

UNCLASSIFIED

AD NUMBER
AD427601
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 30 Apr 1963. Other requests shall be referred to School of Aerospace Medicine, Brooks AFB, TX.
AUTHORITY
SAM USAF ltr, 25 Jul 1973

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 427601

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

AD No. 427601

DDC FILE COPY

427601

607100



RESEARCH AND REPORTS ON
PHOTOCHROMIC MATERIALS WHICH MAY
BE USED AS EYE PROTECTIVE DEVICES

Richard E. Bowman
Richard E. Fox
Alan J. Kresch
J. E. Gordon Taylor

Fundamental Research Department
The National Cash Register Company

SCHOOL OF AEROSPACE MEDICINE
USAF AEROSPACE MEDICAL CENTER (ATC)
BROOKS AIR FORCE BASE, TEXAS

JAN 21 1964

427601

NO OTS

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

"This report is not to be announced or distributed automatically in accordance with AFR 205-43A, Par. 6d."

5) 604100

44

6

RESEARCH AND REPORTS ON
PHOTOCHROMIC MATERIALS WHICH MAY
BE USED AS EYE PROTECTIVE DEVICES ,

10

by

Richard E. Bowman
Richard E. Fox
Alan J. Kresch
J. E. Gordon Taylor

Fundamental Research Department
The National Cash Register Company

AI

SCHOOL OF AEROSPACE MEDICINE
USAF AEROSPACE MEDICAL CENTER (ATC)
BROOKS AIR FORCE BASE, TEXAS

(over)

111-1-2-1-1-1

(7)

Final Engineering Report on Contract AF 41(657)-406

Prepared By:

Alan J. Kresch

Alan J. Kresch
Principal Author

Approved By:

Helmut Schwab

Helmut Schwab
Section Head

Lowell Schleicher

Lowell Schleicher, Head
Fundamental Research Department

B. K. Green

B. K. Green
Manager of Chemical Research

G. J. Wilson

G. J. Wilson
Director of Research

Field 23

*3640	Photodiscoloration	2235	Health physics
*2235	Health physics	3911	Protective clothing
*1722	Eyeglasses	0743	Burns
*1720	Eye	5562	Wounds and injuries

3298.1	N-Heterocyclic compounds	3475.1	O-Heterocyclic compounds
3783.75	Polycyclic compounds	3290	Nitrates
0920	Chlorine compounds	0395.5	Aromatic compounds
3330	Nuclear explosions	5070	Thermal radiation
4696	Spectra (Infrared)	4697	Spectra (Visible and ultraviolet)
4930	Synthesis (chemistry)	4717.5	Spiro compounds

Field 25

7004.9

Identifiers
Photochromic materials
1963

*Spiropyrans

*Irdole

*Trimethylindolinobenzospiropyran (1, 3, 3)

*Dichloro-6'-nitroindolinobenzospiropyran (5', 7')

*Phenyl-6-methoxy-7'-nitrobenzo-beta-naphthospiropyran

FOREWORD

This report was prepared by the Fundamental Research Department of The National Cash Register Company under Contract AF 41 (657)-406. This contract is under the supervision of Mr. Barrett K. Green, Manager of Chemical Research; Mr. Lowell Schleicher, Head, Fundamental Research Department; Dr. Helmut Schwab, Section Head, Fundamental Research Department and Mr. J. E. Gordon Taylor, Group Leader, Fundamental Research Department.

This document is the final report for the contract and summarizes the work of the entire contract period, 1 May 1961 to 30 April 1963. The following individuals of the Fundamental Research Department have contributed to the work of the contract: J. E. Gordon Taylor, Dr. Alan J. Kresch, Richard E. Bowman, Richard E. Fox, Francis D. Thomson, David B. McQuain and Dr. Gerald Feig.

The authors wish to acknowledge the advice given by Professor Jack Calvert, Ohio State University, in the planning of photochemical experiments and in the design of the optical apparatus.

The authors thank Dr. John J. Van Voorhis for his comments and corrections concerning the draft copy of this report.

ABSTRACT

Studies of the thermal switching properties of 5', 7'-dichloro-6'-nitroindolinobenzospiropyran have been completed. Rate constants and equilibrium constants have been obtained for all processes that take place in both ethanol and toluene over a temperature range from 0° to 60° C. The thermodynamic parameters for these processes have been calculated.

Phenomenological equations describing the photochemical switching processes of this compound have been derived and appear to be verified by experimental data. True quantum efficiencies for both the opening and closing processes of the spiro pyran ring (writing and erasing) have been obtained.

The photochemical, thermal and spectral properties of seven other photochromic compounds have been investigated in toluene solutions at 20° C. There appears to be a considerable variance in important parameters (quantum efficiency, thermal rate constants, extinction coefficients, etc.) among the different compounds.

Over two hundred compounds of the indolinobenzospiropyran structure were subjected to standard testing conditions in order to obtain a basis for evaluating their relative sensitivities. The data obtained from this survey indicate a few structural features which improve or diminish the sensitivity of the compounds.

The photochromic behavior of a benzo- β -naphthospiropyran compound was studied in a series of solvents and in several film-forming materials.

Mathematical discussions of a flash-tube activated photochromic filter system and self-attenuating photochromic filter systems are presented.

Studies of the hydrochloride salts of 6'-nitroindolinobenzospiropyran conclusively demonstrate the existence of both an open and closed form.

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	i
ABSTRACT	ii
LIST OF ILLUSTRATIONS	vi
LIST OF TABLES	ix
1. INTRODUCTION	1
2. THERMAL BEHAVIOR OF 5', 7'-DICHLORO-6'-NITRO BIPS . . .	9
2. 1. Discussion of thermal switching	9
2. 2. Experimental	25
2. 2. 1. Elemental analysis	25
2. 2. 2. X-Ray powder photographs	25
2. 2. 3. Solid state analysis of colored and colorless spiropyrans	27
2. 2. 4. Extinction coefficient of the colorless form of 5', 7'-dichloro-6'-nitro BIPS	28
2. 2. 5. Extinction coefficient of the colored form of 5', 7'-dichloro-6'-nitro BIPS	31
2. 2. 6. Absorption spectra of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C	32
2. 2. 7. Thermal equilibrium measurements of 5', 7'- dichloro-6'-nitro indolinobenzospiropyran in ethanol and toluene	33
2. 2. 8. Thermal color disappearance measurements in ethanol and toluene	36
2. 2. 9. Fast and slow thermal color formation in ethanol	37
2. 2. 10. Controlled formation of the U ₁ modification	40
2. 2. 11. Calculation of true first-order rate constants and equilibrium constants	43
2. 3. Calculation of thermodynamic functions from rate constants and equilibrium constants	51

	<u>Page</u>
2.4. Conclusions.	63
3. PHOTOCHEMICAL STUDIES OF 5', 7'-DICHLORO- -6'-NITRO BIPS	71
3.1. Instrumentation for quantitative photochemical measurements.	71
3.2. Filters for isolation of mercury lines	72
3.3. Actinometric determination of light intensities	72
3.4. Solvent absorption	76
3.5. Rate equations for simultaneous reversible photochemical and thermal reactions of BIPS compounds	78
3.6. Quantitative measurement of the photochemical reaction of spiropyrans in solution	86
3.7. Results.	87
4. MEASUREMENTS OF THE THERMAL AND PHOTOCHEMICAL PROPERTIES OF OTHER PHOTOCROMIC COMPOUNDS.	91
4.1. Investigation of six representative BIPS compounds.	91
4.1.1. Molar absorptivity measurements	91
4.1.2. Quantum yield determinations at 366 m μ irradiation	92
4.1.3. Extent of photochemical transformation from colorless to colored form of 7-phenyl-5'-bromo-6'- nitro-8'-methoxy BIPS in ethanol	94
4.2. Some observations on the hydrochloride salts of 6'- nitro BIPS.	95
4.3. Shape of the visible transmittance spectrum to molecular structure	101
4.4. Semi-quantitative survey of the photochromic properties of the indolinobenzospiropyrans	103
4.5. Study of the benzo- β -naphthospiropyrans.	117
4.5.1. Testing procedure	119
4.5.2. Work done in film-forming materials	119

	<u>Page</u>
4.6. Thermal color disappearance in a photochromic filter.	123
5. EYE PROTECTION PROBLEMS	
5.1. Discussion on self-attenuating eye-protective filters.	125
5.2. Self-attenuating sunglasses	130
5.3. Response time of photochromic material.	131
6. SYNTHETIC WORK	
6.1. Variations in substituents.	140
6.2. Basic structural changes	153
6.3. Conclusions on synthetic work	160
7. REFERENCES	161

LIST OF ILLUSTRATIONS

<u>Figure No.</u>	<u>Page</u>
1. Structural formula of BIPS.	1
2. Absorption spectra of 6'-nitro BIPS in ethanol at 6°C	2
3. Switching mechanism of spiropyrans	3
4. Spectrum of "ideal" photochromic dye	5
5. Ultraviolet spectra of 5', 7'-dichloro-6'-nitro BIPS in ethanol at -80°C	13
6. Thermal decoloration of pure colored 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C.	21
7. Initial rapid decoloration of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C	22
8. Initial rapid recoloration after photo-erasure of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C.	23
9. Thermal coloration of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C	24
10. Calibration curve for infrared analysis of U ₂ in KBr.	29
11. Infrared spectrum of colorless 5', 7'-dichloro-6'-nitro BIPS (U ₂) in a KBr pellet	30
12. Infrared spectrum of colored 5', 7'-dichloro-6'-nitro BIPS in a KBr pellet.	30
13. Ultraviolet and visible spectra of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C.	34
14. Rapid thermal color disappearance of colored 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C	38
15. Slow thermal color disappearance of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C	39
16. Recoloration effect after photo-erasure.	41
17. Rapid thermal recoloration of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 20°C, immediately after photo-erasure	42
18. Temperature dependence of K _t	48
19. Temperature dependence of K _p	49

<u>Figure No.</u>	<u>Page</u>
20. Temperature dependence of K_c	50
21. Temperature dependence of k_1	56
22. Temperature dependence of k_2	57
23. Temperature dependence of k_3	58
24. Temperature dependence of k_4	59
25. Temperature dependence of k_5	60
26. Temperature dependence of k_6	61
27. Energy relationships among the various species of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 30°C.	66
28. Entropy relationships among the various species of 5', 7'-dichloro-6'-nitro BIPS in ethanol at 30°C.	67
29. Energy and entropy relationships among the various species of 5', 7'-dichloro-6'-nitro BIPS in toluene at 30°C	68
30. Apparatus for photochemical measurements	73
31. Calibration curve for ferrous-phenanthroline in pH 3.5 buffer.	75
32. Plot of eq. (37) for 5', 7'-dichloro-6'-nitro BIPS in toluene at 20°C with 366 μ radiation	85
33. Infrared spectra of the hydrochloride salts of 6'-nitro BIPS in KBr.	99
34. Infrared spectra of 6'-nitro BIPS in KBr	100
35. Visible transmission spectra of several substituted indolinobenzospiropyrans in toluene	102
36. Modified rapid scanning spectrophotometer	104
37. Sample cell	105
38. Absorption spectrum of 3-phenyl-8-methoxy-7'- nitrobenzo- β -naphthospiropyran in p-dioxane at 25°C.	118
39. Thermal color disappearance in filter 1973-23B	124

<u>Figure No.</u>	<u>Page</u>
40. Optical density versus response time for a photochromic coating, P-136, on a wedge.	133
41. Relative flashtube output versus time	134
42. Normalized output of flashtube, I/I_M , versus normalized time, t/τ	136
43. Normalized plot of optical density versus time for a photochromic filter	138

LIST OF TABLES

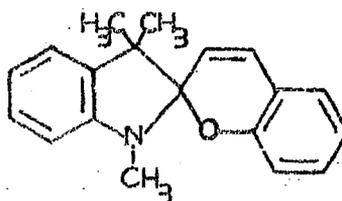
<u>Table No.</u>	<u>Page</u>
1. Elemental analysis of 5', 7'-dichloro-6'-nitro BIPS.	25
2. X-Ray powder photograph data	26
3. Recoloration of ethanolic 5', 7'-dichloro-6'-nitro BIPS solutions after photo-erasure at different times during the initial rapid decoloration	44
4. Equilibrium constants for solutions of 5', 7'-dichloro- 6'-nitro BIPS	46
5. Measured rate constants for solutions of 5', 7'- dichloro-6'-nitro BIPS	52
6. Calculated first-order rate constants for solutions of 5', 7'-dichloro-6'-nitro BIPS	53
7. Thermodynamic functions derived from equilibrium measurements on solutions of 5', 7'-dichloro-6'-nitro BIPS . . .	54
8. Thermodynamic functions derived from rate measurements of solutions of 5', 7'-dichloro-6'-nitro BIPS	62
9. Absorption of light by solvents.	78
10. Data for quantum yield determination of 5', 7'-dichloro- 6'-nitro BIPS in toluene	84
11. Quantum yields of 5', 7'-dichloro-6'-nitro BIPS	88
12. Quantum yield and extinction coefficients for 5', 7'- dichloro-6'-nitro BIPS in toluene using 313 m μ radiation	90
13. Photochemical and thermal data on BIPS compounds.	93
14. Photochemical conversion of 7-phenyl-5'-bromo-6'- nitro-8'-methoxy BIPS.	96
15. Standard test data for indolinobenzospiropyrans	
(Part A-1).	108
(Part A-2).	109
(Part A-3).	110
(Part B-1).	111

<u>Table No.</u>	<u>Page</u>
(Part B-2).112
(Part B-3).113
16. More standard test data on indolinbenzospiropyrans.114
17. Examination of 3-phenyl-8-methoxy-7'-nitrobenzo- β - naphthospiropyran in various solvents.120
Legend for above.121
18. Photochromic properties of 3-phenyl-8-methoxy-7'- nitrobenzo- β -naphthospiropyran in cellulose materials.122
19. Synthesized indolinbenzospiropyrans.151

I. INTRODUCTION

The photochromic spiropyrans are a group of organic compounds characterized structurally, as the name indicates, by a pyran ring which contains a spiro carbon (usually in the position ortho to the pyranic oxygen) and functionally by their ability to undergo a change of color in solution under ultraviolet irradiation. Figure 1 is the structural formula of a typical photochromic spiropyran, specifically 1, 3, 3-trimethylindolino-benzospiropyran, or BIPS.

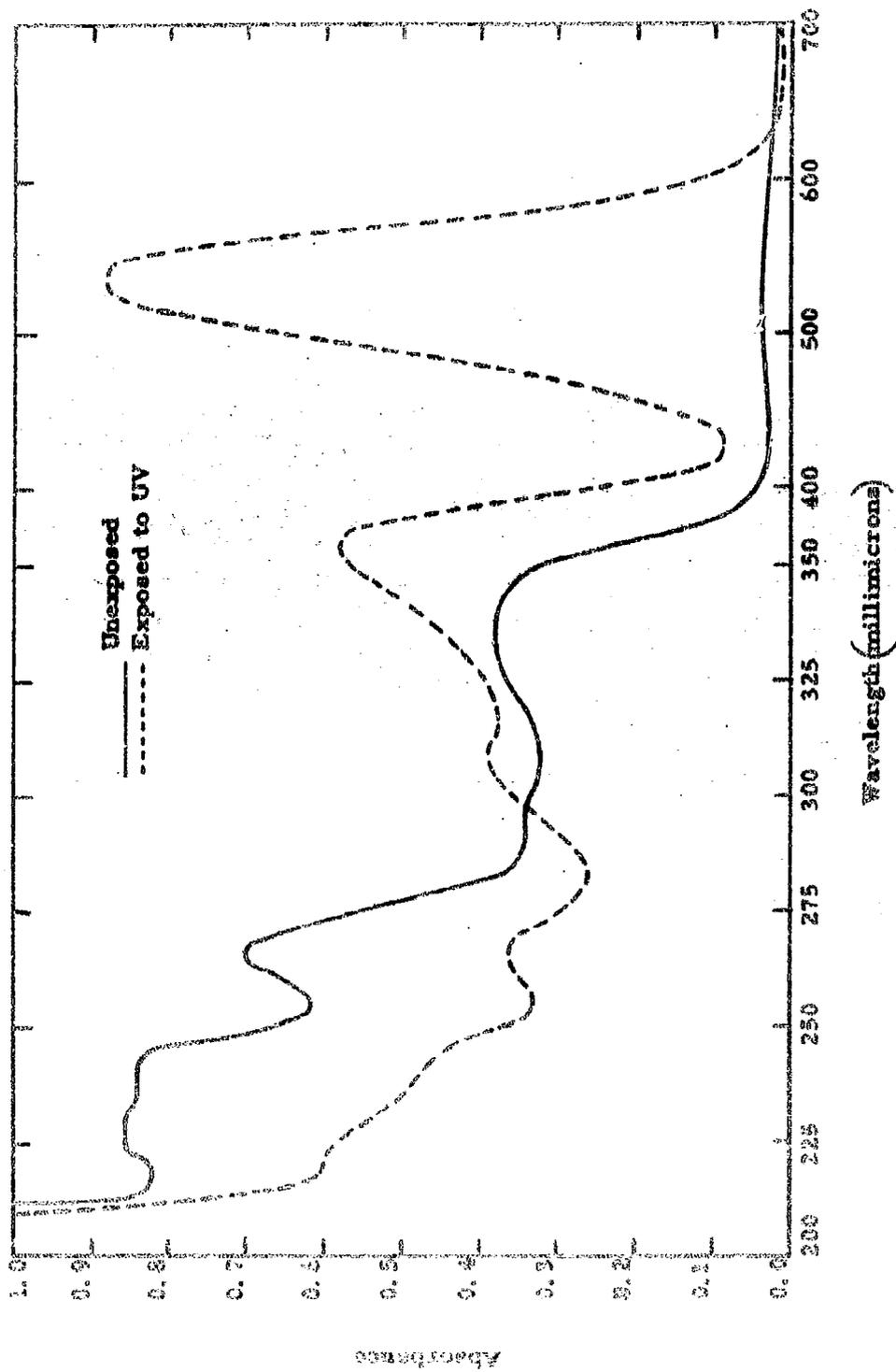
Figure 1



There are several families of photochromic spiropyrans which are differentiated by the particular ring systems joined by the spiro-carbon atom. Within each family of spiropyrans it is possible to prepare an extremely large number of individual compounds by placing various substituents on the aromatic rings. Further variations have been obtained (in this particular family) by replacing the methyl groups at the 1 and 3 positions with other alkyl and aromatic groups. Analogous variations are possible in the other families. Considering the large number of variations possible in each family of photochromic spiropyrans and the number of families (over ten families have been prepared and evaluated by NCR) it is apparent that there are potentially many thousands of photochromic spiropyrans. Over 500 spiropyrans have actually been prepared and evaluated in the NCR laboratories and from this work has come a number of generalizations relating basic structure and substituents with photochromic properties. These generalizations will be presented below following a short description of the photochromic process.

All photochromic spiropyrans thus far prepared are crystalline solids and are generally very lightly colored varying from white to pale or medium green (though some highly colored compounds have been prepared). When a spiropyran is dissolved in a low concentration in any of a wide

Figure 2
Absorption Spectra of 6' - Nitro BIPS in Ethanol at 60° C



On absorption of a photon of sufficient energy (from incident ultraviolet radiation) the bond between the spiro-carbon and pyran-oxygen is broken giving structure II. This structure is no longer restricted by a spiro-linkage and can assume a planar configuration. The conjugated system is now extended in length to include both ring systems with the result that the molecule now absorbs electromagnetic radiation of lower energy (i. e., visible light) than before. Structure II can now be assumed to isomerize rapidly into any of several structures (only III is shown) analogous to merocyanine dyes. Although a rigorous proof for this "open structure" as the colored form of the photochromic spiropyran has not yet been presented, there is a body of supporting evidence for it and very little contradictory evidence; for instance: there is a striking similarity between the absorption spectra of merocyanine dyes and the colored form of spiropyran; the water-organic solvent interfacial tension undergoes a significant lowering when the organic solution of the spiropyran is irradiated and colored; the thermal decoloration process in general follows some combination first-order kinetic steps; etc. The important point is that this hypothesis has been of value in understanding and improving the photochromic properties of the spiropyran in the past and should continue to be valuable in the future.

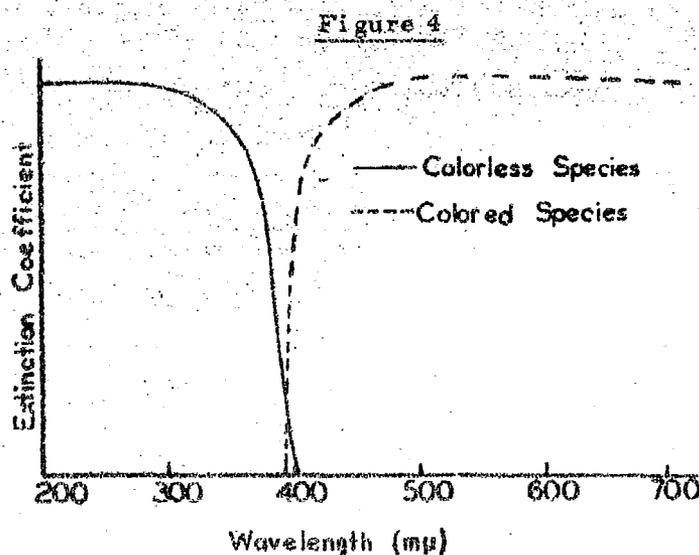
In addition to being photochromic the spiropyran are also thermochromic since a thermal equilibrium exists between the colored and colorless forms of the spiropyran, (see Figure 3). Usually this equilibrium at ambient temperatures is far to the colorless side and, as the temperature is raised, slowly shifts to the colored form. The speed at which thermal equilibrium is reached is, of course, increased as the temperature is raised. As mentioned previously some materials have been prepared which under ambient conditions appear to have the thermal equilibrium shifted far toward the colored form.

The purpose of this research is to obtain a detailed knowledge of both the photochemical and thermal switching mechanisms of spiropyran type compounds. If this is accomplished, compounds could be "tailor-made" with a view towards their intended use. In particular, a detailed a-priori prediction is needed for the optimum chemical system to be used in a reversible eye-protective lens element.

The results of this investigation are contributing more information as to the molecular and optical factors that will affect the performance of

such an eye-protection device. Some of the more important considerations are listed below:

- (1) Incident irradiating light - The intensity of the activating radiation should be high. In many systems it appears that the limiting factor is the rate at which the light can be pumped into the system. The quality of the irradiating beam is of equal importance. The spectrum should be limited to those regions where the colorless modification absorbs and switches efficiently while the colored form does not.
- (2) Molar absorptivities - While the open form should have a uniform high extinction coefficient throughout the visible region it should also have a low extinction coefficient in that part of ultraviolet where the activating radiation is concentrated. The opposite should be true of the closed (colorless) form. The spectrum of an idealized photochromic dye is shown below in Figure 4.



- (3) Quantum efficiencies - It is as important for the quantum yield of the back reaction (colored $\xrightarrow{h\nu}$ colorless) to be small as it is for the quantum yield of the forward reaction to be large. This is because the fraction of the species that is colored at the photostationary state depends upon the ratio of these quantum efficiencies.

(4) Thermal reactions - It is necessary that the thermal equilibrium constant strongly favor the colorless form, otherwise the compound will color in the dark. The absolute magnitude of the individual rate constants are also of importance. If they are too small the system will essentially be irreversible and if they are too large the thermal fade rate might be rapid enough to prevent any effective coloration.

As far as is known, none of the compounds presently available embody all of the characteristics desired, nor are the structural requirements for such a compound known. It is felt that the primary purpose of this work is to attempt to correlate structure with properties in order to obtain the objective of selective synthesis.

The investigation proceeded along two different, but related, approaches. A survey was made of the spectral, thermal and switching properties of a series of spiropyran type compounds. From this semi-quantitative evaluation the effect of certain specific structural groups on some specific property (i. e. fade rate, sensitivity) has been noted. Unfortunately, however, no important generalizations concerning the overall effect of structure on the properties of the compound could be obtained from this approach. Also, the basic mechanism of the switching processes still remained an unknown factor.

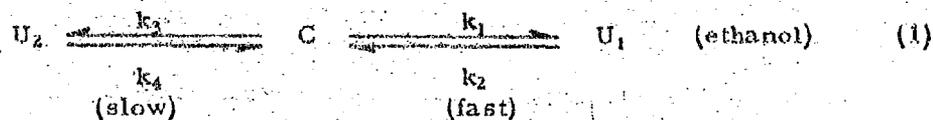
In these measurements, the photochemical switching "efficiency" that was measured was the optical density at one or more wavelengths as a function of radiant energy absorbed from a flashtube. While this is indeed a measure of the practical switching efficiency it leaves many important parameters unknown and gives little information from which extrapolation to other compounds can be made.

The second approach, therefore, was an attempt to determine the detailed mechanism of the switching process. It was felt that a profitable procedure would be to study one particular compound in great detail. Then with the techniques developed, and some general information obtained, other particular compounds could be studied in areas of specific interest. While spiropyran are noted for their individuality it is still felt that some important generalizations might arise from an intensive study of a particular compound.

At present, NCR has synthesized more than 500 spiropyran type molecules. The compound chosen for intensive study was 5', 7'-dichloro-6'-nitroindolinebenzospiropyran (5', 7'-dichloro-6'-nitro BIPS). At room

temperature the colored form of this compound is relatively stable, thus simplifying the experimental set-up for rate studies and making very accurate measurements of the extinction coefficient of the transient colored form a possibility. The photochemical switching mechanism will surely be easier to interpret under those conditions where thermal effects are small. This compound can be prepared in the solid state in either a pure colored or pure uncolored crystalline form. This compound also rapidly decolors when it absorbs visible light thus making both writing and erasing measurements possible.

The thermal switching behavior of this compound has been determined in both a polar and non-polar solvent (ethanol and toluene) at several temperatures and the basic parameters (rate constants, equilibrium constants, activation energies, entropies, etc.) have been determined for each of the processes that take place. This phase of the study has essentially been completed. A kinetic mechanism that is consistent with all thermal switching behavior, observed to date, has been postulated for both ethanolic and toluenic solutions of 5', 7'-dichloro-6'-nitro BIPS. This is described in equation (1) and (2).



Where U_1 and U_2 represent two distinct colorless BIPS species in dynamic equilibrium with the colored modification of the BIPS, C . A large part of this report will be devoted to analysis and discussion of this proposed thermal mechanism.

The photochemical properties of this compound have constituted a more difficult study from both the experimental and theoretical point of view. Small percentages of impurities in the solvents used appear to affect the switching properties. Instabilities in the detector circuits of the instrumentation also appear to cause some inaccuracies in the measurements. Nevertheless, accurate values of quantum efficiencies have been

obtained. Phenomenological equations describing the photochemical switching process have been derived, and appear to be confirmed by the experimental data. The detailed mechanism of this process, however, is still forthcoming.

4. THERMAL BEHAVIOR OF 5', 7'-DICHLORO - 6'-NITRO BIPS

4.1. Discussion of thermal switching. - If pure-colored 5', 7'-dichloro-6'-nitro BIPS is dissolved rapidly in ethanol and the absorbance at the visible peak is followed with time there is observed an initial fast decolorization which is followed by a decolorization to a final equilibrium state whose rate is much slower.

The slow decolorization obeys a first-order rate law. This is expressed in equation (3).

$$\ln (A-A_e) = -k_s t + K_s \quad (3)$$

A = absorbance of colored form at a selected wave length at time t.

A_e = equilibrium absorbance (absorbance at t = ∞)

k_s = first-order rate constant

K_s = intercept of plot. K_s = ln (A_{p-o} - A_e), where

A_{p-o} = extrapolation of first order plot to absorbance at t = 0.

It should be emphasized that A_{p-o} is not the actually obtained absorbance at t = 0.

The initial fast decolorization rate also approximates a first-order rate law as follows:

$$\ln (A-A_p) = k_f t + K_f \quad (4)$$

A_p = The absorbance of colored form calculated from an extrapolation of the first-order slow-rate plot.

k_f = First-order rate constant for fast rate.

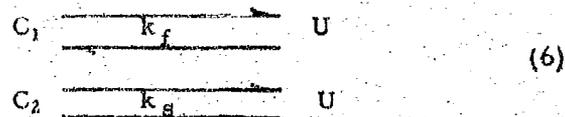
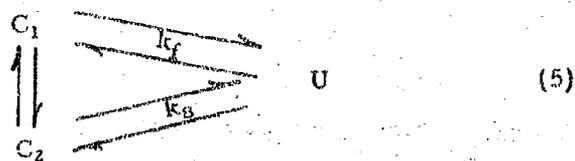
K_f = Intercept of plot. K_f = ln (A_o - A_{p-o}), where

A_o = True absorbance at t = 0.

It should be pointed out that certain liberties are being taken and equation (4) is not a true first-order plot. A_p is not a true equilibrium value but it does change very slowly at small t's when compared to the change in A. A_p is considered a pseudo-equilibrium value.

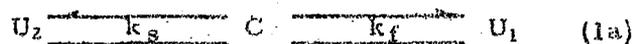
There are several physical systems that can give kinetic results as just discussed. If one chooses the proper ratios among the rate constants many different types of consecutive or simultaneous reactions can be resolved in the first approximation to two or more first-order rates. At

low temperatures the existence of several configurational isomers of the open (colored) form for some of the spiropyrans has been deduced from spectral and photochemical evidence by Fischer.^{1, 2} Molecular models made of these configurations indicated that several of them should be sterically stable³. Therefore it was at first believed that the fast and slow rates were due to the decolorization of different colored species. Possible equations for such reaction mechanisms would be:



Where C_1 and C_2 indicate two different open form configurations and U represents the closed or uncolored form. (It is known that there is both a forward and back reaction as there is an equilibrium color at infinite time.)

The observed kinetics can also be explained by the postulation of two colorless species reacting in the following manner:



It turns out that the latter postulate can adequately explain all observations while the postulate of two colored and one uncolored species cannot.

The rapid recoloration of the BIPS, after light erasure, an effect that is described in detail in sections 2.2.9. and 2.2.10., is the key observation that necessitates the postulation of more than one colorless form participating in the thermal mechanism. The most significant fact about these observations is that there is a recoloration to an optical density that may be orders of magnitude greater than the true equilibrium absorbance. If it is assumed that this recoloration effect is an integral part of the thermal behavior of ethanolic solutions of 5', 7'-dichloro-6'-

nitro BIPS then in any kinetic mechanism that can account for this behavior at least two colorless forms must be postulated. The mechanisms described by equations (5) and (6) are inadequate as they cannot by any reasoning permit a recoloration to a level greater than that of the equilibrium color. The mechanism described by equation (1a) which postulates two uncolored forms is in fact the simplest scheme by which the recoloration effect can be included in the general thermal kinetics.

It is generally agreed that one colorless form (U_2) is the closed spiropyran molecule. This form is predominantly present at thermal equilibrium and is also assumed to be formed from the erasure of the colored species with visible light. This closed form does not have any configurational isomers but could, in theory, have two optical isomers. These optical isomers have not as yet been resolved, but in any event one would expect their kinetic behavior to be identical under the experimental conditions thus described.

Therefore, the second type colorless form (U_1) is in all probability some chemical species quite distinct from the normal closed spiropyran molecule.

The following possibilities exist for the formation of U_1 .

- (1) U_1 is formed during light erasure and is in actuality a long lived excited state. (This excited state then reverts into the colored and U_2 forms of the BIPS giving a recoloration effect.)
- (2) U_1 is originally present in the solid colored form.
- (3) U_1 is formed rapidly in solution after colored form is dissolved in ethanol at room temperature.

The following theoretical considerations and experimental evidence give strong indication that only the third possibility can be correct.

Possibility (1) is doubtful because excited states in solution at room temperature generally have half-lives in the order of milli-to nano-seconds, while the half-life of the recoloration process is approximately 4 minutes. Also, such an excited state would be expected to have some absorption in the red region of the spectrum⁴. In actuality the uncolored form, when measured immediately after light erasure, does not absorb above 430 m μ .

Possibility (Z) is eliminated for the following reasons. A sample of colored 5', 7'-dichloro-6'-nitro BIPS which was dissolved in ethanol at dry ice-acetone temperature and erased at the same temperature did not recolor to any extent, even when raised to room temperature. On the other hand, if the solution was dissolved at room temperature and erased at dry ice-ethanol temperature, recoloration would take place when the solution was again warmed to room temperature. This indicates that the species that recolors is formed during the solution process at room temperature, while at dry ice-ethanol temperature this process is too slow to form any appreciable amounts of U_1 .

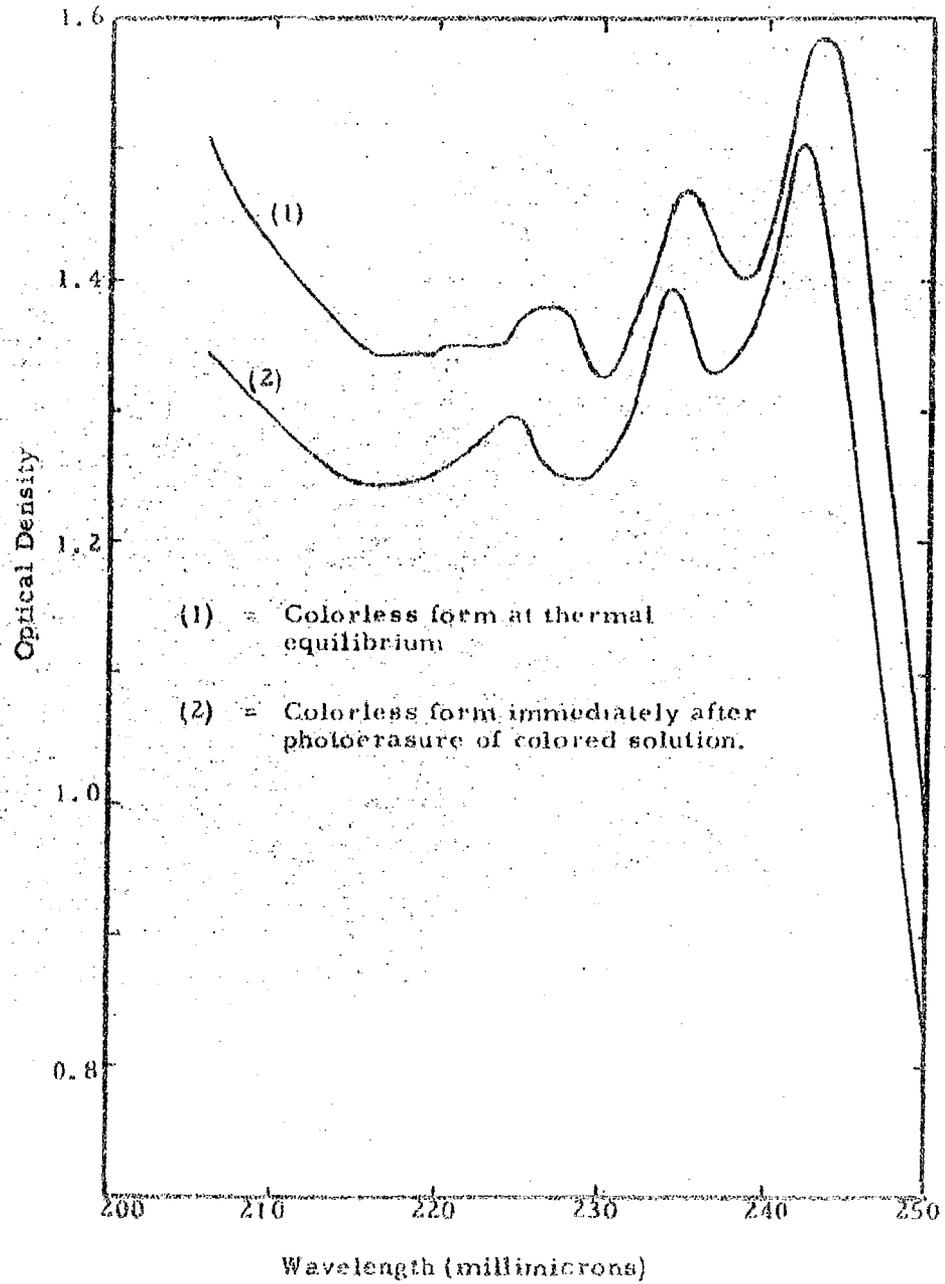
The ultraviolet spectrum at -80°C . of colorless form that was taken after light erasure of colored form dissolved at room temperature differed slightly, but nevertheless significantly, from the ultraviolet spectrum at -80°C of colorless form obtained from light erasure of colored form dissolved in ethanol at -80°C . These spectra are shown in Figure 5. This fact also supports the proposition that U_1 is formed during and immediately after the solution process at room temperature.

The first-order rate constant for the recoloration after light erasure is identical, within experimental error, with k_f (The first-order rate constant for the fast thermal fade). Also the pseudo-equilibrium constants are the same. (At 20°C approximately 10% of the colored species disappears during the course of the initial rapid thermal decoloration. This is equivalent to the observed rapid recoloration, after light erasure, to approximately 1/9 of the initial color.) This would suggest that the fast fade and the recoloration after erasure is in actuality the same kinetic process approached from opposite sides of the pseudo-equilibrium point.

If pure solid uncolored 5', 7'-dichloro-6'-nitro BIPS (U_2) is dissolved in ethanol there is a gradual rise in the optical density of the colored peak until a true thermal equilibrium is reached. This slow coloration obeys a first-order rate law and has a rate constant and equilibrium constant that, within experimental error, is equal to those of the slow decolorization process. Therefore it appears reasonable that the slow thermal fade and the slow coloration of uncolored form may well be the same kinetic process approaching a true equilibrium from opposite directions.

Figure 5

Ultraviolet Spectra of 5', 7'-dichloro-6'-nitro
BIPS in Ethanol at -80° C



In summary, therefore, all kinetic and spectrophotometric observations made to date can be explained by assuming a colored or open form of the 5', 7'-dichloro-6'-nitro BIPS in dynamic equilibrium with two uncolored species. One of these species (U_2) is almost surely the normal closed spiropyran molecule which is formed by dissolving the solid pure uncolored form, by the slow thermal decoloration of the colored form, or by erasure with visible light of the colored species. The other uncolored species (U_1) is of unknown constitution and is formed as a result of the fast thermal decoloration. The rapid recoloration effect after light erasure would be due to the pseudo-equilibration of U_1 with the colored species. The slow coloration of dissolved uncolored form would be due to the true equilibration of all three species. Although the actual mechanism may, in fact, be much more complicated, the mechanism proposed is the simplest one which is completely consistent with our present body of experimental data.

The thermal fade of 5', 7'-dichloro-6'-nitro BIPS in toluene follows a first-order rate law from start to finish and is therefore much simpler than the ethanolic systems. In toluene the following equilibration reaction takes place:

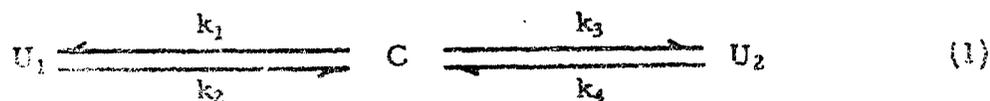


Therefore the slope of a plot of $\ln(A-A_e)$ vs. time (t) yields the rate constant for the reaction since

$$\ln(A-A_e) = -k_t t + \ln(A_0 - A_e) \quad (7)$$

k_t = first-order rate constant for thermal
equilibration in toluene
($k_t = k_5 + k_6$)

As has been shown, the postulate of the dynamic equilibrium



is consistent with qualitative and semi-quantitative observations concerning the kinetics of the ethanolic system. In this section the mathematical expressions for the rate equations will be derived and it will be demonstrated that, within the limits of experimental error, the quantitative observations are also consistent with the proposed mechanism.

The following rate equations describe the proposed kinetic system:

$$\frac{dC}{dt} = -(k_1 + k_3) C + k_2 U_1 + k_4 U_2 \quad (8)$$

$$\frac{dU_1}{dt} = k_1 C - k_2 U_1 \quad (9)$$

$$\frac{dU_2}{dt} = k_3 C - k_4 U_2 \quad (10)$$

Where C , U_1 , and U_2 are now concentrations of the various forms at any time t .

$$C + U_1 + U_2 = T \quad (11)$$

Where T = Total concentration of spiropyran present.

The solutions to these equations are straightforward, although tedious, and can be expressed as follows:

$$C = \frac{1}{k_6} (k_2 k_4 T + A_1 e^{k_7 t} + A_2 e^{k_8 t}) \quad (12)$$

$$U_1 = \frac{1}{k_6} (k_1 k_4 T + A_3 e^{k_7 t} + A_4 e^{k_8 t}) \quad (13)$$

$$U_2 = \frac{1}{k_6} (k_2 k_3 T + A_5 e^{k_7 t} + A_6 e^{k_8 t}) \quad (14)$$

where

$$A_1 = \frac{X'_0 - k_1 X_0}{k_7 - k_8} \quad A_2 = \frac{X'_0 - k_7 X_0}{k_8 - k_7}$$

$$A_3 = \frac{Y'_0 - k_2 Y_0}{k_7 - k_8} \quad A_4 = \frac{Y'_0 - k_7 Y_0}{k_8 - k_7}$$

$$A_5 = \frac{Z'_0 - k_3 Z_0}{k_7 - k_8} \quad A_6 = \frac{Z'_0 - k_7 Z_0}{k_8 - k_7}$$

and

$$X_0 = k_6 C_0 - k_2 k_4 T \quad X'_0 = k_6 [k_3 U_{1-0} + k_4 U_{2-0} - (k_1 + k_3) C_0]$$

$$Y_0 = k_6 U_{1-0} - k_1 k_4 T \quad Y'_0 = k_6 (k_3 C_0 - k_2 U_{1-0})$$

$$Z_0 = k_6 U_{2-0} - k_2 k_3 T \quad Z'_0 = k_6 (k_3 C_0 - k_4 U_{2-0})$$

for

$$k_8 = 1/2 [k_5 + (k_5^2 - 4k_6)^{1/2}] \quad k_7 = 1/2 [-k_5 + (k_5^2 - 4k_6)^{1/2}]$$

$$k_6 = k_1 k_4 + k_2 k_4 + k_2 k_3 \quad k_5 = k_1 + k_2 + k_3 + k_4$$

Where C_0 , U_{1-0} , and U_{2-0} are the values of C , U_1 , and U_2 respectively at $t = 0$.

At large values of t the exponential terms approach zero and the equilibrium values for the three species are given by the following relationships:

$$C_e = \frac{k_2 k_4 T}{k_1 k_5 + k_2 k_4 + k_2 k_3} \quad (15)$$

$$U_1 - e = \frac{k_1 k_4 I}{k_1 k_2 + k_3 k_2 + k_3 k_4} \quad (16)$$

$$U_2 - e = \frac{k_2 k_3 I}{k_1 k_4 + k_2 k_4 + k_3 k_4} \quad (17)$$

For any set of values of the fundamental rate constants k_1, k_2, k_3, k_4 and initial concentrations, U_{1-0}, U_{2-0}, C_0 , the concentrations of C, U_1 , and U_2 can be calculated from equations (12), (13), and (14) at any time t . This, however, is a time consuming process and therefore a program has been designed for our CRC-102D digital computer which from the input data of rate constants and initial concentrations will print out U_1, U_2 and C at predetermined time intervals.

To date, it has not been possible to follow the change in concentration of either of the two colorless forms as a function of time since the true absorbance spectrum of U_1 has not as yet been resolved, and an actual physical separation of the species does not appear feasible. The concentration of colored form C , can be determined spectrophotometrically at any time from its visible absorbance and thus the experimental values of C can be compared with those calculated from eq. (12).

The values of k_1, k_2, k_3 and k_4 were obtained in the following manner - At early times (up to 30 minutes for 5', 7'-dichloro-6'-nitro BIPS) the fast process $C \xrightleftharpoons[k'_2]{k'_1} U_1$ is assumed predominantly responsible for the decoloration. At longer times C and U_1 are in a state of pseudo-equilibrium and the slow process $C \xrightleftharpoons[k'_4]{k'_3} U_2$ is the main cause of decoloration. Thus, for a first approximation at large values of t :

$$\frac{dC}{dt} = -k'_3 C + k'_4 U_2 \quad (18)$$

Equation (18) has the following solution (changing concentrations to absorbances).

$$\ln(A-A_e) \approx -(k'_3 + k'_4)t + \ln(A_{p-o} - A_e) \quad (3a)$$

where $k'_3 + k'_4 = k_s$ (from eq. (3))

Thus a first approximation to $k_3 + k_4$ can be obtained from the first-order plot shown in eq. (3a). At true equilibrium $\frac{dC}{dt} = 0$ and

$$\frac{C_e}{U_2 - e} \approx \frac{k'_4}{k'_3} \approx \frac{A_e}{A_0 - A_e} = K_c \quad (19)$$

Assuming for the first approximation that U_1 is present in negligible concentrations k_2 and k_3 can each be calculated from the slope of Eq. (3a) and from the equilibrium coloration via eq. (19).

Similarly for small values of t :

$$\frac{dC}{dt} \approx -k_1 C + k_2 U_1 \quad (20)$$

Upon integration and substitution -

$$\ln(A - A_p) \approx -(k'_1 + k'_2)t + \ln(A_0 - A_{p-o}) \quad (4a)$$

where $k'_1 + k'_2 = k_f$ (from eq. (4))

Thus $k'_1 + k'_2$ can be obtained from a plot of eq. (4a).

A psuedo-equilibrium (or when $A = A_p$, or after approximately five or six half lives)

$$\frac{C_p}{U_1 - p} \approx \frac{A_{p-o}}{A_0 - A_{p-o}} \approx \frac{A_p}{A_0 - A_p} = \frac{k'_2}{k'_1} \quad (21)$$

Thus from eqs. (4a) and (21) both k_1 and k_2 can be calculated.

The next step is to introduce the perturbation of the fast rate on the slow rate and vice versa in order to correct the values of rate constants. The rate constants for the slow rate ($k'_3 + k'_4$) measure not only the slow decoloration

but also include to a smaller extent the rapid re-equilibration between C and U_1 , while most of C goes to U_2 . As seen from equation (21):

$$\frac{dC}{dU_1} \approx \frac{k'_2}{k'_1} \quad (22)$$

Thus for every molecule of C that goes to U_2 , approximately k'_1/k'_2 molecules of U_1 re-equilibrate with C. Therefore, if $k'_3 + k'_4$ is the rate measured from a plot of equation (3a), then the second approximation will be:

$$(k'_3 + k'_4) \approx (k'_3 + k'_4) + \frac{k'_1}{k'_2} (k'_3 + k'_4) \quad (23)$$

Now $(k'_3 + k'_4)$ may be used in plots of equation (4a) to give new values of A_p and A_{p-o} and thus get second approximations for the fast rate constants $(k'_1 + k'_2)$. This iterative process can be repeated until the change in the rate constants is insignificant. It turns out that for the particular case of the kinetics of 5', 7'-dichloro-6'-nitro BIPS in ethanol the first or second iteration is sufficient.

Thus;

$(k_3 + k_4) = (k'_3 + k'_4)$ and $(k_1 + k_2) = (k'_1 + k'_2)$ to within the error of our experiments. Where k_1 , k_2 , k_3 and k_4 are the values of the rate constants used in equations (12), (13) and (14).

The mathematical treatment of the rate data can be approached in another manner. As has been previously shown, k_7 and k_8 (the constants that appear in the exponential terms) are roots of the quadratic indicial equation. At 20° C in this particular case $k_7 = -3.6 \times 10^{-4} \text{ min}^{-1}$ and $k_8 = -1.7 \times 10^{-1} \text{ min}^{-1}$. Therefore, at small values of time, equation (12) can be approximated in the following manner:

$$C = \frac{1}{k_6} (k_2 k_4 T + A_1 + A_2 e^{k_8 t})$$

since for small values of time $e^{k_7 t} \approx 1$.

At large values of time equation (12) can be approximated in a different manner as follows:

$$C \approx \frac{1}{k_2} (k_2 k_1 T + A_1 e^{k_1 t})$$

since for larger values of time $e^{k_1 t} \approx 0$.

By appropriate substitutions equations (24) and (25) can be changed to a form where pseudo-first-order plots can be made and rate constants determined without using iterative approximations.

It should be pointed out that the mathematical analyses described are possible only because there is a significant difference in the rates of the fast and the slow thermal reactions. If these rates were very nearly the same it would be impossible to separate them from measurements of the colored species alone. Also, if these rates were of different values but of the same order of magnitude, first-order plots would not give straight lines at any value of time. There are, in fact, certain spiropyrans which yield a continuous curved line when plotted for first-order kinetics.

In cases such as these it would probably be necessary to obtain the fundamental rate constants from initial rate data. This is a differential method and, by its very nature, would not yield values of rate constants as accurate as by the analytical methods presently used. It would also be very valuable to be able to spectroscopically follow the change in concentration of each of the colorless species with time in addition to that of the colored form. The techniques required for these measurements appear to be quite involved.

Figures 6, 7, 8, and 9 show theoretical plots of the thermal switching as a function of time for various initial concentrations of all three forms. These plots were made from the output of the CRC-102D computer with the corrected values for k_1 , k_2 , k_3 and k_4 used as input. Figures 6 and 7 show how an ethanolic solution of pure colored form fades with time. Figure 8 should approximate the rapid recoloration to pseudo-equilibrium after light erasure. Figure 9 demonstrates the approach to true equilibrium of a solution initially composed of pure U_2 .

Figure 7

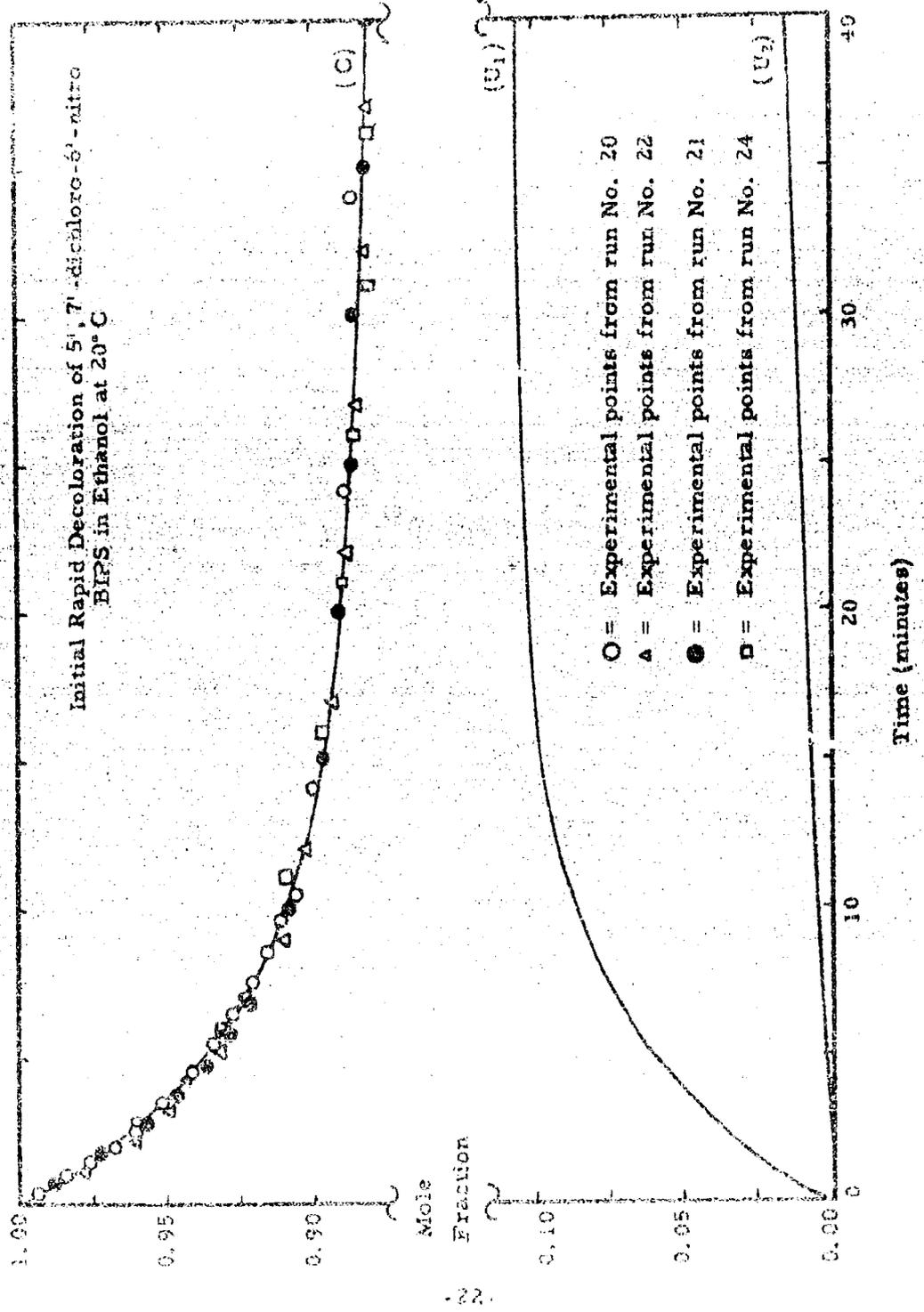
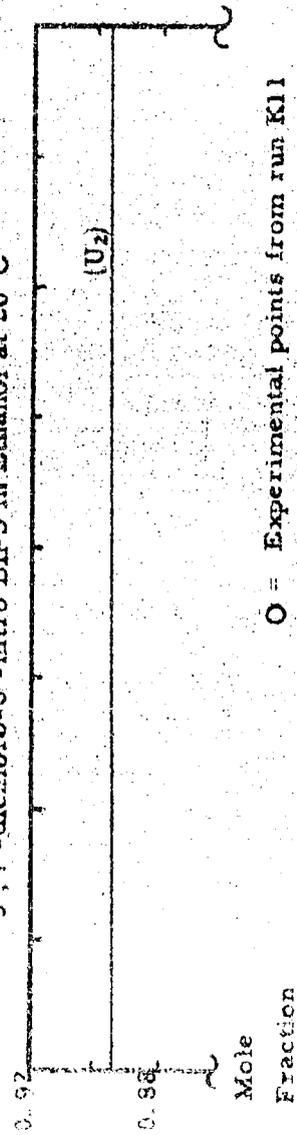


Figure 8

Initial Rapid Recoloration After Photo-erasure of
5, 7'-dichloro-6'-nitro BIPS in Ethanol at 20° C



O = Experimental points from run K11
A = Experimental points from run K11A

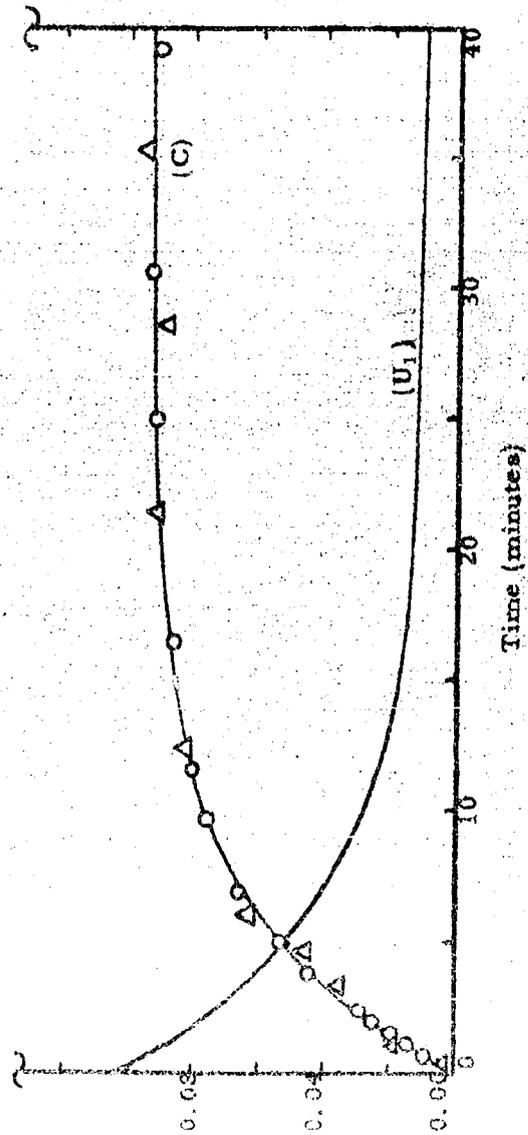
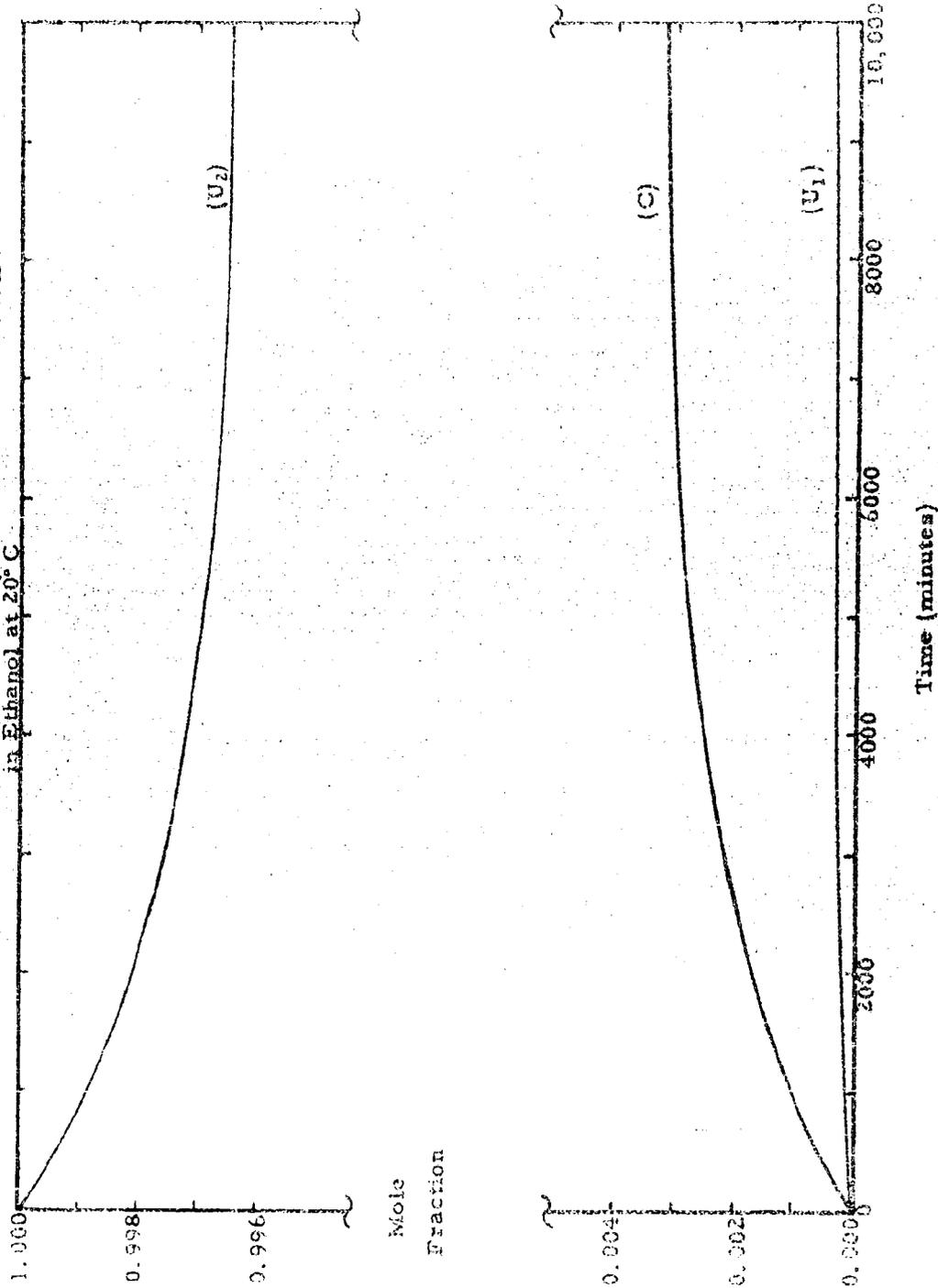


Figure 9

Thermal Coloration of 5,7-dichloro-6'-nitro BIPS
in Ethanol at 20°C



2.2. Experimental

2.2.1. Elemental analysis. - (These were performed by Dr. Carol K. Fitz, Needham Heights, Mass.) Twenty-three (23) milligrams of recrystallized colorless 5', 7'-dichloro-6'-nitro BIPS (U_2) was analyzed for carbon, hydrogen, nitrogen and chlorine. The results are reported in Table 1.

TABLE 1

<u>Element</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>Cl</u>
Analyzed %	58.5	3.8	7.1	18.6
Theoretical %	58.3	4.1	7.2	18.0

2.2.2. X-Ray powder photographs. - X-Ray powder photographs were taken of the following compounds.

(1) Colorless 5', 7'-dichloro-6'-nitro BIPS (U_2) which was first recrystallized from isooctane and subsequently from an ethanol-water mixture.

(2) Colored 5', 7'-dichloro-6'-nitro BIPS, which was prepared by the irradiation of a colorless solution of the compound under a Gates lamp and followed by an immediate filtration of the insoluble colored-form precipitate.

(3) Recrystallized, colorless 5', 7'-dichloro BIPS: An x-ray powder photograph of this compound was taken to make certain that any of the precursors of the dichloronitro compound that did not undergo complete nitration were removed by the purification steps.

An examination of the developed powder camera photographs showed that certain of the strong lines found for each compound were completely absent in the photographs of the other compounds. These results indicate that the solid samples are probably pure crystalline compounds and if there is an impurity of one in the other it is no greater than 3%-4% and probably much less. The "d" values for the strongest lines on the powder photographs of these three compounds are shown in Table 2.

TABLE 2

X-Ray Powder Photograph Data

5', 7'-dichloro-6'-nitro BIPS (Colored)

<u>Strength of Line</u>	<u>"d" value</u>
1	5.29
2	3.33
3	3.73
4	3.60

5', 7'-dichloro-6'-nitro BIPS (Colorless (U₂))

<u>Strength of Line</u>	<u>"d" value</u>
1	5.77
2	4.83
3	5.28
4	3.84

5', 7'-dichloro BIPS (Colorless)

<u>Strength of Line</u>	<u>"d" value</u>
1	7.28
2	3.55
3	5.59
4	5.25

2.2.3. Solid state analysis of colored and colorless spiropyrans

One of several methods devised for determining the extinction coefficient of an unstable colored form was to analyze the solids obtained from a solution whose absorbance at the visible λ_{max} had just been measured. The solids were to be isolated by immediately freezing and then freeze-drying the solution. In this way it was assumed that the ratio of colored to colorless form which existed in the solution would also be retained in the solid, in which state conversion from one form to the other could no longer take place. The material isolated in this way could then be put into a KBr pellet matrix and analyzed for the different components by infrared spectrophotometry. Therefore, by knowing the absorbance of the colored form and calculating its concentration from the above analysis, the extinction coefficient could be obtained.

A calibration curve for the colorless form was prepared from two types of samples: aliquots of standard solutions, and solid samples dissolved directly. In both cases 3 to 10 ml. of solution was used. To this was added 2 ml. of a solution containing 212.2 mg./ml. of potassium bromide and about 0.1% KSCN. This latter material is used as the internal standard in the pellet, as will be shortly explained. To these solutions was also added some excess water to precipitate the BIPS and discourage any photochemical or thermal conversion to the colored form. This mixture was then frozen in dry ice-acetone, (sometimes with difficulty, according to the alcohol-water ratio) and freeze-dried to remove the solvent. After freeze-drying for up to 24 hours the sample was removed as a very fine, intimately mixed powder. About 350 mg. of this mixture was placed in a 1/2" diameter KBr-pellet die and pressed under vacuum and 20,000 lbs. total load for 1 minute. A pellet about 1 mm. thick was obtained. The spectrum of this pellet was scanned, in duplicate runs, from 8 μ to 15 μ on an "Infracord" Perkin-Elmer Model 137 Spectrophotometer, the pellet being turned in its holder before the second scan.

A convenient method for adjusting absorbances to a common pellet thickness is to include an internal standard in the pellet. The KSCN used for this purpose has an absorbance at 2050 cm^{-1} , and is transparent

throughout the rest of the spectrum. The weight ratio of this substance to the KBr is always the same because they are originally in solution together. The use of the ratio of the absorbance of the analysis peak to that of the internal standard peak should eliminate many systematic errors. Absorbances were obtained from the transmittance curve by the standard base line method. The calibration curve is shown on Figure 10.

The precision of this method of analysis was found to be rather poor. Even after several refinements in technique and standardization of conditions the variance of 1 sigma was about $\pm 6\%$. Since it was desired to obtain the extinction coefficient with greater accuracy than could be obtained by this method, the project was discontinued.

Potassium bromide pellets of pure colored 5', 7'-dichloro-6'-nitro BIPS were prepared in a manner analagous to those of the colorless form. The infrared spectra of these two species, in KBr pellets, are shown in Figure 11 and Figure 12.

2.2.4. Extinction coefficient of the colorless form of 5', 7'-dichloro-6'-nitro BIPS. - Solutions were prepared by weighing pure colorless sample on a Cahn Electro-balance (Model M-10), transferring the sample to a volumetric flask, dissolving in the appropriate solvent and diluting to the mark at 20° C. Absorbance readings were made using a Beckman model DU or DK-1 spectrophotometer with constant temperature control at 20° C. In ethanol, absorbance readings were made at the ultraviolet absorption maximum of the colorless form, 243 m μ . In toluene, absorbance readings were taken at a plateau of the colorless form spectrum, 310 m μ . The following values are an average of several runs at different concentrations:

$$\epsilon \text{ (colorless, toluene, 310 m}\mu\text{)} = 5,130 \text{ liter mole}^{-1}\text{cm}^{-1}$$

$$\epsilon \text{ (colorless, ethanol, 243 m}\mu\text{)} = 35,800 \text{ liter mole}^{-1}\text{cm}^{-1}$$

A slight systematic error might possibly be induced due to the equilibration of the uncolored BIPS with some colored form. This equilibrium, however, greatly favors the colorless form in both of these solvents, and therefore any colored form present would introduce an error of no more than a few tenths of a percent, which is well within other experimental errors.

Figure 10

Calibration Curve for Infrared Analysis of U_2 in KBr

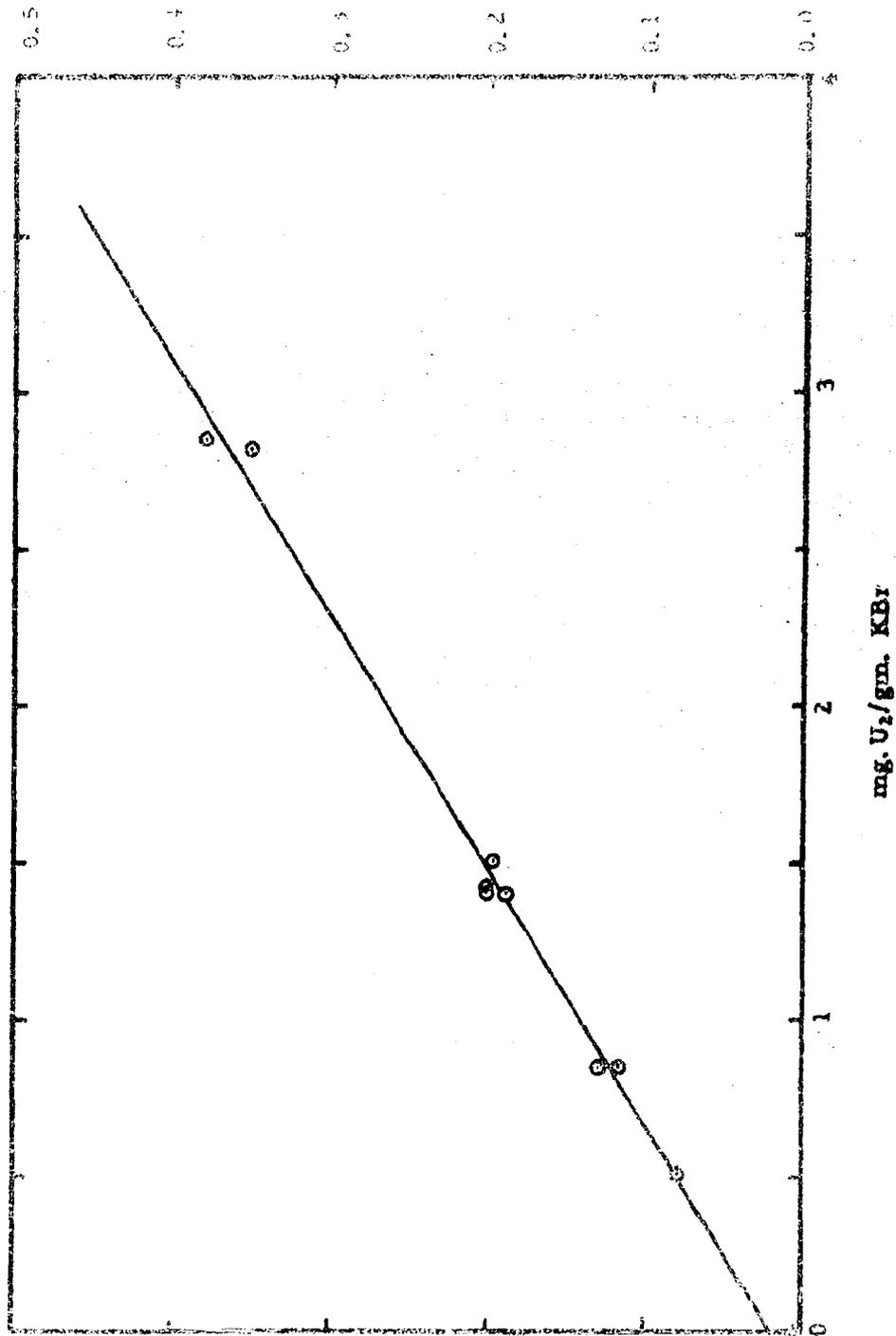


Figure 11

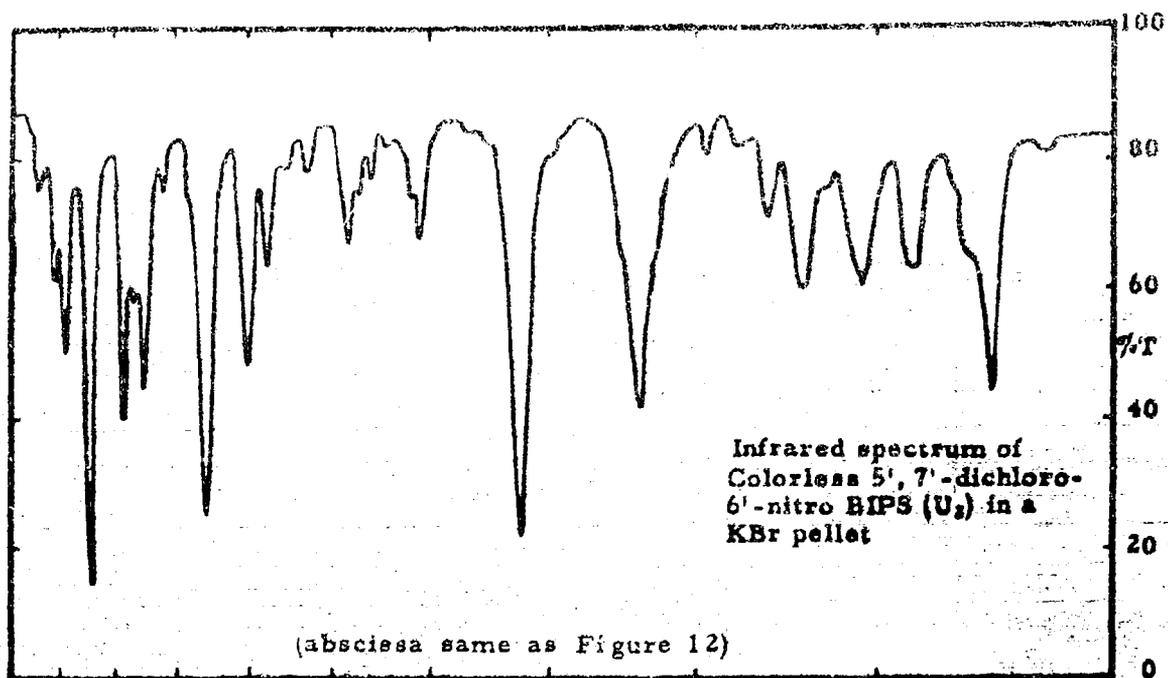
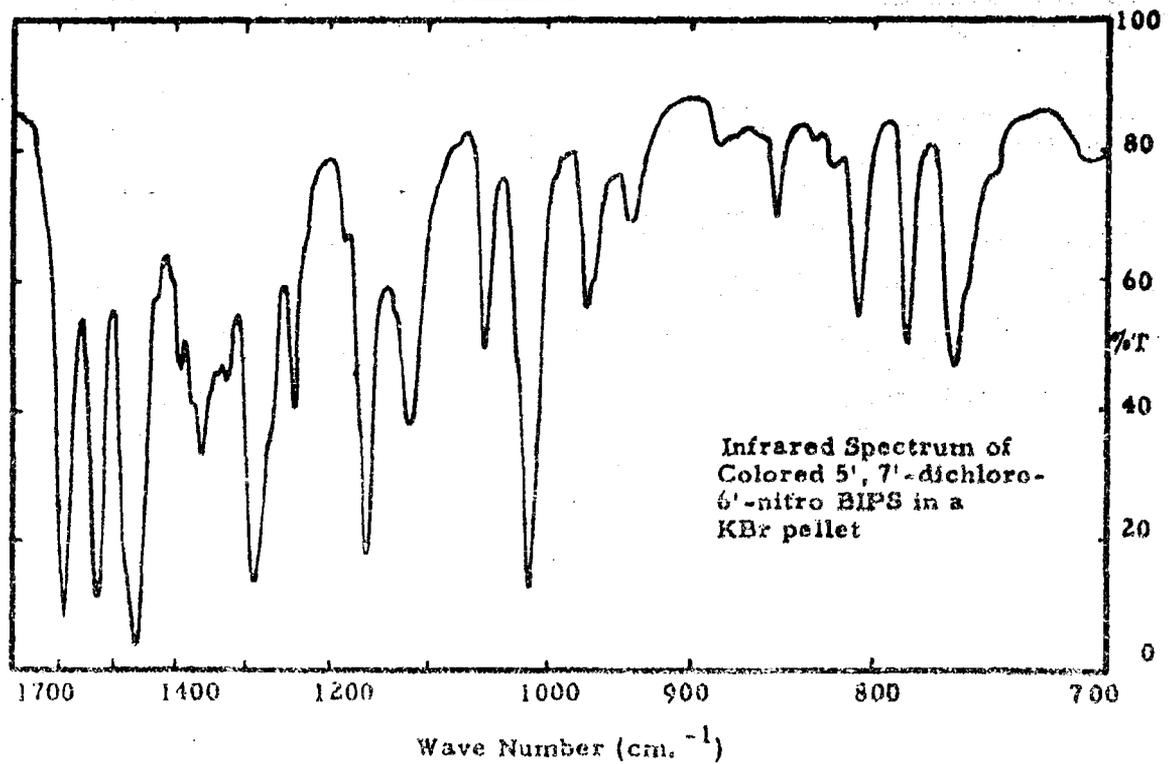


Figure 12



In this range of concentrations used (5×10^{-6} to 5×10^{-4} M) it appears that Beer's Law is obeyed.

2.2.5. Extinction coefficient of the colored form of 5', 7'-dichloro-6'-nitro BIPS.- Fourteen determinations of the extinction coefficient of the colored form of 5', 7'-dichloro-6'-nitro BIPS were made by direct absorbance measurement of solutions of the pure colored form. The solutions were prepared by placing solid colored form on the fritted glass disc of a filter funnel, pouring absolute ethanol over the solid, then filtering the colored solution under vacuum and collecting it in a beaker. The solution was quickly transferred to an absorption cell and set in a Beckman model DK-1 spectrophotometer maintained at 20°C . The preparation of the colored solution was carried out in darkness to prevent the photoreaction (colored $\xrightarrow{h\nu}$ colorless) from taking place. The absorbance of the solution was followed at $531 \text{ m}\mu$ with time; usually sixty minutes. After sixty minutes the solution was completely decolorized with visible radiation and the absorbance of this completely colorless solution was measured at $243 \text{ m}\mu$, the λ_{max} of the colorless form. The total concentration was then calculated by dividing the absorbance at $243 \text{ m}\mu$ by the molar absorptivity at $243 \text{ m}\mu$.

The absorbance of the colored solution at zero time was determined from an extrapolation of a plot of A_{531} versus time. (Where A_{531} = Optical density at $531 \text{ m}\mu$). The thermal fade curves were amenable to extrapolation because of their small slope over the early portion of the fade. Zero time was taken to be the time at which the alcohol was first added to the colored solid. The actual zero time would lie between the time of alcohol addition and the completion of the filtering of the colored solution, since molecules were being dissolved over this entire period (Generally about 10 to 30 seconds). Temperature of the solution during preparation and filtering was not completely controlled at 20°C and some slight changes in temperature were possible during the first several minutes of any given recording of A_{531} versus time. Using Beer's Law the absorbance of the colored form at $531 \text{ m}\mu$ at zero time was then used to calculate the extinction coefficient of the colored form at $531 \text{ m}\mu$.

The solutions ranged in concentration from 5.5×10^{-7} moles per liter to 8.9×10^{-4} moles per liter. Absorption cells of 0.1, 1.0, and 10.0 cm. were employed to enable accurate readings through the entire concentration range. Neutral density screens were used at the higher concentrations to permit measurement by a differential technique. An average value for this extinction coefficient, of 3.93×10^4 liter mole⁻¹ cm.⁻¹ ± 900 liter mole⁻¹ cm.⁻¹ was obtained. Over the range in concentrations used in these measurements, Beer's Law appears to be valid.

The extinction coefficient of the colored modification of this dye was determined in toluene at the visible absorption maximum (594 m μ) by completely analogous procedure.

ϵ (colored, toluene, 594 m μ) = 48,200 liter mole⁻¹ cm.⁻¹ ± 1000 liter mole⁻¹ cm.⁻¹

Another method of obtaining the molar absorptivity (extinction coefficient) of the colored species consists of liberating pure colored form by reaction of the hydrochloride salt of the open spiropyran with a weak organic base. The absorbance of the free colored form is then measured at 531 m μ . The following experimental procedure was employed.

A 1.0 cm. absorption cell was half-filled with 1.5 ml. of an EtOH-HCl solution of the hydrochloride salt of the open 5',7'-dichloro-6'-nitro BIPS in known concentration. To this was added 1.5 ml. of an ethanolic solution containing triethylamine in excess. The solution immediately changed from yellow to red. The cell was quickly shaken to insure good mixing and then placed in a Beckman model DK-1 recording spectrophotometer. The absorbance at 531 m μ was measured versus time and the zero-time absorbance was found by extrapolation.

For two determinations the molar absorptivity of the colored form at 531 m μ (ϵ_{531}) was $39,300 \pm 800$ mole liter⁻¹ cm.⁻¹. This is in excellent agreement with the value determined by the pure colored solution extrapolation technique.

2.2.6. Absorption spectra of 5',7'-dichloro-6'-nitro BIPS in ethanol at 20°C. - The visible and ultraviolet spectra of the colored form and colorless form (U₂) were recorded in ethanol (U.S.I., U.S.P.) at 20° using a

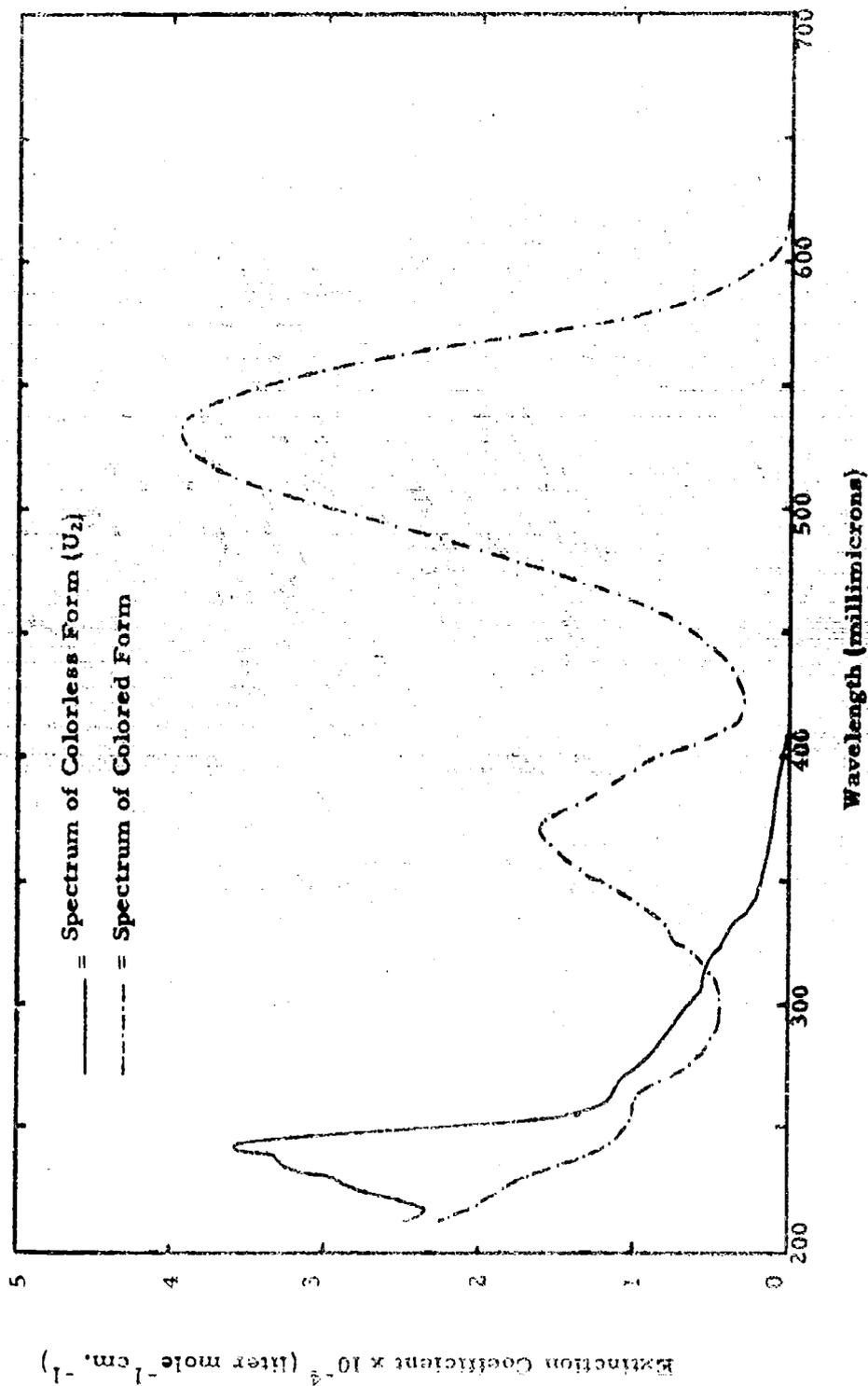
Beckman model DK-1 spectrophotometer and 1.0 cm. path. The colored solution was prepared by dissolving pure colored form in ethanol and quickly filtering. The spectra were recorded at a medium scan speed. The colored form spectrum was recorded first and was completed nine minutes after zero time. (Zero time was taken to be the time when the ethanol was added to the pure colored form.) After the spectrum of the colored form had been recorded, the solution was decolorized with visible light from an electronic flash a sufficient number of times to make certain that very little U_1 species was present in the colorless solution. The spectrum of the colorless form (U_2) was then recorded.

The colored and colorless spectra were re-plotted as molar absorptivity versus wavelength. The visible spectrum of the colored form (700 $m\mu$ - 325 $m\mu$) was corrected for the thermal fade with time by employment of the thermal decoloration rate plot (see Figure 7). The remaining portion of the colored spectrum (325 $m\mu$ - 200 $m\mu$) was obtained by dividing the observed absorbance at any given wavelength by the observed absorbance at 531 $m\mu$ then multiplying the result by 39,300. In the colorless spectrum the value for the molar absorptivity at any given wavelength was obtained by dividing the observed absorbance at that wavelength by the observed absorbance at 243 $m\mu$, then multiplying the result by 35,800. The plot of extinction coefficient versus wavelength appears in Figure 13. It must be noted that the colored spectrum as plotted is not completely correct since slight changes in spectrum do occur in the ultraviolet region with time. These changes, however, are relatively small over the nine minute time period.

2.2.7. Thermal equilibrium measurements of 5',7'-dichloro-6'-nitro indolinobenzospiropyran in ethanol and toluene. - All solutions used in equilibrium studies were prepared by dissolving a preweighed quantity of the colorless spiropyran in ethanol (U. S. I., U. S. P.) or toluene (reagent grade) in volumetric flasks at 20°. Ethanolic solutions were placed in a constant temperature bath in complete darkness at the desired temperature until true thermal equilibrium was established. A portion of the solution was transferred under dark-room conditions from

Figure 13

Ultraviolet and Visible Spectra of 5', 7' -dichloro-6' -
Nitro BIPS in Ethanol at 20°C



the storage vessel to an absorption cell of appropriate path length situated in a controlled temperature cell holder. The cell holder was placed in a Beckman Model DK-1 spectrophotometer where the absorbance of the equilibrium solution was measured at its wavelength of maximum absorbance in the visible region.

The equilibrium absorbance of the toluenic solutions was measured at several temperatures by the above method and at several other temperatures by placing the colorless solution in the controlled temperature absorption cell situated in the spectrophotometer and then following the absorbance of the solution at the wavelength of maximum absorbance until thermal equilibrium was established.

It was noticed that toluene solutions of 5', 7'-dichloro-6'-nitro BIPS were being affected by some indeterminate condition. The absorbance of these solutions increased very slowly at times beyond the calculated time needed for equilibrium to be reached. The equilibrium constant reported here is calculated from the absorbance taken at the time equilibrium should have been reached based on the knowledge of the thermal kinetics for the system.

Since the toluene equilibrium greatly favors the colorless species, relatively concentrated BIPS solutions had to be used in order to get a measurable colored form absorbance. In all cases measurements were made at more than one BIPS concentration and the measured equilibrium constant was extrapolated back to infinite dilution to obtain a more reliable value. It was possible to calculate the concentration of the colorless and colored forms present in the equilibrium mixture since both the molar absorptivity of the colored form at the visible λ_{max} , and the total concentration of each solution was known. The equilibrium constant is defined by the relation:

$$\frac{\text{Concentration of colored form at equilibrium}}{\text{Concentration of colorless form at equilibrium}} = \text{Equilibrium constant}$$

K_c is the equilibrium constant in ethanol and K_t denotes the equilibrium constant in toluene.

2.2.8. Thermal color disappearance measurements in ethanol and toluene. - The experimental procedure, as described below, can be divided into two basic steps:

- (1) Preparation of the solution
- (2) Measurement of the absorbance change of the colored species at λ_{max} , as a function of time.

Solution preparation - A small quantity of pure solid colored form was placed on the fritted glass disc of a Buchner funnel of medium porosity. Solvent was added to the funnel and the colored solution was prepared as in section 2.2.5, describing the determination of the molar absorptivity of the colored form.

Solutions were prepared at temperatures lower than 20° by this method by using a jacketed fritted funnel maintained at the desired temperature. Colored solution was collected in a receiving flask immersed in a constant temperature bath.

At higher than ambient temperatures some solutions were prepared by placing the pure colored form solid on a 13 mm diameter millipore filter pad situated in a Swinny hypodermic adapter. The adapter was attached to a jacketed hypodermic syringe containing solvent at the desired temperature. The solvent was forced through the adapter and channeled through a wide gauge needle into an absorption cell maintained at the desired temperature.

In some cases an alternate procedure was followed. A colorless solution of the spiropyran was situated in an absorption cell in a constant temperature cell holder. The cell was exposed to the radiation of a Braun "Hobby" Electronic flash unit or to a low pressure Mercury arc lamp. At the completion of the irradiation the solution in the cell was shaken to insure homogeneity of color.

Measurement of the change in concentration of the colored species as a function of time - The concentration of the colored species in solution was found to be directly proportional to its absorbance at the λ_{max} in the visible region. Hence, the change in concentration of colored form was easily followed by recording the absorbance at the visible λ_{max} versus time. In cases where color disappearance was fast the recording was done automatically on either a Beckman model DK-1 spectrophotometer

or model DU spectrophotometer equipped with an energy recording attachment (ERA). Where color disappearance was relatively slow (more than a day) the solutions were stored at constant temperature in darkness and small portions were removed at intervals and placed in the spectrophotometer where the absorbance at the λ max and the time were recorded. Examples of first-order rate plots for the fast and slow decoloration are shown on Figures 14 and 15.

2.2.9. Fast and slow thermal color formation in ethanol. - A fast thermal coloration was observed in ethanolic solutions of 5', 7'-dichloro-6'-nitro BIPS when colored solutions were photo-decolorized. This fast color formation presumably occurs as a result of the re-equilibration between U_1 and C following the sudden removal of C from solution by photo-decolorization.

The photo-decolorization was done by successive exposures to an electronic flash lamp when the maximum concentration was present in solution; i. e. at pseudoequilibrium. The solutions used for these runs were prepared as described in Section 2.2.8 and some of them were actually portions of the mother solutions used for measuring the fast and slow color disappearance.

Immediately following photo-decolorization, the sample solution was placed in the spectrophotometer and the increase in absorbance at the visible λ max was recorded versus time until pseudoequilibrium was reached.

At 20°C the absorbance of the solution at the apparent equilibrium state was approximately one-ninth the absorbance of the original colored solution before decoloration. The solution at the apparent equilibrium state was then decolorated in the same manner as the original solution and its recoloration was followed at 531 m μ with time until it again reached an apparent equilibrium. This value was approximately one-ninth the value of the first-recoloration-equilibrium absorbance or approximately one-eightieth of the absorbance of the original pure colored solution. The process was repeated a third time after which very little fast recoloration occurred. A schematic diagram of this effect

Figure 14

Rapid Thermal Color Disappearance of Colored
5',7'-dichloro-6'-nitro BIPS in Ethanol at 20°C.
(1st-Order Rate Plots)

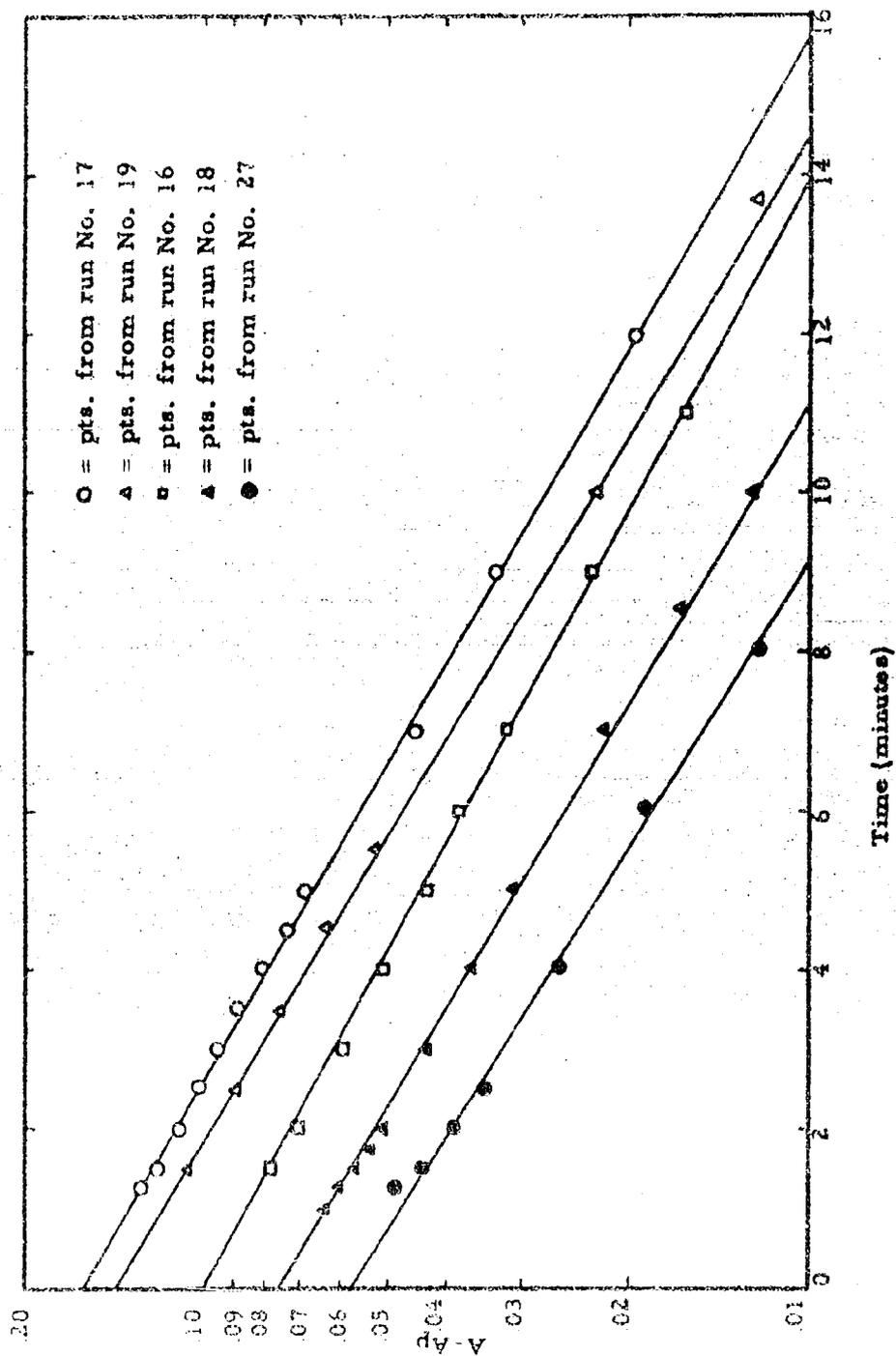
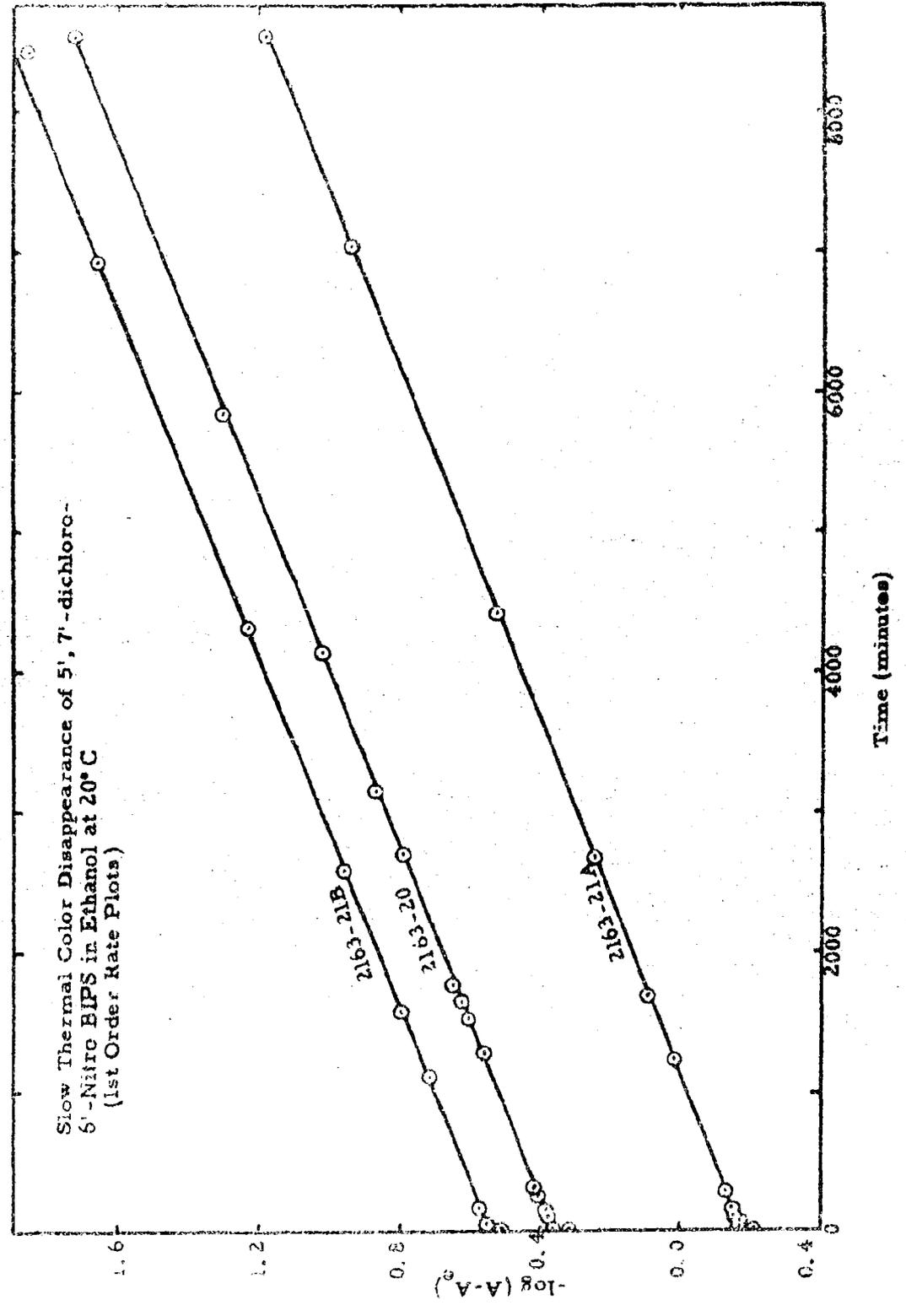


Figure 15



is shown in Figure 16. The first-order rate plot for this process is shown in Figure 17.

The primary experimental difficulty in this type of measurement is that in order to follow the recoloration effect over a few cycles, concentrated solutions must be used initially. These solutions, however, are difficult to erase because they are so concentrated. In addition some thermal recoloration occurs during the time required for complete erasure. These conditions introduce an error in the determination of zero time for the recoloration process and an additional error due to the erasure of some BIPS which has recolorated after being erased by the initial flash of visible light.

The rate of slow thermal color formation at 20°C in ethanol was done by a different method and is described below.

The thermal formation of colored species from the colorless 5', 7'-dichloro-6'-nitro BIPS was measured at 20°C in ethanol by observing the increase in absorbance at 531 m μ at various times until true thermal equilibrium was established. This process is primarily due to slow thermal equilibration between C and U₂ (specified by first order rate constants k₃ + k₄). The solutions used for these determinations were freed of U₁ and C, at the start of each run, by the following procedure.

The colored species present in the original solution was photo-erased. The solution was then allowed to stand for approximately thirty minutes permitting U₁ to reestablish equilibrium with the colored form. This process was repeated several times until U₁ and C were present in only negligible quantities. At this point the run was started and the change of absorbance at 531 m μ was measured at various times until true thermal equilibrium was reached.

2.2.10. Controlled formation of the U₁ modification - As described previously, when colored form of 5', 7'-dichloro-6'-nitro BIPS is dissolved in ethanol a colorless species, U₁, is rapidly formed. This reaction obeys a first-order rate law and has a half-life of approximately four minutes at 20°C. At this temperature, after approximately

Figure 16

Recoloration Effect After Photo-erasure

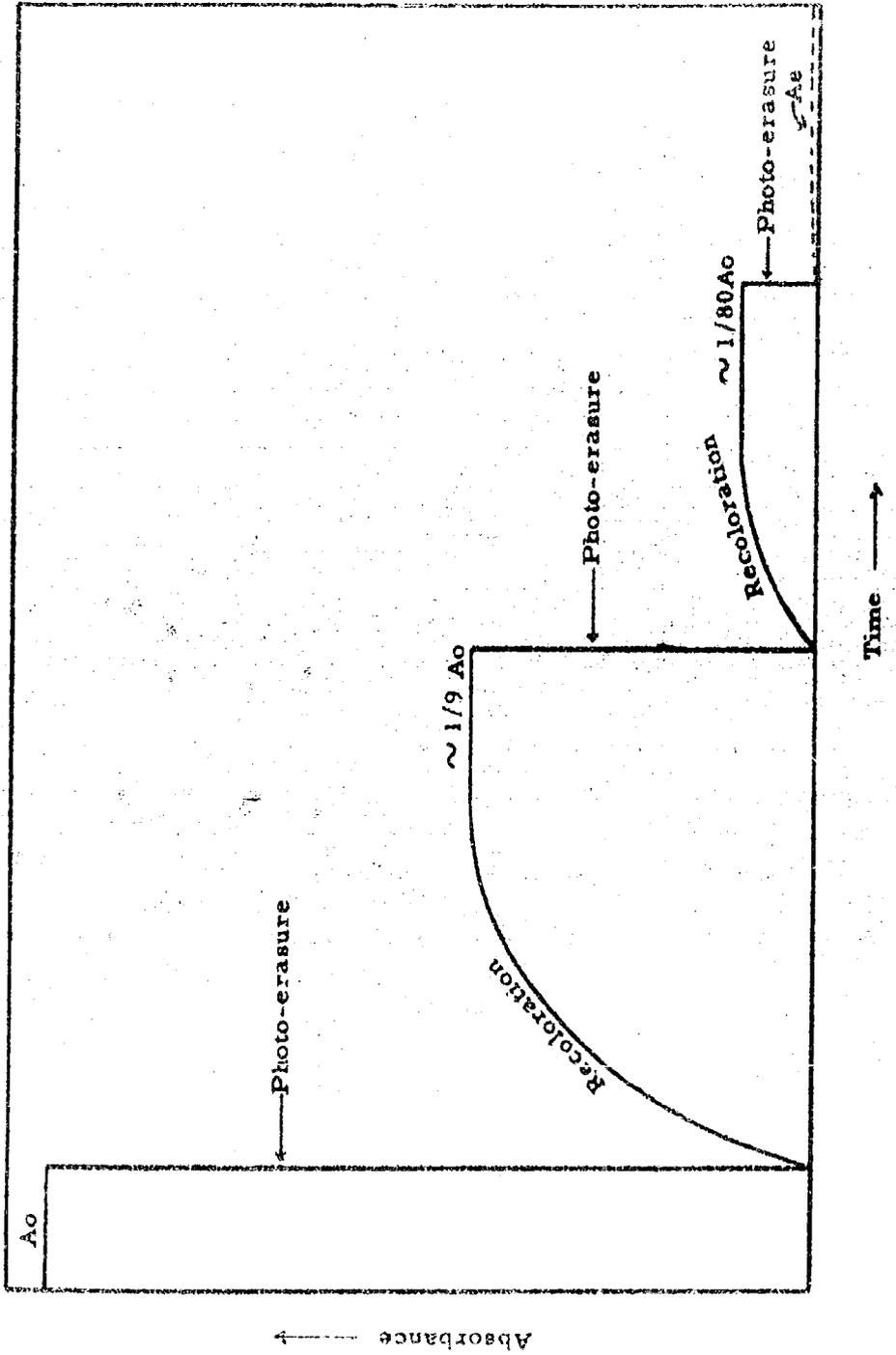
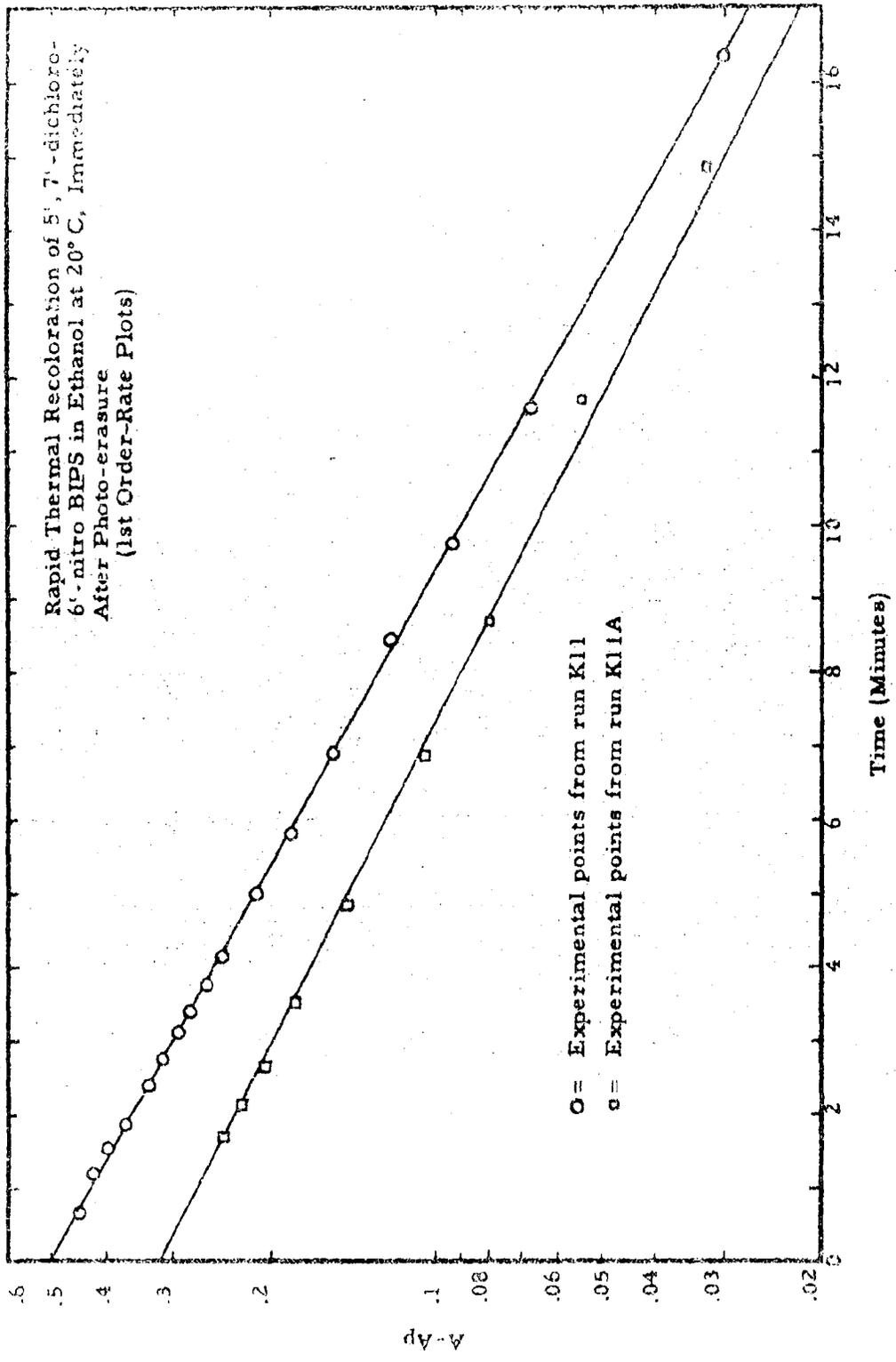


Figure 17



thirty-five minutes, a state of pseudoequilibrium is reached between C and U_1 . At this time the kinetic data indicate that the concentration of U_1 is at a maximum.

A large quantity of colored solution was prepared via the method described in Section 2.2.8, and was collected in a storage bottle at 20°C. Six portions of the solution were taken from the storage bottle and placed in 10 ml. volumetric flasks, then stored in a constant temperature bath at 20°C. A seventh portion was placed in a 0.1 cm. absorption cell maintained at 20°C in a Beckman model DK-1 spectrophotometer where the absorbance change of the solution was followed at 531 m μ continuously for thirty-five minutes. The portions in the volumetric flasks were photo-decolorized at various times between zero time and thirty-five minutes after zero time. Each photo-decolorized solution was permitted to re-color thermally for approximately thirty-five minutes, then the absorbance of each solution was measured at 531 m μ in a 1.0 cm. absorption cell. The total concentration of the solution was found by measuring the absorbance of the completely colorless solution at 243 m μ and dividing this absorbance value by the molar absorptivity of the colorless spiropyran at that wavelength. Three separate runs were made under darkroom conditions. A summary of the results appears in Table 3.

The data in Table 3 clearly demonstrate the fact that as the decoloration time increases the pseudoequilibrium recoloration absorbance also increases. This is exactly what the proposed kinetic mechanism predicts. The photo-decolorization of the colored solution immediately after its preparation results in formation of a minimum quantity of U_1 since U_1 has had no opportunity to be formed via the fast rate mechanism. Consequently, there will be a negligible rapid recoloration in this case since no U_1 is present to reequilibrate. Also, colored solutions which are photo-erased at times intermediate between zero time and thirty-five minutes should produce a quantity of U_1 which in some manner corresponds to the length of time the colored form was permitted to remain in solution.

2.2.11. Calculation of true first-order rate constants and equilibrium constants. - The following equations define the equilibrium constants for the colored species \rightleftharpoons colorless species equilibria.

TABLE 3

Recoloration of Ethanolic 5', 7'-dichloro-6-nitro BIPS Solutions After Photo-Erasure at Different Times During the Initial Rapid Decoloration

Run 2306-39-1 Conc. = $5.00 \times 10^{-5} M$		Run 2306-39-2 Conc. = $1.55 \times 10^{-4} M$		Run 2306-39-3 Conc. = $1.42 \times 10^{-4} M$	
Decolor Time (Min.)	Recolored Absorbance (531 m μ)	Decolor Time (Min.)	Recolored Absorbance (531 m μ)	Decolor Time (Min.)	Recolored Absorbance (531 m μ)
0.75	0.046	0.9	0.191	0.75	0.083
2.25	0.079	2.53	0.247	2.33	0.285
4.5	0.131	4.5	0.341	4.51	0.297
8.0	0.164	8.0	0.440	8.52	0.403
12.0	0.179	12.0	0.498	12.0	0.452
35.0	0.193	35.0	0.574	35.0	0.609

$$K_c = \frac{C_{eq}}{U_{2-eq}} = \frac{k_4}{k_3} \quad (\text{ethanol}) \quad (26)$$

$$K_p = \frac{C_{eq}}{U_{1-eq}} = \frac{k_2}{k_1} \quad (\text{ethanol}) \quad (27)$$

$$K_t = \frac{C_{eq}}{U_{2-eq}} = \frac{k_5}{k_5} \quad (\text{toluene}) \quad (28)$$

where C_{eq} , U_{1-eq} and U_{2-eq} represent the equilibrium concentrations of the various species.

K_c and K_t can be readily calculated from the measured equilibrium absorbances (see section 2.2.7.). K_p is calculated from data obtained from the first-order rate plots. As has been previously demonstrated -

$$K_p \approx \frac{A_{p-0}}{A_0 - A_{p-0}} \quad (21)$$

The calculated values of K_c , K_p and K_t are compiled in Table 4. The values obtained for K_c are quite accurate. As equation (21) clearly shows, the calculation of K_p involves the subtraction of two absorbances. These absorbances are, in this case, of the same order of magnitude. Thus considerable error is introduced in this calculation, especially at higher temperatures in which case A_0 is not much greater than A_{p-0} .

The concentrated BIPS solutions that had to be used in the equilibrium measurements in toluene contributed to the inaccuracies of these measurements. Under these conditions, impurities deviations from ideality, and the extrapolation to infinite dilution calculations all tend to introduce errors in K_t .

The thermodynamic relationship between equilibrium constant and enthalpy is ⁵ -

$$\left(\frac{\partial \ln K_{eq}}{\partial T} \right)_p = \frac{\Delta H^0}{RT^2} \quad (29)$$

where K_{eq} = equilibrium constant

ΔH^0 = standard enthalpy of reaction

R = gas constant

T = absolute temperature

TABLE 4

Equilibrium Constants for Solutions of 5', 7'-Dichloro-6'-NitroBIPS

Temperature (°C)	<u>Measured Values</u>			<u>Values Calculated from lines of Figures 1, 2 and 3</u>		
	<u>K_D</u>	<u>K_C × 10³</u>	<u>K_T × 10³ ^a</u>	<u>K_D</u>	<u>K_C × 10³</u>	<u>K_T × 10³</u>
0	4.95			4.68	2.17	
8	5.42			5.80	2.67	1.20
14	6.21		1.52	6.88	3.08	1.50
20	8.50	3.57	2.15	8.10	3.57	1.87
25			2.50			2.27
30	10.3	4.78	2.65	10.5	4.88	2.65
40	13.7	5.43	3.33	13.4	5.44	3.68
50		6.72	5.05	16.8	6.68	5.05
60		7.82		21.0	8.05	6.70

a - Extrapolated to infinite dilution.

If ΔH^0 is constant over the temperature range in question, equation (29) can be integrated as follows:

$$\ln K_{eq} = - \frac{\Delta H^0}{RT} + \text{Constant} \quad (30)$$

Thus a plot of $\ln K_{eq}$, vs. $\frac{1}{T}$ yields a straight line with a slope of $\Delta H^0/R$. Figures 18, 19, and 20 are plots of the measured equilibrium constants vs. $1/T$. Table 5 is a listing of the measured values of the equilibrium constants and the values obtained from the lines drawn on Figures 18, 19, and 20.

The true rate constants (k_1 , k_2 , k_3 , k_4 , k_5 , and k_6) are related to the measured rate constants (k_f , k_s and k_t) and the equilibrium constants by the following equations:

$$k_f = k_1 + k_2 \quad (31)$$

$$K_p = \frac{k_2}{k_1} \quad (32)$$

$$k_t = \frac{k_f}{K_p + 1} \quad (33)$$

$$\text{and } k_2 = \frac{k_f K_p}{K_p + 1} \quad (34)$$

$$k_3 + k_4 = \left(\frac{k_1 + k_2}{k_2} \right) \cdot k_s \quad (35)$$

$$K_c = \frac{k_4}{k_3} \quad (36)$$

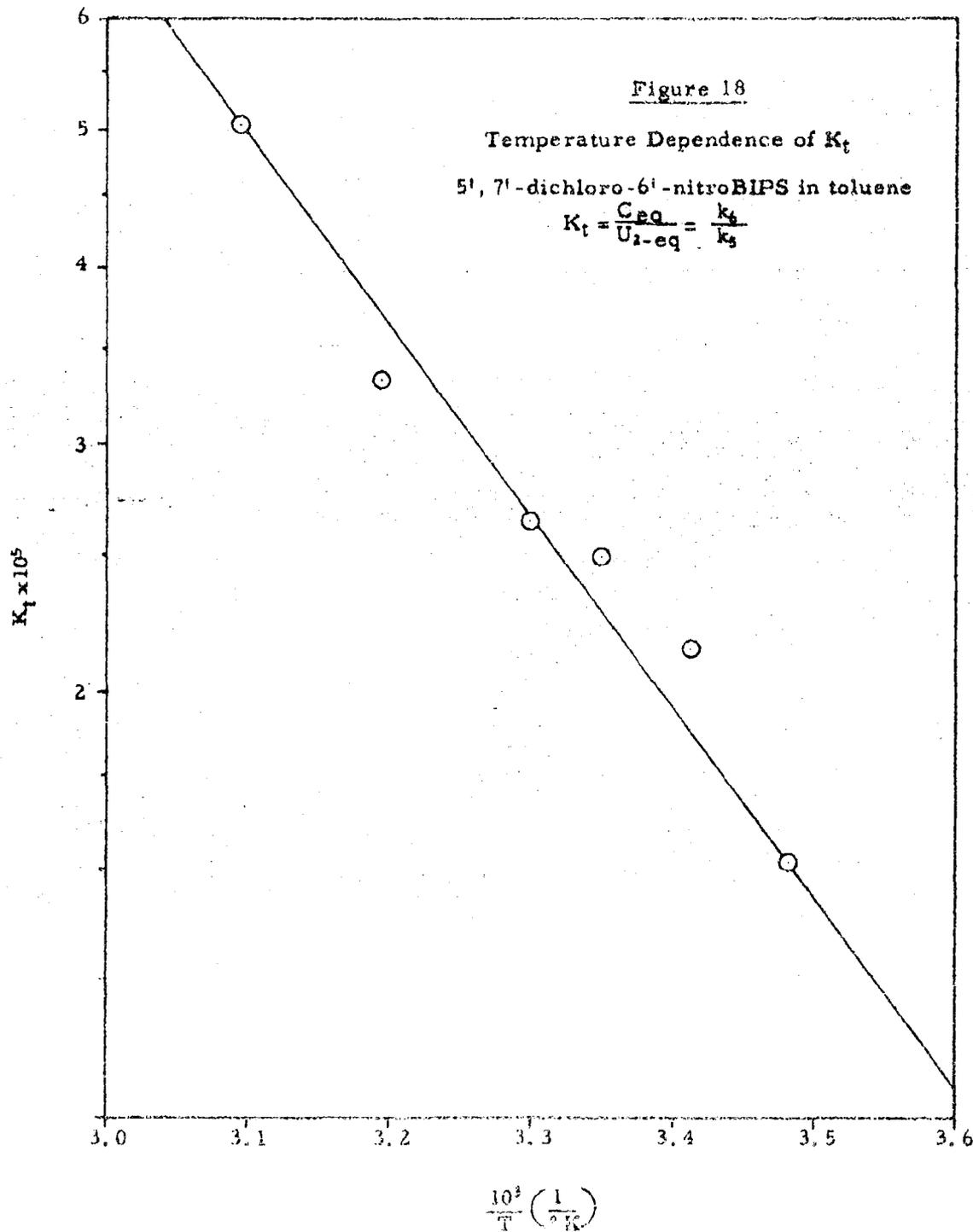
$$\frac{k_1 + k_2}{k_2} = \frac{K_p + 1}{K_p} \quad (37)$$

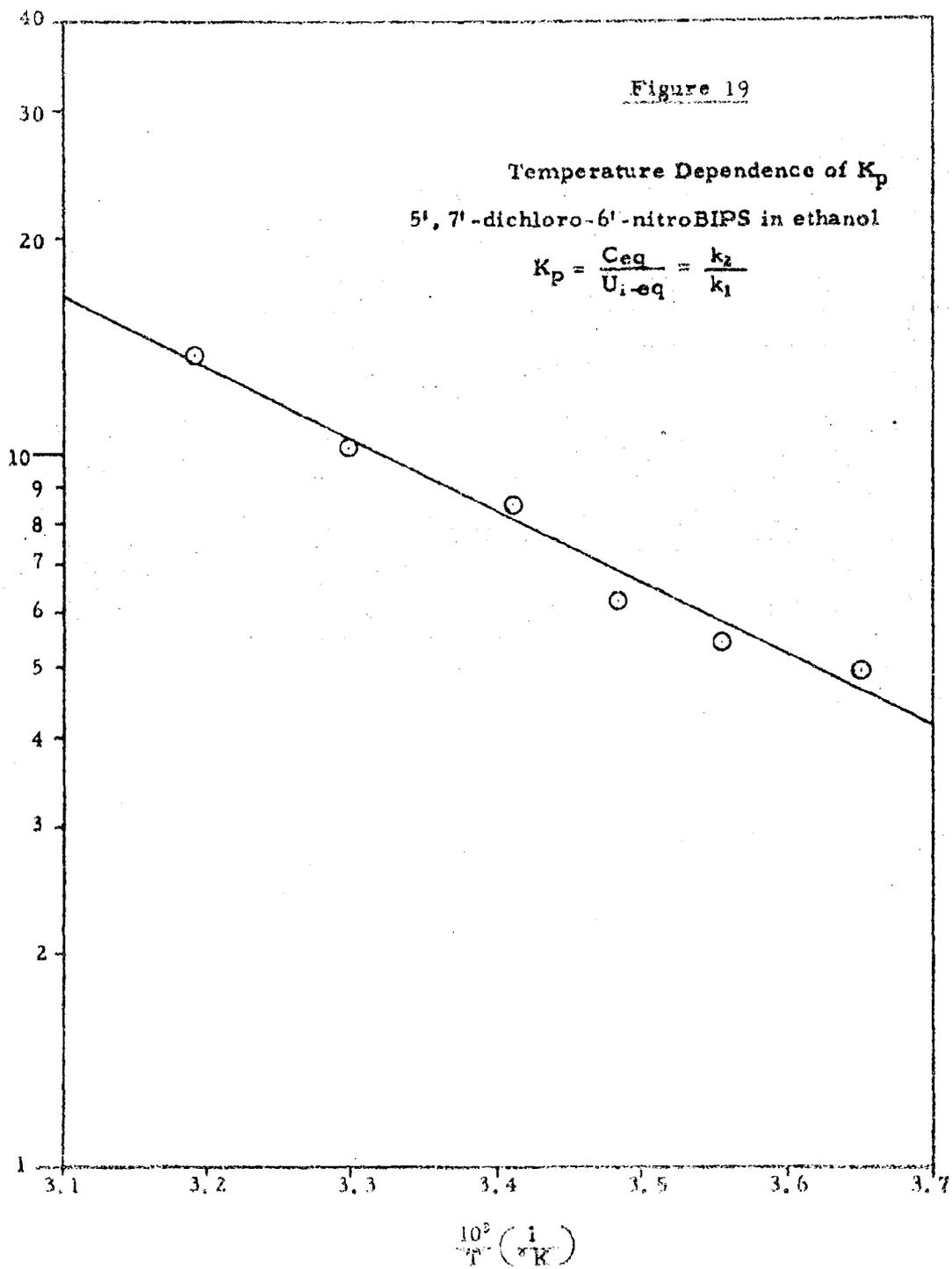
$$k_3 = \frac{(K_p + 1) k_s}{K_p (1 + K_c)} \approx \frac{(K_p + 1) k_s}{K_p} \quad (38)$$

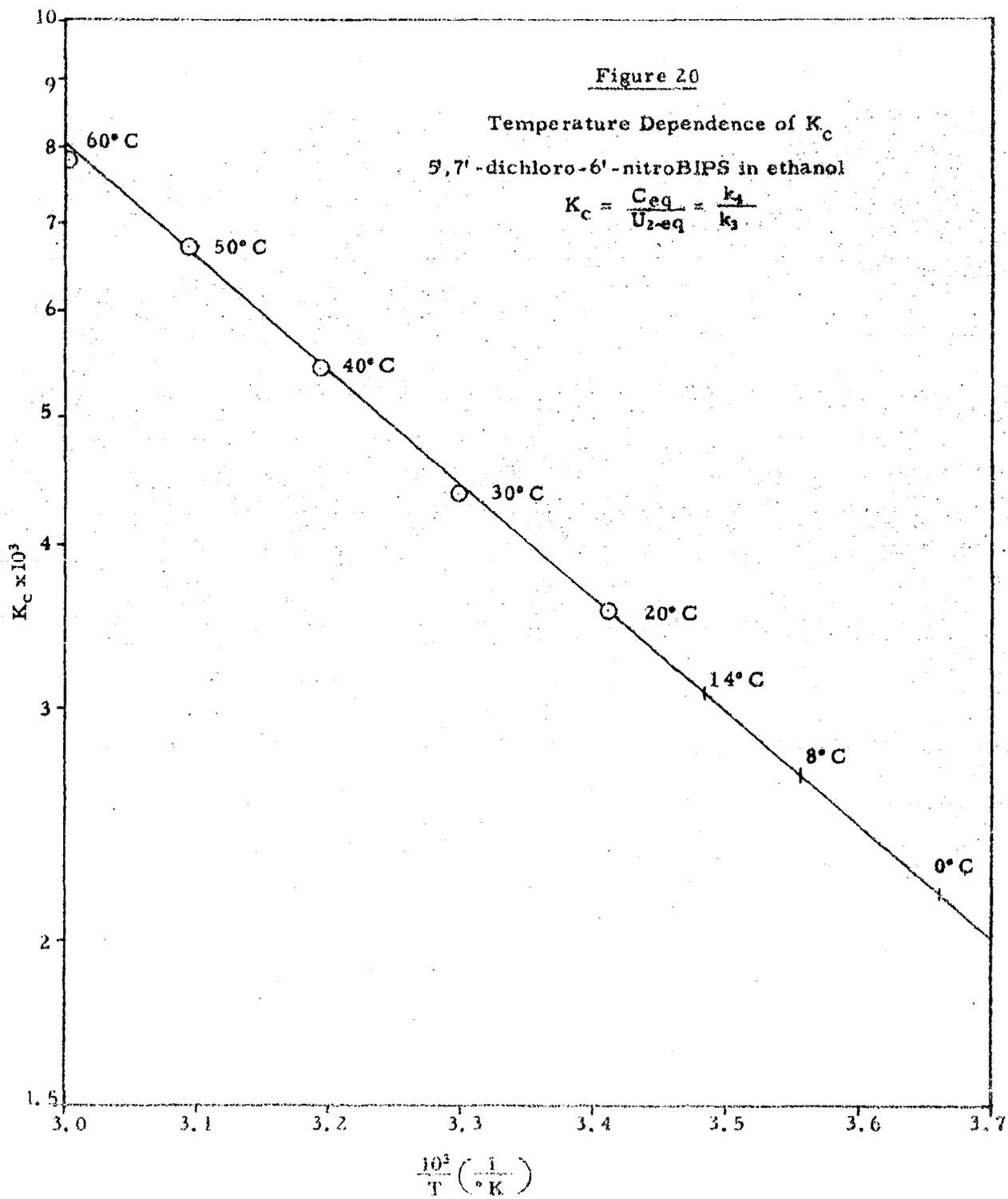
since $1 \gg K_c$,

$$k_4 = \frac{K_c (K_p + 1) k_s}{K_p} \quad (39)$$

$$k_5 + k_6 = k_t \quad (40)$$







$$K_t = \frac{k_6}{k_5} \quad (41)$$

$$k_5 = \frac{k_t}{K_t + 1} \approx k_t \quad (42)$$

since $1 \gg K_t$,

$$k_6 = \frac{K_t k_t}{K_t + 1} = K_t k_t \quad (43)$$

Table 5 is a listing of the measured rate constants at different temperatures. Table 6 lists the calculated true first-order rate constants at different temperatures. In making the calculations described in equations (33), (34), (38), (39), (42) and (43) the values used for the appropriate equilibrium constants were obtained from the lines drawn on Figures 18, 19, and 20.

2.3. Calculation of thermodynamic functions from rate constants and equilibrium constants. - As has been previously demonstrated⁵, ΔH^0 for the equilibria can be obtained from the slope of a plot of $\ln K_{eq}$ vs. $\frac{1}{T}$. Since -

$$\Delta F^0 = -RT \ln K_{eq} \quad (44)$$

The standard free energy (ΔF^0) can be calculated for each equilibrium reaction from the value of the equilibrium constant at a given temperature.

Since -

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0}{T} \quad (45)$$

the standard entropy of reaction (ΔS^0) can also be calculated. These thermodynamic functions are listed for the three equilibrium reactions at 30°C on Table 7.

The Arrhenius equation relates rate constant with activation energy in the following manner -

$$k_r = A \exp(-E_A/RT) \quad (46)$$

or

$$\ln k_r = \ln A - \frac{E_A}{RT} \quad (47)$$

where k_r = rate constant for reaction

E_A = activation energy

A = frequency factor

TABLE 5

Measured Rate Constants for
Solutions of 5', 7'-dichloro-6'-nitroBIPS

Temperature (°C)	k_f (sec. ⁻¹)	k_s (sec. ⁻¹)	k_t (sec. ⁻¹)
0	1.98×10^{-4}	2.26×10^{-7}	
8	4.43×10^{-4}	7.98×10^{-7}	
14	1.01×10^{-2}	2.04×10^{-6}	6.37×10^{-4}
20	3.06×10^{-2}	5.58×10^{-6}	1.55×10^{-2}
30	1.29×10^{-2}	2.88×10^{-5}	6.10×10^{-2}
40	2.84×10^{-2}	1.26×10^{-4}	1.95×10^{-2}
50		4.95×10^{-4}	
60		1.73×10^{-3}	

TABLE 6

Calculated First-Order Rate Constants
for Solutions of 5', 7'-dichloro-6'-nitroBIPS

Temp- erature (°C)	k_1 (sec. ⁻¹)	k_2 (sec. ⁻¹)	k_3 (sec. ⁻¹)	k_4 (sec. ⁻¹)	k_5 (sec. ⁻¹)	k_6 (sec. ⁻¹)
0	3.95×10^{-5}	1.63×10^{-4}	2.74×10^{-7}	5.97×10^{-10}		
8	6.51×10^{-5}	3.78×10^{-4}	9.35×10^{-7}	2.50×10^{-9}		
14	1.28×10^{-4}	8.82×10^{-4}	2.34×10^{-6}	7.23×10^{-9}	6.37×10^{-4}	9.68×10^{-9}
20	3.36×10^{-4}	2.72×10^{-4}	6.27×10^{-6}	2.24×10^{-8}	1.55×10^{-3}	2.90×10^{-9}
30	1.12×10^{-3}	1.17×10^{-3}	3.15×10^{-5}	1.40×10^{-7}	6.10×10^{-3}	1.62×10^{-7}
40	1.98×10^{-3}	2.64×10^{-3}	1.35×10^{-4}	7.39×10^{-7}	1.95×10^{-2}	7.06×10^{-7}
50			5.25×10^{-4}	3.50×10^{-6}		
60			1.81×10^{-3}	1.45×10^{-6}		

TABLE 7

Thermodynamic Functions Derived from Equilibrium
Measurements on Solutions of 5', 7'-Dichloro-6'-NitroBIPS

<u>Process</u>	<u>ΔH°</u> <u>(cal/mole)</u>	<u>ΔF°</u> <u>(cal/mole)</u>	<u>ΔS°</u> <u>(cal/°K mole)</u>
$U_1 \rightarrow C$ (30° C, ethanol)	4,600	-1,400	19.6
$U_2 \rightarrow C$ (30° C, ethanol)	3,900	3,200	2.2
$U_2 \rightarrow C$ (30° C, toluene)	6,100	6,300	-0.7

Therefore, from the slope of a plot of $\ln k_r$ vs. $\frac{1}{T}$ the activation energy for the reaction (E_A) can be calculated, while the frequency factor (A) can be obtained from the intercept of this plot.

Figures 21 through 26 are Arrhenius plots for the six rate constants studied.

From transition state ⁶ theory it is known that -

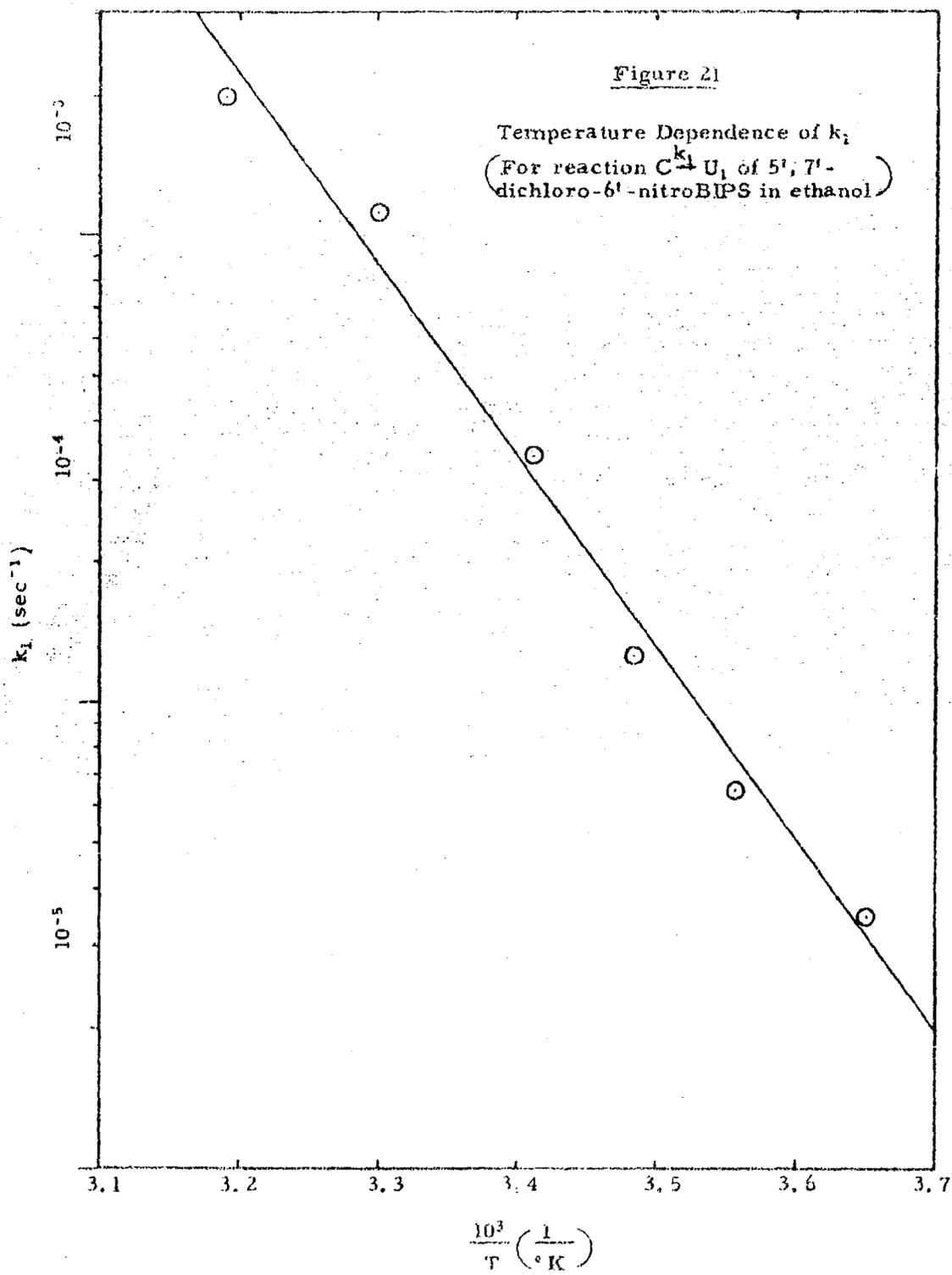
$$\Delta H^\ddagger = E_A - RT \quad (48)$$

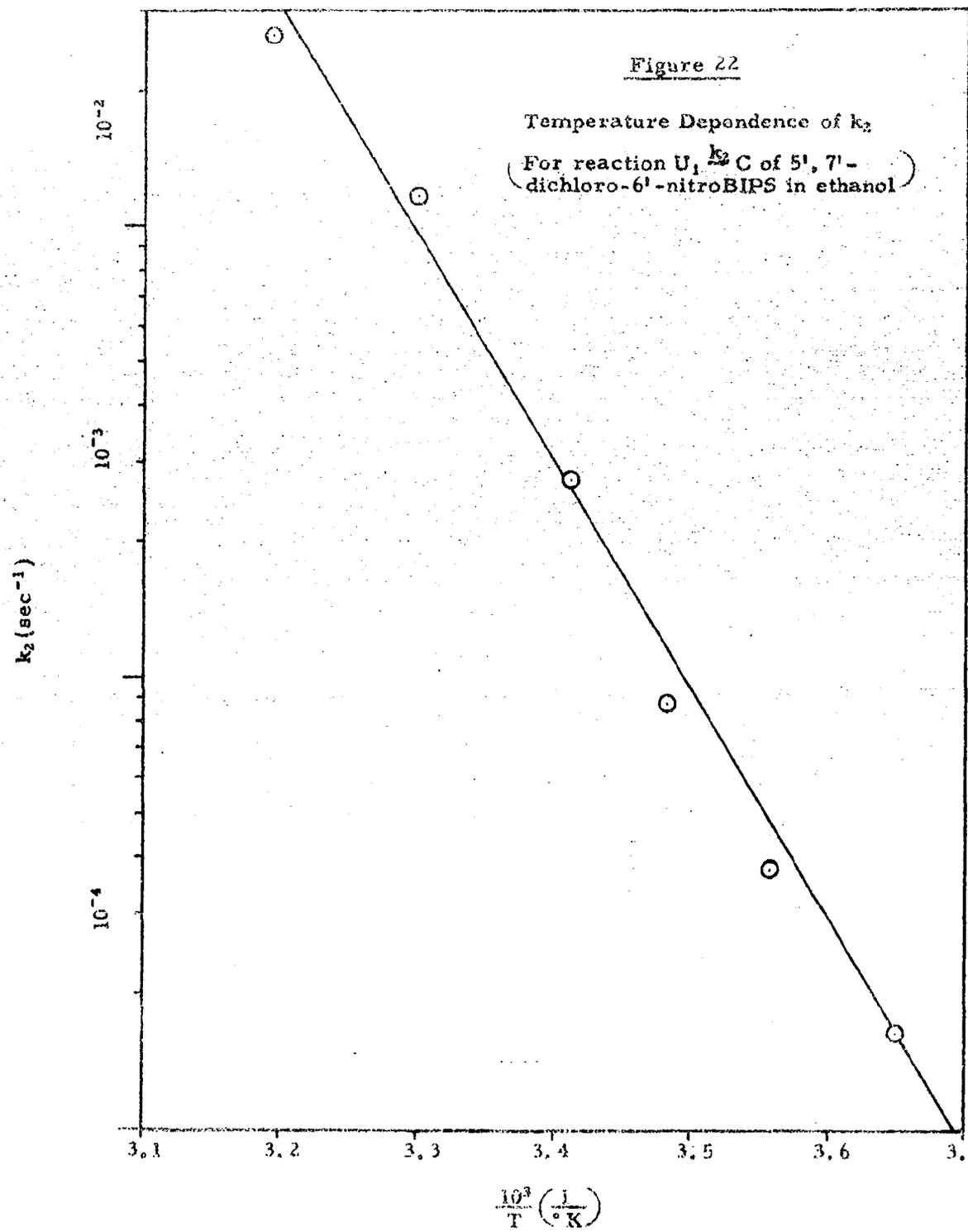
$$\Delta S^\ddagger = R \ln \frac{hA}{kT} \quad (49)$$

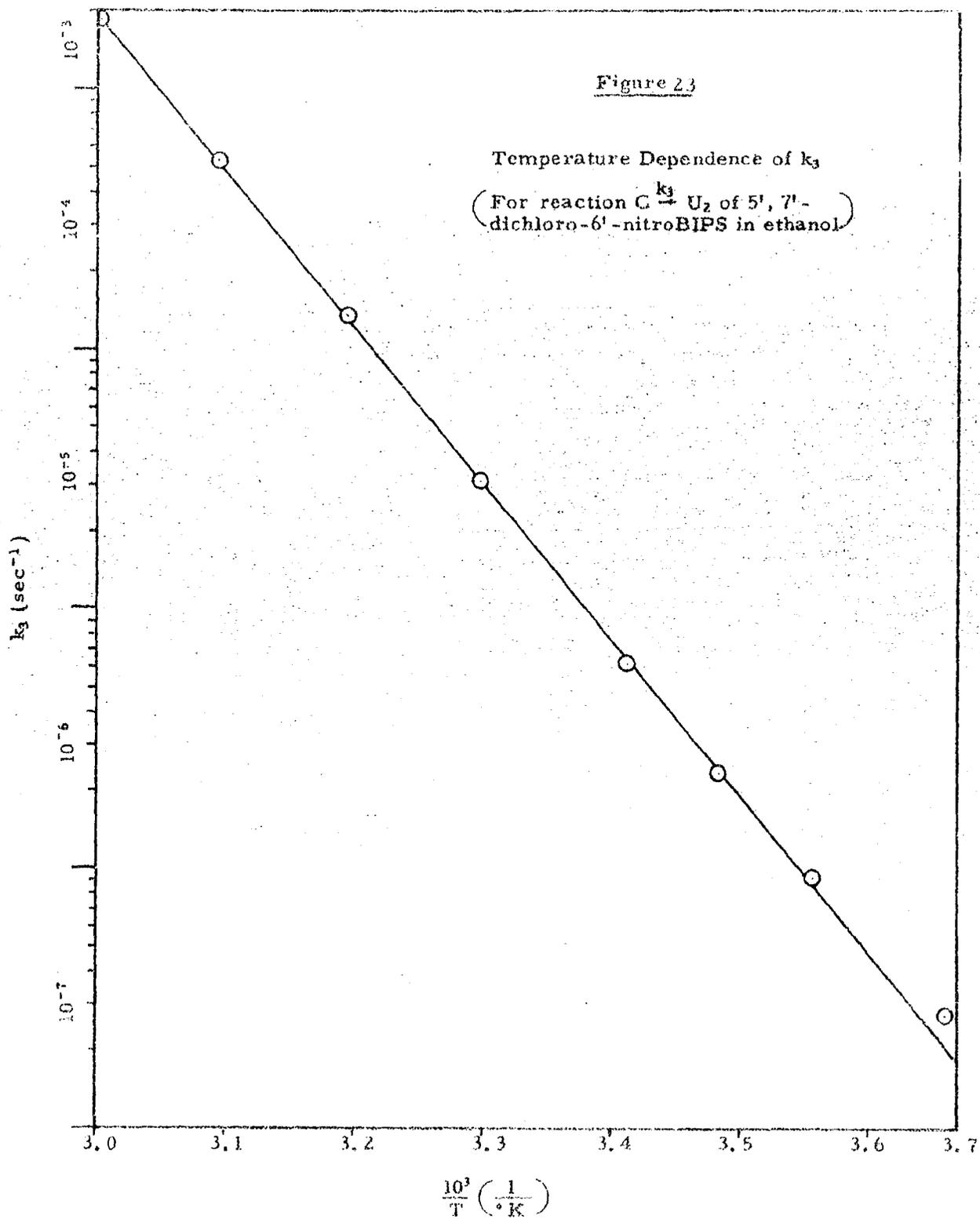
$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (50)$$

where ΔH^\ddagger = enthalpy of activation
 ΔS^\ddagger = entropy of activation
 ΔF^\ddagger = free energy of activation
h = Planck's constant
k = Boltzmann constant

The values of the "thermodynamic" functions are listed for the six rate processes at 30°C on Table 8.







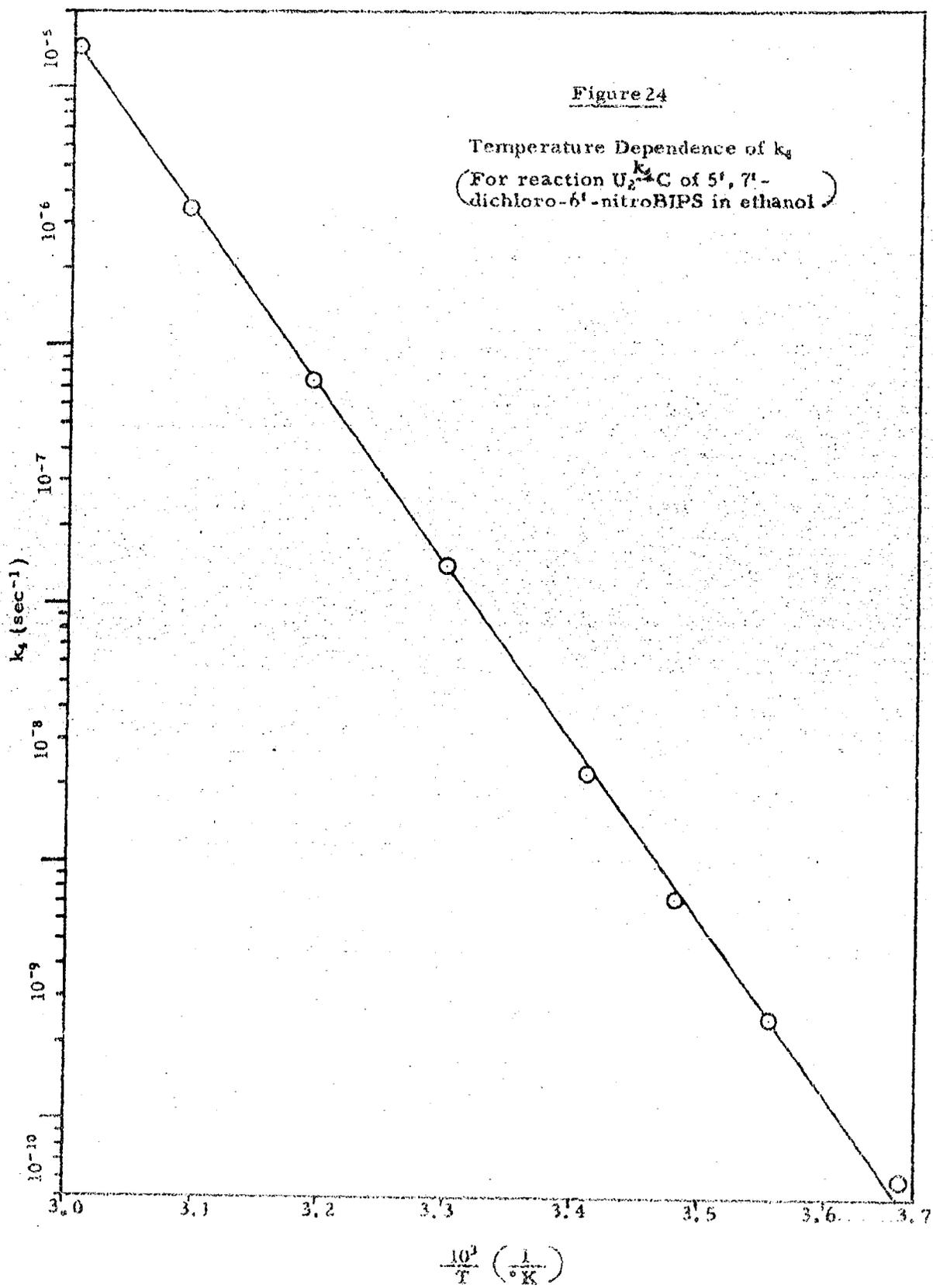


Figure 25

Temperature Dependence of k_5
(For reaction $C \xrightarrow{k_5} U_2$ of 5, 7'-
dichloro-6'-nitroBIPS in toluene)

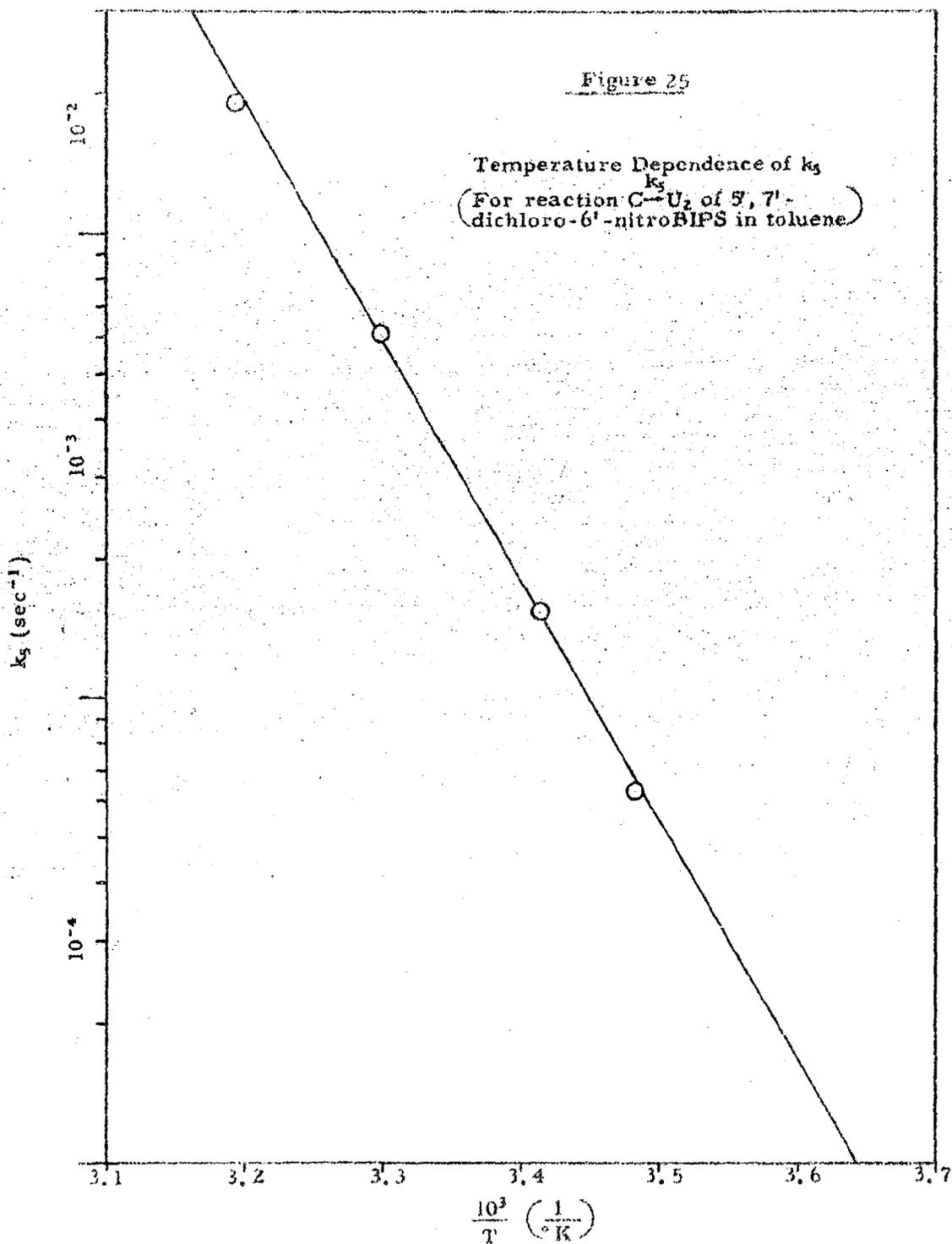


Figure 26

Temperature Dependence of k_6
(For reaction $U_2 \xrightarrow{k_6} C$ of 5', 7'-
dichloro-6'-nitroBIPS in toluene.)

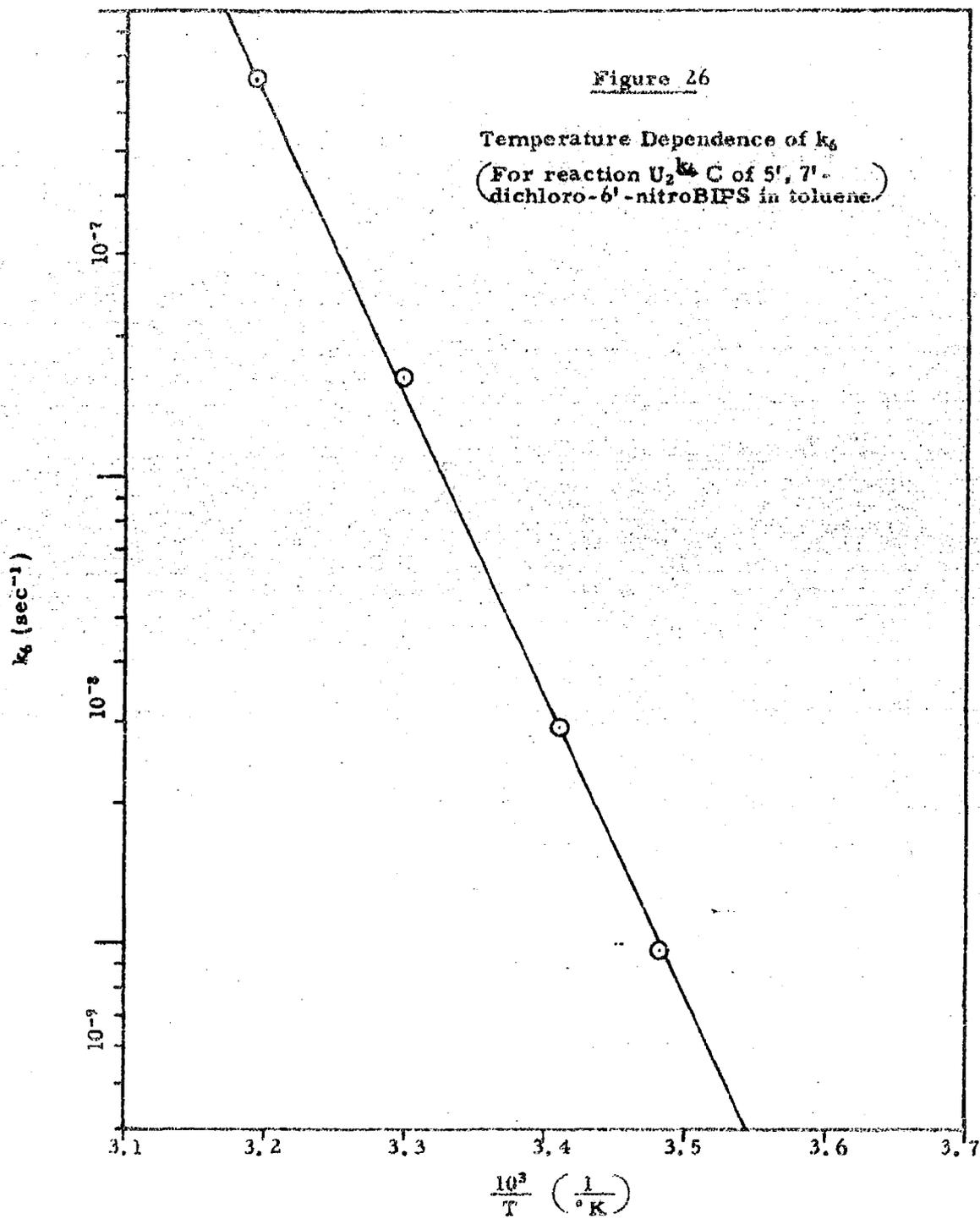
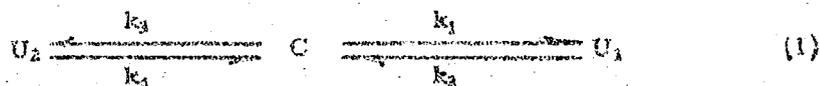


TABLE 8

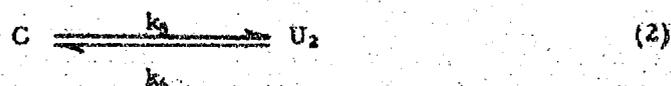
"Thermodynamic" Functions Derived from
Rate Measurements of Solutions of 5, 7'-Dichloro-6'-NitroBIPS

Process	E_A (cal/mole)	A (sec. ⁻¹)	ΔH^\ddagger (cal/mole)	ΔF^\ddagger (cal/mole)	ΔS^\ddagger (cal./°K mole)
$C \xrightarrow{k_1} U_1$ (ethanol, 30°C)	18,700	2.66×10^{10}	18,160	21,400	-11.0
$U_1 \xrightarrow{k_2} C$ (ethanol, 30°C)	22,700	2.26×10^{14}	22,100	19,700	8.0
$C \xrightarrow{k_3} U_2$ (ethanol, 30°C)	27,400	1.81×10^{15}	26,800	23,400	11.2
$U_2 \xrightarrow{k_4} C$ (ethanol, 30°C)	31,300	5.27×10^{15}	30,700	26,600	13.4
$C \xrightarrow{k_5} U_2$ (toluene, 30°C)	23,560	5.19×10^{14}	22,800	20,000	9.0
$U_2 \xrightarrow{k_6} C$ (toluene, 30°C)	29,300	2.32×10^{14}	28,700	26,500	7.2

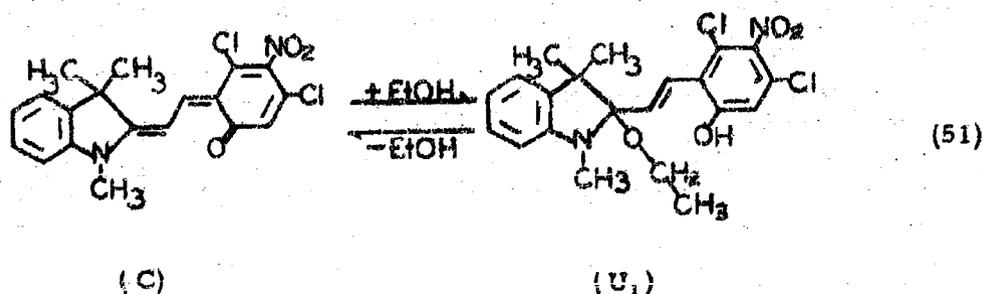
2.4. Conclusions. - It has been demonstrated that ethanolic solutions of 5', 7'-dichloro-6'-nitro BIPS undergo the following thermal reactions -



where U_1 and U_2 represent two distinct colorless BIPS species in dynamic equilibrium with the colored modification of the BIPS, C. In toluene, however, equilibration takes place by only one set of reactions.



One explanation of this behavior is the hypothesis that the fast decoloration reaction in ethanol is due to a nucleophilic attack on the spiro carbon atom of the open spiropyran form by an ethanol molecule⁷. Equation (51) describes this process.



If equation (51) actually does take place then the U_1 formed would not be expected to absorb in the visible since the conjugation length is shortened. It would also explain why in non-polar solvents, where such an attack is impossible, there is observed only one thermal fade rate.

One could also expect that this effect could be greatly magnified by the addition of a base which would act as a much stronger nucleophilic agent than ethanol.

If a strong base such as NaOH, NaOCH₃, etc., is added to a solution of the colored modification of 5', 7'-dichloro-6'-nitro BIPS at room temperature the red or blue color (depending on the solvent) immediately disappears leaving a yellow solution, while at -80°C the original colored BIPS solution remains unchanged. The addition of water or acid, to this yellow solution restores the solution to its original color. This indicates that the colored (open) modification of the spiropyran is in some manner bound to the base but, since color is instantly renewed when acid is added, probably still retains its open configuration.

The yellow base-adduct, just described, does not appear to have any photochromic properties. Ultraviolet irradiation of the yellow solution does not appear to change either the spectrum or the properties of the compound either at room temperature or at -80°C. (It might be assumed that a photochromic splitting of the base adduct might not be observable at room temperature due to a rapid recombination of the base with the spiropyran. However, no photochromic reaction takes place at -80°C, a temperature at which the recombination reaction has been shown to be negligible. If one is willing to assume that this base-adduct has a similar structure to U₁, then it appears very likely that U₁ is non-photochromic.

Figures 27, 28, and 29 are sketches of the various energy and entropy changes that the 5', 7'-dichloro-6'-nitro BIPS undergoes during its thermal transitions. Although the science of thermodynamics does not depend on molecular structure it is possible to make some structural interpretations of the energy and entropy values shown on Figures 27, 28, and 29.

The energy or enthalpy should give a rough measure of bond-strength and resonance stabilization. The entropy is a measure of the possible configurations of the molecules or it can be looked upon as representing a steric factor.

Figure 27 demonstrates that in ethanol U₁ and U₂ have almost the same energy while C is the least favored form energetically by

about 4 Kcal/mole. The activation energies range from approximately 20 - 30 Kcal/mole., which is not unusual for solution processes of this type.

Figure 28 shows the entropy relationships for the processes in ethanol. It is immediately evident that both U_2 and C are of considerably greater entropy than U_1 . High entropy indicates more possible molecular configurations or less steric hindrance. It therefore appears that the U_1 form has considerable steric hindrance. If the U_1 modification actually has the structure as shown in equation (51) it is not unreasonable to assume that things could be cramped around the spiro-carbon atom. A further experimental verification of this structure would be to measure the shift in K_p with butanol as a solvent and with methanol or EtOH - H₂O as a solvent. In the first case the steric effect should be even larger and the equilibrium should be shifted towards the colored species. In the second and third cases the reverse should hold true.

It is believed that the colorless form (U_2) consists of two ring structures joined at right angles to each other at the spiro-carbon atom as shown below:

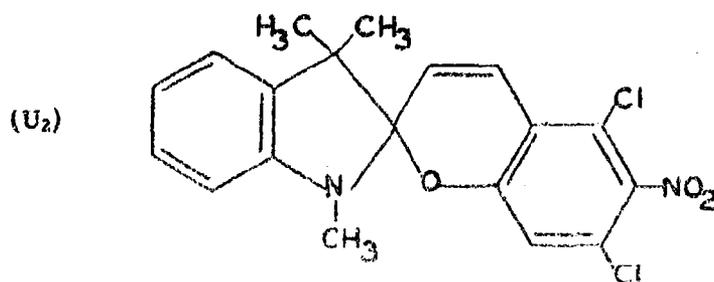


Figure 27

Energy Relationships among the Various Species
of 5', 7'-Dichloro-6'-NitroBPS in Ethanol at 30° C

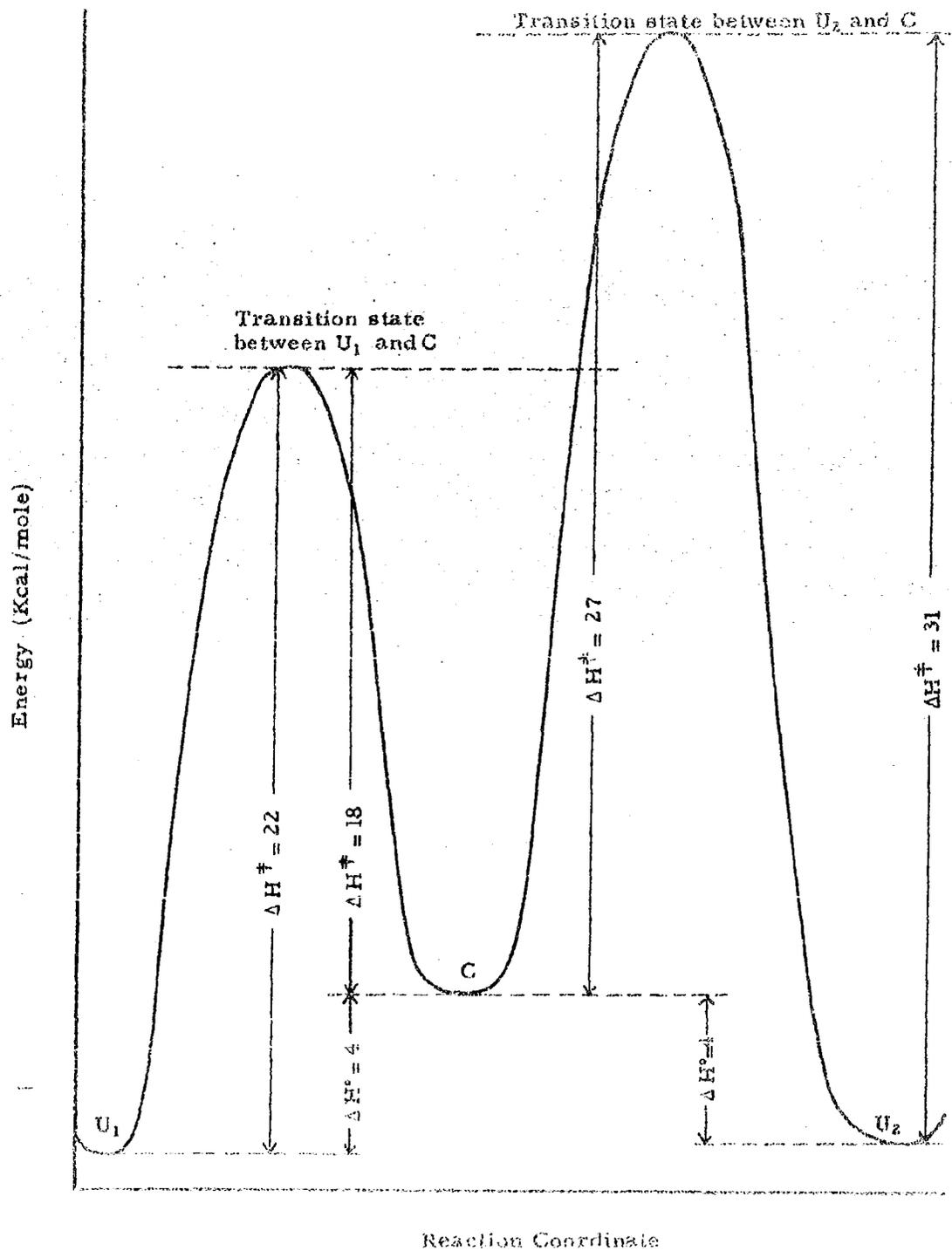


Figure 28

Entropy Relationships among the Various Species of 5', 7'-Dichloro-6'-NitroBIPS in Ethanol at 30° C

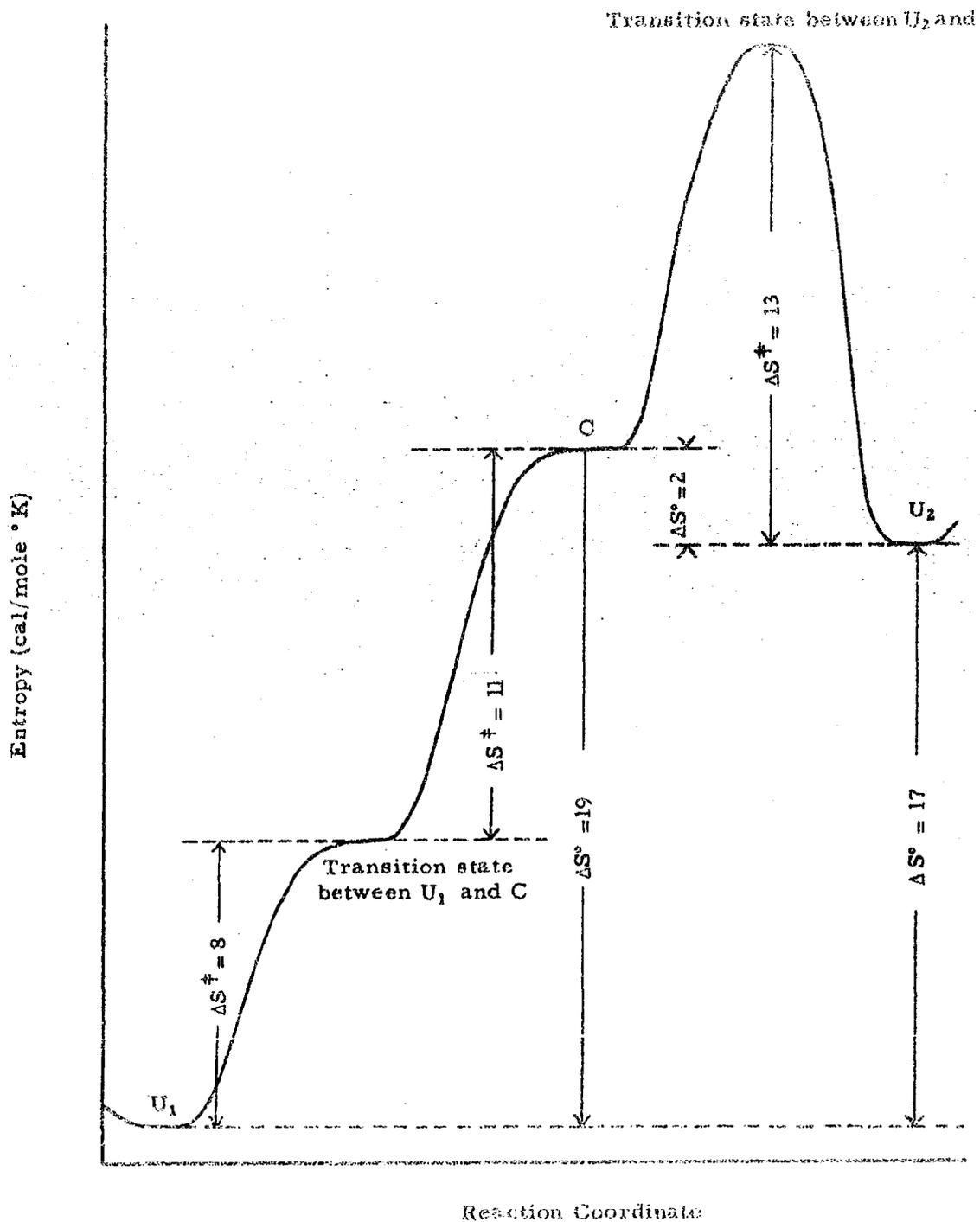
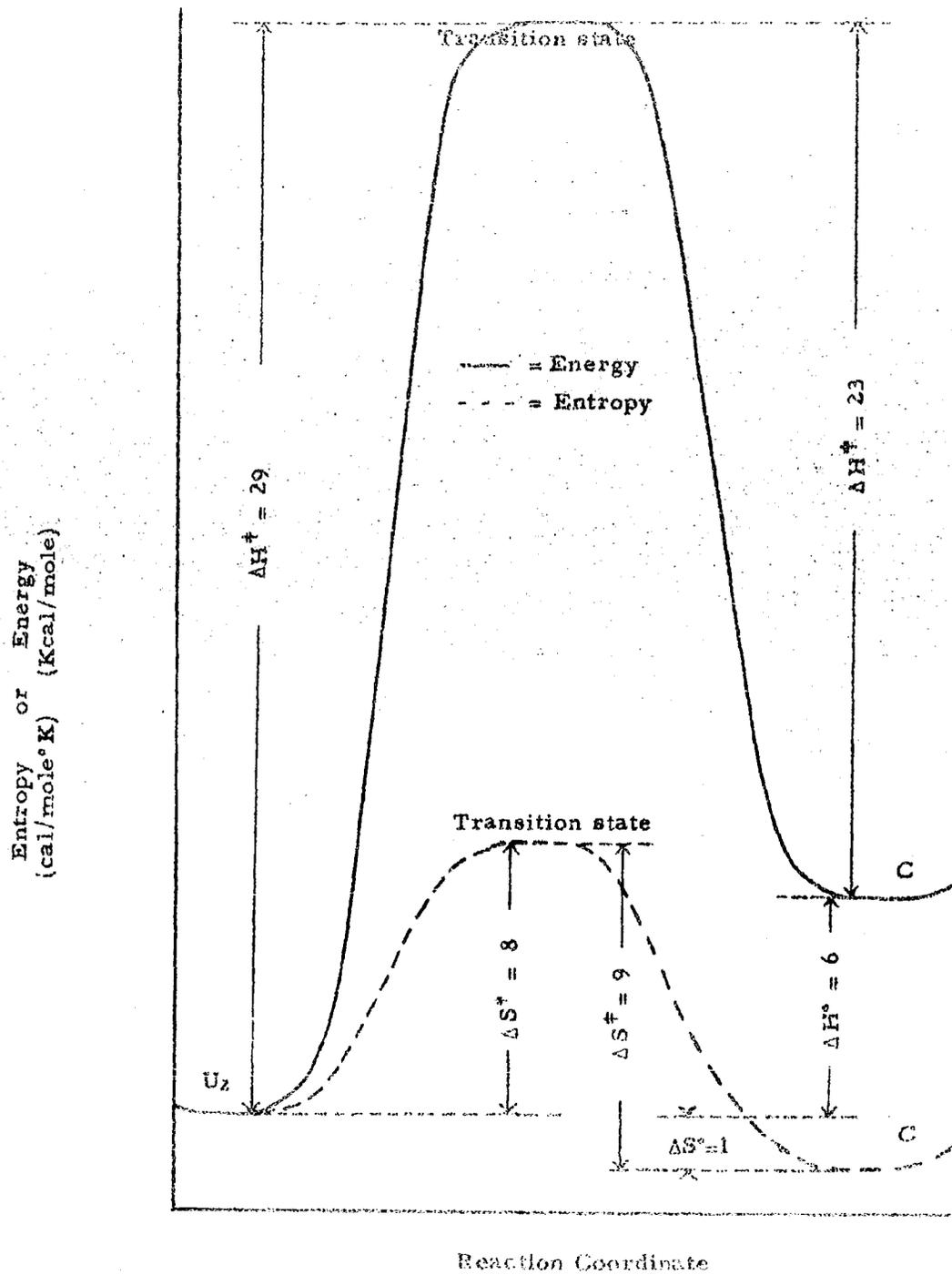
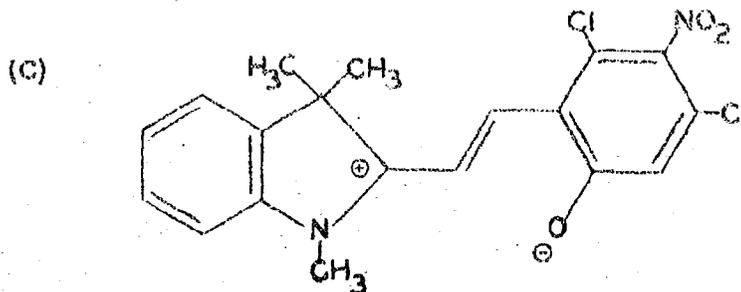


Figure 29

Energy and Entropy Relationships among the Various Species of 5', 7'-Dichloro-6'-NitroBIPS in Toluene at 30° C



It is thought that the bond between the oxygen atom in the ring system and the spiro-carbon atom opens to yield the colored form -



From a comparison of the structures of U_2 and C a conclusion might be reached that there are more configurations available to C than to U_2 and that C should be the entropically favored species. An examination of Figures 28 and 29, however, indicates that there is very little entropy difference between C and U_2 in either ethanol or toluene. The following reasons are offered in explanation of this fact.

1) The colored species (C) is limited to only planar configurations. Any non-planar configurations would break up the conjugation system and thus destroy any visible absorption.

2) The entropy change measured is that of the complete system and therefore the entropy change in the solvent must also be considered. The colored form (C) is more polar than the colorless species (U_2). The solvent molecules would be more strongly attracted to C molecules than to molecules of U_2 . This would result in a decrease in the possible configurations of solvent molecules with an

overall decrease in entropy of the solvent molecules when $U_2 \rightarrow C$. This decrease in entropy would be compensated for by the greater number of configurations possible to the colored form. The overall result could correspond with the very small calculated entropy change.

It is interesting to note that the transition state between C and U_2 is of high entropy than either C or U_2 . This phenomenon indicates that there are more allowable configurations of the BIPS molecule immediately before or immediately after the formation or rupture of the carbon-oxygen bond than there are in the lower-energy vibrational levels of either species.

In summary, it may be stated that the detailed study of the thermal behavior of 5', 7' -dichloro-6'-nitro BIPS has been successfully concluded. The information obtained should be of considerable value in the thermal and photochemical studies of other photochromic compounds.

3. PHOTOCHEMICAL STUDIES OF 5', 7'-DICHLORO-6'-NITRO BIPS

3.1. Instrumentation for quantitative photochemical measurements.

The apparatus, as shown on Figure 30, was designed to perform the following functions:

- (1) Obtain accurate values of quantum efficiencies
- (2) Follow the increase or decrease of color continuously as a function of time
- (3) Allow for simultaneous irradiation and readout either at different or the same wavelengths
- (4) Eliminate errors due to scattered or fluorescent light
- (5) Provide a cross-check on the light absorbed by the reaction solution
- (6) Insure homogeneity of the reaction solution through efficient stirring.

The set-up is essentially a Beckman model DU spectrophotometer, modified so that the sample can be irradiated by an auxiliary light source while in a readout position.

The monochromator section of the DU has been placed on a 6 inch stand, thus allowing access to the under side of the cell compartments. A 10 cm. cell compartment, placed next to the monochromator, frees the reaction compartment from the lamp housing. The reaction compartment has 1 1/4" x 1/2" openings in each end to allow for the entrance and exit of excitation radiation. Contained in the compartment is a thermostatted brass cell holder which can accommodate two 1 cm. reaction cells (4 sides optically clear). In the bottom of the compartment a brass bushing supports a shaft to which is attached a cylindrical magnet about 3/8" in diameter, which protrudes through the bottom of the cell holder and is positioned slightly below the reaction cell. Rotation of this large magnet causes rotation of a small Teflon embedded magnet that stirs the reaction solution.

The optical train is mounted on a small optical bench perpendicular to the readout path of the DU and consists of the following components:

- (1) The light source, a 550 watt Hanovia (673A-10) medium pressure mercury arc contained in a water cooled housing
- (2) A quartz lens 3" diameter, 4" focal length
- (3) A filter for isolating the mercury lines
- (4) A shutter arrangement

With the exception of the light source these components are mounted in telescoping tubing to exclude all stray light.

The cover for the standard cell compartment (between the reaction cell compartment and the D. U. photomultiplier) supports a rotating, cylindrical shutter which is connected through a flexible cable to an identical shutter positioned at the entrance to the photoreaction compartment. The shutters are driven out of phase with each other by an 1800 RPM synchronous motor. Thus no irradiating light enters the reaction cell compartment during readout and vice versa. This system eliminates errors in readout due to stray light caused by scattering and fluorescence and allows readout at or near the irradiating wavelength. Attached to the exit of the photoreaction compartment, is an Aminco photomultiplier detector which is used to determine the total amount of excitation radiation that is absorbed by the sample.

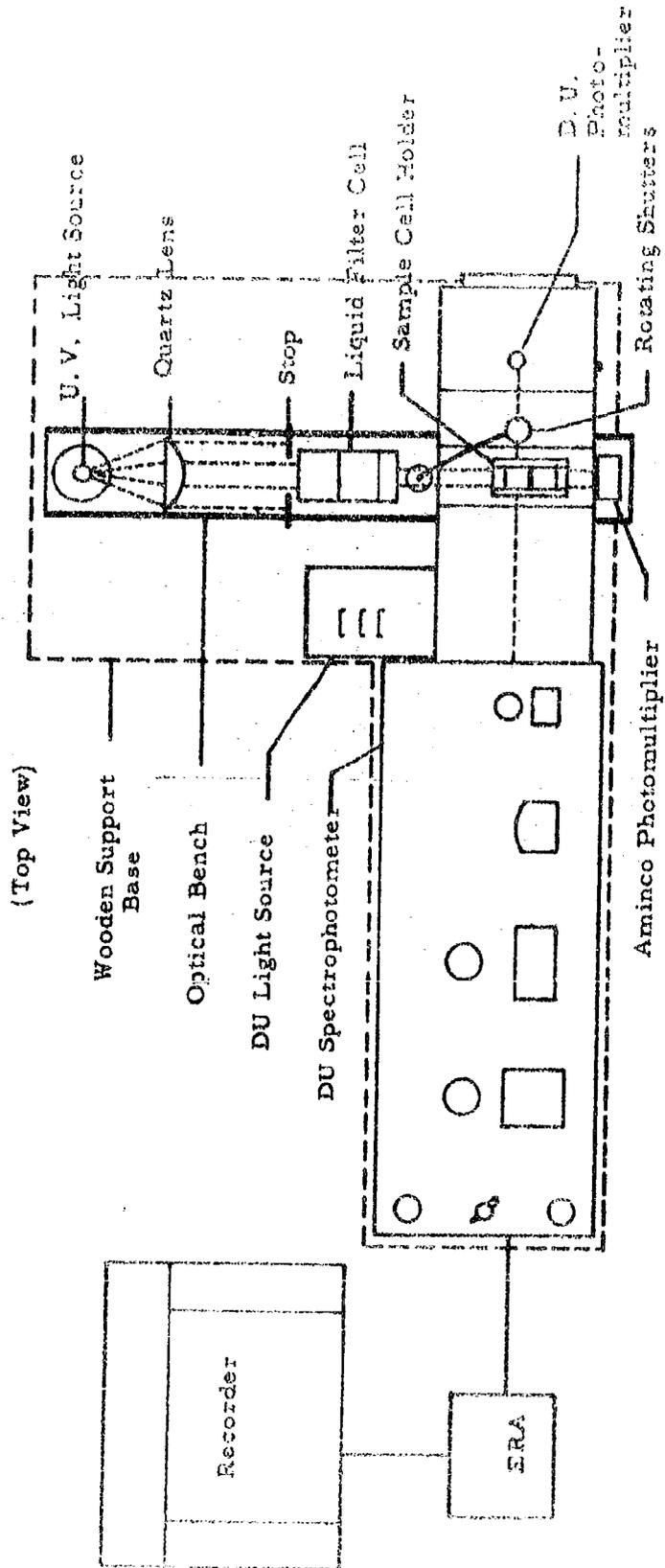
3.2. Filters for isolation of mercury lines - The 366 m μ group of the mercury spectrum was isolated by the use of corning filters No. 7380 and 5860. This combination has a transmittance of 0.18 at 366 m μ , and a band half-width of 22 m μ .

The 313 m μ group was isolated by a combination of solution filters contained in a three compartment quartz windowed cell plus a corning glass filter. The following solutions were used⁸: 5 cm. of 0.178 M nickel chloride, 5 cm. of 0.0005 M potassium chromate; 1 cm. of 0.0245 M potassium biphthalate. The glass filter was a 3 mm. Corning filter No. 9863. This combination has a transmittance of 0.33 at 313 m μ and a band half-width of 12 m μ .

3.3. Actinometric determination of light intensities - The actinometer system used was that described by Hatchard and Parker⁹. Potassium ferrioxalate decomposes with light to give ferrous ions.

Figure 30

Apparatus for Photochemical Measurements



These ions react with o-phenanthroline to give an orange colored complex which can be determined spectrophotometrically.

Appropriate solutions were prepared and a calibration curve constructed (see Figure 31) for the ferrous-phenanthroline complex. The extinction coefficient for the complex calculated from this data is 1.107×10^4 liter/mole cm. at 510 m μ .

After allowing sufficient warm up time for the Hg lamp, each of two 1 cm cells were filled with 2.93 ml of 0.006 M potassium ferrioxalate in 0.1 M H₂SO₄. The sample cell was irradiated for a measured time under conditions identical with those to be used on the photochromic samples. 0.51 ml of phenanthroline-buffer solution was added to each cell and the absorbance of irradiated solution was determined at 510 m μ on a Beckman Model DU spectrophotometer using the non-irradiated solution as a blank. The incident intensity (I) of monochromatic radiation entering the actinometer solution is given by the following equation:

$$I = \frac{A_{510} V}{t \epsilon_{510} \phi P} \quad (52)$$

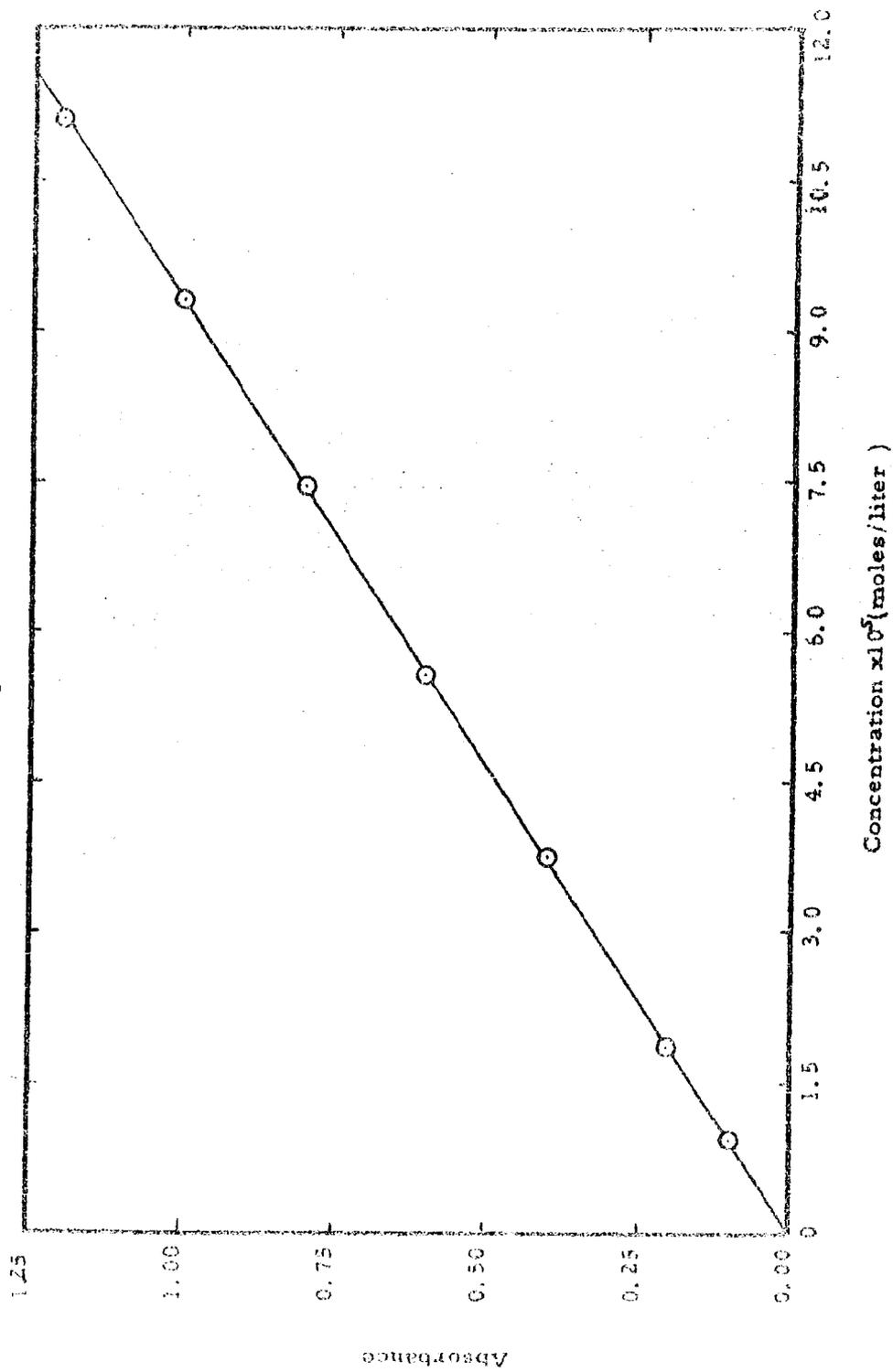
where -

- A₅₁₀ = Absorbance of ferrous-phenanthroline solution at 510 m μ
- V = Total volume of actinometer solution (3.44×10^{-3} liter)
- t = Time in minutes
- ϵ_{510} = Molar absorptivity ferrous-phenanthroline complex at 510 m μ . ($\epsilon_{510} = 11,070$ liter mole⁻¹ cm.⁻¹)
- ϕ = Quantum efficiency of ferrioxalate at irradiating wavelength. ($\phi = 1.21$ mole einstein⁻¹ at 366 m μ and $\phi = 1.24$ mole einstein⁻¹ at 313 m μ)
- P = Path length of irradiating light (cm.)
- I = Incident intensity of radiation on actinometer solution (einstein min.⁻¹)

From this quantity the value of I₀, that is used in the rate equations for photoconversion, can be calculated from the following relationships:

Figure 31

Calibration Curve for Ferrous-Phenanthroline
in pH 3.5 Buffer



$$I_0 = \frac{I}{V_b} \quad (53)$$

Where -

V_b = Volume of BIPS solution irradiated during photo-conversion (liter)

The actinometer system Malachite green leucocyanide was also used to obtain incident light intensities. In an ethanol solution this material turns from colorless to green with a quantum yield of 1.00^{10} at 313 m μ irradiation. A neutral density filter (of measured transmittance) was inserted between the source and the sample to reduce the radiation to a level where the actinometer functions properly. The calculation of incident light intensity is identical to that of the previously described procedure.

Values of light intensity shown below, determined by these two independent systems are in good agreement considering that the constants used in the calculations for Malachite green system were taken from the literature and not redetermined on our own instruments.

	<u>Incident Light Intensity</u>	
	<u>Ferrioxalate</u>	<u>Malachite Green L. G.</u>
Run No. 1	2.17×10^{14} Photons/sec.	1.83×10^{14} Photons/sec.
Run No. 2	2.23×10^{14} Photons/sec.	1.97×10^{14} Photons/sec.

3.4. Solvent absorption - In the determination of quantum yield it is necessary to know the amount of light absorbed by the reacting species. Absorption of light by the solvent due to impurities or to the inherent electron structure of the solvent molecule must therefore be taken into consideration. To determine the absolute absorption of the solvent itself, corrections must be made for reflections at the cell window interfaces and for the absorption of the cell windows¹¹.

Assume a cell having two parallel quartz windows with the angle of incidence at 90°



The reflectivity at an interface is:

$$\rho_j = \left(\frac{n_1 - n_0}{n_1 + n_0} \right)^2 \quad (54)$$

where n_0 and n_1 are the refractive indices of the substances forming the interface at the irradiating wavelength.

let Z'_j = Total light losses at interfaces up to and including j

$$\text{then } Z'_4 = \frac{Z'_3 + \rho_4 - 2Z'_3 \rho_4}{1 - Z'_3 \rho_4} \quad (55)$$

$$\text{where } Z'_3 = \frac{Z'_2 + \rho_3 - Z'_2 \rho_3}{1 - Z'_2 \rho_3} \quad (56)$$

$$\text{and } Z'_2 = \frac{\rho_1 + \rho_2 - 2\rho_1 \rho_2}{1 - \rho_1 \rho_2} \quad (57)$$

From the cell filled with air (empty) the light losses due to absorption and scattering by the windows (Z_w) can be calculated (assuming air to be 100% transparent).

$$Z_w = 1 - (T_{\text{air}} + Z'_4 \text{ air}) \quad (58)$$

where T is the measured transmittance

Using this correction, the absolute transmittances (T_A) of other substances within the cell may be calculated.

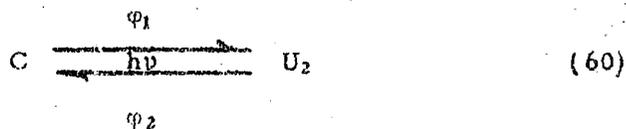
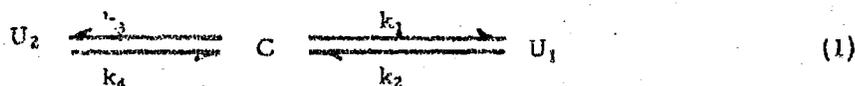
$$T_A = T + Z'_4 + Z_w \quad (59)$$

The data and results for these calculations are compiled in Table 9.

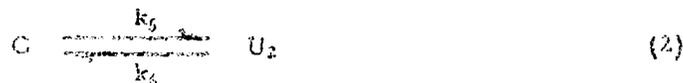
TABLE 9 - Absorption of Light by Solvents

Substance	$n_{1.13}$	Light Losses (Z'_4)	$T_{1.13}$ (10 cm.)	$T + Z'_4$	Window Absorption (Z'_w)	$T_A/10\text{cm.}$ (Absolute Trans.)
Quartz	1.48	---	---	---	---	---
Air	1.00	.136	.842	.978	.022	1.000
Water	1.33	.080	.896	.976	.022	.998
Toluene	1.51	.073	.315	.388	.022	.410

3.5. Rate equations for simultaneous reversible photochemical and thermal reactions of BIPS compounds.¹² - Consider a BIPS compound in ethanol or some other polar solvent being irradiated with monochromatic light of such a wavelength that photochemical switching is possible. In this system the following reactions take place.



As has been mentioned previously, there is reason to believe that there is no photochromic transformation between C and U_1 and vice versa. If this reaction were carried out in a non-polar solvent where there is no fast thermal rate then instead of equation (1) we would have equation (2).



Going back to eq. (1) and eq. (60) the following rate equations describe the formation of C, U_1 , and U_2 as a function of time.

$$\frac{dC}{dt} = -(k_1 + k_2)C + k_3 U_1 + k_4 U_2 - \phi_1 I_{ac} + \phi_2 I_{au_2} \quad (61)$$

$$\frac{dU_1}{dt} = k_1 C - k_3 U_1 \quad (62)$$

$$\frac{dU_2}{dt} = k_2 C - k_4 U_2 + \phi_1 I_{ac} - \phi_2 I_{au_2} \quad (63)$$

$$\text{and } C + U_1 + U_2 = T \quad (64)$$

where C, U₁ and U₂ again represent, respectively, the molar concentration of the colored and two colorless BIPS species (mole liter⁻¹).

T = Total BIPS concentration of all species (mole liter⁻¹)

t = Time (min.)

k₁, k₂, k₃ and k₄ are 1st-order rate constants for the individual processes of eq. (1) (min.⁻¹); φ₁ and φ₂ are quantum efficiencies at the irradiating wavelength for the processes of eq. (60) (mole einstein⁻¹).

I_{ac} and I_{au₂} are the intensities of light absorbed by C and U₂ respectively (einstein min.⁻¹ liter⁻¹).

The following assumptions are implied in allowing the above rate equations to describe the formal reactions:

- (1) φ₁ and φ₂ are independent of concentration.
- (2) There is always perfect mixing in the reaction solution.
- (3) If any intermediates are formed, they are short lived and have no effect on the rate determining steps.
- (4) Absorption of light by the solvent is negligible.

Now -

$$i_{ac} = \frac{\epsilon_c C I_a}{\epsilon_1 U_1 + \epsilon_2 U_2 + \epsilon_c C} \quad (65)$$

$$i_{au_2} = \frac{\epsilon_2 U_2 I_a}{\epsilon_1 U_1 + \epsilon_2 U_2 + \epsilon_c C} \quad (66)$$

Where -

I_a = Total intensity of light absorbed by solution (einstein $\text{min.}^{-1} \text{liter}^{-1}$).

ϵ_c , ϵ_1 and ϵ_2 are the molar absorptivities of C, U_1 and U_2 respectively at the irradiating wavelength ($\text{liter mole}^{-1} \text{cm.}^{-1}$).

Also from the Beer-Lambert law -

$$I_a = I_0 \left[1 - 10^{-(\epsilon_1 U_1 + \epsilon_2 U_2 + \epsilon_c C)P} \right] \quad (67)$$

Where -

I_0 = Intensity of light incident on solution (einstein $\text{min.}^{-1} \text{liter}^{-1}$).

P = Path length of irradiating beam (cm.)

and -

$$(\epsilon_1 U_1 + \epsilon_2 U_2 + \epsilon_c C)P = A \quad (68)$$

where A = Optical density or absorbance at irradiating λ .

By appropriate substitution of eqs. (65), (66), (67) and (68) into eqs. (61) and (63) the following rate equations are obtained

$$\frac{dC}{dt} = \frac{I_0 P (1 - 10^{-A})}{A} (\phi_2 \epsilon_2 U_2 - \phi_1 \epsilon_1 C) - (k_3 + k_4)C + k_3 U_1 + k_4 U_2 \quad (69)$$

$$\frac{dU_1}{dt} = k_1 C - k_2 U_1 \quad (70)$$

$$\frac{dU_2}{dt} = \frac{I_0 P (1 - 10^{-A})}{A} (\phi_1 \epsilon_1 C - \phi_2 \epsilon_2 U_2) + k_3 C - k_4 U_2 \quad (71)$$

In general, this set of equations must be solved by approximation methods. In certain specific cases, listed below, the equations can be simplified.

(1) Very low concentration of BIPS in solution - In this case the approximation $(1 - 10^{-A}) \approx 2.303A$ can be made.

(2) Very high concentration of BIPS in solution - In this case the approximation $10^{-A} \approx 0$ can be made.

Unfortunately, at either very high or very low concentrations of BIPS, it becomes quite difficult to accurately determine small differences in optical density. Or, the cases where the mathematical analysis becomes more simple are the same ones where it becomes more difficult to obtain accurate measurements.

If the thermal rate constants and molar absorptivities are known the quantum efficiencies can be calculated from initial rate data and from measurements at the photostationary state. For example, if a solution of freshly prepared colorless BIPS (U_2) is used, then at $t = 0$, $U_1 = C = 0$, and $U_2 = I$.

Equation (69) reduces to -

$$\left(\frac{dC}{dt}\right)_{t=0} = k_4 T - I_0 (1 - 10^{-\epsilon_2 P T}) \phi_2 \quad (72)$$

or -

$$\phi_2 = \frac{\left(\frac{dC}{dt}\right)_{t=0} - k_4 T}{I_0 (1 - 10^{-\epsilon_2 P T})} \quad (72a)$$

Thus, by extrapolation of $\frac{\Delta C}{\Delta t}$ to $t = 0$, and from the value of the absorbance at $t = 0$, ϕ_2 can be calculated.

At the photostationary state $\left(\frac{dC}{dt}\right) = 0$.

Therefore from eq. (69)

$$\phi_1 = \frac{\left[-(k_1 + k_3) C_p + k_2 U_{1p} + k_4 U_{2p} \right] A_p}{I_0 P (1 - 10^{-A_p}) \epsilon_c C_p + \frac{\phi_2 \epsilon_2 U_{2p}}{\epsilon_c C_p}} \quad (73)$$

where the subscript p indicates the value of the quantity at the photostationary state.

If a solution of freshly prepared colored BIPS is used to obtain the initial rate data then at $t = 0$, $U_1 = U_2 = 0$ and $C = T$. From eq. (69) -

$$\phi_1 = \frac{-\left(\frac{dC}{dt}\right)_{t=0} - (k_1 + k_3) T}{I_0 (1 - 10^{-\epsilon_c P T})} \quad (74)$$

This results in another independent method for obtaining ϕ_1 .

A method of determining whether the mechanisms described by equations (69), (70), and (71) are consistent with experimental evidence is as follows. Measure C, U₁ and U₂ as a function of time and calculate $\frac{\Delta C}{\Delta t}$, $\frac{\Delta U_1}{\Delta t}$, $\frac{\Delta U_2}{\Delta t}$ as a function of time. Substitute these values and the known values of rate constants, molar absorptivities, absorbances, etc., into equations (69), (70), and (71), and see whether the values of ϕ_1 and ϕ_2 calculated from these equations remain constant throughout the photoconversion.

Since C is the only independently measurable species, U₂ and U₁ cannot be determined individually at most times. In ethanol it is necessary to make calculations for quantum yield from initial rate data and from the measurements at the photostationary state as has been previously described. All quantum yield values reported to date have been calculated in the manner described (both ethanol and toluene).

Assuming that U₁ does not exist in toluene and therefore U₂ = T - C, (where T is the total concentration of BIPS present) equation (69) can be rewritten as follows: (assuming k₁ = k₂ = k₄ = 0 and P = 1 cm)

$$\frac{dC}{dt} = \frac{I_0(1-10^{-A})}{A} [\phi_2 \epsilon_2 (T-C) - \phi_1 \epsilon_C C] - k_3 C \quad (75)$$

or rearranging -

$$\frac{\left(\frac{dC}{dt} + k_3 C\right) \cdot A}{I_0(1-10^{-A})} = -(\phi_1 \epsilon_C + \phi_2 \epsilon_2) C + \phi_2 \epsilon_2 T \quad (75a)$$

If the term on the left side of equation (75a) is plotted against C, as shown in Figure 32 and Table 10, the slope of the line will be - ($\phi_1 \epsilon_C + \phi_2 \epsilon_2$) and the intercept $\phi_2 \epsilon_2 T$. From these values ϕ_1 and ϕ_2 can be calculated. The primary disadvantage of this type of calculation is that it is time consuming. The values of ϕ_1 and ϕ_2 obtained from a plot of equation (75a) in Figure 32 agree well with those values obtained from

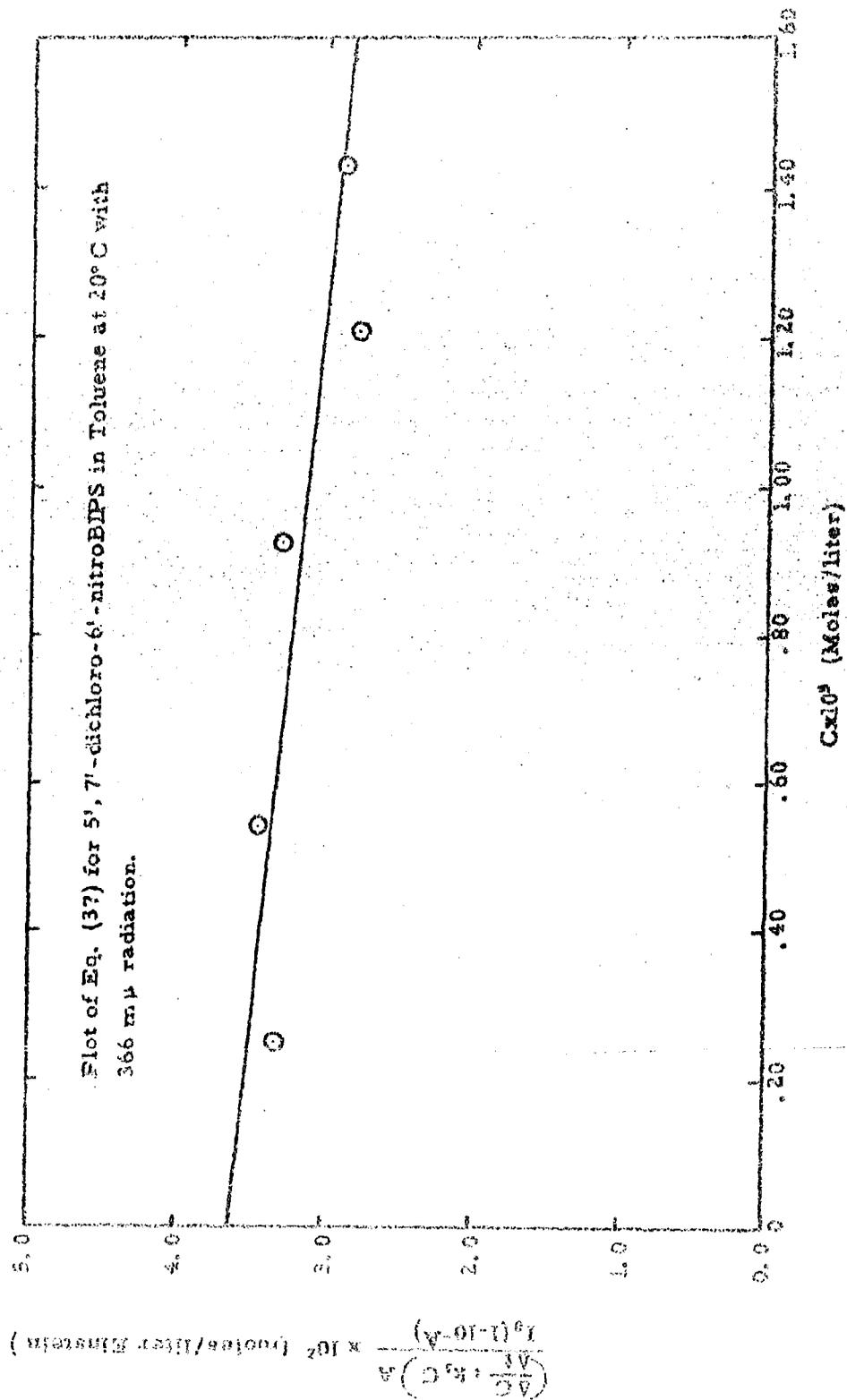
TABLE 10

Data for Quantum Yield Determination
of 5, 7'-Dichloro-6'-Nitro BIPS in Toluene

Run No. 19 at 366 m μ 20 $^{\circ}$ C

<u>t (sec)</u>	<u>C (moles/liter)</u>	<u>$(\frac{\Delta C}{\Delta t} + k_3 C)A/I_0(1-10^{-A})$</u>
39	2.08×10^{-6}	2.77×10^{-2}
99	4.53×10^{-6}	2.86×10^{-2}
189	7.70×10^{-6}	2.79×10^{-2}
279	1.01×10^{-5}	2.31×10^{-2}
369	1.20×10^{-5}	2.40×10^{-2}

Figure 32



$$\frac{\left(\frac{A_0}{A} + k_2 C\right) A}{I_0(1-10^{-A})} \times 10^2 \text{ (moles/liter Einstein)}$$

from initial rate and photostationary state data, as shown below:

Initial rate and photo-stationary state data	- 0.008	0.608
Eq. (37) plot (least squares results)	- 0.013	0.638

3.6. Quantitative measurement of the photochemical reaction of spiropyrans in solution - These reactions were carried out in the same cell as were the actinometry measurements. Three ml. of colorless (U_2) BIPS solution was placed in the thermostatted absorption cell. With the stirrer started, and the readout systems calibrated, the shutter in the ultraviolet irradiation beam was opened. The resulting color formation was followed as a function of time by plotting the transmittance at λ_{max} of the colored form vs. time on a strip chart recorder connected to the DU readout. From this information $\frac{\Delta C}{\Delta t}$ can be calculated.

The transmitted intensity of the irradiating Hg line was also monitored by a photomultiplier - recorder arrangement. From these data the absorbance of the solution at the excitation wavelength [A in eqs. (69) and (71)] can be calculated.

The irradiation was continued until the photostationary state was reached. At this point the shutter was closed and the sample allowed to thermally decolor while the absorbance was still being recorded. From this data the rate constants for the thermal reaction may be calculated as has been previously described. In the case of 5', 7'-dichloro-6'-nitro BIPS in a hydroxylic solvent (ethanol) no initial fast rate of color disappearance was detected. This implies that under the conditions of irradiation, at the photostationary state, C and U_1 are also in a state of thermal equilibrium. Since the equilibrium constant is known, the concentration of U_1 can be calculated.

Since the concentrations of all species, the molar absorptivities of C and U_2 at λ_{exp} , and the total absorbance (A) all are known, at zero

time and at the photostationary state, enough information is available to calculate the quantum efficiencies, ϕ_1 and ϕ_2 as described by equations (72a) and (73).

An alternate method is similar to the one above except that the initial solution contains only colored species. To prepare the solution, a small amount of pure solid colored BIPS was pressed into a 13 mm. type OH Millipore filter pad which in turn was placed in a Swinny Hypodermic adapter. The irradiating-measuring instrument was set into operation with stirrer running and shutter open. A syringe containing approximately 3.5 ml. of solvent was attached to the adapter. On depression of the syringe plunger the solvent dissolved the colored BIPS and immediately swept it into the reaction cell that was already waiting in the irradiation path. In this manner, essentially no time was lost between the dissolving of the BIPS and the start of the irradiation. Thus at $t = 0$, $C = T$, $U_1 = U_2 = 0$, and from equation (74) the quantum efficiency ϕ_1 can be calculated.

3.7. Results. - Quantum efficiencies were obtained for both the forward ($U_2 \xrightarrow{\phi_2} C$) and reverse ($C \xrightarrow{\phi_1} U_2$) photo chemical reactions of 5', 7 -dichloro-6' -nitro BIPS in both ethanol and toluene with a 366 m μ excitation source. The results are summarized on Table 11. It appears that in toluene the forward reaction is more efficient and the reverse reaction less efficient than in ethanol. As is shown on Table 11, there is good agreement for the value of ϕ_1 regardless of whether the pure colored or the pure colorless compound was used as a starting material.

An attempt was made to obtain the quantum efficiencies in toluene using a 313 m μ excitation source. The work progressed in a straight forward manner until the calculation of the quantum efficiency, ϕ_1 , for the back reaction ($C \rightarrow U$) from the photostationary state data was made. On four separate runs this quantity was negative (-.1 to -.3) which is inconceivable. Using an alternate method for determining ϕ_1 by starting with pure colored form, positive values were obtained in the range of 0.2 to 0.4. Although corrections were made for the

TABLE II

Quantum Yields of 5',7-Dichloro-6'-Nitro BIPS

(ethanol, 366 m μ , 20°C)

<u>Conc. (M)</u>	<u>I₀ Einsteins/Min.</u>	<u>Φ_2</u>	<u>Φ_1</u>
<u>Starting with Pure Colorless Form (U₂)</u>			
9.97 x 10 ⁻⁵	1.90 x 10 ⁻⁸	0.312	--
9.97 x 10 ⁻⁵	1.99 x 10 ⁻⁸	0.299	--
9.97 x 10 ⁻⁵	2.01 x 10 ⁻⁸	0.295	0.071
9.97 x 10 ⁻⁵	1.45 x 10 ⁻⁸	0.301	0.074
1.00 x 10 ⁻⁴	1.43 x 10 ⁻⁷	0.314	0.089
1.00 x 10 ⁻⁴	1.40 x 10 ⁻⁷	0.313	--
<u>Starting with Pure Colored Form (C)</u>			
2.40 x 10 ⁻⁵	1.40 x 10 ⁻⁷	--	0.078
4.26 x 10 ⁻⁵	1.40 x 10 ⁻⁷	--	0.091

(toluene, 366 m μ , 20°C)

<u>Conc. (M)</u>	<u>I₀ Einsteins/Min.</u>	<u>Φ_2</u>	<u>Φ_1</u>
4.98 x 10 ⁻⁵	1.44 x 10 ⁻⁷	.623	- .017
4.98 x 10 ⁻⁵	1.47 x 10 ⁻⁷	.582	+ .001

absorption of 313 m μ light by the solvent (see section 3.4), and the values of the important parameters were rechecked (extinction coefficients, rate constants, etc.), non-reproducible or impossible results were still obtained. It appears that there are still unresolved factors influencing this particular system. Results are shown in Table 12.

TABLE 12

Quantum Yield and Extinction Coefficients
for 5', 7'-Dichloro-6'-NitroBIPS in Toluene Using 313 m μ Radiation

<u>Con- centration (mole/liter)</u>	<u>I_0 (Einstein/min)</u>	<u>k_t (min.⁻¹)</u>	<u>ϕ_2</u>	<u>ϕ_1</u>	
4.98x10 ⁻⁵	2.49x10 ⁻⁸	9.67x10 ⁻²	.502	-.127	
4.98x10 ⁻⁵	2.59x10 ⁻⁸	2.21x10 ⁻¹	.478	-.340	
7.02x10 ⁻⁵	2.23x10 ⁻⁸	2.86x10 ⁻¹	.399	---	} Corrections Applied
7.02x10 ⁻⁵	2.25x10 ⁻⁸	9.33x10 ⁻²	.420	-.192	
2.05x10 ⁻⁵	2.24x10 ⁻⁸	9.26x10 ⁻²	---	.232	} Started with Pure Colored Form
8.58x10 ⁻⁶	2.24x10 ⁻⁸	8.72x10 ⁻²	---	.480	

$\lambda_{\max} = 594, m\mu$

Extinction coefficient of colored species at $\lambda_{\max} = 4.8 \times 10^4$ liter/mole cm.

Extinction coefficient of U₂ at 315 m μ = 5.13×10^3 liter/mole cm.

Extinction coefficient of U₂ at irradiating $\lambda = 5.10 \times 10^3$ liter/mole cm.

Extinction coefficient of C at irradiating $\lambda = 1.29 \times 10^3$ liter/mole cm.

k_t = measured overall thermal rate constant.

4. MEASUREMENTS OF THE THERMAL AND PHOTOCHEMICAL PROPERTIES OF OTHER PHOTOCROMIC COMPOUNDS

4.1. Investigation of six representative BIPS compounds. - In addition to the intensive investigation done on 5', 7' -dichloro-6' -nitro BIPS at several temperatures, a program was undertaken to study the thermal and photochemical properties of six other compounds in toluene at 20°. The study of these other compounds gives some indication of the similarities and differences that can be expected among various spiropyrans.

The study of these compounds in toluene proceeded via the following steps.

1. Determination of the molar absorptivity of the colorless form at an absorption maximum in the ultraviolet region.
2. Determination of the molar absorptivity of the colored form at the visible absorption maximum.
3. Determination of the molar absorptivity of both the colorless and colored forms at the wavelength used for the photochemical measurements.
4. Determination of the thermal rate constants at the temperature used for the photochemical measurements.
5. Measurement of the photochemical color formation versus time using an irradiating wavelength of 366 m μ .
6. Calculation of quantum yield using the constants obtained in steps 1 through 5.

4.1.1. Molar absorptivity measurements. - The determinations of the molar absorptivities of the colorless species have been described previously. Molar absorptivity determinations of the colored forms in toluene were more difficult due to the relatively fast thermal color disappearance rates. Attempts were made to determine the molar absorptivity of the colored forms in the same manner as that used for ethanol solutions. In several cases, the absorbance versus time curve obtained was "S" shaped, at first increasing then decreasing with time. It is believed

that minute particles of undissolved colored form were passing through the millipore pad and dissolving in the absorption cell, thus giving the initial rise in color.

An alternate method was devised which made use of the reaction between the colored salt and a weak organic base. Since the salts were completely insoluble in toluene the following procedure was used: A small amount of solid salt was placed on a millipore filter and inserted into the Swinny adapter. A toluene solution containing 0.5 ml. triethylamine per 50 ml. was forced through the filter. The action of the amine on the salt produced colored form that was transferred, in the same motion into the reaction cell. The absorbance versus time curve showed the normal first-order decay and extrapolation back to zero time was done with little difficulty. The concentration was determined from the decolorized solution by its UV absorbance. The amine appeared to have little or no effect. The UV absorption spectrum and the extinction coefficients obtained in this region in pure toluene were applied in determining the solution concentrations except in the case noted on Table 13.

All extinction coefficients (colored and colorless) obtained at irradiating wavelengths (step 3) were determined by using the filtered mercury arc light source and photomultiplier detector as the measuring device. In this way no irregularities would arise due to differences in spectral band widths as might have been the case if the measurements had been made on the DU spectrophotometer. The values obtained for all extinction coefficients determined are incorporated into Table 13.

4.1.2. Quantum yield determinations at 366 m μ irradiation. - In order to obtain an indication of the effect of various substituents on the efficiency of color formation, quantum yield determinations were made on several different compounds of the BIPS series. All the runs were made on toluene solutions of the samples for the following reasons:

1. Calculations are simplified since it is probable that no solvated species similar to U_1 will be found in this system.
2. Both the thermal and photochemical reactions proceed at a faster rate allowing more work to be accomplished in a shorter time.

TABLE 13

Photochemical and Thermal Data on BIPS Compounds

Solvent: Toluene	Irradiating Wavelength: 366 m μ						Temp: 20 $^{\circ}$ C
Compound (BIPS)	$\lambda_{\text{max-C}}$ (m μ)	$\epsilon_{\lambda_{\text{max-C}}}$ $\times 10^{-4}$ (liter/mole cm)	$\epsilon_{\lambda_{\text{max-U}_2}}$ $\times 10^{-3}$ (liter/mole cm)	$\epsilon_{\lambda_{\text{Irr-U}_2}}$ $\times 10^{-3}$ (liter/mole cm)	$\epsilon_{\lambda_{\text{Irr-C}}}$ $\times 10^{-3}$ (liter/mole cm)	k_t (min. $^{-1}$)	ϕ_2 (moles/Einstein)
5', 7'-DiCl-6'-NO $_2$	594	4.82 ^b	5.13 ^a (315m μ)	.964	8.49 ^b	.099	0.553 ^b
7- α -5'-Br-6'-NO $_2$ - 2-OCH $_3$	591	3.70	10.7 (293m μ)	5.11	6.43	.868	0.717
5'-NO $_2$	605	5.18	9.10(337m μ)	3.93	19.6	1.55	0.759
5-Cl-5', 7'-DiCl- 6'-NO $_2$	604	4.77	6.67(304m μ)	.896	5.58	.092	0.353
5-Cl-6'-NO $_2$	613	3.96	9.90(313m μ)	3.51	16.8	1.25	0.985
5-OCH $_3$ -6'-NO $_2$	613	5.99	11.1(318m μ) ^c	3.16	13.6	1.75	0.217
7- α -6'-NO $_2$	612	5.33	11.0(309m μ)	4.39	18.2	1.70	0.655

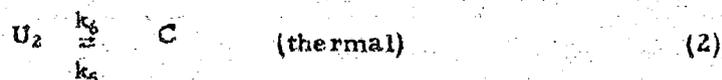
where:

 $\lambda_{\text{max-C}}$ = wavelength of maximum absorbance of colored form. $\epsilon_{\lambda_{\text{max-C}}}$ = molar absorptivity of colored form at $\lambda_{\text{max-C}}$. $\epsilon_{\lambda_{\text{max-U}_2}}$ = molar absorptivity of colorless form at $\lambda_{\text{max-U}_2}$. $\epsilon_{\lambda_{\text{Irr-U}_2}}$ = molar absorptivity of colorless form at 366 m μ . $\epsilon_{\lambda_{\text{Irr-C}}}$ = molar absorptivity of colored form at 366 m μ . k_t = thermal rate constant ϕ_2 = quantum yield for reaction $U_2 \xrightarrow{h\nu} C$ ^a - Corrected Value ^b - Recalculated from Corrected Value of $\epsilon_{\lambda_{\text{max-U}_2}}$ ^c - Measured in toluene - triethylamine mixture

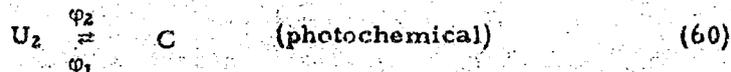
3. Toluene solutions more nearly simulate the systems being used in the eye protection device.

The general procedures for determining quantum efficiencies and for determining light intensities by use of the chemical actinometer have been previously described. In addition to following the color formation at the visible λ_{max} , the total absorption of the excitation radiation was also followed with time in all of the determinations reported here.

Due to the absence of the U_1 species in toluene, the only reactions of concern are -



and



Since the thermal equilibrium lies greatly in favor of U_2 , k_6 is insignificant compared to k_5 and therefore $k_5 \approx k_t$ where k_t is the observed rate constant for the thermal color disappearance reaction. The method used in the calculation of the quantum efficiencies has been previously described. The results are tabulated on Table 13.

4.1.3. Extent of photochemical transformation from colorless to colored form of 7-phenyl-5'-bromo-6'-nitro-8'-methoxy BIPS in ethanol -

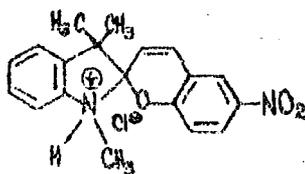
The seven solutions prepared for use in the determination of the molar absorptivity of the colorless form at 260 m μ in ethanol were also used to determine, qualitatively, the extent to which the phototransformation (colorless $\xrightleftharpoons{h\nu}$ colored) takes place under conventional laboratory lamps. An absorption cell of suitable path length was filled with the solution at 20°C and was subsequently irradiated under a mercury arc lamp (George W. Gates, MIL-2F-C) or Blak Ray (Ultraviolet Products, Inc.; Model XX-4). The absorbance of the solution being irradiated was checked periodically in a Beckman model DK-1 spectrophotometer. The irradiation was discontinued when the absorbance at 560 m μ appeared to level off (photostationary state). The concentration of the colored form present at the photostationary state was calculated from the absorbance at 560 m μ and

the known value for ϵ_{560} . The percent transformed was obtained from the ratio of colored form present at the photostationary state to the total spiropyran present before irradiation. The average conversion was 94.7% under the Gates lamp and 92.9% when using the Blak Ray. The results of the work are tabulated in Table 14.

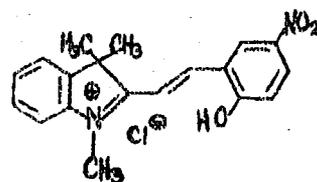
It must be kept in mind that the data in Table 14 are not quantitative since some variations in irradiation conditions among the various samples is probable. Also, the photostationary absorbance values are subject to error due to the readout procedure used. However, the data convincingly demonstrate a high percent of photoconversion in all cases and suggest that very close to total conversion might be possible with a lamp of higher intensity than those used here. It should be remembered also that at room temperature even if the reverse photochemical reaction $C \xrightarrow{h\nu} U_2$ is negligible the thermal reactions, $C \xrightleftharpoons[k_4]{k_3} U_2$ and $C \xrightleftharpoons[k_2]{k_1} U_1$, are not.

4.2. Some observations on the hydrochloride salts of 6'-nitro BIPS

Evidence gathered to date has shown that the salt can exist in both an open and a closed form. At room temperature, in both the solid and in solution, the open modification appears to be the more stable compound. Possible structures of these salts are diagrammed below.



(I = closed form)



(II = open form)

The reaction of hydrogen chloride with 6'-nitro BIPS was carried out at several temperatures in both toluene and ethanol. Two distinct products were obtained, depending upon the temperature at which the reaction took place.

TABLE 14

Photochemical Conversion of 7-phenyl-5'-bromo-6'-nitro-8'-methoxy BPS

Solution No.	Total Concentration Before Irradiation	Path (cm.)	A_{660} at Photostationary State	Concentration of Colored Form at Photostationary State	% Transformed
2306-16-1	5.34×10^{-6} M	1.0	0.193	5.22×10^{-6} M	97.3 ^a
2306-16-2	1.01×10^{-5} M	1.0	0.353	9.54×10^{-6} M	94.5 ^a
2306-16-3	2.90×10^{-5} M	1.0	0.983	2.66×10^{-5} M	91.7 ^a
2306-16-4	7.22×10^{-5} M	0.1	0.252	6.81×10^{-5} M	94.4 ^a
2306-16-5	1.06×10^{-4} M	0.1	0.364	9.84×10^{-5} M	92.8 ^b
2306-16-5	1.06×10^{-4} M	0.1	0.379	1.03×10^{-4} M	97.2 ^a
2306-16-6	2.96×10^{-4} M	0.1	1.022	2.76×10^{-4} M	93.2 ^b
2306-16-6	2.96×10^{-4} M	0.1	1.032	2.79×10^{-4} M	94.2 ^a
2306-16-7	4.96×10^{-4} M	0.1	1.697	4.59×10^{-4} M	92.6 ^b
2306-16-7	4.96×10^{-4} M	0.1	1.713	4.63×10^{-4} M	93.3 ^a

^a Irradiation under Gates lamp.

^b Irradiation under Blak Ray.

The preparations were accomplished by bubbling hydrogen chloride through solutions of the spiropyran at -78° , room temperature, and at the boiling points of ethanol and toluene. In each case the reaction product precipitated from solution as a yellow solid. Each reaction was carried out in solutions prepared from colorless or "closed" spiropyran as starting material.

The first indication that the products were two different salts came from the speed of reaction itself. The reaction at -78° proceeded extremely fast in the nearly complete absence of colored or "open" form of the spiran. This suggested that the colorless or "closed" form rather than the open form was reacting with hydrogen chloride in salt formation. On the other hand, the reaction in boiling solvent presumably took place between the open form, present in abundance, and the acid. The solid hydrochloride salts were removed from the reaction solution by filtration, washed with pentane and dried. Elemental analyses were performed without further purification. The open salt melted at $266-269^{\circ}$. The closed salt apparently isomerized to the open salt at 130° and melted at $264-265^{\circ}$. The samples gave a mixed melting point of $264-265^{\circ}$.

Anal. Calcd. for $C_{19}H_{19}N_2O_3 Cl$: C, 63.6; H, 5.3

found (closed salt): C, 61.6; H, 5.4
found (open salt): C, 64.0; H, 5.4

A small quantity of the salt prepared in boiling solvent was dissolved in toluene at room temperature. Weak organic base was added to this solution whereupon an immediate color change, yellow to blue, occurred. This same test when applied to the salt prepared at low temperature, gave only a trace of color. The salt prepared at room temperature gave results intermediate between the low and high temperature ones.

Titration of ethanolic solutions of each reaction product with standardized sodium hydroxide revealed that both were monohydrochloride salts.

Infrared spectra of the two salts were recorded on a Perkin-Elmer model 137 spectrophotometer, in KBr pellets. The spectra showed

distinct differences. (Figure 33). These spectra differed from the infrared spectra of the colorless and colored forms of 6'-nitro BIPS, (Figure 34).

The following experimentation strengthens the argument for the existence of two types of salts.

(1) A portion of the solid low temperature reaction product was decomposed in aqueous ammonium hydroxide. The product was washed several times with water giving a gray solid, m.p. 177-178°. (The melting point of the colorless 6'-nitro BIPS is 177-178°). The infrared spectrum of this material was identical with the infrared spectrum of colorless 6'-nitro BIPS.

Anal. Calcd. for $C_{11}H_{13}N_2O_3$:	C, 70.8;	H, 5.6
Found:	C, 71.2;	H, 5.7

(2) A portion of the high temperature reaction product was decomposed in aqueous ammonium hydroxide yielding a nearly black solid product which was washed several times with water. This product melted at 177-178°. The infrared spectrum of this black material was identical with the infrared spectrum of the pure colored 6'-nitro BIPS previously prepared by precipitation from non-polar solvent.

Anal. Calcd. for $C_{11}H_{13}N_2O_3$:	C, 70.8;	H, 5.6
Found:	C, 70.4;	H, 5.6

(3) A portion of the salt prepared at low temperature was dissolved completely in ethanol then refluxed for ten minutes. A precipitate formed on refluxing and after fifteen minutes the contents of the flask had solidified. The infrared spectrum of this product was no longer that of the closed salt but was identical to the infrared spectrum of the "open" form salt. The solubility of the closed salt is apparently greater than that of the open salt in ethanol. This rearrangement of the closed salt to the open salt also occurs in the solid. The original closed salt has completely isomerized to the open salt after standing for six months at room temperature.

Figure 33

Infrared Spectra of the Hydrochloride Salts of 6'-Nitro BIPS in KBr

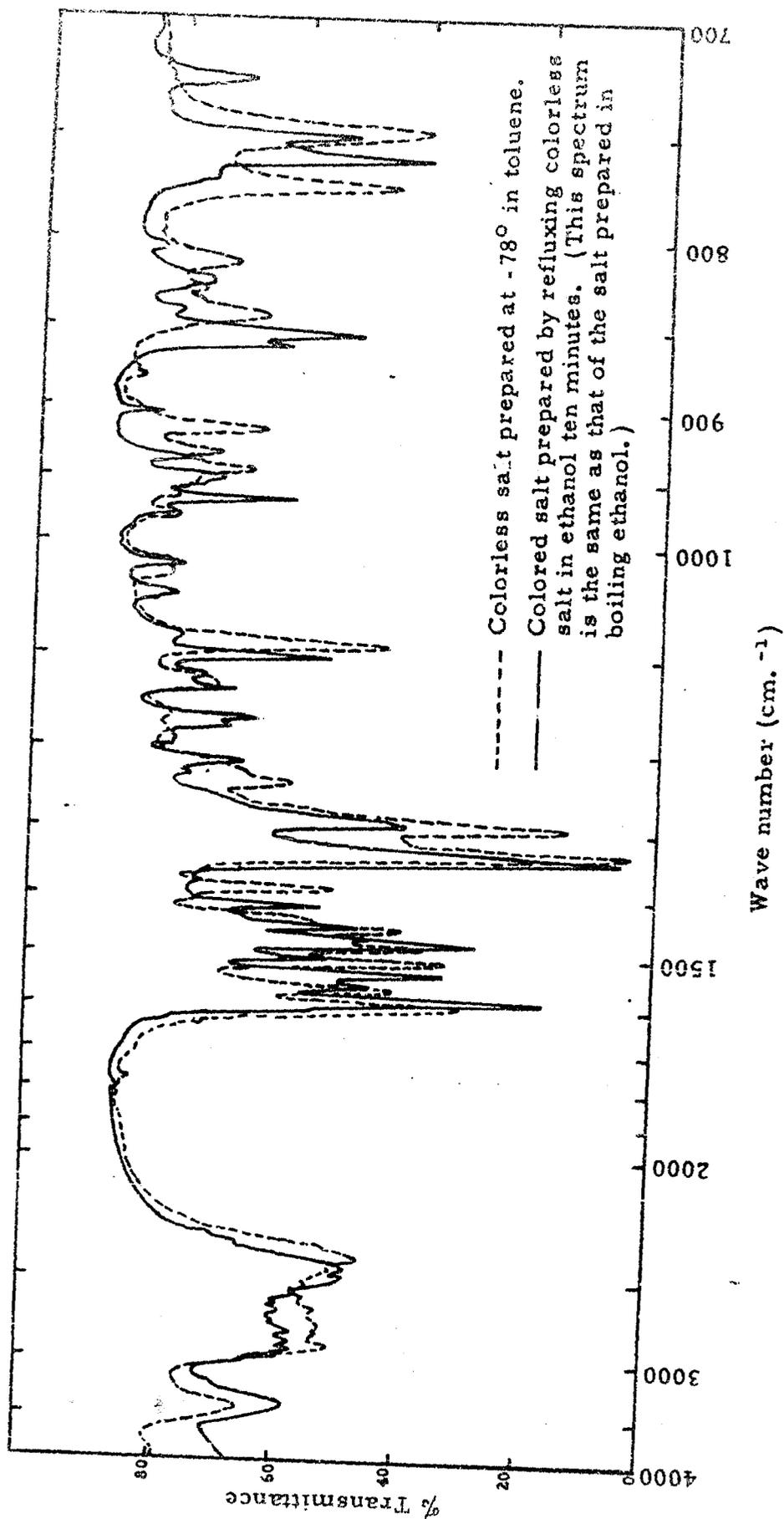
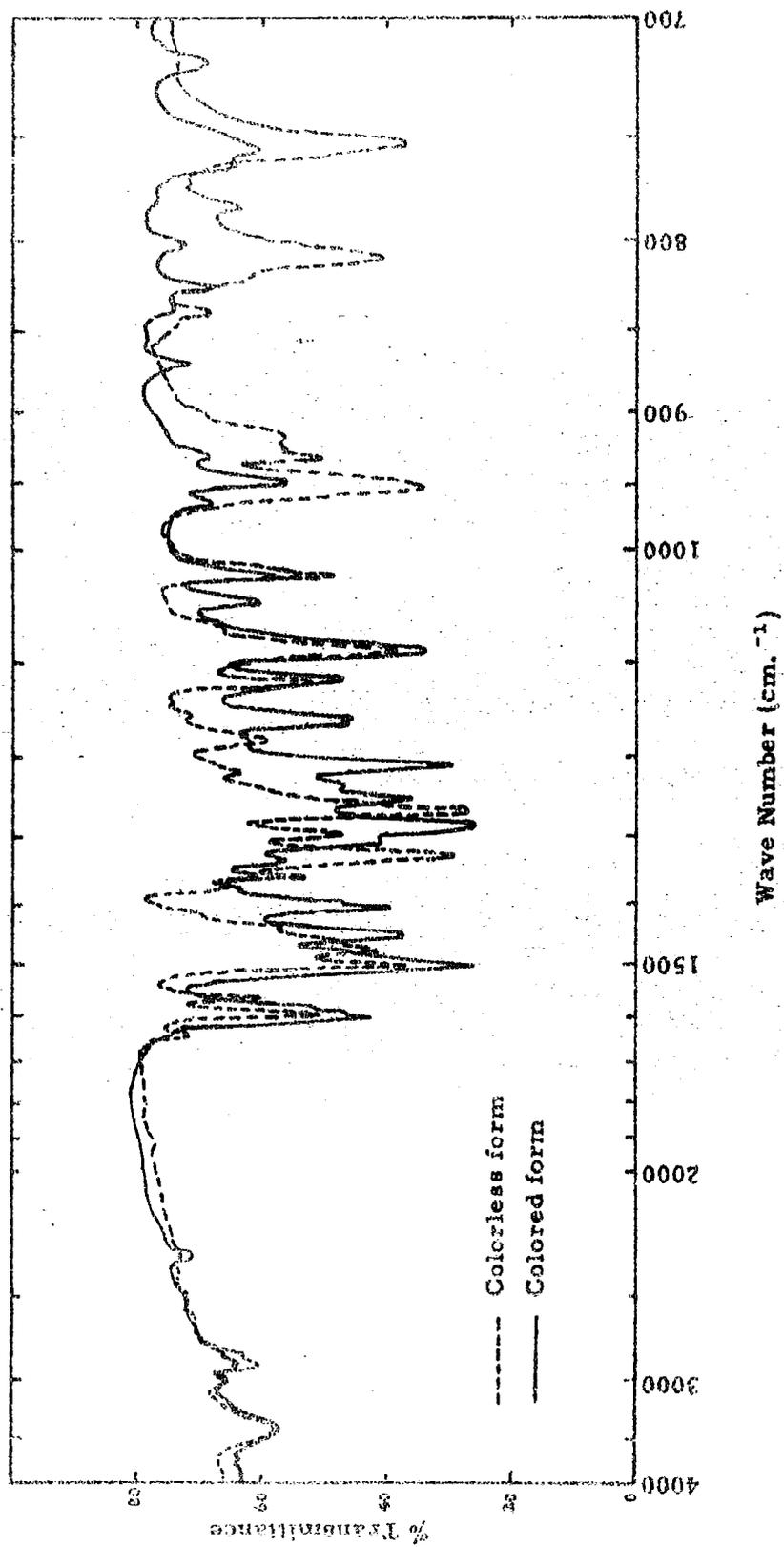
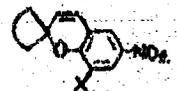
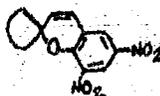
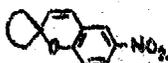


Figure 34
Infrared Spectra of 6'-Nitro BIPS in KBr



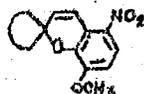
4.3. Shape of the visible transmittance spectrum to molecular structure. - The various indolinobenzospiropyran compounds show distinct differences in the shape of the visible transmittance spectrum. Examination of the visible spectra of all the compounds tested under the standard conditions reveals that in most cases a definite curve shape accompanies certain substituent combinations on the benzopyran half regardless of the substitution on the indoline portion of the molecule. Four general types of curve shape have been identified and are described in the following paragraphs.

Type I. The curve shows two maxima of different intensity. They are sometimes resolved, while at other times the maximum of lesser intensity appears as a shoulder to the shorter wavelength side of the larger maximum. Figure 35, Column 1 shows representative spectra of this type. This curve shape was usually found among compounds of the following type:

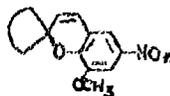


where $x = \text{halogen}$

Type II. The spectrum shows two resolved maxima of low intensity, usually separated by 30-40 millimicrons. (See Figure 35, Column 2.) Compounds of the general structure below show this curve.



Type III. Spectra of this type are very broad, rounded curves which sometimes show the presence of two maxima. (See Figure 35, Column 3.) Curves exhibiting this broad spectrum are produced by compounds having the structure given below.



Type IV. The curve is less broad than Type III but usually shows the presence of three maxima and is associated with compounds of the following structure. (Figure 35, Column 4).

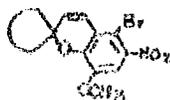
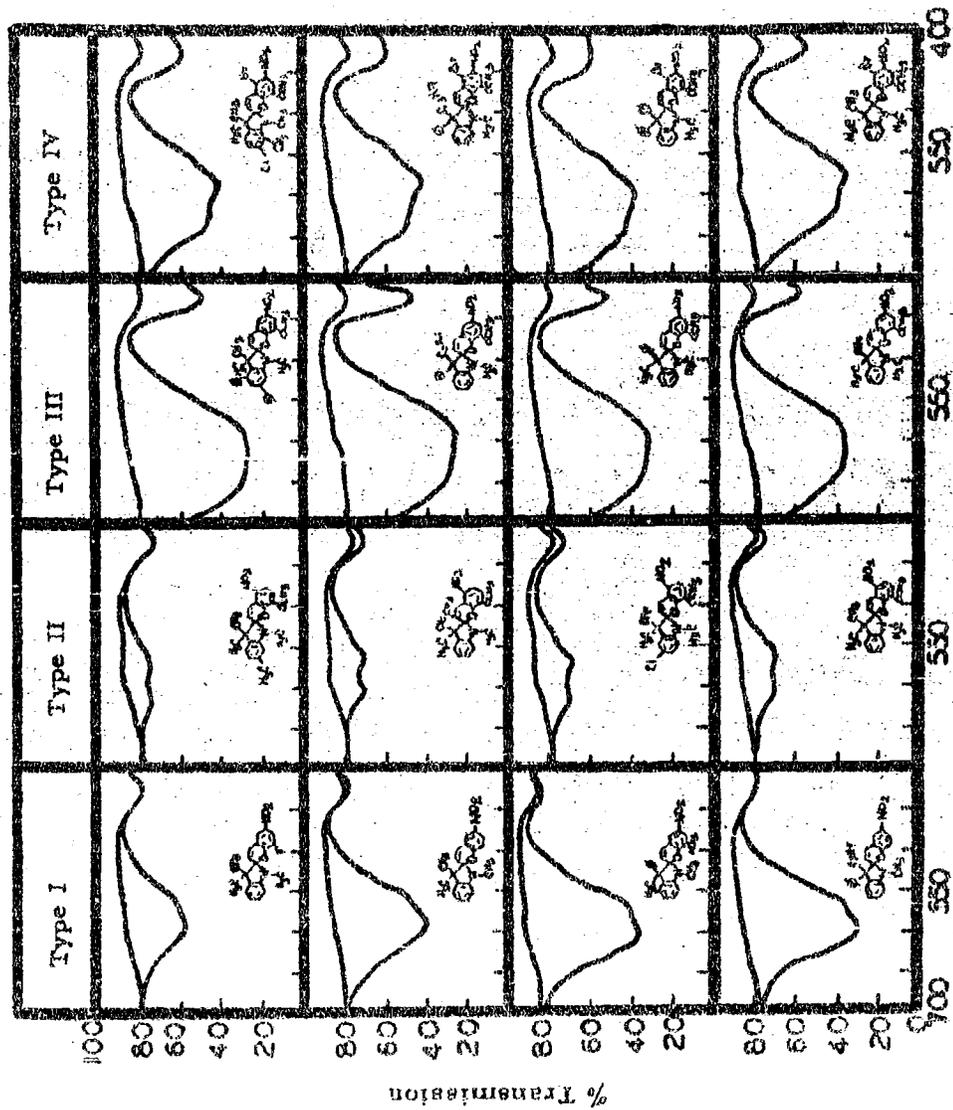


Figure 35

Visible Transmission Spectra
of Several Substituted Indolinbenzospiropyrans
in Toluene



4.4. Semi-quantitative survey of the photochromic properties of the indolinbenzospirans. - This project was undertaken to obtain an overall picture of the properties of the variously substituted indolinbenzospirans (specifically, those properties that will determine the performance of an eye-protective lens element). The information required was obtained by making use of a modified rapid scanning spectrophotometer (Model A-1, American Optical Co.). The modification consisted of placing an electronic flash lamp in the sample compartment as shown in Figure 36. The sample cell was constructed of two glass plates separated by a Teflon spacer 0.050 inch thick. The glass plates are held firmly between two steel frames as illustrated in Figure 37.

The operation of the instrument consists of placing the sample cell on the movable platform outside the light path of the spectrophotometer and directly in front of the flash lamp. After irradiation (filtered by Corning filter No. 9863) the cell in the carriage is quickly moved along the metal track into the spectrophotometer light path. At this point the spectrum is displayed on the oscilloscope and immediately photographed. The flash output is controlled electronically so that each sample receives equivalent exposure.

The sample solutions were prepared in toluene at a concentration of 5.0×10^{-4} mole per liter.

This method enabled a rapid evaluation of a large number of compounds with the basic structure I. One important advantage of the method was that it permitted the recording of the entire visible spectrum at one time within one second after the sample was irradiated. Many compounds having short half-lives of the colored species were studied in this way for

Figure 36
Modified Rapid Scanning Spectrophotometer

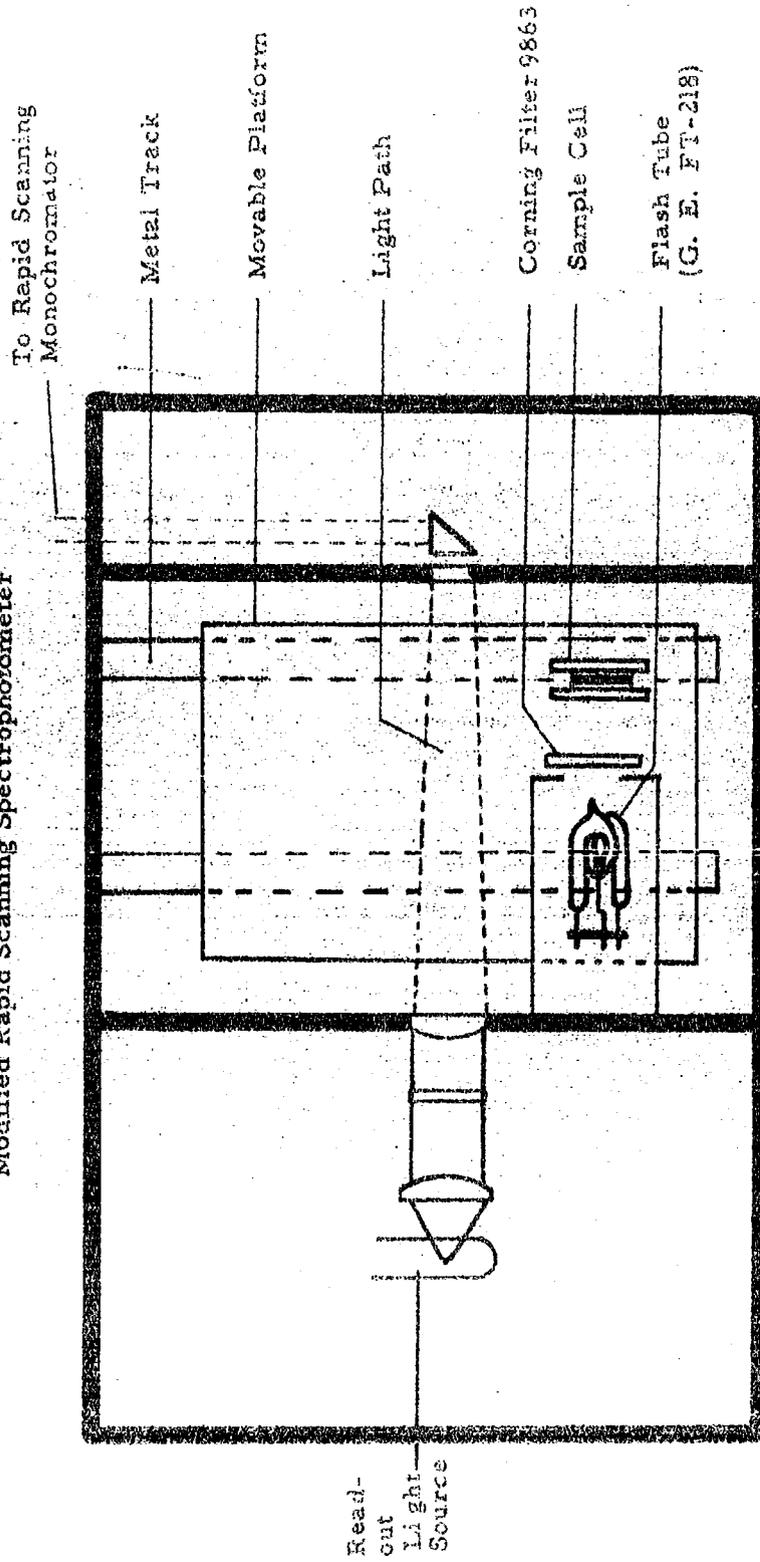
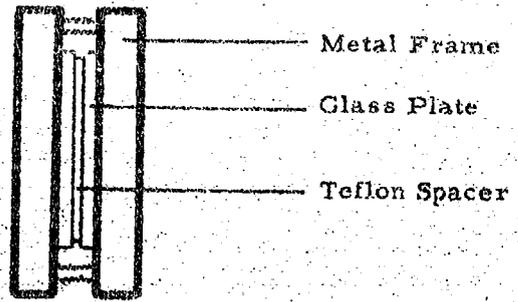
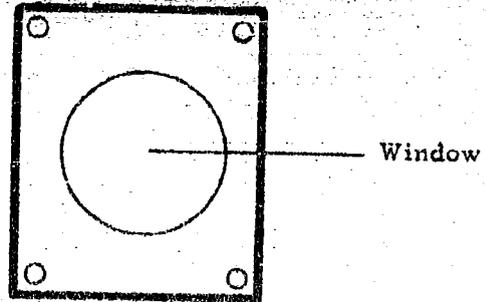


Figure 37

Sample Cell

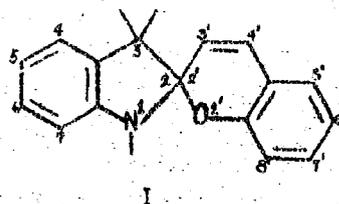


Side View



Front View

the first time. Conventional recording spectrophotometry could not offer this feature since the time delay between irradiation of the sample and recording its spectrum is too great for fast-fading compounds.



The photographed transmittance spectrum, 400 to 700 m μ , of each sample allows several different types of variables to be obtained. Although the absolute accuracy of these variables is probably not as good as that obtained on more conventional spectrophotometers with stable samples, the advantage of scanning and recording the whole visible spectrum in one-sixtieth of a second by far outweighs this drawback. The following variables may be obtained from these determinations: 1) wavelength of maximum absorbance, λ_{max} , 2) The change in transmittance at λ_{max} upon exposure to a standard amount of excitation energy (electronic flash), ΔT . This may also be converted to absorbance or optical density changes, ΔA or $\Delta O.D.$, 3) The integrated absorption, $\int 1-T$, of the colored sample. This measurement gives an indication of the breadth of the absorption and relates to its neutral density equivalent.

The stability of the colored form as determined by the half-life data gives an indication as to whether the particular material being studied may be considered as a component for a self deactivating lens element.

Some 212 samples of the indolinobenzospiropyran family have been tested according to the foregoing procedures. In order to monitor the instrument response and light source output a standard sample was chosen. Periodic determinations on this sample showed the reproducibility of the measurements to be better than $\pm 2\%$ transmission.

Table 15 lists 140 of the samples examined on the modified Rapid Scanning Spectrophotometer. The Fischer's Base and salicylaldehyde components which combine to form the indolinobenzospiropyrans are listed vertically and horizontally respectively. Data that concern

a particular compound is given at the intersection of the components forming that compound. In this way the effect of the various substituents on the Fischer's Base or salicylaldehyde can be observed by noting the values of the different properties in their respective files or columns. The basis for putting a compound in this table was that it be of a group of six or more compounds prepared from a common salicylaldehyde. Of the remaining samples that were tested and not listed only a few were photochromic under the stated conditions. Those found to be photochromic are listed separately in Table 16.

All Fischer's Bases presently synthesized are listed. Only salicylaldehydes containing a nitro substituent are listed, (two exceptions). It has been found that a non-nitrosubstituted salicylaldehyde combination with Fischer's Base will not produce a compound showing photochromism under the standard test procedure (with two exceptions).

Also contained in Tables 15 and 16 is the data relating to the stability of the colored form.

From these tables then can be obtained the photochemical and thermal data for many compounds. In this way the over-all performance of a material may be judged relative to other materials under the same conditions.

A general statement may be made that in the family of indolino-benzospiropyrans there is a relatively small shift of λ_{max} due to the addition of substituents to the basic structure. Almost all samples tested in toluene fall within the range of 570 to 670 m μ . The upper end of this range is somewhat hard to determine for two reasons: 1) The compounds whose absorption is in this region are considerably less sensitive than those of other regions. The small amount of absorption obtained makes it difficult to determine the point of maximum absorption. 2) The instrument becomes somewhat unreliable in this long wavelength region.

Molecules with 6'-methoxy-8' nitro and 5-nitro substituents tend to peak near the upper end of the range while those at the lower end are of a miscellaneous variety.

TABLE 15

(Part A-1)

Standard Test Data for Indolinebenzospiropyrans

Fischer's Bases	Benzopyran Substituents											
	6'-Nitro				5', 7'-Dichloro-6'-Nitro				5'-Bromo-6'-Methoxy-8'-Nitro			
	$t_{1/2}$	ΔA	$\int 1-T$	λ_{max}	$t_{1/2}$	ΔA	$\int 1-T$	λ_{max}	$t_{1/2}$	ΔA	$\int 1-T$	λ_{max}
Unsubstituted	.16	.32	.22	595	5.7	.08	.07	585	-	.05	.05	60
1-Amyl	.30	.36	.25	605	-	-	-	-	-	-	-	-
1-Amyl-5-Nitro	-	-	-	-	-	-	-	-	-	-	-	-
1-Phenyl	.03	.29	.25	615	.15	.07	.05	610	-	-	-	-
2-Ethylidene	-	.02	.02	-	-	-	-	-	-	-	-	-
2-Propylidene	-	-	-	-	-	-	-	-	-	-	-	-
3-Ethyl	.25	.37	.27	600	-	-	-	-	-	.05	.05	60
3, 3-Diethyl	.27	.37	.25	600	-	-	-	-	-	-	-	-
3-Ethyl-3-Phenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Ethyl-5-Chloro	-	-	-	-	-	-	-	-	-	.06	.07	66
3-Ethyl-7-Phenyl	.19	.32	.27	600	-	-	-	-	-	-	-	-
3-Heptyl-3-Phenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Pentyl-3-Phenyl	-	-	-	-	-	-	-	-	-	-	-	-
3, 3-Diphenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Phenyl	.41	.44	.31	605	-	-	-	-	-	.06	.06	67
3-Phenyl-3-n-Propyl	.53	.45	.29	605	4.5	.14	.11	590	-	-	-	-
3-Phenyl-7-Phenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-n-Propyl	-	-	-	-	-	-	-	-	-	-	-	-
3, 3-Di-n-Propyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Phenyl-3-Propyl-5-Nitro	-	-	-	-	-	-	-	-	-	-	-	-

$t_{1/2}$ in minutes, ΔA in Absorbance Units, $\int 1-T$ in Absorption Units, λ_{max} in $m\mu$, N.P. - not photochromic

TABLE 15

(Part A-2)

Standard Test Data for Indolinobenzospiropyrans

Wischer's Bases	Benzopyran Substituents											
	6'-Nitro-8'-Methoxy				6', 8'-DiNitro				6'-Methoxy-8'-Nitro			
	$t_{1/2}$	ΔA	$\Omega-T$	λ_{max}	$t_{1/2}$	ΔA	$\Omega-T$	λ_{max}	$t_{1/2}$	ΔA	$\Omega-T$	λ_{max}
Unsubstituted	.37	.36	.33	600	-	.02*	.01*	-	-	.04	.04	660
1-Amyl	-	-	-	-	-	-	-	-	-	.04	.06	-
1-Amyl-5-Nitro	V. F.	.55	.47	630	-	-	-	-	-	-	-	-
1-Phenyl	.01	.34	.33	615	.19	.04*	.05*	590	-	N. P.	-	-
2-Ethylidene	-	.01	.03	-	.09	.24*	.17*	595	-	-	-	-
2-Propylidene	-	-	-	-	-	-	-	-	-	-	-	-
3-Ethyl	-	.04	.06	-	.08	.14*	.13*	595	-	.04	.05	640
3,3-Diethyl	-	.10	.09	-	-	-	-	-	-	.04	.05	680
3-Ethyl-3-Phenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Ethyl-5-Chloro	-	-	-	-	-	-	-	-	-	-	-	-
3-Ethyl-7-Phenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Heptyl-3-Phenyl	.64	.42	.37	600	-	-	-	-	-	-	-	-
3-Pentyl-3-Phenyl	.68	.51	.43	600	-	-	-	-	-	-	-	-
3,3-Diphenyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Phenyl	.64	.41	.36	605	.48	.42	.30	605	-	.04	.05	660
3-Phenyl-3-n-Propyl	.58	.48	.40	600	-	-	-	-	-	-	-	-
3-Phenyl-7-Phenyl	.47	.42	.37	605	-	-	-	-	-	-	-	-
3-N-Propyl	-	-	-	-	-	-	-	-	-	.04	.05	670
3,3-Di-n-Propyl	-	-	-	-	-	-	-	-	-	-	-	-
3-Phenyl-3-n-Propyl-5-Nitro	V. F.	.37	.40	630	-	-	-	-	-	-	-	-

$t_{1/2}$ in minutes, ΔA in Absorbance Units, $\Omega-T$ in Absorption Units, λ_{max} in m μ , N. P. - Not Photochromic, V. F. very fast, * saturated solution.

TABLE 15

(Part A-3)

Standard Test Data for Indolinobenzospiropyrans

Fischer's Base	Benzopyran Substituents											
	5'-Bromo-6'-Nitro-8'-Methoxy				5,6'-Dinitro-8'-Methoxy				5'-Nitro-8'-Methoxy			
	$t_{1/2}$	ΔA	$\int I-T$	λ_{max}	$t_{1/2}$	ΔA	$\int I-T$	λ_{max}	$t_{1/2}$	ΔA	$\int I-T$	λ_{max}
Unsubstituted	.68	.34	.31	575	14.0	.27*	.21*	605	-	.10	.09	
1-Amyl	.98	.34	.27	585	-	-	-	-	-	-	-	
1-Amyl-5-Nitro	-	-	-	-	-	-	-	-	-	-	-	
1-Phenyl	V. F.	.12	.14	610	.70	.24	.24	630	-	-	-	
2-Ethylidene	.82	.21	.21	580	10.1	.26*	.19*	610	-	.09	.08	
2-Propylidene	-	-	-	-	-	-	-	-	-	-	-	
3-Ethyl	.84	.30	.26	580	-	-	-	-	-	.10	.09	
3,3-Diethyl	1.1	.26	.23	585	-	-	-	-	-	-	-	
3-Ethyl-3-Phenyl	.66	.30	.36	585	-	-	-	-	-	-	-	
3-Ethyl-5-Chloro	.23	.27	.36	585	-	-	-	-	-	-	-	
3-Ethyl-7-Phenyl	.66	.32	.27	585	-	-	-	-	-	-	-	
3-Heptyl-3-Phenyl	-	-	-	-	-	-	-	-	-	-	-	
3-Pentyl-3-Phenyl	-	-	-	-	-	-	-	-	-	-	-	
3,3-Diphenyl	.24	.35	.31	595	-	-	-	-	-	-	-	
3-Phenyl	.66	.31	.27	585	-	-	-	-	-	-	-	
3-Phenyl-3-n-Propyl	.74	.30	.27	585	-	-	-	-	-	-	-	
3-Phenyl-7-Phenyl	-	-	-	-	-	-	-	-	-	-	-	
3-n-Propyl	.62	.35	.28	580	-	-	-	-	-	-	-	
3,3-Di-n-Propyl	.70	.32	-	595	-	-	-	-	-	-	-	
3-Phenyl-3-n-Propyl-5-Nitro	-	-	-	-	-	-	-	-	-	-	-	

$t_{1/2}$ in Minutes, ΔA in Absorbance Units, $\int I-T$ in Absorption Units, λ_{max} in m μ .
 H. P. - Not Photochromic, V. F. - Very fast, * saturated solution.

TABLE 15

(Part B-1)

Standard Test Data for Indolinobenzospiropyrans

Fischer's Base	Benzopyran Substituents										
	6'-Nitro				5', 7-Dichloro-6'-Nitro				5'-Bromo-6'-Methoxy-8'-N		
	$t_{1/2}$	ΔA	β -T	λ_{max}	$t_{1/2}$	ΔA	β -T	λ_{max}	$t_{1/2}$	ΔA	β -T
4, 6-Diphenyl	.09	.41	.28	605	5.4	.07	-	595	-	-	-
4, 7-Dimethoxy	.09	.23	.17	600	-	-	-	-	-	-	-
4, 7-Dimethyl	-	-	-	-	11.0	.10	.08	585	-	-	-
5-Amino	-	N. P.	-	-	-	-	-	-	-	-	-
5-Chloro	.20	.36	.27	605	1.1	.08	.07	590	-	.07	.06
5-(β -Hydroxyethyl)	.10	.28	.20	600	-	-	-	-	-	-	-
5-Methoxy	.19	.10	.08	600	21.0	.05	.05	595	-	-	-
5, 7-Dimethoxy	-	-	-	-	-	-	-	-	-	-	-
5-Methyl	.11	.28	.21	605	16.7	.05	.03	585	-	-	-
5, 7-Dimethyl	-	-	-	-	10.8	.08	.05	585	-	-	-
5-Nitro	V. F.	.45	.37	610	-	-	-	-	-	-	-
5-Phenyl	.14	.33	.24	615	-	-	-	-	-	.03	.03
5, 7-Diphenyl	.13	.09	.09	610	-	-	-	-	-	-	-
6, 7-Benzo	-	.02	.02	-	-	-	-	-	-	-	-
6-Chloro-7-Methyl	-	-	-	-	-	-	-	-	-	-	-
6-Methyl	.13	.33	.23	600	-	-	-	-	-	-	-
7-Chloro	.18	.36	.27	610	-	-	-	-	-	-	-
7-Methoxy	.09	.26	.20	600	-	-	-	-	-	-	-
7-Methyl	.06	.29	.20	595	-	-	-	-	-	-	-
7-Nitro	-	-	-	-	-	-	-	-	-	-	-
7-Phenyl	.12	.35	.24	600	5.7	.06	.04	580	-	.03	.03

$t_{1/2}$ in Minutes, ΔA in Absorbance Units, β -T in Absorption Units, λ_{max} in N. P. - Not Photochromic, V. F. - Very fast.

TABLE 15

(Part B-2)

Standard Test Data for Indolinobenzospiropyrans

Fischer's Bases	Benzopyran Substituents											
	6'-Nitro-8'-Methoxy				6', 8'-DiNitro				6'-Methoxy-8'-Nitro			
	$t_{1/2}$	AA	β -T	λ_{max}	$t_{1/2}$	AA	β -T	λ_{max}	$t_{1/2}$	AA	β -T	λ_{max}
4, 6-Diphenyl	.18	.49	.43	610	-	-	-	-	-	-	-	-
4, 7-Dimethoxy	.13	.10	.18	630	1.4	.32	.26	580	-	.01	.02	670
5-Amino	-	N. P.	-	-	-	-	-	-	-	-	-	-
5-Chloro	.19	.44	.39	605	.19	.30	.24	605	-	.03	.04	-
5-(β -Hydroxyethyl)	.25	.31	.28	620	-	-	-	-	-	-	-	-
5-Methoxy	.16	.08	.09	620	-	-	-	-	-	N. P.	-	-
5, 7-Dimethoxy	-	-	-	-	-	-	-	-	-	-	-	-
5-Methyl	.22	.25	.24	620	-	-	-	-	-	-	-	-
5, 7-Dimethyl	-	-	-	-	-	-	-	-	-	-	-	-
5-Nitro	V. F.	.52	.44	620	V. F.	.25	.24	605	-	.01	.03	-
5-Phenyl	.30	.32	.31	620	.08	.20	.17	610	-	.03	.03	670
5, 7-Diphenyl	-	-	-	-	-	-	-	-	-	-	-	-
6, 7-Benzo	-	N. P.	-	-	-	-	-	-	-	-	-	-
6-Chloro-7-methyl	-	-	-	-	-	-	-	-	-	-	-	-
6-Methyl	.29	.24	.24	610	-	-	-	-	-	.02	.03	670
7-Chloro	-	-	-	-	-	-	-	-	-	-	-	-
7-Methoxy	.19	.25	.24	610	-	-	-	-	-	.02	.01	-
7-Methyl	.13	.26	.27	610	.08	.11*	.11*	600	-	.01	.02	670
7-Nitro	-	.04	.05	-	-	-	-	-	-	-	-	-
7-Phenyl	.24	.33	.32	620	-	-	-	-	-	.02	.02	670
4, 7-Dimethyl	-	-	-	-	-	-	-	-	-	-	-	-

$t_{1/2}$ in Minutes, AA in Absorbance Units, β -T in Absorption Units, λ_{max} in m μ .
 N. P. - Not Photochromic, V. F. - Very Fast, * Saturated solution.

TABLE 15

(Part B-3)

Standard Test Data for Indolinobenzospiropyrans

Fischer's Bases	Benzopyran Substituents											
	5'-Bromo-6'-Nitro-8'-Methoxy				5', 6'-Dinitro-8'-Methoxy				5'-Nitro-8'-Methoxy			
	$t_{1/2}$	ΔA	β -T	λ_{max}	$t_{1/2}$	ΔA	β -T	λ_{max}	$t_{1/2}$	ΔA	β -T	λ_{max}
4, 6-Diphenyl	.60	.39	.31	585	-	-	-	-	-	-	-	-
4, 7-Dimethoxy	-	.03*	.03*	580	-	-	-	-	-	.03	.04	610
4, 7-Dimethyl	1.6	.24	.20	585	-	-	-	-	-	-	-	-
5-Amino	-	-	-	-	-	-	-	-	-	-	-	-
5-Chloro	.22	.32	.29	585	2.9	.27*	.25*	620	-	.11	.08	570
5-(β -Hydroxyethyl)	-	-	-	-	-	-	-	-	-	-	-	-
5-Methoxy	2.8	.16	.15	610	-	-	-	-	-	-	-	-
5, 7-Dimethoxy	-	-	-	-	-	-	-	-	-	-	-	-
5-Methyl	1.2	.27	.23	580	-	-	-	-	-	-	-	-
5, 7-Dimethyl	2.3	.24	.21	580	-	-	-	-	-	-	-	-
5-Nitro	-	-	-	-	-	.59	.45	600	-	.02	.01	-
5-Phenyl	.48	.31	.27	590	-	-	-	-	-	.04	.06	610
5, 7-Diphenyl	-	-	-	-	-	-	-	-	-	-	-	-
6, 7-Benzo	-	-	-	-	-	-	-	-	-	-	-	-
6-Chloro-7-methyl	.16	.33	.27	590	-	-	-	-	-	-	-	-
6-Methyl	.82	.34	.27	580	-	-	-	-	-	.06	.06	570
7-Chloro	-	-	-	-	-	-	-	-	-	-	-	-
7-Methoxy	1.0	.21	.20	585	-	-	-	-	-	.04	.05	620
7-Methyl	1.4	.25	-	580	-	-	-	-	-	.03	.05	570
7-Nitro	-	-	-	-	-	-	-	-	-	-	-	-
7-Phenyl	.35	.31	.26	580	6.0	.26	.22	610	-	.06	.07	575

$t_{1/2}$ in Minutes, ΔA in Absorbance Units, β -T in Absorption Units, λ_{max} in $m\mu$,
N. P. - Not Photochromic, * Saturated solution.

TABLE 16

More Standard Test Data on Indolinbenzospirograns

Compound (BIPS)	t_R (min)	ΔA (Absorbance Units)	$\int 1-T$ (Absorption Units)	λ_{max} (m μ)
6'-Nitro-8'-Fluoro	.24	.17 *	.15 *	570
6'-Nitro-8'-Iodo	.36	.18 *	.16 *	600
6'-Nitro-8'-Allyl	.37	.24	.22	605
5-Chloro-6'-Nitro- 8'-Chloro	.16	.20 *	.16 *	605
5-Chloro-6'-Nitro- 8'-Bromo	.16	.24 *	.20 *	605
5-Chloro-6'-Nitro- 8'-Iodo	.17	.28	.21	615
5-Chloro-6'-Nitro- 8'-Allyl	.33	.38	.30	605
6'-Nitro-7'-Bromo	1.71	.21	.15	590
3'-Methyl-6'-Nitro 7'-Chloro	.15	.16	.13	585
5'-Chloro-6'-Nitro	2.6	.24	.15	590
7'-Nitro	.09	.15	.14	650
5', 7'-Dimethoxy-6', 8'-Dinitro	2.7	.12 *	.07 *	560
5-Nitro-8'-Methoxy	V. Fast	.11	.19	565
7-Methoxy-7'-Chloro	.47	.14	.12	600

* Data on saturated solution

The change in transmittance of the sample upon exposure to the constant energy flash source, as obtained from the photographed spectrum at λ_{max} , has been converted to a change in absorbance and thus presented in Table 15 as ΔA . These values are intended, along with the integrated absorption values to be the basis on which the relative sensitivities of the various compounds are established.

The time elapsed between exposure and readout is not definitely known but is somewhat less than one second. With this type readout, the time factor will have little effect on the ΔA values except for those compounds whose thermal color disappearance is extremely fast. It is felt therefore that the values listed indicate, in almost all cases, the maximum color obtained under the specific conditions. As was mentioned it must be kept in mind that a change in conditions, especially a change in the quality of exposing radiation, might produce different results.

The compounds falling at the top of the list as far as ΔA is concerned are of various structure. Molecules having 6'-nitro, 6'-nitro-8'-methoxy, and 5', 6'-dinitro-8'-methoxy substituents (originally substituents on their respective salicylaldehydes) all show reasonable sensitivity. By addition of the appropriate substituent(s) to the Fischer's Base half of the above molecules, a quite significant gain in sensitivity can be achieved. It should also be mentioned that a number of substituents on the Fischer's Base will decrease the sensitivity. Such groups as 3-phenyl-3-n-propyl, 4,6-diphenyl, and 5-nitro are shown to increase the sensitivity of 6'-nitro, and 6'-nitro-8'-methoxy BIPS by a factor approaching two. Because of the inherent insolubility of the 5', 6'-dinitro-8'-methoxy BIPS, relatively few of this series have been synthesized. On preparing the 5-nitro derivative it was found to be the most sensitive compound available. This opens another area for more work. No mention has been made of the 5'-bromo-6'-nitro-8'-methoxy BIPS because of the fact that no significant increase in sensitivity has been observed by addition of substituents to the Fischer's Base half of the molecule. The 6'-methoxy-8'-nitro and 5'-bromo-6'-methoxy-8'-

indolinobenzo-*spiro*pyrans were prepared and studied in the hope of finding a sensitive red absorber. These compounds show very poor sensitivity and further substitution has produced little if any improvement in sensitivity.

Integrated absorption ($\int 1-T$) is the integrated percent absorption over the visible range from 460 to 700 m μ . This is related to the neutral density equivalent of the colored sample and when used in conjunction with the ΔA value gives an indication of the breadth of the absorption band. The ΔA and $\int 1-T$ values are therefore the quantities which describe the sensitivity of the sample relative to some other sample under the same conditions.

The integrated absorption is obtained by dividing the area between the transmittance curve for the colorless form and the curve for the colored form by the total area under the transmittance curve for colorless form. The area measurements were taken directly from the photographed spectrum of each sample by use of a Kueffel and Esser No. 4236 compensating polar planimeter. The limited range of 460-700 m μ was necessary because of the inability to adjust the 100% line of the rapid scanning spectrophotometer to the proper position below 450-460 m μ . Since the region of concern in these determinations was near 600 m μ , this malfunction had no effect on the values obtained.

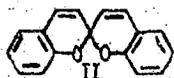
The series of compounds within the family of indolinbenzo-*spiro*pyrans that show the largest ratio of $\int 1-T/\Delta A$ contain the 6'-nitro-8'-methoxy substituents on the benzopyran half of the molecule. Substituents on the Fischer's Base component seem to have little effect on this value.

The half-lives ($t_{1/2}$) of the colored forms of all samples that showed reasonable sensitivity were determined at room temperature (22-23°C) on a Beckman DU spectrophotometer with the energy recording attachment. The calculation of half-lives was made from two (2) points, based on the assumption that the thermal fade followed first-order kinetics.

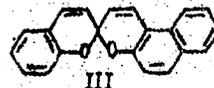
Compounds with 1-phenyl and 5-nitro substituents showed very short and in many cases unmeasurable half-lives. Substituents on both

the Fischer's Base and benzopyran halves have an effect on $t_{1/2}$. Many of these compounds whose sensitivity was so low as not to warrant the half-life determination were observed by the eye to be quite fast.

4.5. Study of the benzo- β -naphthospiropyrans. - Many compounds having the basic structure II and III react with ultraviolet light to produce a colored form exhibiting a very broad visible absorption spectrum. (Figure 38)



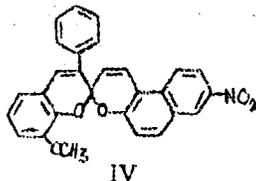
Dibenzospiropyran



Benzo- β -naphthospiropyran

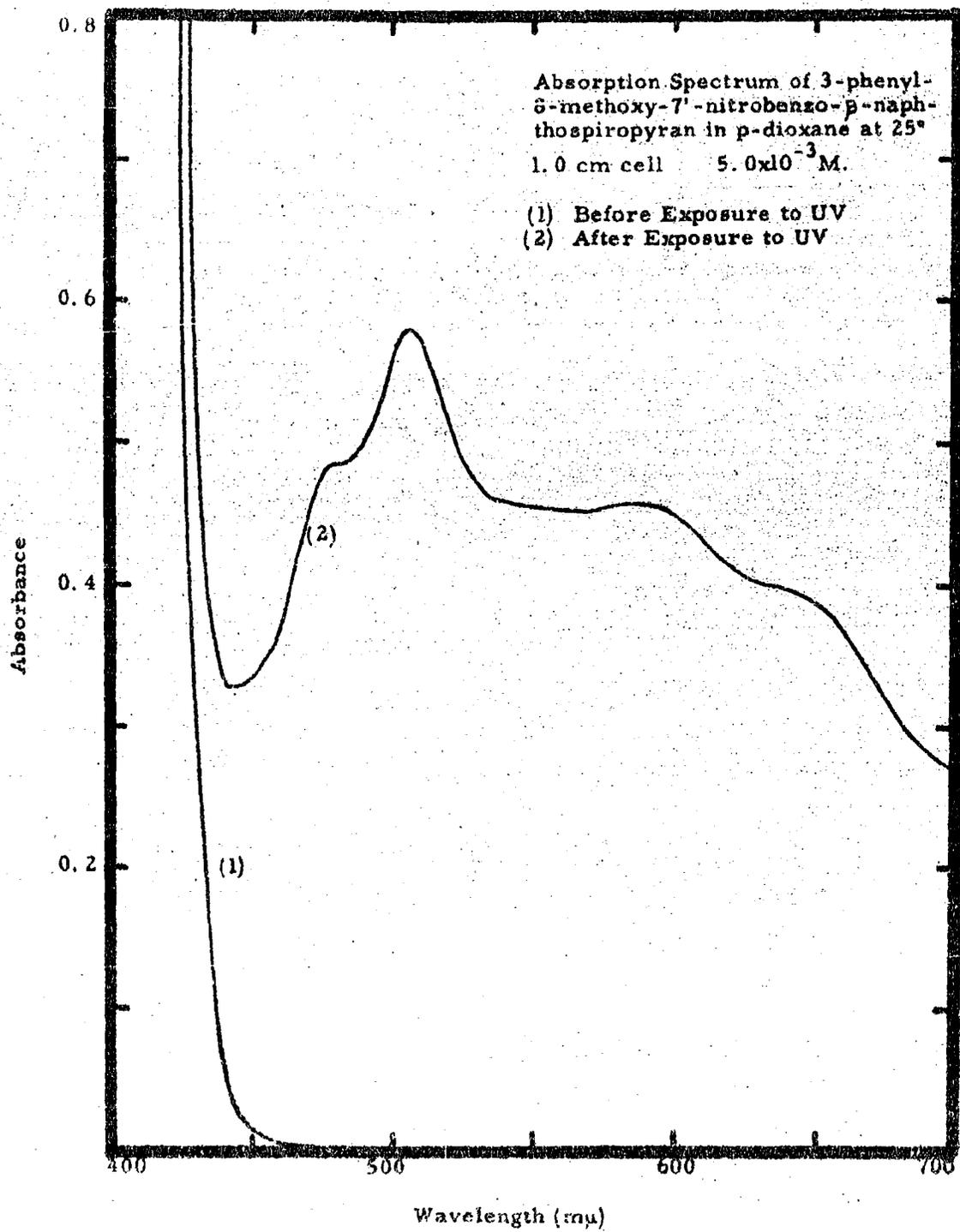
The efficiency of color formation appears substantially less among members of these groups than among indolinobenzospiropyrans. The fact that neutral or near-neutral density is produced when compounds analogous to II and III are exposed to ultraviolet radiation is sufficient reason to explore these compounds to determine if any increase in efficiency can be obtained. Certainly, use of a single material to obtain complete protection from visible radiation is more desirable than employment of several compounds in conjunction with permanent filters for this same protection. Very little experimental work on compounds of type II and III has been done in the past.

In order to obtain some understanding of the properties of materials of this type, a single compound (IV) was selected and examined for photochromic properties in a series of solvents. The structure for this compound is given below.



(3-phenyl-8'-methoxy-7'-nitrobenzo- β -naphthospiropyran)

Figure 38



4.5.1. Testing procedure - A small amount of the sample compound was placed in a Pyrex test tube and dissolved in the solvent to be tested. The sample solution was irradiated under a mercury vapor arc lamp. Each sample solution was examined for the following features: Color of the solution before irradiation; qualitative relative density of the coloration; and qualitative rate of color fade after the irradiation.

The purpose of this qualitative study was to disclose, if possible, the solvent or class of solvents which most favored photochromism in the selected compound. Marked variation in the photochromic properties was observed as the solvent was changed. A sample solution, prepared with p-dioxane as solvent, produced the greatest amount of color. In general, solvents containing ether linkages favored the phototransformation more than other types. Table 17 provides a list of the solvents tested to date.

4.5.2. Work done in film-forming materials - Compound IV has been placed in several film-forming materials and was found to be photochromic. Ethyl cellulose, N-50 viscosity grade and N-300 viscosity grade were dissolved in p-dioxane at several concentrations. An equal quantity of compound IV was added to each solution. When the solutions were exposed to ultraviolet radiation, they changed from light yellow to red-gray. Solutions containing the highest percent of cellulose lost the color faster than those of less concentration prepared from the same viscosity grade and color fade was faster in the lower viscosity grade than in the higher grade. (See Table 18)

Compound IV was found to be photochromic in polymeric solutions of polyvinyl chloride, Styron 689, and polyvinylpyrrolidone. Crude laminates prepared from Compound IV in the following polymeric solutions in p-dioxane were photochromic when exposed to the flash of a Braun "Hobby" unit: polyvinyl chloride (Geon Resin, B. F. Goodrich, 400 x 742); ethyl hydroxyethyl cellulose (EHEC High, Hercules); and Styron 689 (Dow). The laminate containing the ethyl hydroxyethyl cellulose seemed to give the largest amount of color of the several laminates prepared.

TABLE 17

Examination of 3-phenyl-8-methoxy-7'-nitrobenzo- β -naphthospiropyran in various solvents

Solvent	Source	Color before UV	Color after UV	Color fade
Chloroform (Fisher, C 574)	Fisher	yel	gray	S
Carbon tetrachloride	Fisher	V. L. yel	r-g	F
Nitrobenzene	Fisher N-91	yel	No C	-
Decalin	Eastman P 1905	yel	r-g	F
Acetonitrile	Sohio (crude)	yel	No C	-
p-dioxane	M. C. and B. 2347	yel	r-g	VS
N, N-Dimethylformamide	M. C. and B. 5974	yel	green-g	MF
Silicone Fluid	A. H. Thomas 6407j	clear	pur-r	S
o-dichlorobenzene	Eastman p 494	yel	r-g	MF
Halocarbon oil 11-14	Halocarbon Prod.	clear	N-C	-
Methylcyclohexane	Eastman S 946	clear	r-g	MF
Dodecene oxide	Beco Chem FMC	yel	r-g	VF
Caproic Acid	-	yel	N-C	-
n-hexane	M. C. and B. 5093	yel	r-g	S
Cyclohexanone	Eastman 972	yel	N-C	-
Mesityl oxide	Eastman T 582	yel	N-C	-
2, 3-Dichloro-p-dioxane	Eastman 3603	blue	N-C	-
Naphtha Solvent	Fisher N-3	clear	r-g	S
n-butyl ether	Eastman 173	yel	r-g	S
ethyl phthalate	Fisher E-162	yel	gray	VF
Cellaflex CEF	Celanese	yel	N-C	-
n-hexyl ether	Carbide and Carb.	yel	pur	ppt.
Ethyl ether	Fisher E-133	yel	g-black	S
Ethyl Acetate	-	yel	N-C	-
Tetrahydrofuran	-	yel	gray	S

TABLE 17, LEGEND

The symbols used in Table 17 (previous page) are explained below:

Colors

r-g = red-gray

pur = purple

N-C = no color
change

Color Disappearance

S = Slow

F = Fast

VS = Very Slow

MF = Moderately Fast

VF = Very Fast

TABLE 18

Photochromic Properties of 3-phenyl-8-methoxy-7'-nitrobenzo- β -naphthospiropyran
in Cellulose Materials.

Polymer Type*	% Polymer by Weight	Color after UV Irradiation	Time for Color to Fade \dagger
Ethyl Cellulose (Hercules, N-50)	0.1	gray-black	50 sec.
"	1.0	red-gray	30 sec.
"	10.0	red-gray	3 sec.
"	20.0	red-gray	1-2 sec.
Ethyl Cellulose (Hercules N-300)	1.0	red-gray	1 min.
"	5.0	red-gray	35 sec.
"	10.0	red-gray	10 sec.
Ethyl Hydroxyethyl Cellulose (Hercules High)	1.0	gray-black	2.5-3 min.
"	3.0	gray-black	2.5-3 min.
None (Pure p-dioxane)	-	gray-black	1-min.

* The polymer was dissolved in p-dioxane (M. C. and E. SC 2347)

\dagger The approximate time required for the color to disappear after irradiation.

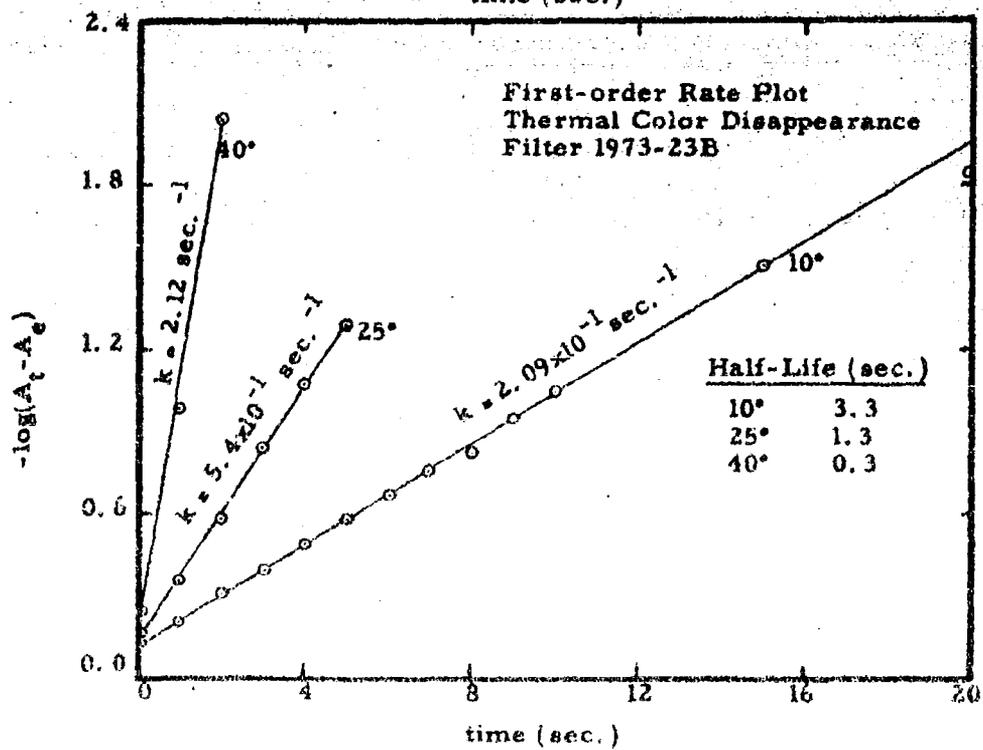
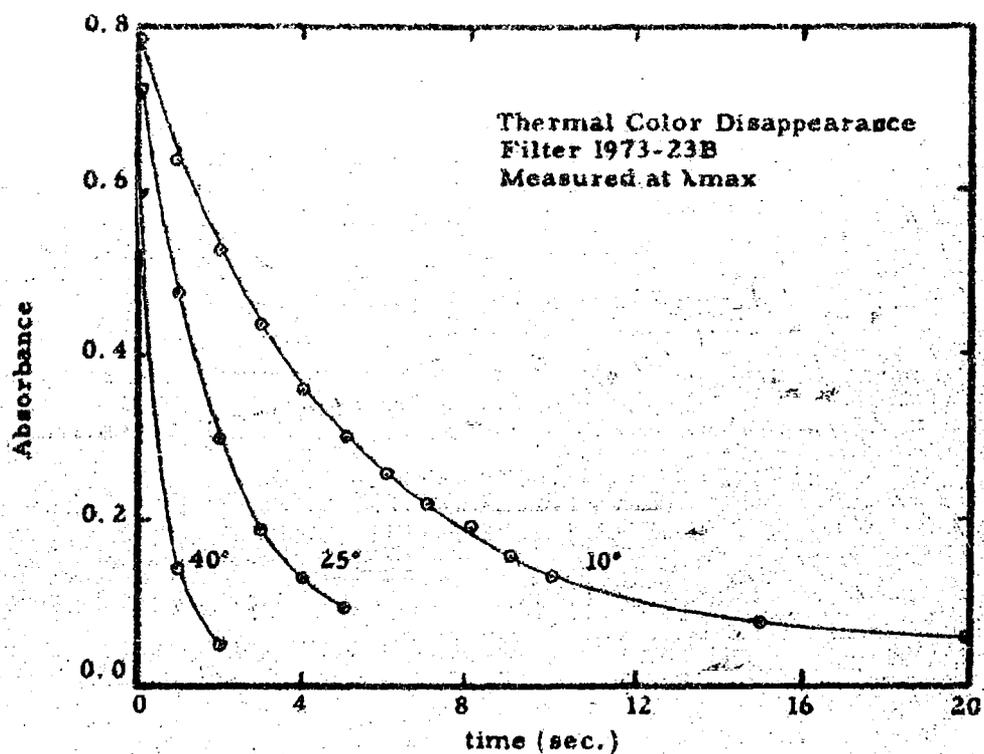
4.6. Thermal color disappearance in a photochromic filter -

At the outset of this contract solutions of several available spiropyran compounds were capable of becoming deeply colored when exposed to ultraviolet radiation and thermally decolorized within several seconds after removal of the radiating source. It was of interest to study the thermal reversibility of these photochromic compounds in polymeric media in connection with their potential use in eye protection systems. It has been shown that these compounds in polymeric media do color deeply under ultraviolet radiation and thermally decolor in very short times, a highly desirable property where eye protection is to be applied to air crew personnel.

One such compound, 1-phenyl-5'-bromo-6'-nitro-8'-methoxyindolino-benzospiropyran, was dissolved in an acryloid B-72-mesitylene mixture. The solution was placed between glass plates and heated from ten to twenty minutes in an oven then cooled to room temperature. A quantitative study was made of the thermal color loss in this filter by recording the absorbance at the visible λ_{max} versus time at three temperatures.

These data were plotted as absorbance versus time and as $-\log (A_t - A_e)$ versus time in Figure 39. At 25° over seventy-five percent of the color had faded within three seconds and the filter had completely changed from the colored (closed) condition to the transparent condition in approximately ten seconds.

Figure 39



5. EYE PROTECTION PROBLEMS

5.1. Discussion on self-attenuating eye-protective filters - Many people have had the opinion that the ultimate goal in eye protection against nuclear explosions would be the development of a self-attenuating system. The motive force for the operation of such a system would be the radiant energy from the nuclear explosion. Based upon present available data for electromagnetic radiation emitted from nuclear flashes, it is the opinion of NCR that current photochromic materials lack the necessary sensitivity to function satisfactorily as self-attenuating filters. There is, unquestionably, enough ultraviolet energy released from a nuclear detonation to activate the photochromic dyes, but not in a sufficiently short period of time (perhaps, 50 to 100 microseconds) to protect the eye adequately from the intense early light emitted from the nuclear device. Therefore, an auxiliary system has been proposed for the activation of the photochromic materials to insure rapid closure of the filter to a good protective density.

It is the opinion of NCR that current photochromic materials cannot function as self-attenuating filters to provide the necessary protection against nuclear flashes. However, it may be possible to use photochromic materials in self-attenuating filters where the time of closure and density requirement are not so stringent for the application.

In this section, a simplified analysis of a self-attenuating chemical-switch device will be presented. This presentation is intended only to be an approximate approach to the eye protection problem involving nuclear detonations and to lend some thought to the critical problem for a self-attenuating filter.

There is some indication that for effective eye protection against nuclear weapons a dynamic light-filter should reach its maximum optical density in a time period no later than 10^{-4} seconds after the initial detonation. During this period of time there is a rapid increase in the rate of emission of thermal radiation from the fireball. Let us assume that the maximum value is reached in approximately 10^{-4} seconds, at which time the surface temperature of the fireball is about $14,000^{\circ}\text{K}$.

In general, the total rate of emission of radiation will be the product of the intensity of thermal radiation and the surface area of the fireball, or

$$Q_s = 4\pi r^2 I_s \quad (76)$$

where Q_s = the total rate of emission of thermal radiation
 r = radius of fireball, and
 I_s = the intensity of radiation at the fireball's surface.

If the assumption is made that during the first 100 microseconds Q_s increases linearly with time, then it can be written that

$$E_s = \frac{Q_s t}{2} = 2\pi r^2 I_s t \quad (77)$$

in which E_s = the total energy emitted by the fireball in time t . The values of Q_s , r , and I_s are now those for these parameters at time t .

The Stefan-Boltzmann law for black-body radiation states that

$$I_s = \sigma T^4 \quad (78)$$

wherein T = the absolute temperature of the surface of the fireball at time t , and

$$\sigma = 5.7 \times 10^{-12} \frac{\text{watts}}{\text{cm}^2 \text{ degree}^4}$$

By combining equations (77) and (78) the following expression can be written for E_s :

$$E_s = 2\pi r^2 t \sigma T^4 \quad (79)$$

At a distance R from ground zero, a set of goggles with a normal surface area S will receive $S/4\pi R^2$ of the total fireball energy in time t . If, at present, atmospheric absorption is neglected, then equation (79) can be rewritten as

$$E_i = \frac{r^2 t \sigma T^4 S}{2R^2} \quad (80)$$

in which E_i = the total incident energy impinging on the goggles in time t . If the values of E_i , T and S are known, the total number of quanta, n , that

strike the filter can, in theory, be calculated by integration of Planck's equation for the distribution of energies in a black-body radiator. However, for the sake of simplicity, the value of n will be approximated in the following manner.

The total radiant energy incident on the filter will be looked upon as being made up of n photons, each of which carries energy, $h\nu_a$. In this case, ν_a is some type of "average" frequency and h is Planck's constant. Therefore, the total incident energy is

$$E_i = nh\nu_a \quad (81)$$

and

$$n = \frac{qr^2 \sigma T^4 S}{2h\nu_a R^2} \quad (82)$$

The following reasons are cited to indicate why all of the n photons will not be able to cause a photochemical change in the light filter:

- (1) Some of these photons will not reach the filter due to atmospheric absorption.
- (2) Some of the photons will not be absorbed by the phototropic material.
- (3) Some of the photons will not be of the proper energy needed to cause photochemical change.
- (4) Only a fraction of the photons which are absorbed by the active elements in the device will be effective in the switching, since the quantum efficiency will probably be less than unity.

The number of molecules, m , that will be switched in time t , will be only a fraction, q , of the theoretical number of impinging photons and can be expressed as

$$m = qn = \frac{qr^2 \sigma T^4 S}{2h\nu_a R^2} \quad (83)$$

The optical density or absorbance, A , is defined as

$$A = \epsilon cl, \quad (84)$$

in which

- ϵ = molar extinction coefficient per unit path length,
- c = molar concentration, and
- l = path length or filter thickness.

An expression can now be written for the absorbance, A, as

$$A = \frac{\epsilon m}{NS} \quad (85)$$

since

$$c = \frac{m}{NSl} \quad (86)$$

in which N represents Avogadro's number. The following equation is obtained by combining equations (83) and (85)

$$A = \frac{\epsilon q r^2 t \sigma T^4}{2N h \nu_a R^2} \quad (87)$$

Let us now consider a specific case of an observer 10,000 feet away from ground zero of a 20 kiloton nuclear explosion. Under these conditions, let us calculate the optical density, A, that a dynamic self-attenuating filter will have after 10^{-4} seconds. The following numerical values are needed for the solution of equation (87):

$$T \approx 14,000^\circ\text{K} \text{ (Approximate surface temperature of fireball at } 10^{-4} \text{ second)}$$

$$r = 50 \text{ feet (Radius of fireball at } 10^{-4} \text{ second)}$$

$$t = 10^{-4} \text{ sec.}$$

$$\sigma = 5.7 \times 10^{-12} \frac{\text{Watts}}{\text{cm.}^2 \text{ degree}^4}$$

$$\epsilon = 5 \times 10^4 \frac{\text{liter}}{\text{mole cm.}} \quad \text{or} \quad 5 \times 10^7 \frac{\text{cm.}^2}{\text{mole}} \quad \text{(Approximate value for photo-chromic dyes)}$$

$$N = 6.0 \times 10^{23} \text{ molecules/mole}$$

$$h = 6.6 \times 10^{-34} \text{ watt sec.}^2$$

$$R = 10,000 \text{ feet (Slant range)}$$

$$\nu_a = 7 \times 10^{14} \text{ sec.}^{-1} \text{ (Estimated from General Electric Radiation Calculator)}$$

$$q \approx 0.45 \text{ molecules/quantum (This value was obtained by assuming that the average surface temperature of the fireball during the first 100 microseconds is approximately } 9500^\circ\text{K. Then about 50 percent of the radiation will be of the proper wavelengths to be effective in photochemical switching. It was also assumed that 10 percent of this radiation is absorbed by the atmosphere and that the quantum efficiency of the absorbed radiation is unity. Thus, } q = 0.5 \times 0.9 \times 1 = 0.45, \text{ which is a very optimistic estimate.)}$$

Based upon these values and equation (87), an optical density, A , was calculated to be 2.2×10^{-2} for this example. This value for the optical density is smaller by a factor of over 100 than the minimal optical density that is generally believed to be needed to afford adequate eye protection.

The numerical values of the parameters that were used in equation (87) were, when necessary, estimated in a manner so as to give a higher value of optical density than would actually be obtained. The quantum efficiency in coloring photochromic materials is, in general, much less than unity. Moreover, it is probable that more than 10 percent of the ultraviolet radiation, which is the radiation needed to color the filter, will be absorbed by the atmosphere. A nuclear fireball, also, does not behave like a perfect black-body radiator. Therefore, less radiation even than that calculated would actually be available to initiate the switching process.

If an optical density of 2.2 were required within 100 microseconds, then a material with an impossibly high extinction coefficient of 5×10^6 liter/mole cm. would be necessary.

If the observer were closer than 10,000 feet from ground zero then a higher optical density could be expected since the radiation flux would be greater. At 5,000 feet, for example, an optical density in the filter of approximately 0.1 could be expected within 100 microseconds. At distances closer than 5,000 feet, other hazardous effects from the nuclear bomb will probably become more important than eye protection.

Although the first thermal pulse generates radiation of very high intensity, its duration is comparatively short. Therefore, although the intensity of radiation in the first 100 microseconds is probably great enough to cause flashblindness and produce retinal burns, the radiant energy in this period of time comprises only a small fraction of the total radiant energy of the nuclear explosion. It appears that the photon flux from the first pulse is too small to color significantly the filter.

If q was greater than unity (resulting from a quantum efficiency greater one), one photon could initiate a reaction that would color more than one molecule. Assuming this amplification to be large enough, self-activation might be a feasible result. In this case, however, the process

would be irreversible and it remains doubtful as to whether any simple techniques could change the photochromic material back to its original uncolored form.

A photopolymerization system might, indeed, provide the amplification needed for self-activation but once the polymer was formed, it would not be easy to change it back to the original monomeric system. A photopolymerization system might in all likelihood have too long an induction period for rapid closure of the filter.

5.2. Self-attenuating sunglasses. - In this section, a simplified analysis of a self-attenuating sunglass system, using a chemical-switch principle, will be presented. The general approach to this problem will be analagous to that described in the previous section. Effects of "fatigue", simultaneous heat erasure and other allied problems will not be considered.

If sunlight of intensity, I , is incident on sunglasses of area, S , for time, t , then the total energy, E_i , impinging on the glasses can be expressed by the following equation:

$$E_i = t I S \quad (88)$$

If this energy is imagined to be composed of n quanta of average frequency, ν_a , then

$$E_i = n h \nu_a \quad (89)$$

or

$$n = \frac{t I S}{h \nu_a}$$

Again, only a fraction, q , of these photons will be effective in producing chemical switching. Equation (89) can then be modified to give the expression

$$m = q n = \frac{q t I S}{h \nu_a} \quad (90)$$

in which m is the number of molecules switched in time t . By combining equations (85) and (90) the following expression is obtained:

$$A = \frac{\epsilon q t I}{h \nu_a N} \quad (91)$$

or

$$t = \frac{h \nu_a N A}{q \epsilon I}$$

Let us now take a specific example and use equation (91) to calculate the time needed to have the glasses reach an optical density of 2.0. The numerical values used in the solution of equation (91) are listed below:

$$h = 6.6 \times 10^{-27} \text{ erg sec.}$$

$$N = 6.0 \times 10^{23} \text{ molecules/mole}$$

$$A = 2.0$$

$$\epsilon = 5 \times 10^7 \text{ cm.}^2/\text{mole}$$

$$I \cong 10^6 \text{ ergs/cm.}^2 \text{ sec.} \quad (\text{Estimated from the solar constant by assuming that approximately 30 percent of sunlight is absorbed by the atmosphere.})$$

$$\nu_a \cong 10^{15} \text{ sec.}^{-1}$$

$$q \cong 8.5 \times 10^{-3} \text{ molecules/quantum}$$

Assuming the sun to have an effective black-body temperature of 5760°K , then about 17 percent of the total energy will consist of quanta which can be effectively used to color photochromic materials (i. e., wavelengths of light less than 435 millimicrons). If the quantum efficiency is estimated at 0.05, then $q \cong 0.17 \times 0.05$ or 8.5×10^{-3} molecules/photon. By substituting these values into equation 16, it is calculated that the time required for the self-attenuating sunglasses to obtain an optical density of 2.0 is approximately 20 seconds.

5.3. Response time of photochromic material. - In the presently studied eye-protective system, a flashtube is triggered in a very short time after the flash from a nuclear detonation is electronically detected. The ultraviolet light from the flashtube colors a photochromic material which in turn filters the intense visible (and ultraviolet) radiations from the remainder of the nuclear blast.

One of the requirements for an eye-protective device against thermal radiation from nuclear bombs is a rapid closure time. At the present state of the art, the closure time of photochromic goggles is in the range of 100 - 125 microseconds.

It may be considered that the closure time of photochromic goggles will be dependent upon the response time of the photochromic material. However, it can be shown that the response time of the

photochromic material is dependent upon that for the flashtube. The response or rise time of the energy from the flashtube is the slow step in the closure of the photochromic goggles.

There appears to be no real good spectral data available for the ultraviolet output of flashtubes. Nevertheless, it seems likely that data showing the efficiency of the spectral distribution of ultraviolet light in coloring photochromic materials would be very helpful in more thoroughly analyzing the light-coupling problem. Perhaps, a determination of the spectral efficiency of ultraviolet light, especially that which corresponds to the wavelengths of the more prominent mercury lines, in coloring the photochromic materials will be sufficient. Data of this nature have recently been obtained and are presented in an earlier section of this report.

Experimentally determined response times, optical density versus time, of a photochromic coating are shown in Figure 40. This response curve was measured with a 3-inch, Xenon flashtube, supplied by Edgerton, Germeshausen and Grier, Inc., (Boston, Mass.). The ultraviolet light produced by this flashtube was used to color the photochromic material. The flashtube was triggered with 1800 volts from a 100 microfarad, oil-filled capacitor employing 5-foot lead wires. The optical density produced in the photochromic material on a quartz wedge does not necessarily represent maximum density of the material. The rise time of the flashtube is presented in Figure 41.

An empirical equation which describes approximately the output of a flashtube that is used to produce the ultraviolet energy for coloring photochromic filters can be expressed as

$$\frac{I}{I_M} = \left(\frac{t}{\tau}\right)^2 \exp [2 (1-t/\tau)] \quad (92)$$

in which

- I = intensity of flashtube output at time t,
- I_M = intensity of flashtube output at time τ , and
- τ = rise time of flashtube, i. e., the time at which the maximum intensity is reached.

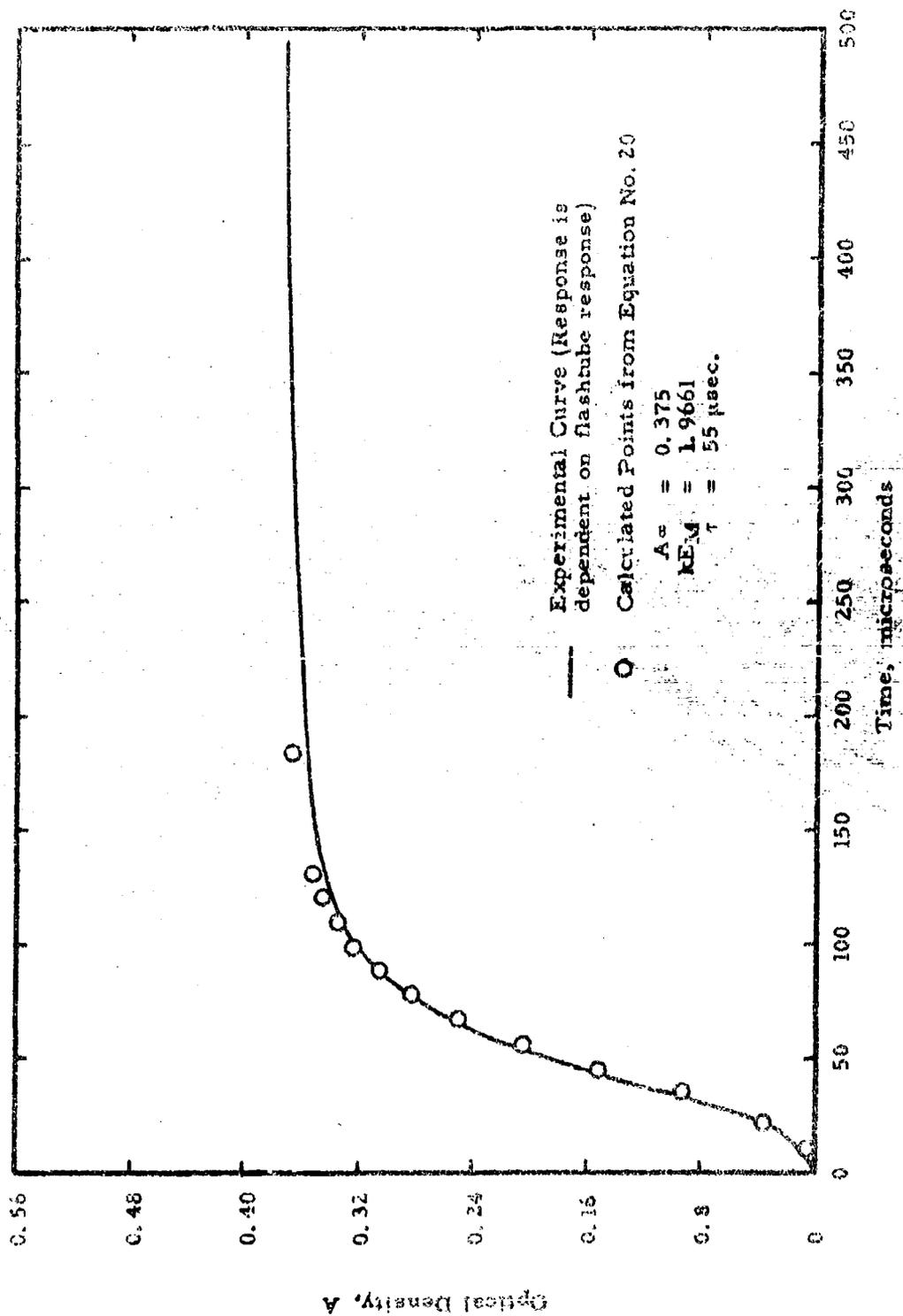


Figure 40. Optical Density versus Response Time for a Photochromic Coating, F-136, on a Wedge

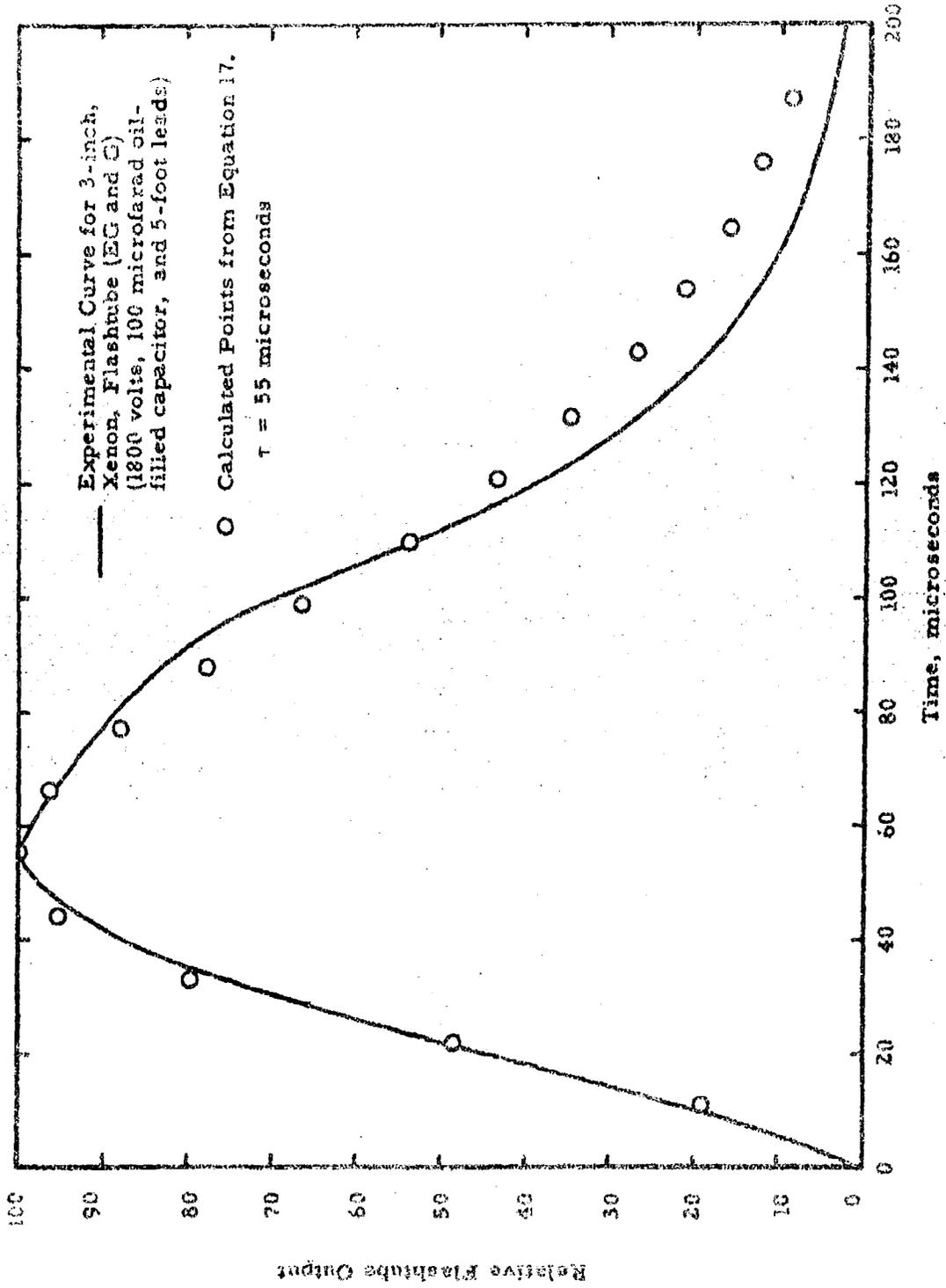


Figure 41. Relative Flashtube Output versus Time

A plot of equation (92), I/I_M versus t/τ , is made in Figure 42. Using 55 microseconds for the value of τ , equation (92) is compared in Figure 41 to the flashtube output curve, which was experimentally determined.

It has been experimentally observed that under the condition when most of the incident light is absorbed by the colorless species, then the rate of color formation may adequately be described as a first-order reaction with respect to both concentration of the colorless form and intensity of the incident light. Such is the case of many photochromic films and solutions presently being used in eye-protective devices. The rate of color formation may be expressed as

$$\frac{dA}{dt} = kI(A_M - A) \quad (93)$$

wherein

- A = optical density of colored photochromic species;
- A_M = expected optical density if all of the photochromic material were converted to the colored form; and
- k = an efficiency factor which includes the fraction of light of proper wavelengths to cause switching and that hits the filter, the fraction of light absorbed by the photochromic material, and the quantum efficiency of the photochemical process.

By combining equations (93) and (92) and integrating the resulting expression, one obtains

$$A = A_M \left\{ 1 - \exp \left[-kE_M \left(1 - e^{-\frac{-2t}{\tau}} \cdot \left[2 \left(\frac{t}{\tau} \right)^2 + 2 \left(\frac{t}{\tau} \right) + 1 \right] \right) \right] \right\} \quad (94)$$

Equation 94 can be rewritten generally as

$$\frac{A}{A_\infty} = \frac{1}{1 - e^{-kE_M}} \left\{ 1 - \exp \left[-kE_M \left(1 - e^{-\frac{-2t}{\tau}} \cdot \left[2 \left(\frac{t}{\tau} \right)^2 + 2 \left(\frac{t}{\tau} \right) + 1 \right] \right) \right] \right\} \quad (95)$$

where

- E_M = the total energy output of the flashtube, and
- A_∞ = the experimentally observed optical density which the filter reaches after the completion of the flash.

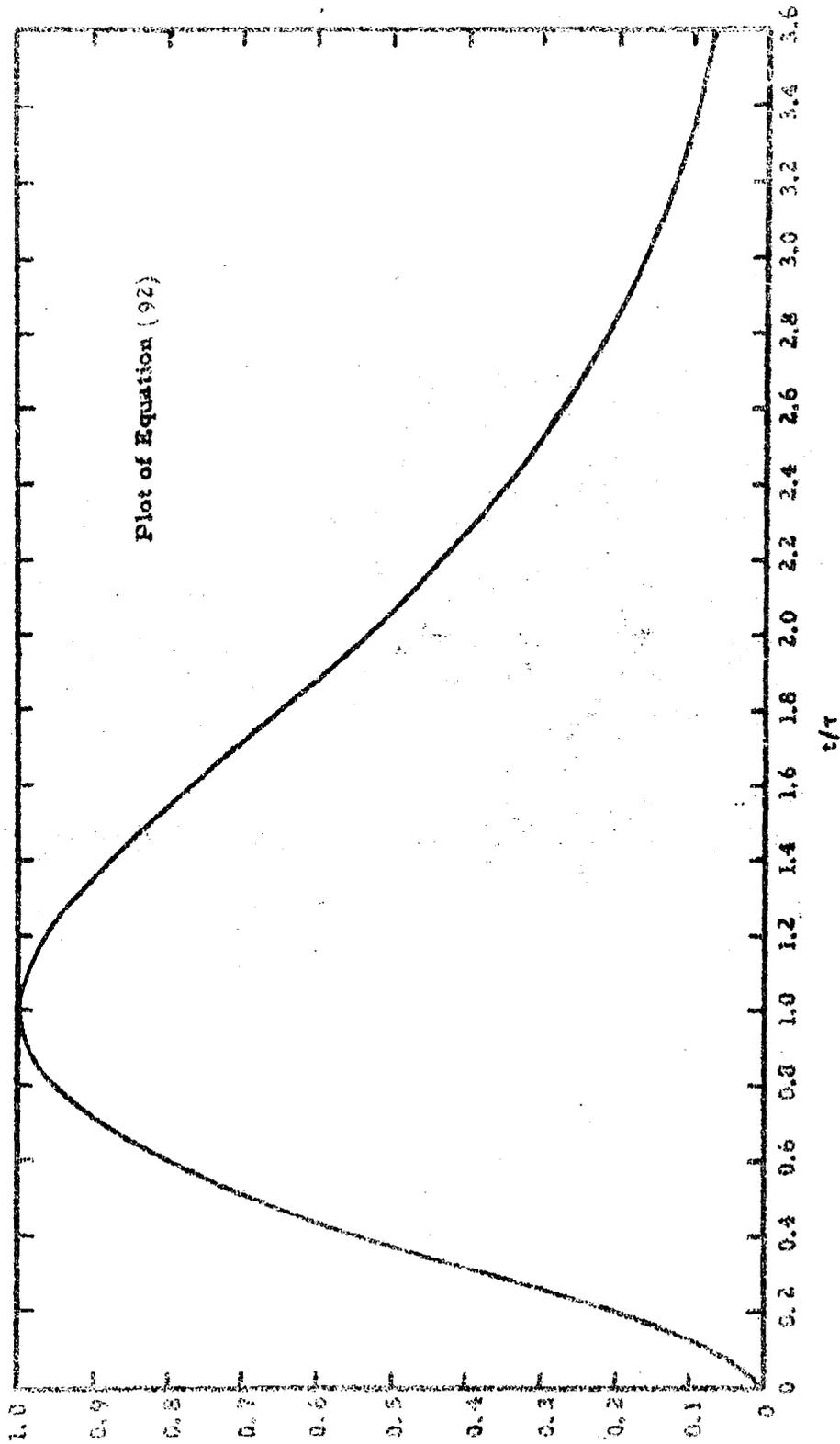


Figure 42. Normalized Output of Flashtube, $1/I_M$ versus Normalized Time, t/τ .

A normalized plot of equation (95), A/A_∞ versus t/τ , for six different values of kE_M is made in Figure 43. The limiting curve is for a value of kE_M less than 0.1 and represents the slowest possible response. In Figure 40 calculated values from equation (95) are compared to the experimental data. In making these calculations, the following values of parameters were used:

$$\tau = 55 \text{ microseconds, } A_\infty = 0.375, \text{ and } kE_M = 1.9661$$

It should be pointed out that the mathematical expressions are based upon several assumptions and limited experimental data. Nevertheless, it is believed that these equations and, in particular, the normalized plots shown in Figures 42 and 43 can be used to predict the rise times of flashtubes needed to insure a given closure time for the photochromic filters.

If the intensity of the visible radiation from the fireball, that is incident on the photochromic filter, is known as a function of time, then calculations could be made as to the amount of visible light that transmitted through the filter and incident on the eye. From the Beer-Lambert law -

$$I_t(t', T, d, R) = I_i(t', T, d, R) \cdot 10^{-A} \quad (96)$$

where

$I_t(t', T, d, R) = I_t$ = Transmitted intensity of visible radiation from the fireball, through the filter. I_t is a function of time after detonation (t'), the surface temperature of the fireball (T), the fireball diameter (d) and the distance from the fireball (R).

$I_i(t', T, d, R) = I_i$ = Incident intensity of visible radiation from the fireball impinging on the photochromic filter.

If the flash tube is triggered at a time α , after the bomb is detonated, then -

$$t' = t + \alpha$$

From equations (95), (96) and (97).

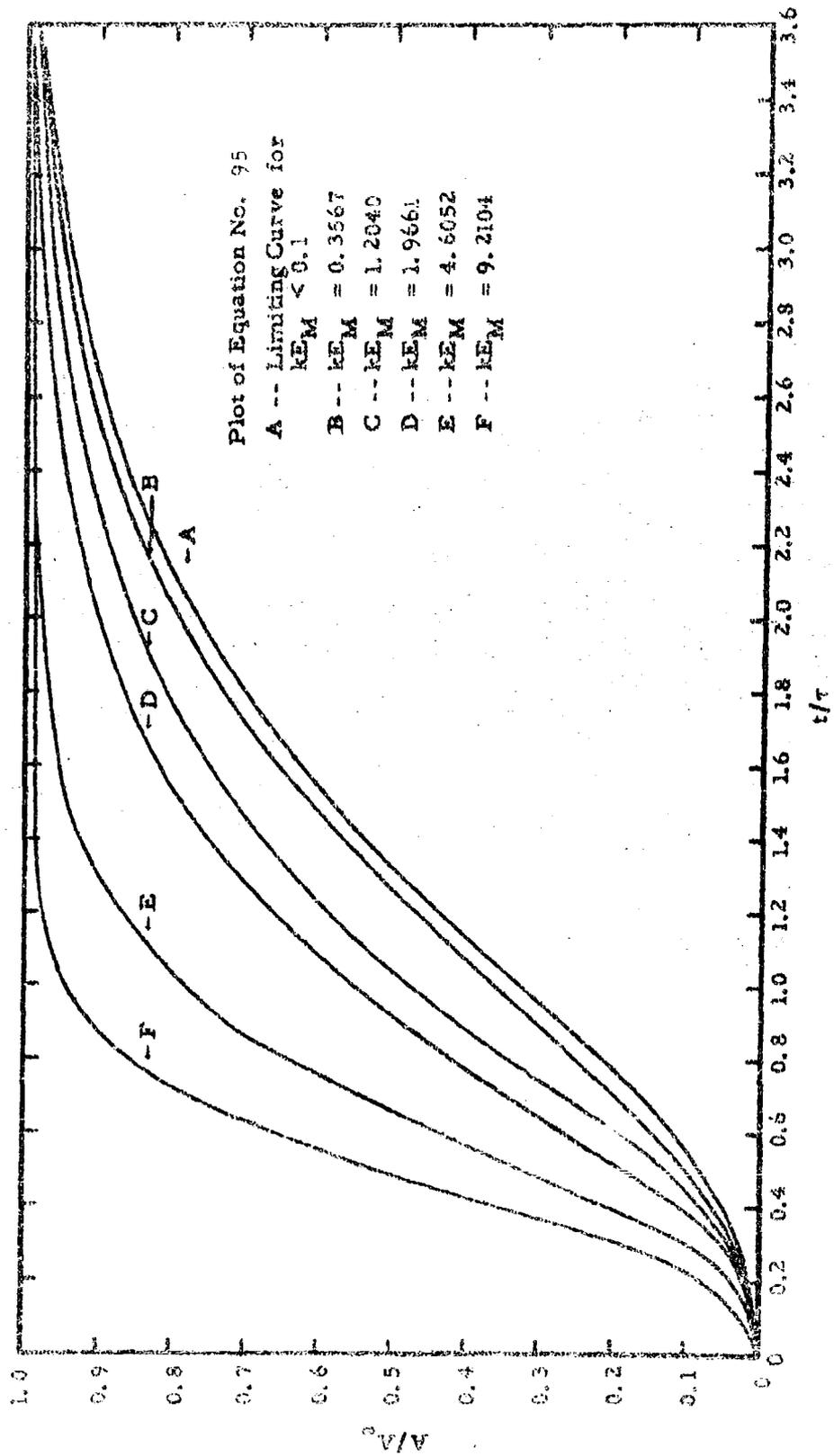


Figure 43. Normalized Plot of Optical Density versus Time for a Photochromic Filter

$$I_i(t + \infty, T, d, R) = I_i 10^{-\frac{A_\infty}{1 - e^{-kE_M}} \left\{ 1 - \exp \left[-kE_M \left(1 - e^{-2(t/\tau) [2(t/\tau)^2 + 2(t/\tau) + 1]} \right) \right] \right\}} \quad (94)$$

Therefore, if accurate information concerning the fireball becomes available, the calculation of the light transmitted through the photochromic filter as a function of time can be accomplished.

6. SYNTHETIC WORK

Synthetic work under the contract was kept at a minimum since the major emphasis of the contract was to study in detail various aspects of the photochromic mechanism in spiropyrans. Only such syntheses which could help elucidate the structural requirements for photochromic behavior or could substantially enhance certain desirable properties (quantum yield, extinction coefficients, rate of thermal fade, etc.) of the spiropyrans were attempted.

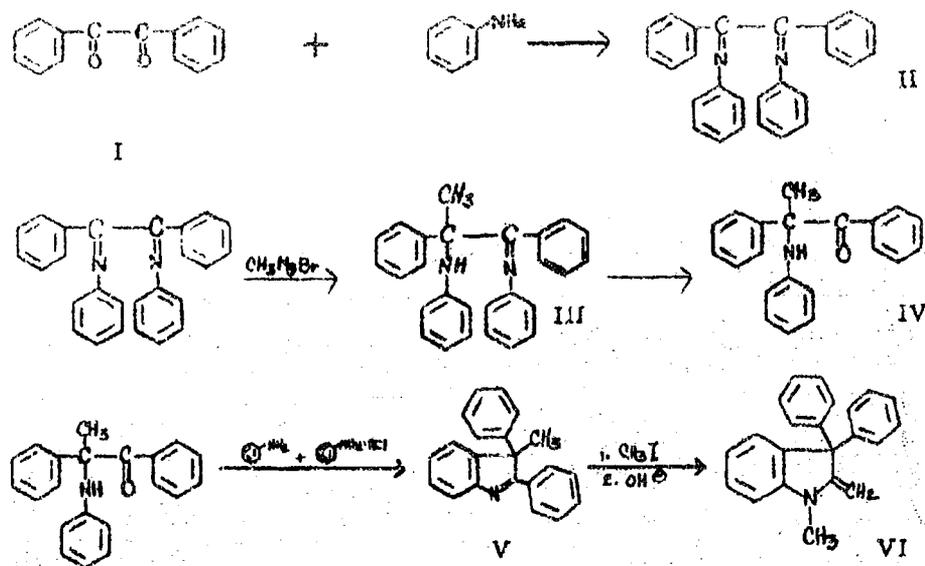
The following syntheses and attempted syntheses therefore fall into two groups: 1) Variations in substituents on the parent indolinobenzospiropyran to determine the effect of such substituents on overall sensitivity (amount of coloration produced for a given amount of UV irradiation) and 2) Basic structural variations on the spiropyran molecule.

6.1. Variations in substituents. - The work done in the latter months of the previous contract (AF 41 (657)-215) and various references in the literature gave an indication that some significant changes in the characteristics of the indolinobenzospiropyrans might be obtained if various substituents other than the methyl groups were contained at the "3" position. Consequently various indolines were prepared which contained either an aryl and an alkyl group or two aryl groups in this position. Indolinobenzospiropyrans were prepared from these indolines and preliminary tests indicated that a moderate increase in sensitivity had been achieved.

It was then decided to determine whether this was a steric or an electronic effect. To determine this the syntheses of indolines containing an electron withdrawing group and an electron donating group on the 3-phenyl substituent were started. These indolines have not yet been successfully prepared and an analysis of the effects is therefore not available.

A second indication for synthetic work also came from the analytical program. It was noted that indolinobenzospiropyrans which contained the 5-nitro substituent were very sensitive and had fast fade rates. Very few 5-nitro substituted compounds were available for testing so a short synthetic program was started to furnish a sufficient number of such compounds and similar compounds so that their general characteristics could be determined.

Preparation of 1-methyl-2-methylene-5,3-diphenylindoline.



In 500 ml. round bottom flask were placed 63 g. (0.31 mole) of benzil, 90 g. (0.96 mole) of aniline and 1 drop of hydrochloric acid and the mixture was heated for an hour at 160-170° in a carbon dioxide stream. The brown oily melt was stirred in ethanol and upon scratching a large quantity of yellow crystals formed, which consisted of 60 g. of dianil contaminated with monoanil. Through recrystallization from ethanol, in which the dianil was much less soluble than the monoanil, 38 g. of benzil dianil (II) was obtained with a melting point of 139-142°.

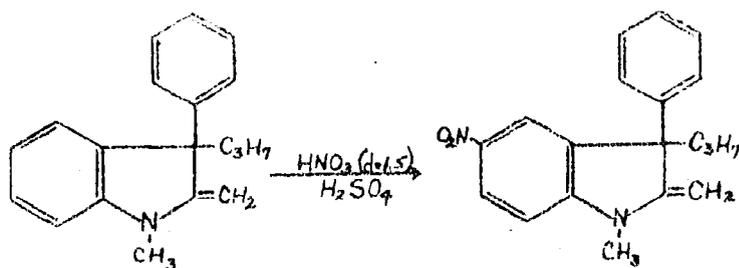
A suspension of 32 g. (0.089 mole) of benzil dianil in 100 ml. of ether was added to a solution of 0.3 mole of methyl magnesium bromide in 100 ml. of ether. The solution was refluxed for 3 hours and then decomposed by pouring into water. The water solution was extracted with ether and 11 g. of a yellow solid (melting point of 147-153°) was obtained from the ether layer. This was identified as α -methyl- α -anilinobenzil anil (III).

The 11 g. (0.03 mole) of α -methyl- α -anilinobenzil anil was added to 200 ml. of 12% hydrochloric acid and refluxed for 1 hour. The hydrochloride was obtained as a white solid with a melting point of 138-141°. This hydrochloride was dissolved in ethanol, water was added and 7 g. of yellow solid with a melting point of 141-142° was obtained and identified as α -methyl- α -anilindesoxybenzoin (IV).

In a 100 ml. round bottomed flask were placed 7 g. (0.024 mole) of α -methyl- α -anilino-desoxybenzoin, 17 g. (0.18 mole) of aniline, and 1.5 g. (0.015 mole) of aniline hydrochloride. The solution was heated to 170° for 3 hours, cooled to room temperature and washed with water several times to yield 3 g. of white powder with a melting point of 144-146° which was identified as 2-phenyl-3-methyl-3-phenylindolenine (V).

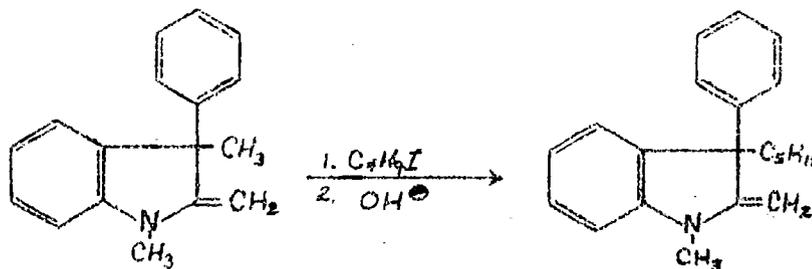
This 2-phenyl-3-methyl-3-phenylindolenine was methylated by refluxing with methyl iodide for three hours. The yellow solid obtained was recrystallized from acetone-ether to give 1.6 g. of yellow crystals with a melting point of 221-223° which was identified as 1,2-dimethyl-3,3-diphenylindolinium iodide. This iodide was decomposed with base, extracted with ether to yield a light green oil which was identified as 1-methyl-2-methylene-3,3-diphenylindoline (VI) by condensation with various salicylaldehydes.

Preparation of 1-methyl-2-methylene-3-phenyl-3-n-propyl-5-nitroindoline.



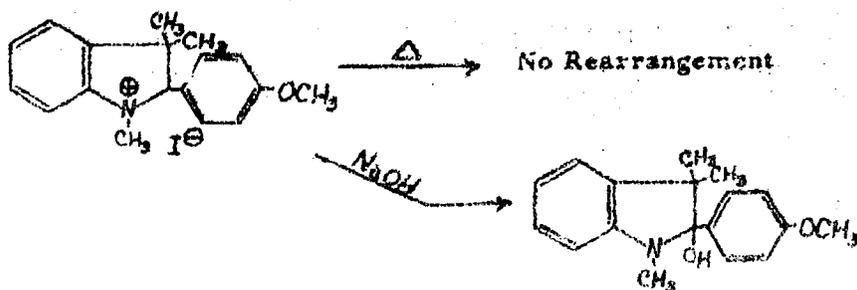
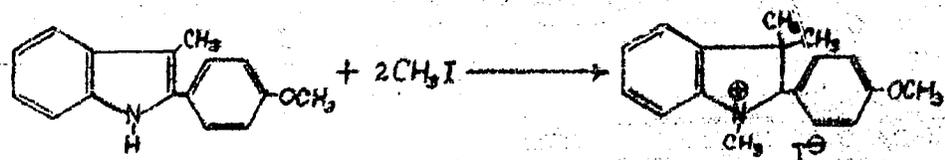
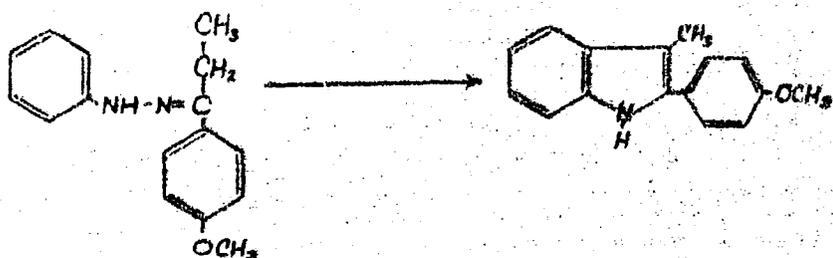
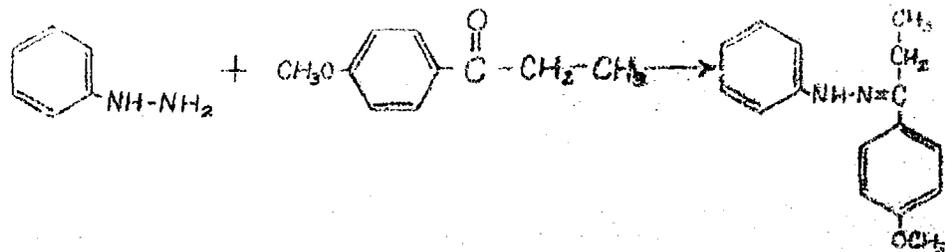
A 5.8 g. sample of 1-methyl-2-methylene-3-phenyl-3-n-propylindoline was added to 52 g. of sulfuric acid holding the temperature below 50°. The solution was cooled to 15° and 1.5 g. of nitric acid (d = 1.5) was added at a rate to maintain the temperature of the solution below 20° C. It was allowed to stand one hour at room temperature, then poured into ice water. On neutralizing with sodium hydroxide, 5 g. of 1-methyl-2-methylene-3-phenyl-3-n-propyl-5-nitroindoline was obtained as a yellow solid.

Preparation of 1-methyl-2-methylene-3-phenyl-3-n-pentylindoline.



1,3-dimethyl-3-phenyl-2-methyleneindoline (31 g. ; 0.13 moles), 48 g. (0.25 mole) of n-butyl iodide, and 35 g. of n-butyl alcohol were reacted in an autoclave for five hours at 130°. The pink solid obtained was recrystallized from ethanol to give a melting point of 227-229°. This iodide was decomposed with base, extracted with ether, and the product was distilled at 125-140°/0.3-0.5 mm. to yield 7 g. of 1-methyl-3-phenyl-3-n-pentyl-2-methyleneindoline.

First attempted preparation of 1,3-dimethyl-3-(p-methoxyphenyl)-2-methylene indoline.



A 100 g. (0.66 mole) sample of 4-methoxy proptophenone (Aldrich Chemical Co.) and 71 g. (0.66 mole) of phenylhydrazine were refluxed in 100 ml. of 95% ethanol containing a few drops of glacial acetic acid for 30 minutes. The reaction mixture was cooled and the product was removed by filtration and recrystallized from ethanol to give 53 g. (0.2 mole, 30% yield) of the hydrazone.

This hydrazone was refluxed for 30 minutes in 2 N sulfuric acid. The reaction mixture was cooled and filtered and the product was recrystallized from ethanol to give 32 g. (0.135 mole, 67.5% yield) of 2-(p-methoxyphenyl)-3-methyl indole, m. p. 126-127°.

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.3

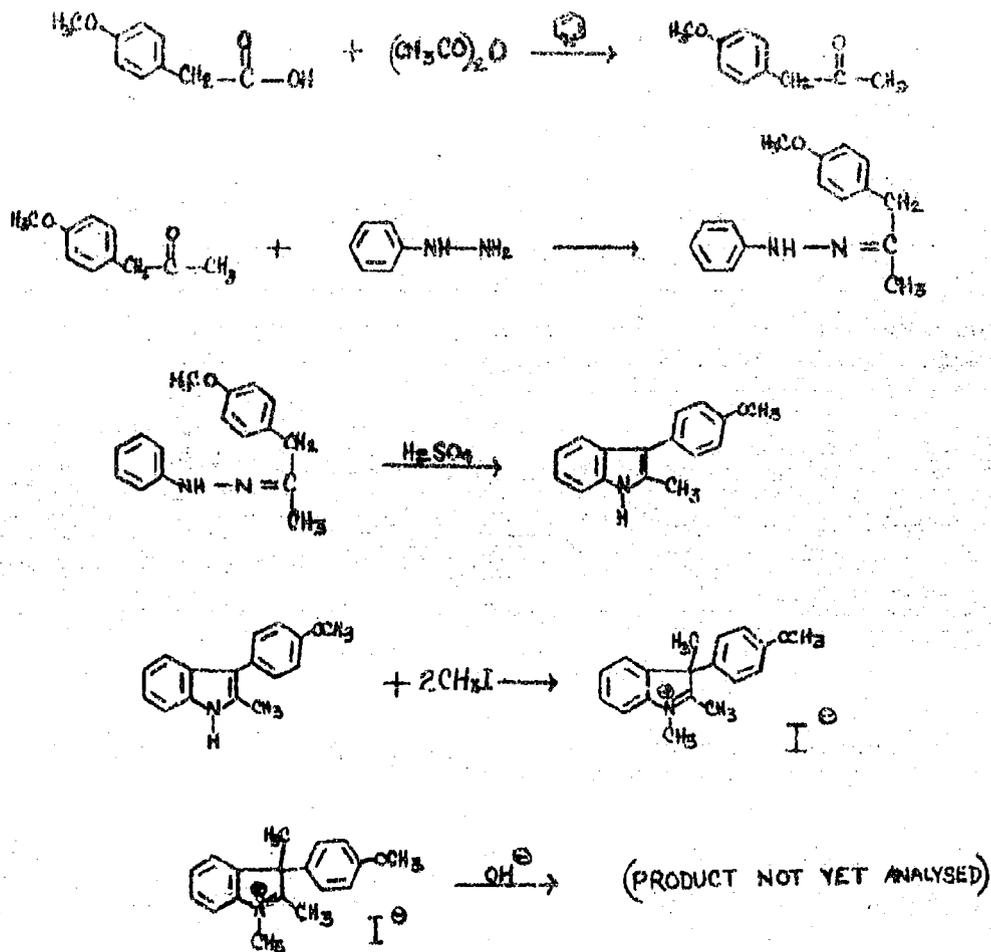
Found: C, 81.2; H, 6.1

A 30.0 g. (0.127 mole) sample of 2-(p-methoxyphenyl)-3-methylindole was heated to 125° for five hours in an autoclave with 54 g. (0.38 mole) of methyl iodide and 30 ml. of methanol. The reaction mixture was washed with acetone and filtered to give 5.1 g. (0.0205 mole, 16% yield) of what was assumed to be 1,3,3-trimethyl-2-(p-methoxyphenyl) indoleninium iodide, m. p. 203-205°.

A small portion of this indoleninium iodide was heated above its melting point to cause it to rearrange to the 1,2,3-trimethyl-3-(p-methoxyphenyl) indoleninium iodide salt. The resulting melt was treated with base and extracted with ether. The ether extract was evaporated and the residue was refluxed with a small amount of 5-nitrosalicylaldehyde. No photochromic product could be found in this reaction mixture. It was then concluded that no rearrangement had occurred on heating the indoleninium salt.

A second small portion of the 1,3,3-trimethyl-2-(p-methoxyphenyl) indoleninium iodide was treated with base and extracted with ether. An IR spectrum of the dried and evaporated ether extract showed a strong O-H absorption band indicating that the product is probably the 1,3,3-trimethyl-2-(p-methoxyphenyl) indolin-2-ol.

Second attempted preparation of the desired indoline was then tried.

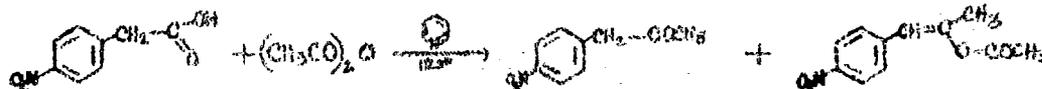


Using the method of G. G. Smith(13) 66 g. (1.0 mole) of p-methoxyphenylacetic acid (Matheson, Coleman and Bell, m. p. 85-87°) was dissolved in 400 g. of pyridine and 970 g. of acetic anhydride in a 2-liter 3-necked flask fitted with a thermometer, a mechanical stirrer and a reflux condenser which was fitted with a drying tube. The well stirred mixture was heated at 125-130° for 78 hours. The pyridine and unreacted acetic anhydride were removed under vacuum and the residue was hydrolyzed with aqueous sodium hydroxide. The hydrolysis mixture was extracted with ether. The ether extract was evaporated and distilled to give 61 g. (0.405 mole, 40% yield of crude anisylacetone, b. p. 132-140°/5 mm. Lit. value 117-122°/5-6 mm. G. G. Smith).

A 44 g. (0.405 mole) portion of phenylhydrazine and 61 g. (0.405 mole) of anisylacetone were refluxed for 1 hour in 75 ml. of ethanol containing few drops of acetic acid. The reaction mixture was cooled and treated with a large volume of water which caused the formation of two layers. The organic layer was drawn off and vacuum distilled to give 21 g. (0.085 mole, 21% yield) of what was assumed to be 2-methyl-3-(p-methoxyphenyl) indole, b. p. 205-210° /1 mm.

The 2-methyl-3-(p-methoxyphenyl) indole was methylated in the usual manner with 3 equivalents of methyl iodide in an autoclave at 125°, the salt obtained was decomposed with base and distilled but has not yet been characterized.

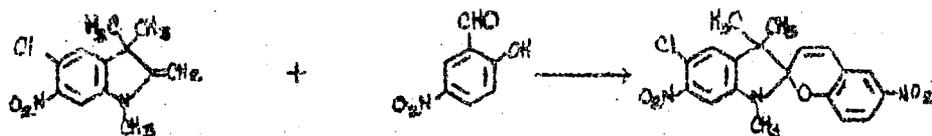
Attempted preparation of 1-(p-nitrophenyl)-2-propanone.



A 500 ml. three-necked flask was fitted with a mechanically driven sealed stirrer, a thermometer, adjusted so that the bulb extended into the reactants, and a reflux condenser. A mixture of 54.0 g (0.3 mole) of p-nitrophenylacetic acid, 120 g. (1.5 moles) of pyridine and 290 g. (2.85 moles) of acetic anhydride was heated with stirring for a period of 24 hours at 120°. The pyridine and excess acetic anhydride were removed by vacuum distillation. Fractional vacuum distillation of the residue yielded the enol acetate of 1-(p-nitrophenyl)-2-propanone. An attempted alkaline hydrolysis to the ketone resulted in the loss of the compound.

Preparation of photochromic compounds. Following is a typical preparation of an indolinobenzospiropyran. Table 19 lists the other spiropyran prepared during the contract period.

Preparation of 5-chloro-6,6'-dinitroindolinobenzospiropyran.



To a solution of 6.6 g. of 5-nitrosalicylaldehyde in 50 ml. of 95% ethanol was added 10 g. of 1,3,3-trimethyl-2-methylene-5-chloro-6-nitroindoline. The resulting mixture was refluxed for two hours. The reaction mixture was cooled and the precipitate which formed was removed by filtration and recrystallized from ethanol. This gave 5-chloro-6,6'-dinitroindolinobenzospiropyran with a m. p. of 249-250°.

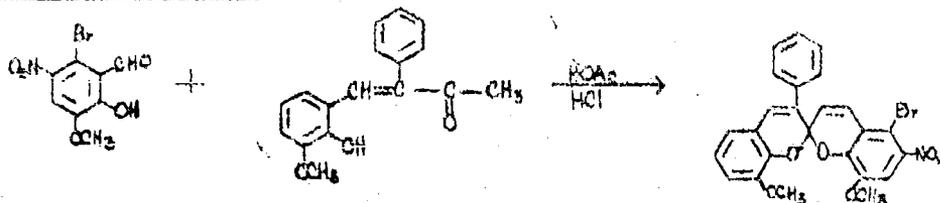
Anal. Calcd. for $C_{19}H_{16}N_3O_5Cl$: C, 56.79; H, 4.01

Found: C, 56.9; H, 4.0

TABLE 19
Synthesized Indolinbenzospiropyrans

Compound	Formula	m. p.	%C		%H		%N	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
5-chloro-6,6'-dinitro	$C_{19}H_{16}N_3O_5Cl$	249-50°	56.79	56.9	4.01	4.0	-	-
5-chloro-6,6'-dinitro-8'-methoxy	$C_{20}H_{18}N_3O_6Cl$	268-70°	55.63	55.4	4.20	4.1	-	-
5-chloro-6,5',6'-trinitro-8'-methoxy	$C_{20}H_{17}N_4O_8Cl$	200-1°	50.37	50.6	3.59	3.6	-	-
3,3-diphenyl-5'-bromo-6'-nitro-8'-methoxy	$C_{30}H_{23}N_2O_4Br$	230-1°	64.8	64.9	4.17	4.3	-	-
3-phenyl-3-n-propyl-6'-nitro-8'-methoxy	$C_{27}H_{26}N_2O_4$	171-2°	73.2	-	5.92	-	6.33	6.4
3-phenyl-3-n-propyl-5,6'-dinitro-8'-methoxy	$C_{27}H_{25}N_3O_6$	138-40°	66.51	-	5.16	-	5.6	5.6
3-phenyl-3-n-pentyl-6'-nitro-8'-methoxy	$C_{29}H_{29}N_2O_4$	170-1°	74.01	-	6.42	-	5.94	6.0
1-phenyl-5',6'-dinitro-8'-methoxy	$C_{25}H_{21}N_3O_6$	-	65.35	65.5	4.6	4.6	-	-

Preparation of 8-methoxy-3-phenyl-5'-bromo-6'-nitro-8'-methoxy-
dibenzospiropyran.



This compound was incorrectly referred to as 3-phenyl-8-methoxy-5'-bromo-6'-nitrobenzo- β -naphthospiropyran in Quarterly Report No. 1 of the contract.

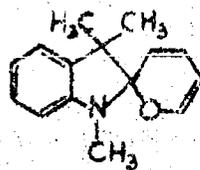
In a 125 ml. Erlenmeyer flask were placed 2.75 g. (0.01 mole) of 3-methoxy-5-nitro-6-bromosalicylaldehyde and 2.2 g. (0.01 mole) of 3-methoxy-2-hydroxystyryl- α -phenyl methyl ketone and 30 ml. of glacial acetic acid. The solution was saturated with dry hydrogen chloride and allowed to stand overnight at room temperature.

Green crystals (4.5 g., yield of 85%) were obtained by filtering and washing several times with ether. The pyrylium salt was hydrolysed by dissolving in acetone and adding ammonium hydroxide until the solution changed from blue to yellow. The yellow solid obtained was decolorized with Norite and recrystallized two times from an acetone-water solution to yield yellow needles with a melting point of 207-209°.

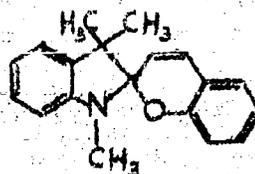
Anal. Calc. for $C_{25}H_{18}NO_6$ Br: C, 59.06; H, 3.56

Found: C, 59.3; H, 3.7

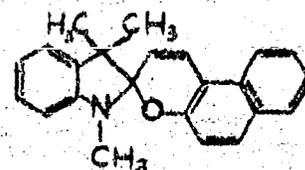
6.2. Basic structural changes. - Several correlations between structure and photochromic properties have been observed in the course of previous investigations of the spiropyrans and it appeared highly advisable to quickly survey several other immediately apparent structural variations before proceeding too far with an evaluation of the ultimate utility of these compounds. The previously observed difference in sensitivity between the indolino- β -naphthospiropyran series (NIPS) and the indolinobenzospiropyran series (BIPS) suggested that possibly



IPS



BIPS

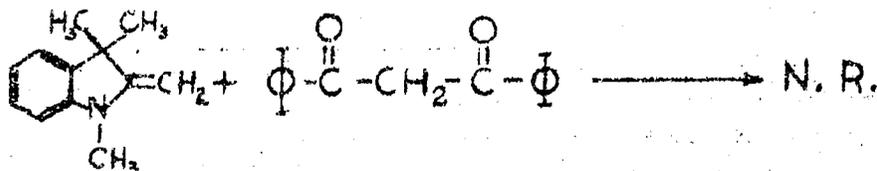


NIPS

a comparable change in sensitivity could be obtained in the indolino-spiropyran series (IPS). The dramatic change in thermal fade rate produced by replacing the 1-methyl group with a phenyl also led to speculation concerning the affect of a similar replacement by an acyl group. A short review of the preparations and results of these and other structural variations is given in the following sections.

Attempted synthesis of indolinospiropyran. - Various attempts were made to synthesize indolinospiropyran (IPS) compounds by methods analogous to the preparations of the BIPS compounds. The few attempts which did give a product yielded no photochromic material.

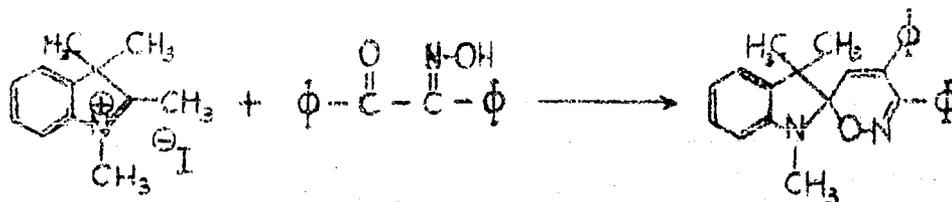
Attempted preparation of 4', 6'-diphenylindolinospiropyran. -



A 3.5 g. (0.02 mole) sample of Fischer's Base was refluxed three hours with 4.5 g. (0.02 mole) of dibenzoyl methane in ethanol. Work-up of the reaction mixture by the usual method used for BIPS preparations (see Engineering Reports and Final Report on Contract AF 41(657)-215) gave no identifiable product.

This reaction was unsuccessfully repeated with a 45 hr. reflux time. Other attempts using basic conditions (sodium methoxide and triethylamine separately) were also unsuccessful.

Attempted preparation of 4', 5'-diphenylindolinospirooxazina.

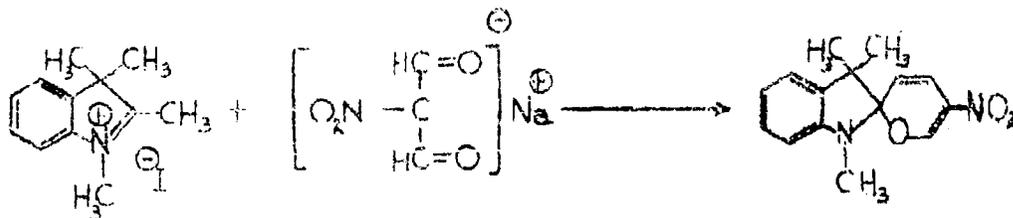


A 3.01 g. (0.01 mole) sample of 1, 2, 3, 3-tetramethylindoleninium iodide and 2.25 g. (0.01 mole) of α -benzil monoxime were refluxed 22 hours in ethanol in the presence of 1.0 g. (0.01 mole) of triethylamine. The reaction mixture was evaporated to give a viscous mass which was triturated with ether. The solid which separated on trituration washed with ether and recrystallized from methanochloroform was found to be the indoleninium iodide. The ether washings were evaporated and the residue was purified of unreacted oxime by recrystallization from benzene to give 0.25 g. of a bright yellow solid, m.p. 183-5°, probably not the assumed 4', 5'-diphenylindolinospirooxazine. This material was not photochromic but did give a deep red melt.

Anal. Calcd. for $C_{25}H_{24}N_2O$: C, 82.1; H, 6.4; N, 7.4

Found: C, 74.8; H, 6.7; N, 6.9

Attempted preparation of 5'-nitroindolinospiropyran.



A 3.01 g. (0.01 mole) sample of 1,2,3,3-tetramethylindoleninium iodide and 1.57 g. (0.01 mole) of sodium nitromalonate were refluxed for 1.5 hours in 100 ml. of ethanol containing 1.0 g. (0.01 mole) of triethylamine. The reaction mixture was cooled to induce precipitation and the crystalline product (0.65 g.) was removed by filtration and washed on the filter with methanol. Recrystallization of 0.20 g. of this product from methanol gave 0.18 g. of orange needles, m.p. 235 -6°, of the assumed structure shown above for 5'-nitroindolinospiropyran.

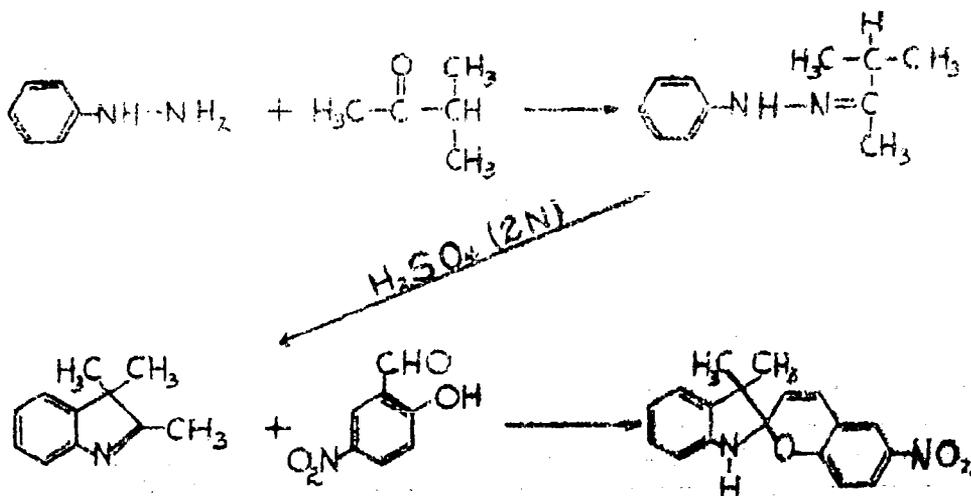
This product was not photochromic.

Anal. Calcd. for $C_{15}H_{16}N_2O_3$: C, 66.2; H, 5.9; N, 10.3

Found: C, 65.2; H, 5.7; N, 10.3.

C, 65.4; H, 5.8; N, 10.2.

Preparation of 3,3-dimethyl-6'-nitroindolinobenzospiropyran.



A 32.4 g. (0.3 mole) sample of phenylhydrazine and 23.8 g. (0.3 mole) of methyl isopropyl ketone were refluxed for 2.5 hours in 150 ml. of absolute ethanol containing 10 drops of concentrated sulfuric acid. The reaction mixture was filtered to remove insolubles and the filtrate was dried over molecular sieve. The dried solution was filtered and vacuum distilled to give 34 g. of the hydrazone.

A 33.5 g. (0.19 mole) sample of this hydrazone was heated for 1 hour on a steam bath in 350 ml. of 2N sulfuric acid. The reaction mixture was cooled, made alkaline and extracted with ether. The ether solution was washed, dried, evaporated and distilled to give 16.6 g. of 2,3,3-trimethylindolenine in two fractions ($n_D^{28.5}$ 1.5433 and 1.5466).

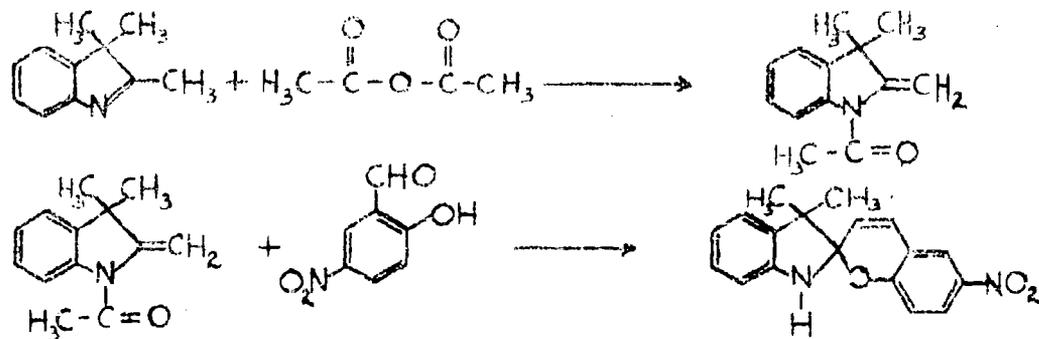
A 1.59 g. (0.01 mole) sample of 2,3,3-trimethylindolenine and 1.67 g. (0.01 mole) of 5-nitro salicylaldehyde were refluxed for 2 hours in ethanol

containing 30 drops of triethylamine. The solution was cooled, filtered and the product was recrystallized from ethanol to give 1.65 g. of light green solid, m. p. 205.5° - 207°, assumed to be the 3,3-dimethyl-9-nitro-indolinobenzospiropyran. This material was not photochromic.

Anal. Calcd. for $C_{18}H_{16}N_2O_3$; C, 70.1; H, 5.2; N, 9.1

Found: C, 69.7; H, 5.3; N, 6.6

Attempted preparation of 1-acetyl-3,3-dimethyl-6'-nitroindolinobenzospiropyran.



A 3.18 g. (0.02 mole) sample of 2,3,3-trimethylindolenine, 1.5 g. of fused sodium acetate and 100 ml. of acetic anhydride were heated on a steam bath in a 250 ml. flask fitted with a condenser and a drying tube. After four hours the reaction mixture was evaporated (still on steam bath) with a water aspirator. The residue was taken up in ether and filtered. The ether solution was washed, dried, evaporated and vacuum distilled to give 1.65 g. of product which showed carbonyl absorption on infra-red analysis and differed radically from the IR spectrum of the indolenine.

The assumed 1-acetyl-3,3-dimethyl-2-methyleneindoline (1.58 g. 0.008 mole) was refluxed with 1.34 g. (0.008 mole) of 5-nitrosalicylaldehyde in 50 ml. of absolute ethanol for a period of 18 hours. Only a viscous red residue remained on evaporation of the solvent from the reaction mixture. This red residue was taken up in benzene and the mixture was filtered to give a bright yellow solid, *m. p.* 204-205.5°, on the filter. This material was not photochromic and by IR analysis was identical with the product

obtained from condensation of 2, 3, 3-trimethylindolenine and 5-nitrosalicylaldehyde reported in Section 6.1.4. Evidently the acetyl group had been cleaved in the reaction.

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.1; H, 5.2; N, 9.1

Found: C, 70.2; H, 5.2; N, 7.4

6.3. Conclusions on synthetic work. - The preliminary investigations of structural modifications described above have given no indication of photochromic properties in spiropyrans lacking the benzene ring in the benzopyran half of the molecule or with the 1-methyl group replaced by a hydrogen. Attempts to replace the 1-methyl group with an acyl group have not been successful.

The syntheses involving less radical changes, i. e., changes only in substituents, produced moderate improvement in various functional properties. The photochromic compounds successfully prepared in this section are included in the table of compounds evaluated in section 4.4.

7. REFERENCES

1. R. Heiligman-Rim, Y. Hirschberg and E. Fisher, Durham Symposium on Reversible Photochemical Processes. (April, 1962).
2. *ibid.*
3. W. Gensler, Seminar on Photochromic Materials, NCR internal report FU-1013, 3, (1960).
4. S. McClynn, personal communication.
5. I. M. Klotz, "Chemical Thermodynamics," p. 127, Prentice-Hall, Inc., (1953).
6. A. Frost and R. Pearson, "Kinetics and Mechanism," Chapter 5, John Wiley and Sons, Inc., (1953).
7. W. Gensler, personal communication.
8. R. E. Hunt and W. Davis, J. Am. Chem. Soc., 69, 1415 (1947).
9. C. G. Hatchard and C. A. Parker, Proc. Royal Soc., A235, 518 (1956).
10. J. G. Calvert and H. J. L. Rechen, J. Am. Chem. Soc., 74, 2101 (1952).
11. A. Vasicek, "Optics of Thin Films."
12. G. Zimmerman et. al, J. Am. Chem. Soc., 82, 3249 (1960).
13. G. G. Smith, J. Am. Chem. Soc., 75, 1134, (1953).

DISTRIBUTION LIST

CONTRACT AF 44(657)-406

Copies

Agency

1 original plus
2 copies

Research Secretariat
School of Aerospace Medicine
USAF Aerospace Medical Center (ATC)
Brooks Air Force Base, Texas