium to occur, one would expect the enthalpy values to be rather small. This was exactly what the data indicated.

Because of the available equipment, only the four temperature studies of the allopolar dyes (V) and (IX) could be obtained. However, since the solvent system used for this study was 2,6-lutidine-methanol, runs above 45° C were impossible. Therefore, the results from temperature studies below that of ice-water are needed to give a more complete picture.

As this paper indicates only two allopolar dyes were used. Therefore, before this study can be more meaningful, the allopolar dyes whose synthesis were attempted will have to be prepared.

Since the only solvent system tried was 2,6-lutidine-methanol, it might be possible to achieve better estimates of the thermodynamic values by trying other miscible solvent systems.

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