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TECHNICAL REPORT
68-68-CM

SYNTHESIS OF CHROMOTROPIC COLORANTS

by
Ralph A. Coleman, John Kazan
and
Mary Louise Vega

American Cyanamid Company
Bound Brook, New Jersey

Contract No. DA19-129-AMC-269(N)

June 1968

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Clothing and Organic Materials Laboratory
TS-157

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1KO-24401-A113

Series: TS-157

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FOREWORD

This report covers the final year of effort in a three-year program in the synthesis of colorants intended for use in the development of a dynamic camouflage system for the individual combat soldier. It includes a review of the work accomplished over the entire three-year period. The study was initiated under Project 1KO-24401-A113 by Mr. Frank J. Rizzo, Project Officer, assisted by Dr. Edward M. Healy. The present work was completed with Dr. Healy as Project Officer and Mr. A. O. Ramsley as Alternate Project Officer. These individuals are assigned to the Textile Dyeing Division, Clothing & Organic Materials Laboratory.

At American Cyanamid Company the Project Leader was Dr. Ralph A. Coleman. The research chemists who were assigned to the project are Dr. John Kazan and Mrs. Mary-Louise Vega.

S. J. KENNEDY
Director
Clothing & Organic Materials Laboratory

Approved:

DALE H. SIELING, Ph.D.
Scientific Director

FELIX J. GERACE
Brigadier General, USA
Commanding

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ABSTRACT

The work described in this report, which represents the final phase (Part III) of a study of photochromic colorants potentially useful for a chameleon-type camouflage system, has been mainly concerned with the preparation and evaluation of new and modified photochromic systems. Of the photochromic compounds prepared, only the metal derivatives of 1,5-diselenocarbazonate, an analog of dithizone (diphenylthiocarbazone), exhibit this phenomenon to a practical extent. Preliminary studies on the selenocarbazonates indicate that they may possess properties superior to those of the corresponding dithizonate compounds.

A number of thermochromic compounds prepared during the second year of this study would not function in plastic media, making them impractical for use in a chromotropic camouflage system.

The facile alkylation of o-nitrobenzyl cyanide at low temperatures, using dimethyl sulfoxide as the solvent and aqueous sodium hydroxide as the base, represents a new and mild procedure for carrying out this type of reaction. The resulting dimethyl compound, 2-methyl-2-(o-nitrophenyl)propionitrile, undergoes an interesting cyclization upon catalytic reduction to give 2-amino-3,3-dimethyl-3H-indoline 1-oxide in addition to the expected aminonitrile.

A three-year project review with recommendations for future effort is included.

SYNTHESIS OF CHROMOTROPIC COLORANTS

THREE-YEAR PROJECT REVIEW WITH RECOMMENDATIONS

A synthetic organic study of colorants having chromotropic properties that may be applied to the development of a chameleon-type system for textile fibers has been conducted over a three-year period. The preparative methods and pertinent properties of over 100 new compounds are recorded in the three annual reports. Structural formulas for these new compounds were deduced from elemental analyses, infrared, ultraviolet and visible spectral curves, and, occasionally, nuclear magnetic resonance data. The spectral characteristics of the stable and metastable states were determined in liquid solvents. The rates and extent of photochromism are described by the thermal return half-life and the percent conversion at photoequilibrium during exposure to a bright tungsten lamp. Some studies of stability to sunlight were made.

Most of the compounds studied belonged to the metal dithizonate system, which was originally chosen because of its relatively good light stability. Combinations of 15 different substituted dithizones with nine different metal ions made available a large variety of compounds which yielded a full spectrum of colors and showed a large range in photochromic properties. In general, the spectral, photochromic and lightfastness properties differed greatly by varying the metal ion, while small changes in color and lightfastness were found when the substituent was varied on the dithizonate ligand. Practically, however, only the mercury and palladium compounds gave large changes in color when exposed to sunlight.

Among the most interesting developments was the discovery that the mercury and zinc diphenylselenocarbazonates are more efficiently converted by light into their metastable state than are the corresponding dithizonates. On the other hand, metal salts of diphenylcarbazone, the oxygen analog of dithizone, showed very little photochromic activity. Attempts to modify the dithizone structure by removing a nitrogen atom or by replacing a nitrogen with a carbon atom were unsuccessful. In a somewhat related class, the metal complexes of 1-mercapto-2-phenylazonaphthalene were found to be only slightly photochromic.

Variations of the well-known photochromic indolinospiropyrans were made with the hope that a more light-stable photochromic compound would result. However, replacing either or both of the ethylenic carbons in the spiropyran system by nitrogen made the photochromism disappear. When a methine group in the nonphotochromic pyridospiropyrans is replaced by nitrogen, the compounds become thermochromic. Considerable effort was made to take advantage of this thermochromism, but the color changing properties of the molecule depend on its equilibrium with a molecule of water. As a result, variations of moisture in the atmosphere and in polymeric substrates were much greater than that required for suitable control of the system.

Photochromic systems similar to salicylidene-anils and nitrobenzylpyridines that depend upon shifts of tautomeric equilibria were investigated, but the color changes were very small or absent. Other tautomeric types involving transfer of a proton from a phenolic group to a benzophenone carbonyl failed to give good color changes.

Attaching a photochromic compound, phenylmercury dithizonate, to a nylon fiber by means of a "reactive hook" was successfully carried out. The dithizonate in this system retained its photochromicity while being non-extractable.

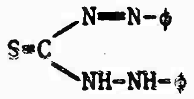
Recommendations:

From this work it is recommended:

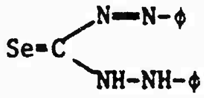
1. That more metal selenocarbazonates be prepared and evaluated for spectral properties, photochromism, lightfastness and toxicity. Also, application of selenocarbazonates on textile fibers should be studied.
2. Application studies of mercury and palladium dithizonate in fibers be made. It is suggested that the compounds also be incorporated in cotton and nylon by impregnating the fiber with dithizone, then after-treating with a mercury or palladium salt.
3. Since the better photochromic compounds are not substantive to cotton and nylon, other fiber reactive mercury dithizonate derivatives which are more compatible with conventional dyebaths should be investigated.

I. GENERAL INTRODUCTION

The work presented in this report concludes a three-year program designed to provide colorants which might be useful in a chameleon-type camouflage system for the protection of personnel and equipment. The main emphasis of the program has been the development of photochromic compounds, since a prior study(1) in this area indicated that such materials provided the most feasible approach to a practical "chameleon" camouflage system. Of the many new and available systems prepared and investigated during that study and the present program(2,3), only the derivatives of diphenylthiocarbazone (dithizone) (I), which were intensively studied during the first year of the program, and its recently prepared analog, diphenylselenocarbazone (II), showed promise as practical photochromic colorants.

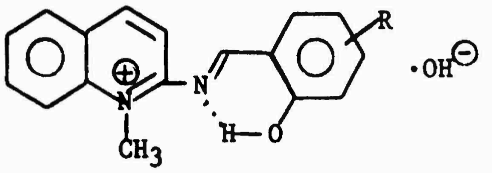


I

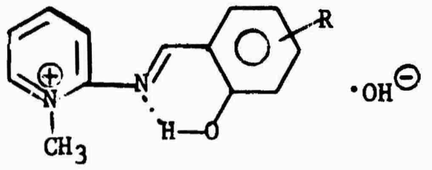


II

A new thermochromic system (structures III and IV),discovered during the second year of the program as a result of a study into the preparation of modified spiropyrans, would not function in polymeric substrates due to a critical dependence of the thermochromic mechanism on trace quantities of water.



III



IV

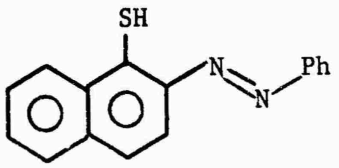
Inasmuch as the first year of the program(2) was concerned with an intensive study of the dithizonate system, the emphasis during the second year(3) was directed toward the preparation of new photochromic compounds and the fundamental modification of the dithizonate and spiropyran systems. It was hoped that the investigation into the preparation of new and modified systems, which has continued during the current year, might provide colorants with improved photochromic characteristics, in particular, greater photostability. The recent preparation of 1,5-diphenylselenocarbazone (II) and its derivatives may provide such colorants. These compounds represent a new, previously unreported class of photochromic materials which may have properties superior to those of existing systems. Preliminary studies on a limited number of derivatives indicate that they have faster return rates, with higher conversions, than the corresponding sulfur analogs.

Although some of the compounds prepared this year exhibit photochromism to a limited degree, only the selenocarbazonates exhibit this property to a practical extent.

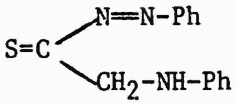
II. SYNTHESIS

A. Introduction

As indicated in Section I, the synthesis program for the current year has been concerned with the preparation of new photochromic compounds and the fundamental modification of the existing dithizonate (diphenylthiocarbazonate) and spiropyran systems. Synthetic studies were conducted on five classes of compounds, three of which represent analogs of dithizone (I). The latter are metal derivatives of 1,5-diphenylselenocarbazone (II), 2-phenylazo-1-naphthalenethiol (V) and 2-anilino-*N*-phenyliminothioacetamide (VI). However, since Compound VI could not be prepared, its derivatives were not investigated. The fourth class of compounds are the salicylaldehyde derivatives of 2-imino-1,3,3-trimethyl-3*H*-indoline (VII) and the fifth group is represented by the azobispyrrole (VIII).

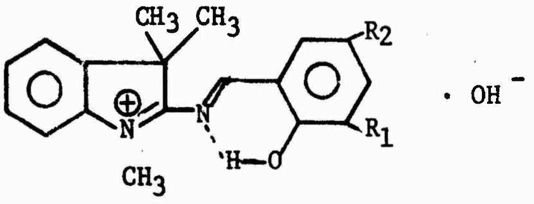


V

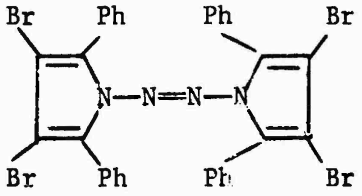


$S{=}C(N{=}N\text{-}Ph)(CH_2\text{-}NH\text{-}Ph)$

VI



VII



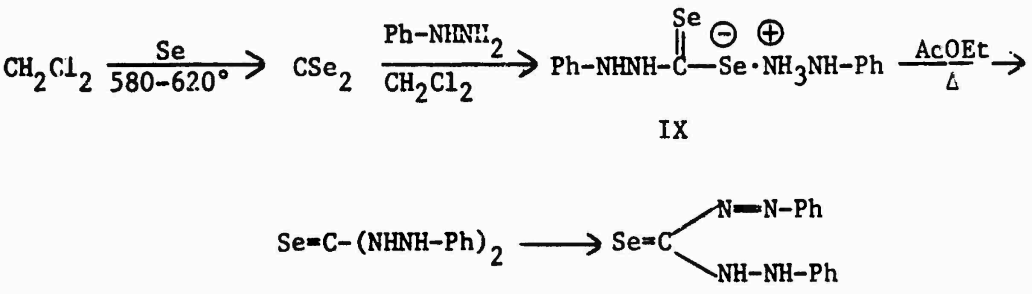
VIII

Only a few derivatives of the selenocarbazone (II) were prepared and evaluated because sufficient quantities of the ligand for synthetic purposes were not obtained in time.

B. Results and Discussion

1. Derivatives of 1,5-Diphenylselenocarbazone

The synthesis of 1,5-diphenylselenocarbazone (II) and a limited number of its derivatives has been achieved. Compound II was prepared by the sequence indicated below:



$$CH_2Cl_2 \xrightarrow[580\text{-}620°]{Se} CSe_2 \xrightarrow[CH_2Cl_2]{Ph\text{-}NHNH_2} Ph\text{-}NHNH\text{-}\overset{\overset{Se}{\|}}{C}\text{—}Se^{\ominus}\cdot{}^{\oplus}NH_3NH\text{-}Ph \xrightarrow[\Delta]{AcOEt}$$

IX

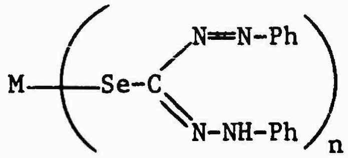
$$Se{=}C\text{-}(NHNH\text{-}Ph)_2 \longrightarrow Se{=}C(N{=}N\text{-}Ph)(NH\text{-}NH\text{-}Ph)$$

X II

Although this series of reactions did give the desired ligand, the over-all yield was very low due to the poor yields experienced in the conversion of the salt IX to the carbazone II. The selenocarbazide (X) was not characterized. The chief difficulty in this conversion was the decomposition of a considerable portion of the salt IX with the formation of elemental selenium. A variety of solvents was tried in order to minimize this side reaction, with ethyl acetate and a nitrogen atmosphere giving the best results. The highest yield of the selenocarbazone was 30%, even under these conditions.

The carbazone was isolated as a dark brown solid which, when dissolved, gave a dark yellow to brown solution, depending on concentration. The compound has an absorption maximum in the visible region at 415 mμ, but the band exhibits a shoulder extending to 600 mμ that may account for the observed color. Quantitative measurements were not made because sufficiently pure material was not available at the time.

Three derivatives (XI) of Compound II were prepared: chloromercury 1,5-diphenylselenocarbazonate (M=ClHg, n=1), mercury bis(1,5-diphenylselenocarbazonate) (M=Hg, n=2), and zinc bis(1,5-diphenylselenocarbazonate) (M=Zn, n=2).



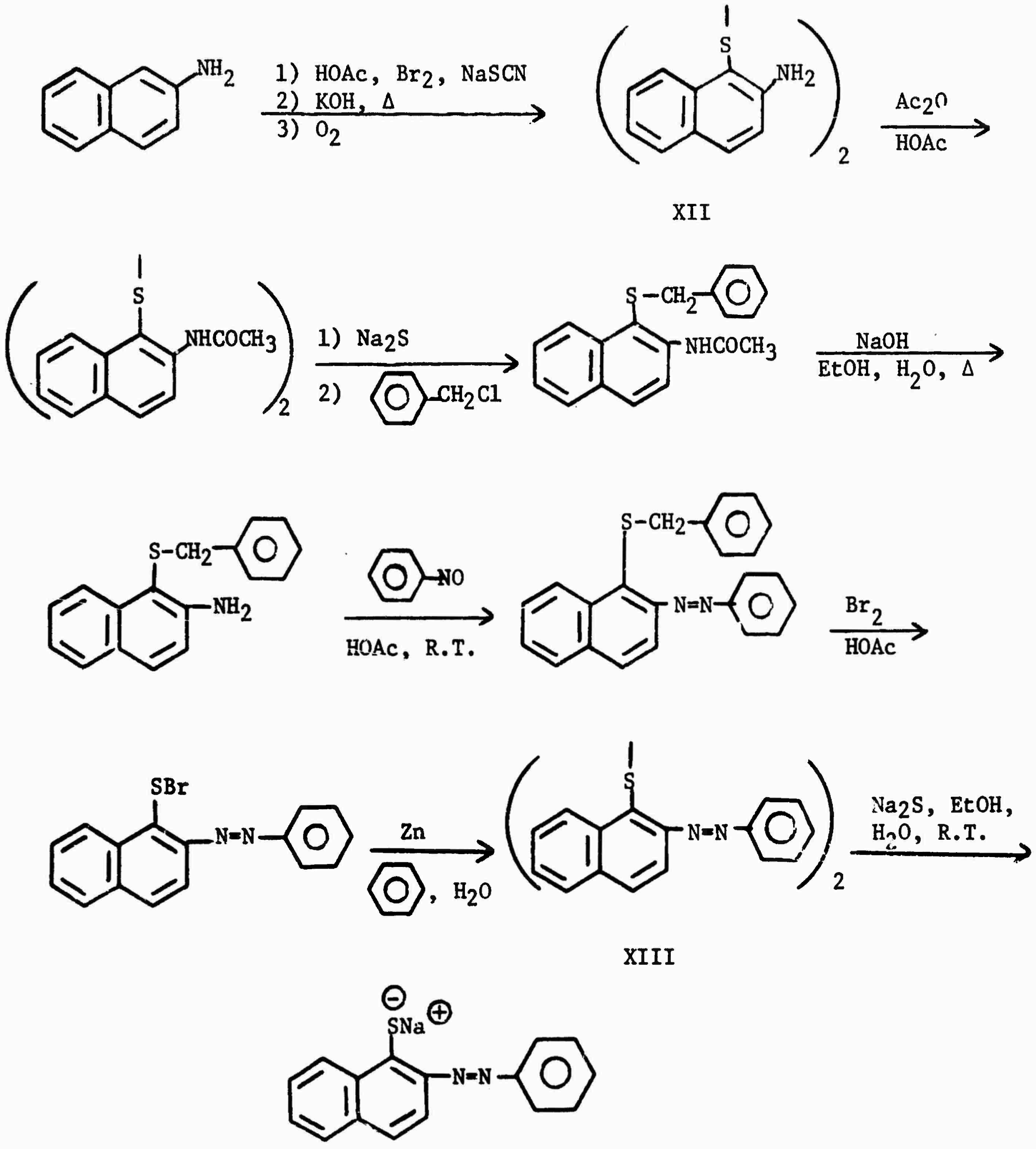
XI

The bis compounds were prepared by treating the ligand in tetrahydrofuran with the stoichiometric amounts of mercuric chloride and zinc acetate, while an excess of mercuric chloride was used for the preparation of the chloromercury compound. Sodium bicarbonate was used in the synthesis of the bis derivatives to neutralize the acid formed. Purification was achieved by chromatography followed by recrystallization. All of the chelates made are photochromic (see Data Sheets 107, 108, 109), with the mercury derivatives exhibiting high conversions and rapid return rates. The metastable form of the zinc compound absorbs in the near infrared region (700 mμ); however, this derivative does not convert to the extent of the mercury chelates.

2. Derivatives of 2-Phenylazo-1-naphthalenethiol

Several metal derivatives of 2-phenylazo-1-naphthalenethiol (V) were prepared, inasmuch as they may be considered analogs of the dithizonates and thus might have photochromic properties. Although Compound V was isolated several years ago by Burawoy and co-workers(4), its metal complexes have not been reported.

Attempts to prepare V from 2-phenylazo-1-naphthol using phosphorus pentasulfide were unsuccessful. Therefore, the compound was prepared as its sodium salt (XIV), by the somewhat long, but straightforward procedure reported in the literature(4,5).



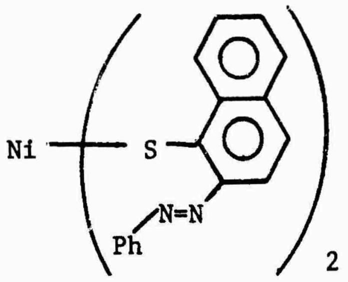
XIV

An attempt to circumvent some of the steps to XIV by treating Compound XII with nitrosobenzene to give the disulfide XIII directly, failed.

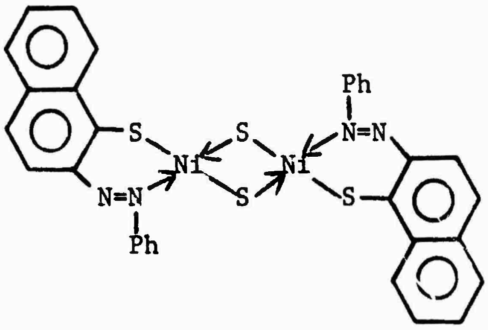
The metal derivatives of V were synthesized by allowing a solution of the sodium salt XIV to react with an excess of the metal ion. The metal sulfides formed along with the desired chelates were removed during the purification process. Attempts to react V with metal salts were unsuccessful inasmuch as it is very rapidly oxidized by air to XIII. The sodium salt XIV was allowed to react with the following metal ions:

Hg^{+2}, Zn^{+2}, Cd^{+2}, Pb^{+2}, Bi^{+2}, Ag^{+1}, Pd^{+2}, Ni^{+2}, Cu^{+2}, and Co^{+2}.

Of these, the first eight gave crystalline products after purification, but copper and cobalt produced black solids which were too insoluble to purify. The analyses for seven of the compounds are correct for the desired chelates. However, the analysis for the nickel derivative does not fit the empirical formula for the expected bis compound XV. It does agree with a structure such as XVI, which is proposed because similar chelates are formed by nickel in the presence of sulfides(6). The large excess of sulfide ion present in the solution of the sodium salt XIV might have led to the formation of XVI. A molecular weight determination on this material is not possible due to the high melting point and low solubility.



XV

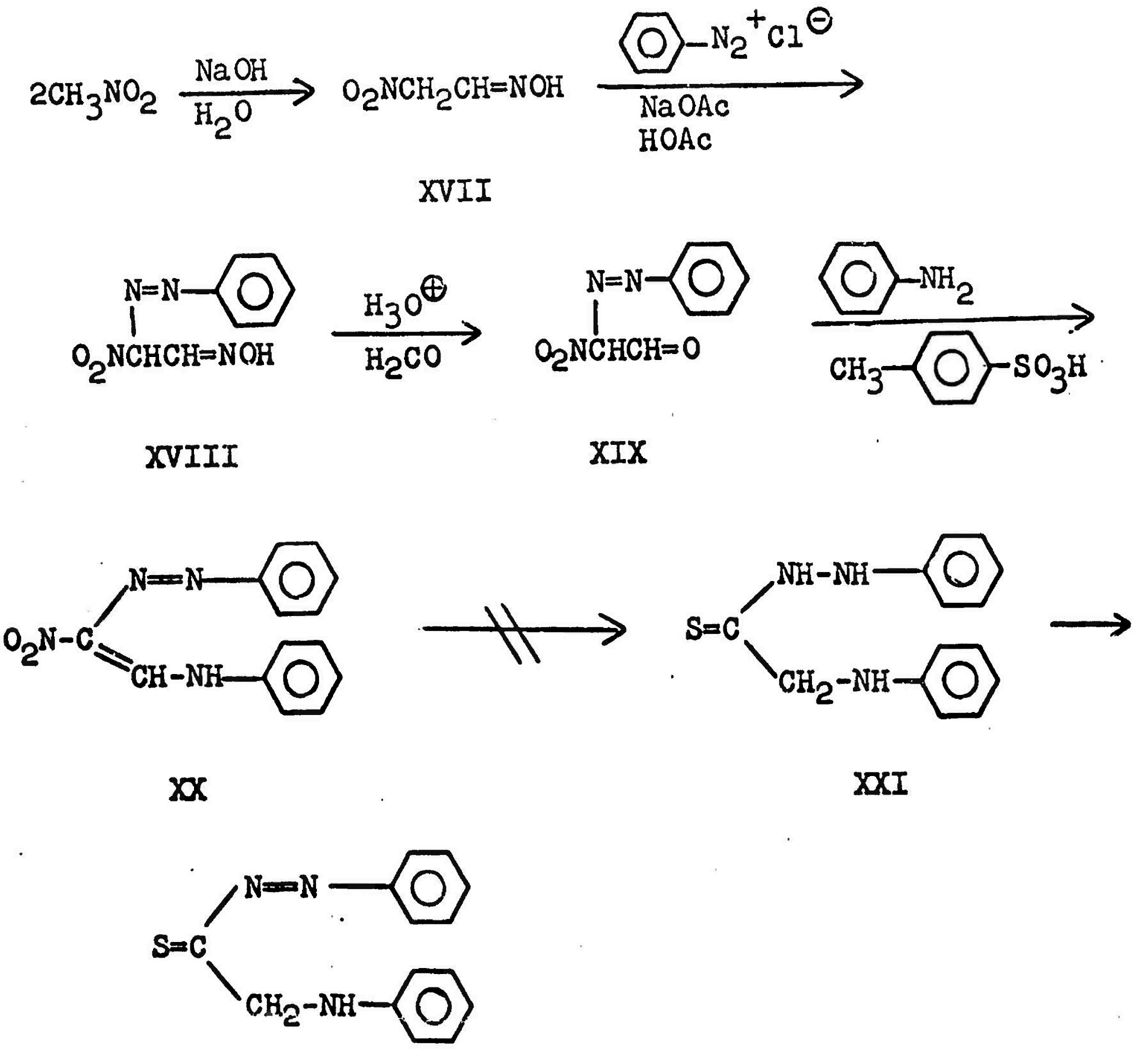


XVI

Although a number of the metal derivatives of V were photochromic, they only showed this phenomenom to a limited degree (see Data Sheets 92 to 98). In addition, they appear to have poor light stability in the presence of oxygen which, along with the small degree of conversion, precludes their use in a camouflage system.

3. Attempted Preparation of 2-Anilino-N-phenyliminothioacetamide

The synthesis of 2-anilino-N-phenyliminothioacetamide (VI) has been unsuccessful. The synthetic route chosen for the preparation is indicated as follows.



XVII

XVIII

XIX

XX

XXI

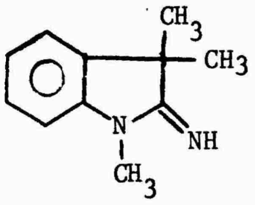
VI

The first three steps in this sequence were carried out successfully; however, all attempts to convert XX to XXI failed. Both ammonium sulfide and sodium sulfide were tried under various conditions, but in all cases the only products isolated were tars or intractable solids. As a consequence of these results, this problem was abandoned.

4. Modified Spiropyrans

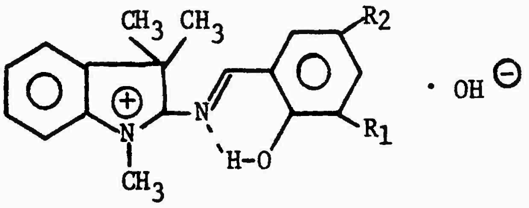
a. Derivatives of 2-imino-1,3,3-trimethyl-3H-indoline

A number of salicylaldehyde derivatives (VII) of 2-imino-1,3,3-trimethyl-3H-indoline (XXII) have been prepared.



XXII

The compounds were synthesized by treating the appropriate salicylaldehyde with the imine XXII, in the presence of p-toluenesulfonic acid.



VII

a) $R_1 = H, R_2 = NO_2$

b) $R_1, R_2 = Br$

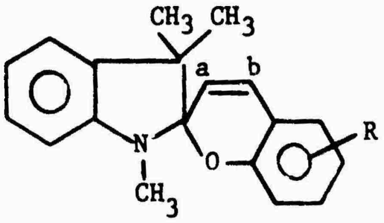
c) $R_1 = H, R_2 = Cl$

d) $R_1, R_2 = NO_2$

e) $R_1 = NO_2, R_2 = Cl$

Only salicylaldehydes with electron withdrawing groups gave crystalline products with XXII. All others produced tars. The structural assignment for these materials is based on their analyses and infrared spectra, which indicate the presence of a molecule of water, and on the analytical and spectral similarity of the analogous N-methyl pyridinium and quinolinium compounds whose N.M.R. spectra confirmed the hydrogen bonded structure depicted above.

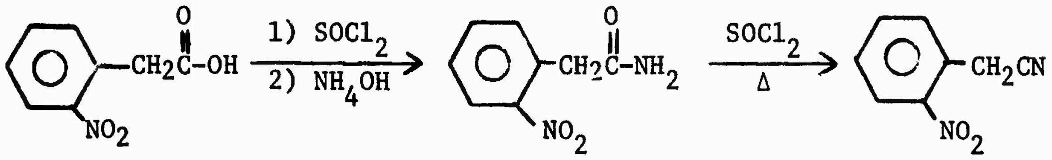
Unfortunately, these compounds did not exhibit either photochromism or thermochromism (see Data Sheets 100 to 104). The lack of thermochromism is surprising, since the analogous pyridinium and quinolinium derivatives do undergo this phenomenon. Previous work(3) and the present results indicate that exchanging nitrogen for carbon in the a and b positions of the spiropyran system (XXIII) destroys the photochromism of this system.



XXIII

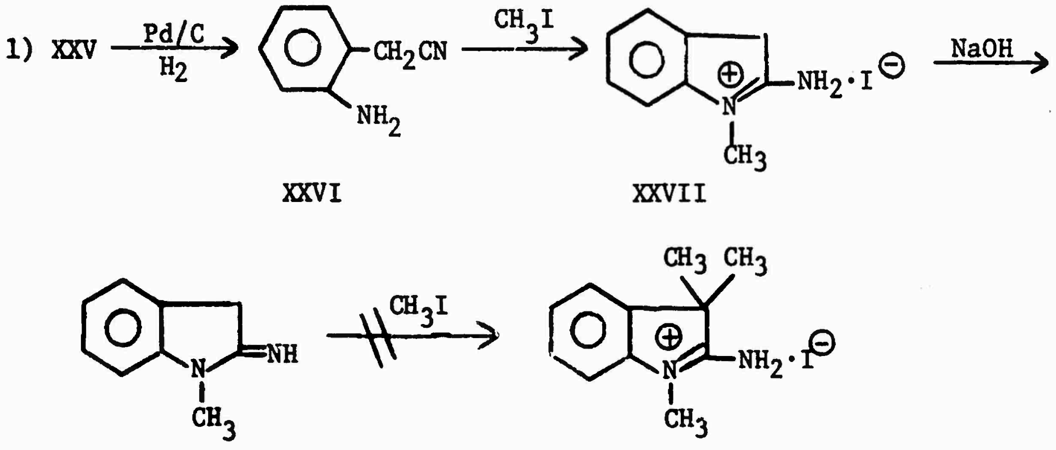
Two synthetic sequences (1 and 2) were investigated for the preparation of the hydroiodide XXIX of 2-imino-1,3,3-trimethyl-3H-indoline (XXII).

Compound XXV, the starting material in both sequences, was prepared by the series of reactions depicted below:



XXIV XXV

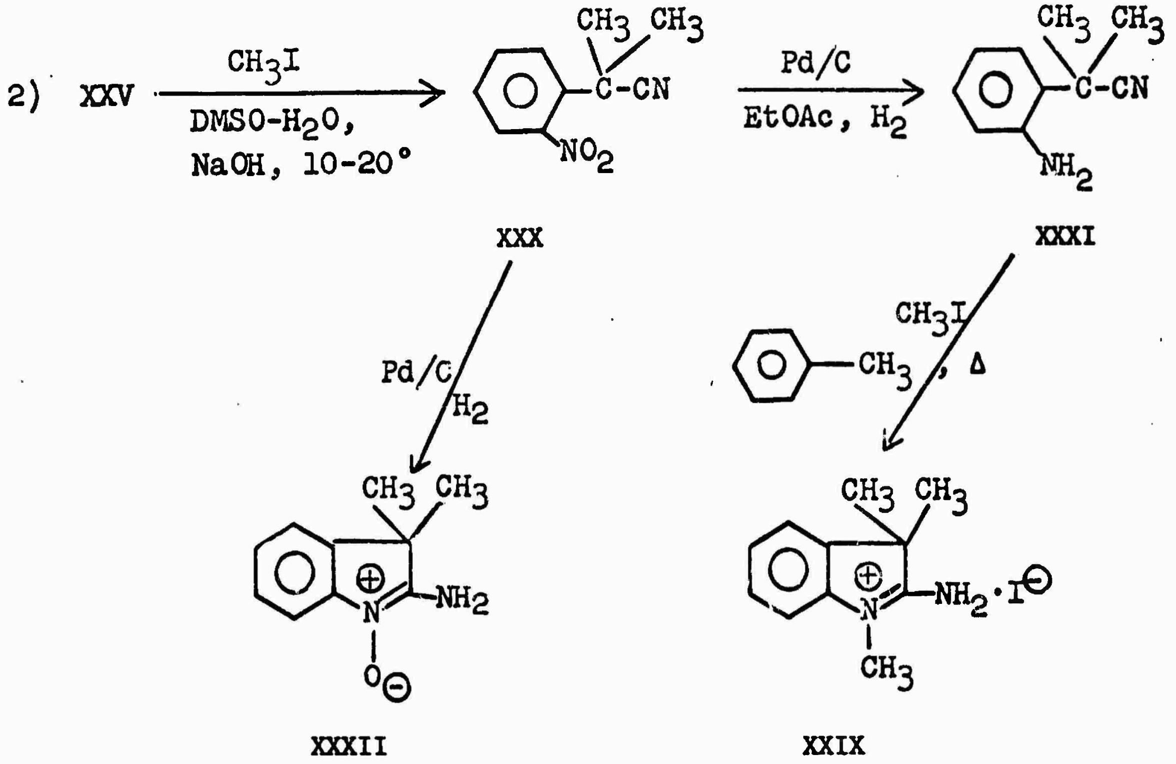
Sequence 1, a literature procedure(7), did not give XXIX because the last step, which is reported to proceed in low yields, would not work.



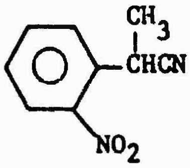
XXVI XXVII

XXVIII XXIX

However, the hydroiodide XXIX was successfully synthesized by sequence 2, utilizing reactions developed in this laboratory.



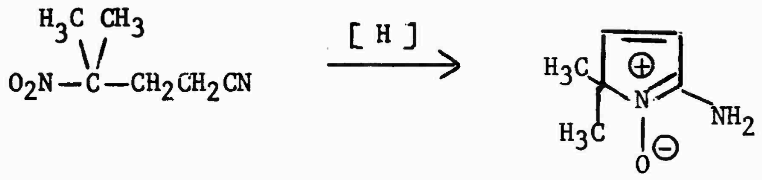
The key step in sequence 2 is the facile alkylation (better than 80% purified yield) of compound XXV at low temperature using dimethyl sulfoxide as the solvent and aqueous sodium hydroxide as the base. This result is interesting in view of the steric hindrance provided by the nitro group and the fact that in other solvents, under more stringent conditions, only the monoalkylation product XXXIII was obtained in low yield.



XXXIII

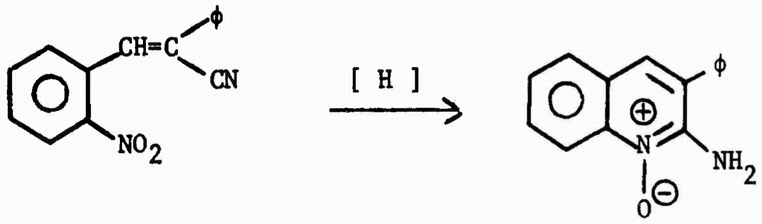
The dialkylated compound (XXX) produced anomalous results upon reduction. Whereas o-nitrophenylacetonitrile (XXV) is reduced cleanly in ethanol to the aminonitrile XXVI using palladium on charcoal as the catalyst, compound XXX gives a mixture of XXXI and XXXII containing about two-thirds of the former and one-third of the latter. There are analogies in the literature for this type of cyclization: Buckley and Elliott(8) (Equation 3) and Bauer(9) (Equation 4) report the formation of compounds such as XXXIV and XXXV from the appropriate nitronitriles using both catalytic and chemical reduction methods.

3)



XXXIV

4)



XXXV

Compound XXXII is a colorless crystalline solid, melting at 268°, which is soluble in hydroxylic organic solvents, hot water and dilute hydrochloric acid. The N.M.R. spectrum of the compound shows a singlet at 8.5τ (C-CH_3 protons) and a multiplet at 2.48τ characteristic for a 1,2-disubstituted benzene ring. The position of the signal for the NH protons could not be determined, since the spectrum had to be run in deuterated methanol. The relative ratio of protons is 6/4/1.9 (NH protons were estimated from the integration of the CD_3OH signal). The infrared spectrum does not show nitrile or amino absorption bands, but has a broad, strong band peaking at 3100 $cm.^{-1}$ and a medium band at 1660 $cm.^{-1}$. The analysis suggests the empirical formula $C_{10}H_{12}N_2O$. The mass spectrum of the compound confirms the formula and gives a molecular weight of 176 (calculated 176.2) for the parent peak; in addition, the fragmentation pattern also supports the structure indicated.

When the reduction of XXX was carried out in ethyl acetate, the expected aminonitrile XXXI was obtained in 72% yield, along with a small quantity (approximately 1/100 of the amount obtained with ethanol as the solvent) of XXXII. The structural assignment of XXXI is based on its analysis, and infrared and N.M.R. spectra. The infrared spectrum shows a triplet at 3300 $cm.^{-1}$ (NH_2), a sharp singlet at 2210 $cm.^{-1}$ (C≡N), and a broad singlet at 750 $cm.^{-1}$ (ortho substituted benzene ring).

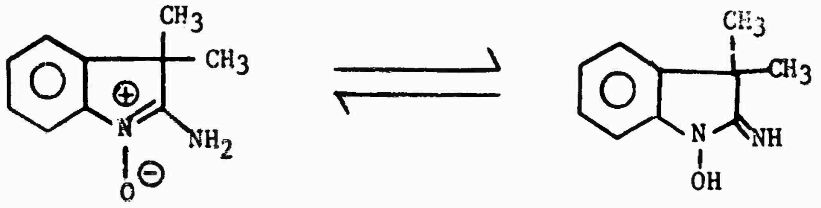
The N.M.R. spectrum of XXXI has a singlet at 8.35τ $(CH_3)_2C$-), a singlet at 5.88τ and an aromatic multiplet in the range 2.75 to 3.5τ. The relative intensities for these signals are: 5.3/1.9/4.0. A sharp singlet at 8.77τ (relative intensity at 0.6) which increases with time indicates that XXXI forms a new compound on standing. An indication that this change was occurring was also provided by the analysis of aged material which showed considerable deviation from the theoretical. The product of the change has not been identified.

Compound XXXI reacts with methyl iodide in refluxing toluene to give XXIX in 75% yield. The structure of XXIX is confirmed by analysis, a positive Beilstein test, and its infrared and N.M.R. spectra. The infrared spectrum shows a triplet (NH_2) with peaks at 3090 cm.$^{-1}$ (strong), 3200 cm.$^{-1}$ (medium) and 3300 cm.$^{-1}$ (weak); a single strong peak at 1610 cm.$^{-1}$ (C=N), and a strong peak at 770 cm.$^{-1}$ (o-substituted aromatic). The N.M.R. spectrum is summarized below:

Tau	Relative Intensity	Assignment	Remarks
0.17	1.6	NH_2	Disappears on deuteration
2.53	4	ArH	Multiplet
6.35	3	NCH_3	Singlet
8.37	6	$C(CH_3)_2$	Singlet

b. Derivatives of 2-amino-3,3-dimethyl-3H-indole 1-oxide. Attempted preparation.

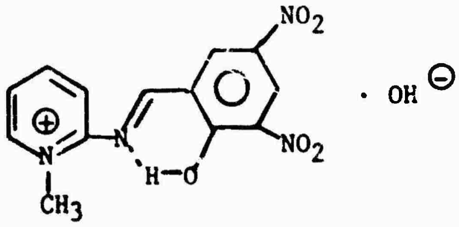
Since 2-amino-3,3-dimethyl-3H-indole 1-oxide (XXXII) can exist as the tautomer XXXIIa, which is similar to the base XXII, it was hoped that it might react in a similar manner. However, attempts to prepare salicylaldehyde derivatives of this compound were unsuccessful. The only products obtained in these reactions were starting materials.



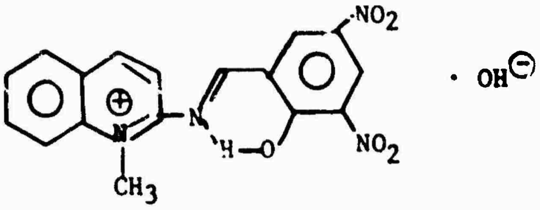
XXXII XXXIIa

c. Derivatives of 1,2-dihydro-2-imino-1-methylpyridine and 1,2-dihydro-2-imino-1-methylquinoline

The 3,5-dinitrosalicylaldehyde derivatives XXXVI and XXXVII of these bases were prepared by methods analogous to those described for five similar compounds reported in last year's publication(3).



XXXVI

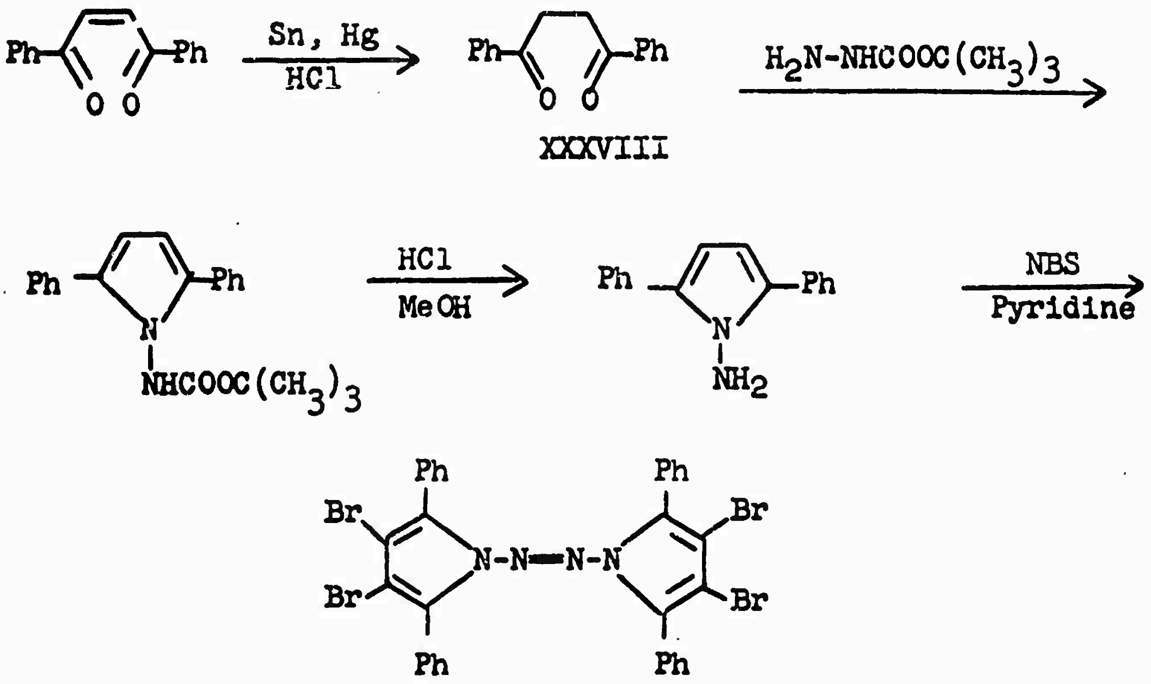


XXXVII

These derivatives are thermochromic (see Data Sheets 105 and 106), but do not exhibit photochromism. They behave in a manner similar to the thermochromic compounds prepared last year (3).

5. Synthesis of 1,1'-Azobis(3,4-dibromo-2,5-diphenylpyrrole)

This compound (VIII), which represents a new photochromic system, was reported by Carpino in 1965(10). It exhibits solid state photochromism (see Data Sheet 91) but does not function in solution or plastic media. The absence of photochromism in these media and the instability of the compound preclude its use in a camouflage system. The compound was prepared by the following sequence:



VIII

C. Experimental

The procedures for the preparation of the compounds described in this report are given below. Following the name of each compound is a Roman numeral which refers to its structure given earlier in the report. When an Arabic numeral also follows the name, a correspondingly numbered data sheet in the Appendix contains the analytical data and the chromotropic evaluation of the compound.

2-Phenylhydrazonium 3-Phenyldiselenocarbazate (IX)

A solution of carbon diselenide in dichloromethane (total weight 95 g) preparation by the literature method(11) was added dropwise with stirring to 10 g phenylhydrazine in 250 ml of methylene chloride. The addition took 2 hours, 15 minutes. A crystalline precipitate began to form approximately 10 minutes after the addition was started. The mixture was stirred for 1.5 hours after the selenide was added, giving 15 g of a tan microcrystalline solid, m.p. 66.5-67.5° (d). The material was stable at 0°, but decomposed within 24 hours when allowed to remain at room temperature. The compound was analyzed without further purification because of its instability. Therefore, the analyses of two different batches are reported:

Anal. Calcd. for $C_{13}H_{16}N_4Se_2$: C, 40.4; H, 4.17; N, 14.5; Se, 40.8

Found: C, 39.1; H, 3.95; N, 14.7; Se, 40.8

Found: C, 40.1; H, 4.15; N, 14.3; Se, 40.0

1,5-Diphenylselenocarbazone (II)

Compound IX (3 g, 0.00778 mole) was refluxed under nitrogen in 150 ml of ethyl acetate for 25 minutes (hydrogen selenide evolution had ceased). The resulting mixture was cooled and filtered giving 0.75 g elemental selenium. The solvent was evaporated from the filtrate giving a brown oil, to which was added 50 ml of a 10% solution of potassium hydroxide in methanol at -10°. The resulting red mixture was stirred for 1 hour at approximately -10° and poured into 200 ml of 2N sulfuric acid at -5° which had been saturated with sodium chloride. A black-brown precipitate formed and the mixture was filtered, keeping the material cold. The precipitate was washed with water and air dried, giving 0.8 g of a greenish-brown solid, melting with slow decomposition between 50 and 65°. A portion was extracted with pentane in a Soxhlet apparatus. A dark brown solid precipitated from the pentane and was submitted for analysis. Melting point 65-70° (d) (chars).

Anal. Calcd. for $C_{13}H_{12}N_4Se$: C, 51.5; H, 3.99; N, 18.5; Se, 26.0

Found: C, 51.5; H, 4.10; N, 17.4; Se, 26.2

General Procedure for the Preparation of Selenocarbazonates (XI) (107, 108, 109)

The selenocarbazone II was dissolved in tetrahydrofuran and 1 or 2 equivalents of the appropriate metal salt (mercuric chloride for the mercury derivative and zinc acetate for the zinc compound) in THF was added with stirring. A small amount of water was added followed by sodium bicarbonate in the preparation of the bis derivatives; in the case of the chloromercury compound, an excess of mercuric chloride was used and no water or base was added. The mixtures were stirred for 15 minutes and drowned in water. The product, which was isolated by filtration or extraction with methylene chloride, was purified by chromatography on silica gel followed by crystallization (the crystallization solvents are reported on the data sheets).

Di-(2-Phenylazonaphthyl)disulfide (XIII)

This compound and its precursors were synthesized by procedures described by Burawoy et al.(4,5). The yields of the compounds were essentially the same as those reported in the literature.

Metal Derivatives of 2-Phenylazo-1-naphthalenethiol (V) (92-99)

The mercury, zinc, cadmium and lead derivatives of this compound were prepared as follows: Finely ground di-(2-phenylazonaphthyl)disulfide, XIII, (5 g, 0.0095 mole) was suspended in 500 ml 3A alcohol. Sodium sulfide nonahydrate (10 g, 0.417 mole) in 100 ml. of water was added and the mixture was stirred for 24 hours at room temperature. The blood red solution was diluted to 1200 ml with water and filtered through Filter-Cel. The filtrate was further diluted to 1500 ml and divided into five 300-ml portions, each containing approximately 0.0038 mole of the sodium salt, XIV. An excess of the solid metal salt (mercuric acetate, zinc acetate, cadmium chloride, lead acetate, and bismuth trichloride) was added to each solution, precipitating the chelate along with the metal sulfide. The reaction with bismuth trichloride gave a mixture containing the disulfide, XIII, and was repeated (see below). Filtration and crystallization gave the pure chelates.

The nickel, palladium, silver and bismuth derivatives could not be prepared by the above procedure and were synthesized as follows: The sodium salt XIV was prepared as indicated above. The reaction mixture was filtered without dilution and the filtrate was diluted with ethanol to a standard volume which, when divided, gave portions containing 0.0038 mole of the ligand salt. Palladium chloride, nickel acetate and silver nitrate were dissolved in 100 ml. 7.5 N ammonium hydroxide and the respective solutions were added to the stirred solution of the salt, precipitating the chelates. For the bismuth derivative, bismuth subacetate was dissolved in 100 ml 50% acetic acid and this solution was allowed to react with the ligand solution. The products were purified as indicated above.

Both variations were tried with copper and cobalt, producing black solids which were too insoluble to purify. High boiling solvents such as nitrobenzene caused decomposition.

Nitrophenylazoacetaldehyde Oxime (XVIII)

To a solution of methazonic acid(12) (XVII) (0.653 mole) in 80 ml water was slowly added 50 ml glacial acetic acid, keeping the temperature below 25°. The resulting solution was cooled to -5° and an aqueous solution of phenyldiazonium chloride prepared at -5 to +5° from 92 g (1 mole) aniline, 240 ml. conc. hydrochloric acid, 150 ml water and 70 g (approximately 1 mole) sodium nitrite (excess nitrous acid destroyed with sulfamic acid) was added with stirring. The mixture was stirred for 1.5 hours at 0-20° during which time a yellow-orange precipitate formed. Filtration, washing with water (approximately 1.5 liter) and drying gave

54 g of an orange-yellow solid, m.p. 155-157°. Crystallization from benzene-ethanol gave three crops of crystals totaling 45 g (67%), m.p. 172-173° (d). A portion recrystallized from acetonitrile melted at 174-175° (d).

Anal. Calcd. for $C_8H_8N_4O_3$: C, 46.1; H, 3.87; N, 26.9; O, 23.1

Found: C, 45.8; H, 3.88; N, 27.1; O, 23.0

Nitrophenylazoacetaldehyde (XIX)

The oxime XVIII (10 g, 0.0482 mole) was refluxed with stirring for 5 minutes in a mixture of 100 ml 5N sulfuric acid, 10 ml. dioxane and 100 ml 36% formaldehyde solution. The hot mixture was poured into 1 liter ice and water and filtered. The solid was washed with water and dried, giving 6 g (65%) of a yellow-orange microcrystalline material, m.p. 155-157°. A portion crystallized from methanol gave yellow-orange needles, m.p. 157-158° (d).

Anal. Calcd. for $C_8H_7N_3O_3$: C, 49.7; H, 3.65; N, 21.8; O, 24.8

Found: C, 49.8; H, 3.65; N, 21.7; O, 25.0

Nitrophenylazoacetaldehydeanil (XX)

Compound XIX (4.2 g, 0.002175 mole), aniline (2.2 g, 0.00239 mole) and p-toluenesulfonic acid (0.1 g, 0.000527 mole) were refluxed in 250-ml benzene with azeotropic removal of the water formed. When no further water was produced, the dark red solution was cooled and extracted twice with saturated sodium bicarbonate and once with water. Drying of the solution and evaporation of the solvent gave 5.7 g of an orange-red solid. Crystallization from ethanol gave two crops of orange needles, total weight 4.6 g (79%). The m.p. of the first crop was 110-111°. The second crop melted at 108-109°. A portion recrystallized from ethanol gave orange needles, m.p. 110-111°.

Anal. Calcd. for $C_{14}H_{12}N_4O_2$: C, 62.7; H, 4.51; N, 20.9; O, 11.9

Found: C, 62.6; H, 4.32; N, 21.2; O, 12.2

Attempted Preparation of Anilinothioacetic Acid, 2-Phenylhydrazide (XXI)

a. Ammonium sulfide method: Compound XX was suspended in methanol or tetrahydrofuran, or mixtures thereof, which had been saturated with ammonia, and ammonia and hydrogen sulfide were passed through in a ratio of greater than 2 to 1. This procedure gives fair to good yields in the conversion of formazans to thiocarbazides*. These reactions were

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*Procedure developed under American Cyanamid Company sponsored research.

carried out at temperatures ranging from -20 to +20°. The only products isolated were tars or intractable dark brown solids which thin-layer chromatography indicated had a multitude of components.

b. Sodium sulfide method: Compound XX was added to sodium sulfide in ethanol at low temperatures. The results were similar to those reported above.

o-Nitrophenylacetamide (XXIV)

o-Nitrophenylacetic acid (5- g, 0.276 mole) was stirred with 100 ml thionyl chloride at room temperature for 3 hours. At the end of this time, the acid had dissolved and the evolution of gas had ceased. The excess thionyl chloride was removed under reduced pressure and the resulting red oil was dissolved in 100 ml methylene chloride that had been dried over Linde 5A sieves. To the vigorously stirred solution was added slowly in portions (caution--violently exothermic reaction) 100 ml 15 N ammonium hydroxide, causing the precipitation of a tan solid. Filtration of the mixture and washing of the precipitate with water until the washings were neutral gave 45 g of a brown solid. Recrystallization from ethanol gave two crops of pale yellow plates totaling 39.4 g (81%), m.p. 161-162° (lit.[13] 160-161°).

o-Nitrobenzylcyanide (XXV)

Compound XXIV (40 g, 0.22 mole) was refluxed with 80 ml. thionyl chloride for 1.25 hours. At the end of this period, the gas evolution had slackened. The excess thionyl chloride was removed under reduced pressure and water was added to the residual oil (caution). Filtration gave 35 g of a yellow solid which, when crystallized from 20% benzene-cyclohexane, gave two crops of pale-yellow needles, total weight 39.1 g (81%), m.p. 81.5-82.5° (lit.[14] 82-84°).

o-Aminobenzylcyanide (XXVI)

This compound was prepared by a literature procedure(14) in which an alcoholic solution of o-nitrobenzylcyanide (XXV) was hydrogenated in a Parr apparatus, using a 5% palladium on charcoal catalyst. After filtering off the catalyst, adding an equal volume of water to the filtrate, and storing in a refrigerator, compound XXVI was isolated in 79% yield, m.p. 69.5-70.5° (lit(14) 70-72°).

2-Amino-1-methyl-3H-indolinium Iodide (XXVII)

Compound XXVI (1 g, 0.0062 mole) was refluxed for 18 hours with 10 ml toluene and 5 ml methyl iodide. Evaporation of the solvent gave 1.9 g of a yellow-orange solid. Recrystallization from ethanol-ethyl acetate gave three crops of colorless needles, total weight 1.3 g (77%), m.p. 261-262° with gradual decomposition beginning at 240° (lit.(7) does not report melting point, but claims gradual decomposition above 260°).

2-Methyl-2-(o-nitrophenyl)propionitrile (XXX)

To 200 ml dimethylsulfoxide was added 22 g (0.136 mole) Compound XXV and 80 ml (122 g, 0.86 mole) methyl iodide. The solution was cooled to 10° and a solution of 12 g (0.3 mole) sodium hydroxide in 61 ml water was added dropwise with stirring, keeping the temperature below 18°, the addition taking approximately 15 minutes. Five minutes after the addition of the base was complete, the color of the solution had changed from deep purple to amber-red. When the temperature of the mixture had dropped to 10°, the ice bath was removed and the temperature was allowed to reach 20°. The mixture was poured into one liter of water and the excess methyl iodide was removed under reduced pressure. Filtration gave 24.4 g of an orange-red solid which, when recrystallized from hexane (charcoal decolorization), gave 20 g (Crop I) of off-white needles, m.p. 88-89°; Crop II weighed 1.2 g, m.p. 88-89°; total yield 21.2 g (82%). A portion recrystallized from hexane for analysis melted at 88.5-89.5°.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.1; H, 5.29; N, 14.7; O, 16.8

Found: C, 62.8; H, 5.17; N, 14.6; O, 16.6

2-Methyl-2-(o-aminophenyl)propionitrile (XXXI) and Compound XXXII

Compound XXX (5 g, 0.0263 mole) was suspended in 30 ml. of ethyl acetate in a Parr hydrogenation apparatus with 150 mg of 10% palladium-on-charcoal. The mixture was hydrogenated under an initial pressure of 40 psi. The hydrogen uptake slowed when 6.5 psi had been absorbed (theoretical 6.3 psi) and the reaction was terminated. The mixture was filtered and the solvent was removed from the filtrate giving 3.4 g of a yellow oil containing a white solid. Dilution with ether and filtration gave 100 mg of a white solid, m.p. 254-256° (d) (XXXII). Evaporation of the ether from the filtrate gave 3.2 g (72%) of XXXI in the form of a yellow oil. Compound XXXII (also prepared in larger quantity when ethanol was used as the solvent in the reduction) was recrystallized from water, m.p. 268-269° (d) and submitted for analysis.

Anal. Calcd. for $C_{10}H_{12}N_2$ (XXXI): C, 75.0; H, 7.56; N, 17.5

Found: C, 74.8; H, 7.63; N, 18.0

Calcd. for $C_{10}H_{12}N_2O$ (XXXII): C, 68.2; H, 6.86; N, 15.9; O, 9.08

Found: C, 68.4; H, 6.79; N, 16.0; O, 8.86

2-Amino-1,3,3-Trimethyl-3H-indolium Iodide (XXIX)

To 100 ml toluene was added 6 g (0.00375 mole) XXXI and 7 ml (16 g, 0.1125 mole) methyl iodide. The resulting mixture was stirred and refluxed for 18 hours, then cooled and filtered to give 10.2 g of crude material, which when recrystallized from acetonitrile-ethyl acetate, gave 3 crops of crystals: Crop I, 5.8 g, m.p. 280-281° (d) (Lit. (7) 275-280°); Crop II, 1.5 b, m.p. 278-280° (d); and Crop III, 1.2 g, m.p. 277-279° (d). The total yield was 8.5 g (75%). A portion of Crop I was submitted for analysis:

Anal. Calcd. for $C_{11}H_{15}N_2I$: C, 43.8; H, 5.00; N, 9.27; I, 42.0
Found: C, 43.6; H, 4.87; N, 9.15; I, 42.0

2-(o-Nitrophenyl)propionitrile (XXXIII)

To 100 ml of methanol was added with stirring 5 g (0.0309 mole) of Compound XXV, 15 ml (22.95 g, 0.159 mole) methyl iodide and 13.6 g (0.099 mole) potassium carbonate. The resulting mixture was stirred at room temperature for 17 hours, poured into 300 ml water and extracted with ether. The ether extracts were combined and dried over sodium sulfate and Drierite. Filtration and evaporation of the solvent gave 4.4 g of an amber oil, which was chromatographed on 50 g of Merck acid-washed alumina, using benzene as the eluent. The first, and main, yellow band was collected, giving 3.7 g (68%) of a yellow oil whose infrared and N.M.R. spectra were consistent with the indicated structure. The oil crystallized on standing and was recrystallized from ether-pet. ether, giving off-white needles, m.p. 43-43.5°.

Anal Calcd. for $C_9H_8N_2)_2$: C, 61.4; H, 4.58; N, 15.9; 0, 18.2
Found: C, 61.4; H, 4.77; N, 16.1; 0, 18.0

General Procedure for the Preparation of Salicylaldehyde Derivatives of 2-Imino-1,3,3-trimethyl-3H-indoline (VII) (100 to 104)

2-Amino-1,3,3-trimethyl-3H-indolium iodide (XXIX) was treated with 6N sodium hydroxide. The resulting base XXII was extracted with ether and the ether extracts were combined and dried over sodium sulfate. Filtration followed by evaporation of the solvent gave XXII as a yellow oil. The oil was dissolved in 150 ml of toluene along with an equivalent amount of the appropriate salicylaldehyde and a few crystals of p-toluenesulfonic acid. The resulting mixture was refluxed for 4 hours with azeotropic removal of the water. Evaporation of the solvent gave the products as oils or solids. In the first instance, the oil was triturated with petroleum ether until solidification occurred and the resulting solid was purified by crystallization. The solid products were purified by crystallization.

Attempted Preparation of Derivatives of 2-amino-3,3-dimethyl-3H-indole 1-oxide (XXXII)

Compound XXXII was combined with an equivalent amount of 5-nitrosalicylaldehyde and a trace of p-toluenesulfonic acid. This mixture was refluxed in three different solvents: ethanol, butanol and toluene. In all cases, starting materials were recovered.

1,4-Diphenylbutane-1,4-dione (XXXVIII)

This compound was prepared in 77% yield by the reduction of 1,4-diphenyl-2-butene-1,4-dione as described in the literature(15).

1,1'-Azobis(3,4-dibromo-2,5-diphenylpyrrole) (VIII)

This compound and its precursors were prepared by literature methods(10) in approximately the same yields reported. The melting point of VIII is 167° (d) (Lit.(10) 159-163° d). The analytical sample was prepared by two recrystallizations of the crude product from ethyl acetate.

III. EVALUATION

A. Methods

1. Photochromic Studies

The photochromic evaluations in this report were carried out in solution at room temperature. Dried methylene chloride was used in the majority of the evaluations. Reagent grade toluene was used where noted.

For the standard evaluation procedure, 1.00 to 5.00 mg of each compound was dissolved in 50 ml of dried methylene chloride. Dilutions were made as necessary to obtain suitable spectra. Spectra of the unirradiated and irradiated solutions were run on the Cary 14 recording spectrophotometer in 1-cm cells. Unirradiated and irradiated spectra were run from 700 mμ to 350 mμ in most cases. The visible spectra mode gave a spectrum of the unirradiated form as the monochromatic light was too weak to produce the photochromism. For irradiated spectra, the near infrared recording mode of the Cary 14 was used in which the full intensity of the 108-watt CPR projection lamp is filtered through an infrared absorbing KG-3 filter and directed onto the sample. The irradiation by this bright light converted photochromic compounds into their metastable state and at the same time the spectra were obtained by the Cary 14 lead sulfide detector.

The percent conversion of the compounds while under irradiation by the CPR lamp was calculated from the absorbance of the spectral band during irradiation relative to an estimated absorbance of the band at 100% conversion.

The thermal return half-life of each photochromic compound was measured by first exposing the sample to the Cary CPR lamp until the new absorption band came to an equilibrium, as measured by the lead sulfide-infrared detector. Then with the wavelength set at this absorption band, the visible mode light source, photomultiplier and multipots were quickly put in place and the transmittance of the sample was recorded as a function of time. The time for half of the absorbance of this band to disappear is easily calculated from the recording.

2. Thermochromic Studies

The studies were made with monochlorobenzene solutions and cellulose acetate films containing the compounds. All spectra were measured on the Cary 14. Two approaches to the evaluation of solutions of the thermochromic materials were taken:

(1) Measurements were made with the solutions open to the air. The solution was placed in a cell containing a thermocouple. This cell was placed in a specially built Dewar with optical windows, thereby affording a method of controlling the temperature. This entire assembly was placed in the Cary 14 and the full, visible spectra measured at various temperatures.

(2) Measurements were made with the solutions in stoppered cuvettes, which contained Linde 5A sieves as a drying agent. In this case, the solution was boiled in the cuvette for 25 minutes, after which a few 5A sieves were added and the cuvette stoppered immediately. The cell was then placed in the Cary 14 and the spectra were measured at various temperatures. Temperature had no effect on the spectra of the solutions prepared in this manner.

Several of the thermochromic compounds were also studied in cellulose acetate films as well as on 13 fibers: acetate, Acrilan®, Arnel®, cotton, Creslan®, Dacron®, Dynel®, nylon, Orlon®, silk, viscose rayon, wool, Zefran®. The thin film studies entailed the chilling of each film to -70°, followed by heating to +150° and observing the colors at these temperatures.

B. Results and Discussion

1. Photochromic Studies

The only compound evaluated that showed photochromism in the solid state was 1,1'-azobis-(3,4-dibromo-2,5-diphenylpyrrole) (VIII) which changed from lemon-yellow to scarlet. Solutions of this compound in dry methylene chloride were found not to be photochromic. Clear films containing this compound were not photochromic and bubbled and bleached when exposed to light. It would appear from this bleaching of the color that the compound is light-unstable.

Eight metal chelates of 2-phenylazo-1-naphthalenethiol (V) were evaluated in methylene chloride and the results tabulated in Table I.

TABLE I

PHOTOCHROMIC PROPERTIES OF METAL CHELATES OF 2-PHENYLAZO-1-NAPHTHALENETHIOL (V) IN METHYLENE CHLORIDE

Compound No.	M	n	Unactivated			Activated		Return Time and Comments
			$\lambda_{max.}$ (mμ)	A	ε	$\lambda_{max.}$ (mμ)	A	
92	Hg	2	473	0.824	10,620	473	0.672	$t_{\frac{1}{2}}$ = 4.5 min.
93	Cd	2	538	0.928	13,770	538	0.783	Immediate but incomplete recovery.
94	Pb	2	530	0.444	11,210	530	0.401	Ditto
95	Zn	2	560	1.187	12,710	560	1.097	Ditto
			448	0.524	5,590	435	0.482	Ditto
96	Pd	2	580	0.323	7,150	580	0.321	No change
			(482)*	0.212		(482)*	0.198	Immediate but incomplete recovery.
97	Ni	?	482			482		No change.
98	Ag	1	450	0.910	4,489	440	0.801	Immediate but incomplete recovery.
99	Bi	3	488	0.695	13,070	488	0.678	No change.

*$\lambda_{min.}$ (mμ)

The immediate but incomplete recoveries noted in Table I would indicate that the return rates of these compounds are very fast, and that the compounds do suffer some decomposition upon irradiation. Since the incomplete recovery appears only on the first exposure to light, it seems likely that the loss of compound was due to the presence of a small amount of impurity, such as oxygen. The films described below containing the compounds did not show this loss during the first exposure period; however, an exposure of one hour bleached the films almost completely.

Three of the compounds were cast in cellulose acetate films and studied. In the case of the cadmium compound (93) the acetate film did not exhibit the change in transmittance at 538 mμ upon irradiation that was noted in the solution study.

The silver compound (98) in cellulose acetate film exhibited a transmittance change upon irradiation, but the wavelength shift from 450 to 440 mμ was not noted. In the case of the mercury compound (92), the $t_{\frac{1}{2}}$ was 1.5 minutes compared to 4.5 minutes in solution.

Although some of these compounds exhibit a small change in transmittance upon irradiation, none are practical for use in photochromic systems. Perhaps further modifications would produce more useful changes, but as the compounds now exist they are not suitable for use as photochromic materials.

Another series of compounds evaluated were some salicylaldehyde derivatives of 2-imino-1,3,3-trimethyl-3H-indoline. The spectral data are tabulated in Table II. These compounds did not exhibit any photochromic or thermochromic properties.

TABLE II

PHOTOCHROMIC PROPERTIES OF THE SALICYLALDEHYDE DERIVATIVES OF 2-IMINO-1,3,3-TRIMETHYL-3H-INDOLINE

Compound No.	$\lambda_{max.}$ (mμ)	ε
100	295	13,120
101	347	3,410
102	341	3,250
103	400 (sh)	8,240
	360	15,130
104	368	4,640

Two other compounds, 2-(2-hydroxy-3,5-dinitrobenzylideneamino)-1-methylpyridinium hydroxide (105) and 2-(2-hydroxy-3,5-dinitrobenzylideneamino)-1-methylquinolinium hydroxide (106), were evaluated in methylene chloride. Neither was found to be photochromic, but they did exhibit thermochromism which will be discussed under that section.

The last series of compounds to be evaluated were three metal complexes of 1,5-diphenylselenocarbazone. These compounds were evaluated in reagent grade toluene. It would appear that this particular series of compounds does not need the extreme "dry" conditions that other compounds have demanded. These compounds did exhibit good photochromic properties as may be seen in Table III.

TABLE III

SPECTRAL DATA FOR METAL COMPLEXES OF 1,5-DIPHENYL-SELENOCARBAZONE**

Compound No.	Unactivated		Activated	
	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
107	479	19,400	597	11,700
108	483	50,930	600	24,150
109	418 (sh)	-	418 (sh)	-
	530	71,221	700	30,290

**Solvent: Reagent grade toluene, as is.

Comparisons of the photochromic properties of the chloromercury selenocarbazonate (107) with the properties of the chloromercury dithizonate* and the photochromic properties of the mercury bis(selenocarbazonate) (108) with the properties of the mercury bis(dithizonate)* (Table IV) show that the seleno compounds offer good conversion as well as faster thermal-return rates than the dithizonates.

TABLE IV

COMPARISON OF THE PHOTOCHROMIC PROPERTIES OF THE SELENO- AND THIO-CARBAZONATES**

Compound	Percent Conversion	Thermal Return Half Life
Chloromercury Selenocarbazonate (107)	98.5	18 sec.
Chloromercury Thiocarbazonate*	98.0	95 sec.
Mercury Bis(selenocarbazonate) (108)	91.0	55 sec.
Mercury Bis(thiocarbazonate)	76.3	135 sec.

**Evaluations in reagent grade toluene.

Because of a lack of time, light stability studies have not been carried out on the seleno compounds, but if the light stabilities are as good as or better than those of the dithizonates, this group of compounds might provide a good photochromic series.

2. Thermochromic Studies

Chlorobenzene solutions of five previously prepared(3) compounds and two newly synthesized compounds (105 and 106) (Table V) will change color upon heating to boiling (130°) and cooling (Table VI). Usually, no color is observed unless the solution has been boiled at

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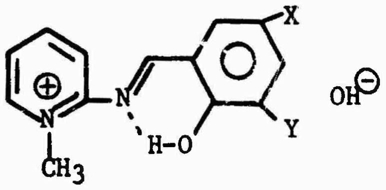
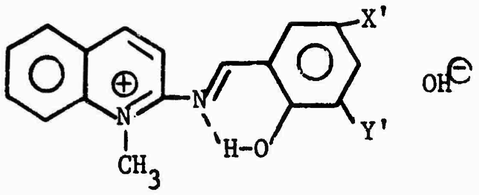
*Synthesized under American Cyanamid sponsored research.

TABLE V

THERMOCHROMIC COMPOUNDS



Compound Number	X	Y
80	NO_2	H
87	Br	Br
105	NO_2	NO_2



Compound Number	X'	Y'
84	NO_2	H
88	Br	Br
89	Cl	NO_2
106	NO_2	NO_2

TABLE VI

COLOR CHANGES OF THERMOCHROMIC COMPOUNDS

Compound Number	Visible Spectrum Stable Form λ_{max}, mμ	ε	Color Change on Heating in Chlorobenzene from Room Temperature to 130°	Color Change on Heating in Dry Chlorobenzene from 5° to 50°
80	520	200	Orange to magenta	No change
84	422	1,600	Yellow to purple	Orange to purple
87	552	1,160	Red to deep purple	Pinkish lavender to bluish lavender
88	356	11,960	Golden yellow to bright blue	Greenish yellow to blue
89	462	5,140	Orange to dark green	Amber to greenish yellow
105	409 (sh) 364	4,580 10,025	Orange to bright pink	-
106	406 (sh) 356 353	 10,175 10,730	Yellow to red	-

least once. If the boiled solution, while exposed to the atmosphere, is cooled, it will return to its original color, but if the solution is tightly stoppered and cooled it will retain its new color for some time.

As an example, a solution of compound 89 in chlorobenzene, boiled for 35 minutes in a flash fitted with a drying tube, turned to a Prussian blue color. Removing the drying tube for a minute and replacing it caused the solution to turn green. Further boiling of the solution brought back the deep blue color. The solution was too sensitive to exposure to the atmosphere to obtain spectrophotometric data on the blue species.

However, spectral data were obtained on the blue form of compound 88 in chlorobenzene (Figure 1). The solution was boiled under a slow flow of dry nitrogen in a cuvette that had a seven-inch long by eight-millimeter diameter tube sealed to it. The cuvette, with a thermocouple in the boiling solution, was placed in a special Dewar flask with optical windows and the spectra recorded at temperatures of 130, 100, 79.5, 71, and 62°C. The spectra at continuously decreasing temperatures show an apparent isosbestic point at 458 millimicrons and a progressive loss in strength at 590 millimicrons. The temperature was then brought back to 100°C., and held there for three hours without nitrogen gas flow. During this time both the 590 millimicron band and the isosbestic point at 458 millimicrons lost strength.

It appears that moisture plays a big role in these systems. The blue color is the anhydrous form and the yellow is a hydrated molecule.

$$X.H_2O \longrightarrow X + H_2O$$

$$\text{yellow} \longrightarrow \text{blue}$$

The set of curves going through the isosbestic point indicates that the amount of moisture in the system is constant for these curves. The variation in the 590 millimicron peak is due to variations in the equilibrium constant with temperature.

$$K = \frac{(X)\ (H_2O)}{(X \cdot H_2O)}$$

If all the water is removed, as with molecular sieves, then the blue form exists at all temperatures. Only when a trace amount of water is present is the thermochromic effect observed.

The spectral data also indicate that there is another form present which is light yellow. This hypothesis is necessary to explain the loss in strength at the isosbestic wavelength during the three-hour standing period. It must also be assumed that during this period moisture is diffusing into the solution to cause this change. This form, which is the normal form in solutions equilibrated with the atmosphere, is possibly the dihydrate.

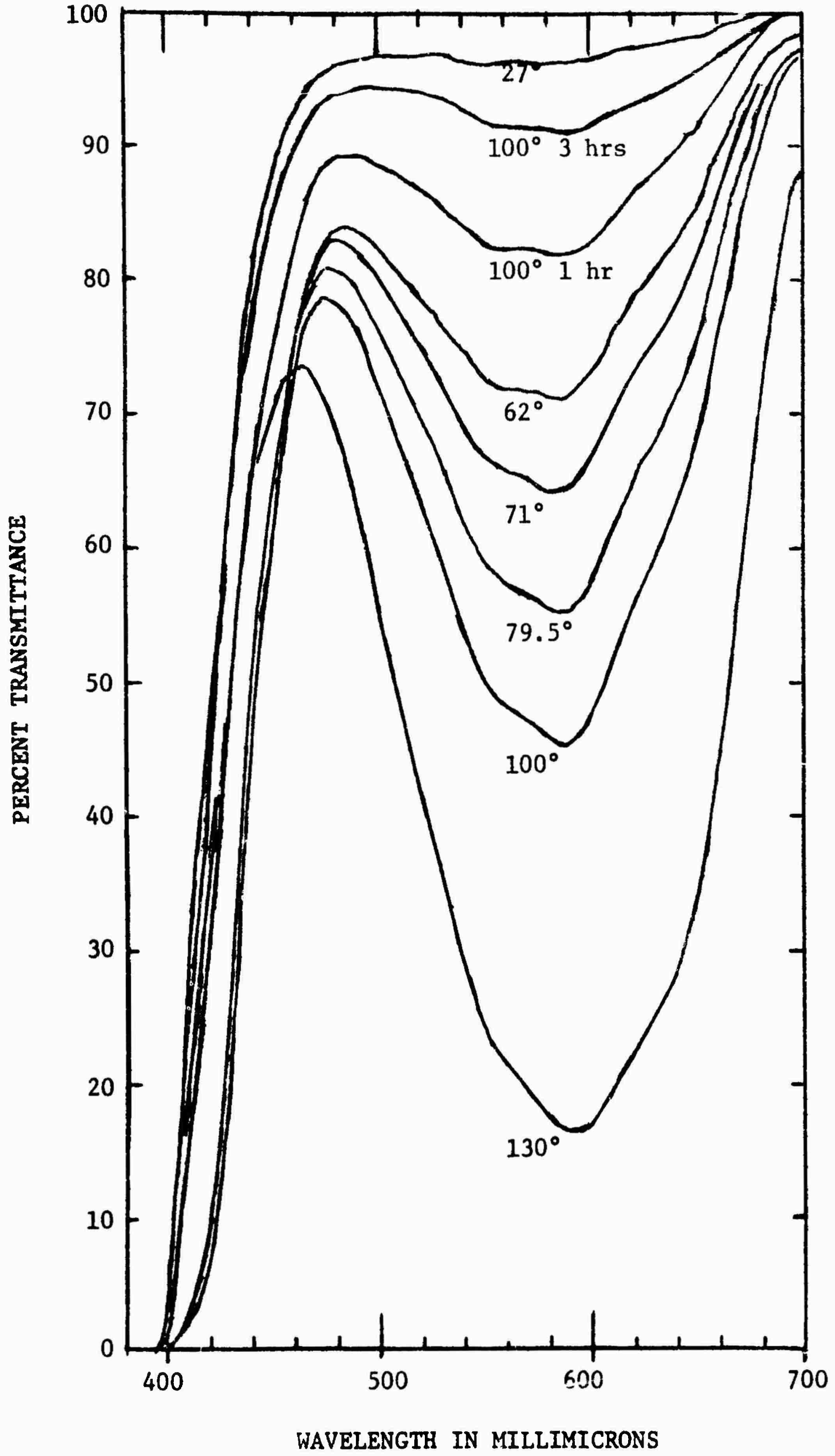


Figure 1. Spectrophotometric curves of Compound 88 in boiled chlorobenzene. The bottom five curves have equal moisture content. The top three curves have increasing amounts of moisture, going from 100° 1 hour to 27°.

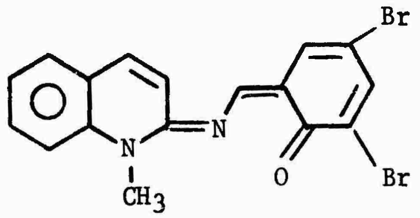
Therefore, the overall equilibrium appears to be:

$$A\cdot 2H_2O \rightleftharpoons A\cdot H_2O \rightleftharpoons A + H_2O$$

light yellow   yellow   blue

Probable structures assigned to the components of the equilibrium would be:

A is



$A\cdot H_2O$ is the structure given in Table V for compound 88.

$A\cdot 2H_2O$ is the mono hydrate of compound 88 in Table V.

It is apparent that the thermochromic behavior of these compounds depends on the precise control of a very small amount of moisture, making evaluations in solution very difficult.

Compound 88 was disperse-dyed on multifiber fabric, giving a very weak dyeing. The fabric was then dried and heated to 150°. No color changes could be induced in the fibers that did take up the dye. Other studies made with this compound included casting it in poly(methylmethacrylate), polystyrene, and cellulose acetate films. In no instance could a color change be induced by either chilling the yellow films to -70° or heating to 150°. Some of this material was cast in a block of poly(methylmethacrylate); again, intense heating or chilling produced no color changes.

Compound 80 was also cast, in ACRYLITE® films. Heating these films beyond 120° decomposed the compound and no thermochromism could be observed between -70° and 105°.

Unfortunately, these thermochromic compounds, because of their exact moisture requirement, do not afford a practical system as they now stand.

IV. CONCLUSIONS AND RECOMMENDATIONS

Several compounds have been prepared which represent modification of the dithizonate and spiropyran classes. Although a number of these materials did show photochromism, only the derivatives of 1,5-diphenylselenocarbazone exhibited this phenomenon to a useful degree. Preliminary evaluation of the few compounds of this class that have been prepared indicates that they have faster return rates with higher conversions than the corresponding sulfur derivatives.

1,1'-Azobis(3,4-dibromo-2,5-diphenylpyrrole), a recently reported literature compound which undergoes solid state photochromism, would not undergo this phenomenon in solution or plastic media, making it valueless as a practical chromotropic colorant.

The thermochromic compounds reported last year were evaluated in plastic media and it was found that they were not thermochromic under these conditions. As a result, these materials cannot be used as part of a "chameleon" camouflage system.

As a result of the favorable photochromic behavior of the selenocarbazonates, it is recommended that an extensive study of this system be undertaken. The derivatives of all the metals that will chelate with the selenocarbazone ligand should be prepared. Evaluations with respect to photochromism, spectral properties, light stability and toxicity should be carried out and the results compared with other known photochromic systems, particularly the dithizonate class.

V. REFERENCES

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APPENDIX

DATA SHEETS

The following data sheets summarize the experimental results obtained on the compounds synthesized or evaluated during the third year of the contract.

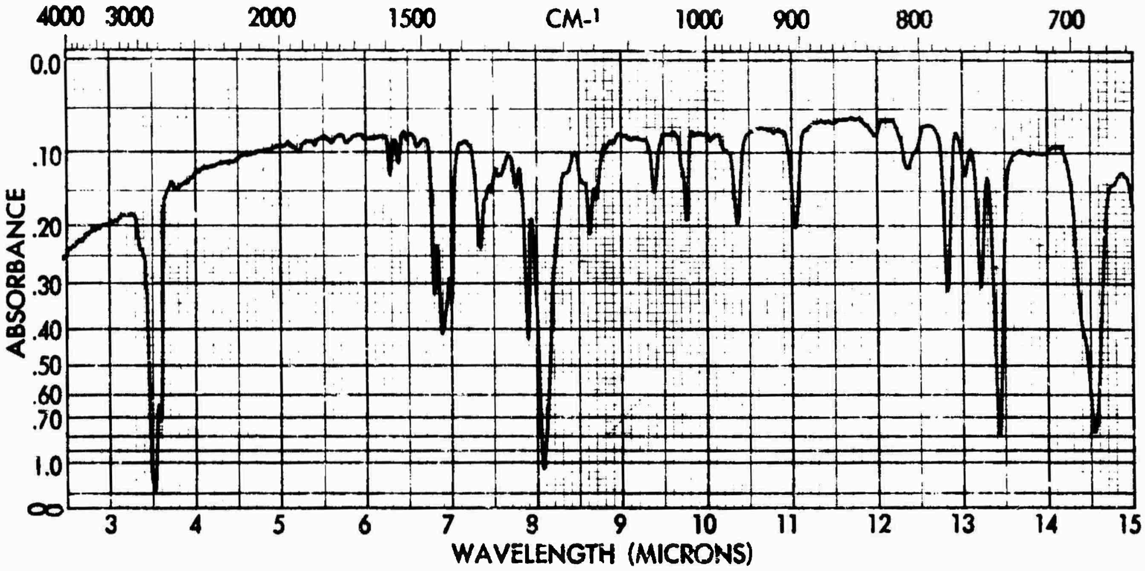
Infrared Spectra - The infrared spectrum for each compound is given at the top of the data sheet. All of the spectra presented were obtained from Nujol mulls on the Perkin-Elmer Model 137 "Infracord."

Physical Properties and Synthesis - In the center of each data sheet are listed the compound number, name, structural formula, molecular weight, melting point, appearance of the solid, synthesis procedure, percent yield, and microanalytical data.

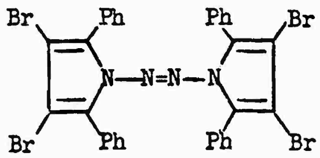
Spectral Data - The ultraviolet-visible spectral data listed in the lower left of the data sheets were obtained on the Cary 14 spectrophotometer. The color specifications for the unirradiated and irradiated solutions are based on visual observations of the standard solution as run on the Cary 14. These color specifications are quite subjective and depend on the concentration as well as the percent conversion obtained with the light source used. The $\lambda_{max.}$ values are given in millimicrons. Shoulders on main absorption bands are indicated by "(sh)". The absorption intensity at $\lambda_{max.}$ is listed under ε, the molar absorptivity, this value having the units liters/mole-cm.

Photochromic Properties - The percent conversion values are, in all cases, estimated. The conversion values listed are those obtained at room temperature during irradiation of an unstirred solution with visible light from the near-infrared source of the Cary 14. The thermal return rates are expressed as half-lives, i.e., the time required for the concentration of metastable species generated by irradiation to decrease to one-half in the absence of irradiation.

Remarks - This section lists the solvent (or mixture of solvents) used in the purification of the compound, the photochromic properties obtained in solution, and any observations of unusual solubilities.



Compound No.: 91 **Name:** 1,1'-Azobis(3,4-dibromo-2,5-diphenylpyrrole)



Mol. Wt.: 785 M.P.: 167° d.

Appearance: Lemon-yellow needles

Synthetic Procedure: Pg. 21 % Yield: 70

Analysis:	C	H	N	S	O	Br
Found	48.9	2.23	7.14			40.1
Calc.	48.9	3.18	7.14			40.8

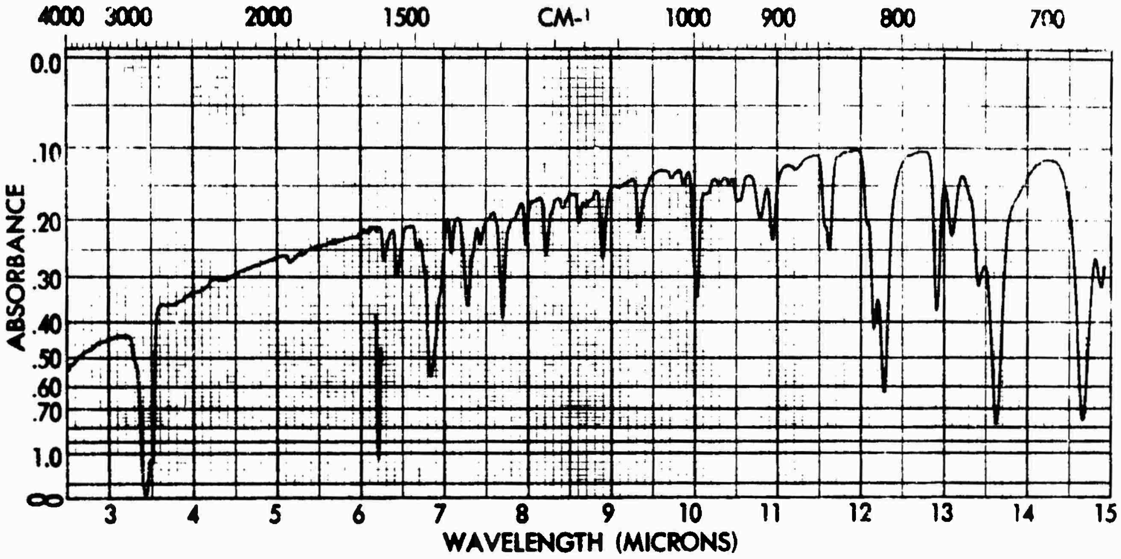
Spectral Data

	Color	λ Max.	ε
Unirradiated	Yellow	423	18,130
Irradiated	-*	-	-

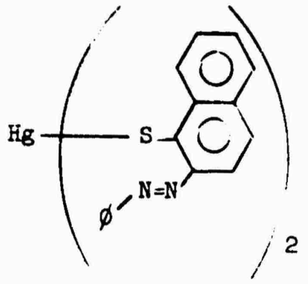
Thermal Return, Half-Life:

% Conversion:
(Cary 14 NIR Source)

Remarks: *In solution this compound irreversibly bleached upon irradiation. It is photochromic in the solid state, going from lemon-yellow to bright scarlet. C.A. films of this material became badly bubbled upon irradiation. Recrystallization solvent: methylcyclohexane.



Compound No.: 92 **Name:** Mercury bis(2-phenylazo-1-naphthalenethiolate)



Mol. Wt.: 727 **M.P.:** 250-1° (d)

Appearance: Orange-red needles

Synthetic Procedure: Pg. 15 **% Yield:** 80

Analysis:	C	H	N	S	O	Hg
Found	52.8	2.79	7.28	8.86		27.1
Calc.	52.9	3.05	7.70	8.82		27.6

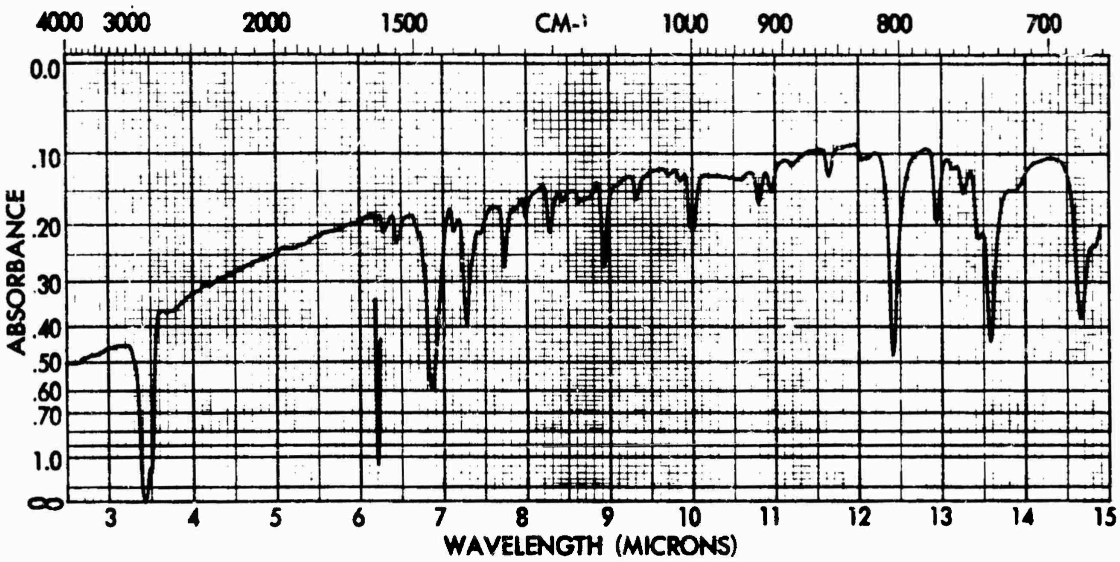
Spectral Data

	Color	λ Max.	ϵ
Unirradiated	Orange	473	10,620
Irradiated	"	473	8,310

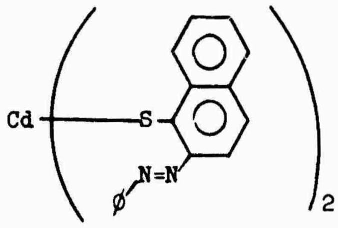
Thermal Return, Half-Life: 4-1/2 min.

% Conversion:
(Cary 14 NIR Source)

Remarks: No change in color could be detected; there was a definite change of intensity observed upon irradiation. C.A. film did not exhibit any changes upon irradiation. Purification solvents: chlorobenzene-butanol and tetrahydrofuran-methanol.



Compound No.: 93 **Name:** Cadmium bis(2-phenylazo-1-naphthalenethiolate)



Mol. Wt.: 638 M.P.: 288-9° (d)

Appearance: Maroon needles

Synthetic Procedure: Pg. 15 % Yield: 58

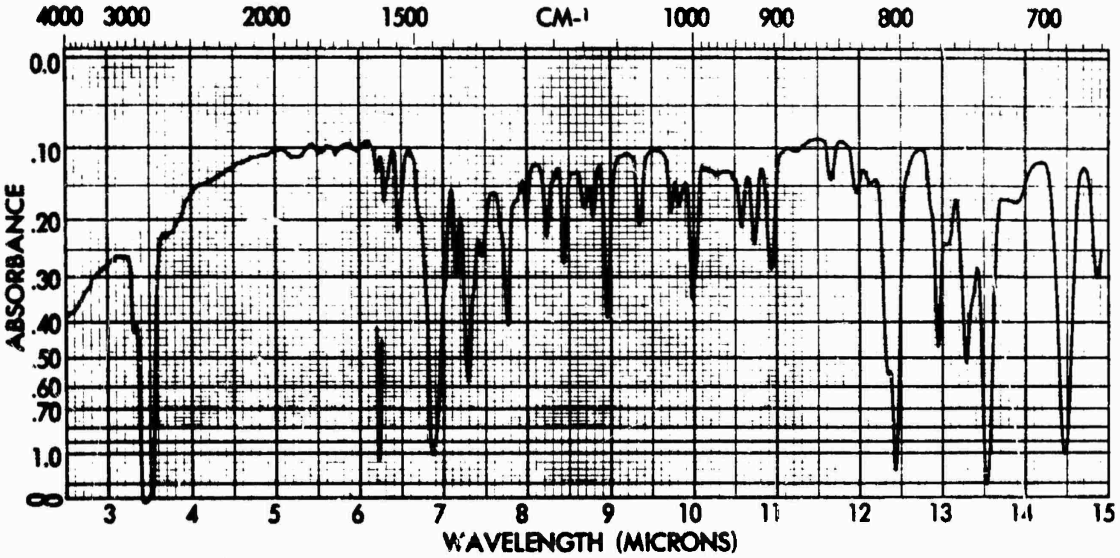
Analysis:	C	H	N	S	O	Cd
Found	60.2	3.17	8.78	9.81		17.9
Calc.	60.1	3.47	8.77	10.0		17.6

Spectral Data

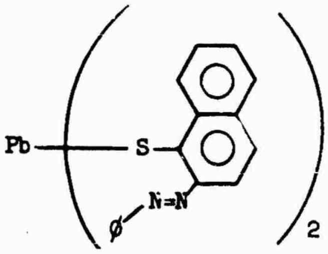
	Color	λ Max.	ε
Unirradiated	Reddish-orange	538	13,770
Irradiated		538	11,600

Thermal Return, Half-Life: Immediate but incomplete recovery.
% Conversion:
(Cary 14 NIR Source)

Remarks: Change in intensity but no color change upon irradiation. No changes observed in C.A. film upon irradiation. Purification solvent: tetrahydrofuran-methanol.



Compound No.: 94 **Name:** Lead bis(2-phenylazo-1-naphthalenethiolate)



Mol. Wt.: 733 **M.P.:** 237-8° (d)

Appearance: Maroon crystalline solid

Synthetic Procedure: Pg. 15 **% Yield:** 36

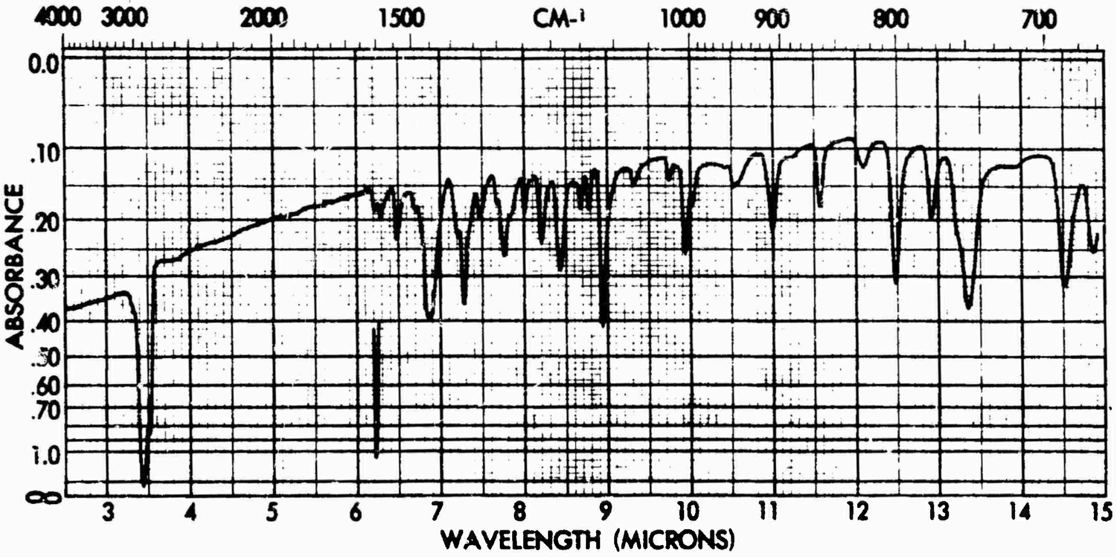
Analysis:	C	H	N	S	O	Pb
Found	52.2	2.72	7.59	9.11		28.9
Calc.	52.4	3.02	7.64	8.74		28.2

Spectral Data

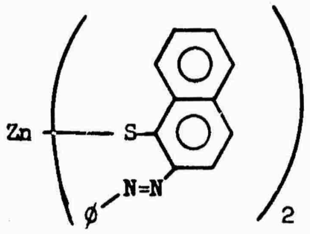
	Color	λ Max.	ε
Unirradiated	Reddish-orange	530	11,210
Irradiated		530	10,210

Thermal Return, Half-Life: Immediate but incomplete recovery.
% Conversion:
(Cary 14 NIR Source)

Remarks: Change in intensity, but no change in color upon irradiation. Purification solvent: chlorobenzene-butanol.



Compound No.: 95 **Name:** Zinc bis(2-phenylazo-1-naphthalenethiolate)



Mol. Wt.: 591 M.P.: 253-4° (d)

Appearance: Dark purple needles

Synthetic Procedure: Pg. 15 % Yield: 80

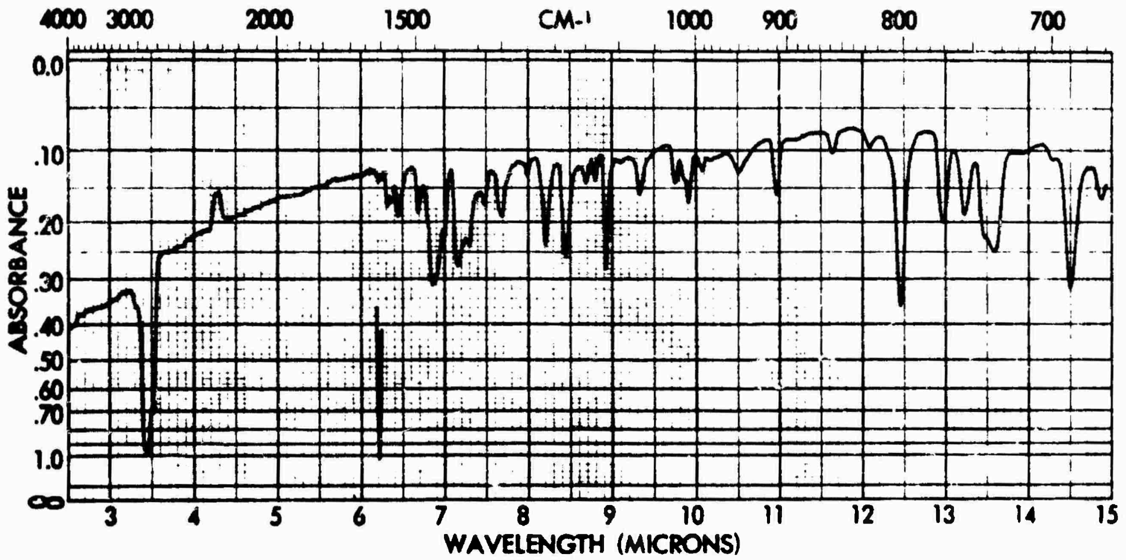
Analysis:	C	H	N	S	O	Zn
Found	64.8	3.48	9.15	11.1		11.5
Calc.	64.9	3.75	9.46	10.8		11.0

Spectral Data

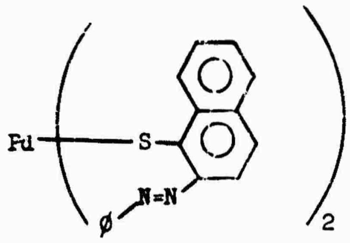
	Color	λ Max.	ϵ
Unirradiated	Red	560 448	12,710 5,590
Irradiated		560 435	11,750 5,060

Thermal Return, Half-Life: Immediate but incomplete recovery.
% Conversion:
(Cary 14 NIR Source)

Remarks: Purification solvent: tetrahydrofuran-methanol



Compound No.: 96 **Name:** Palladium bis(2-phenylazo-1-naphthalenethiolate)



Mol. Wt.: 632 **M.P.:** 270-1°

Appearance: Dark purple microcrystalline solid.

Synthetic Procedure: Pg. 15 **% Yield:** 67

Analysis:	C	H	N	S	O	Pd
Found	60.5	3.65	8.36	10.1		17.4
Calc.	60.7	3.51	8.85	10.1		16.8

Spectral Data

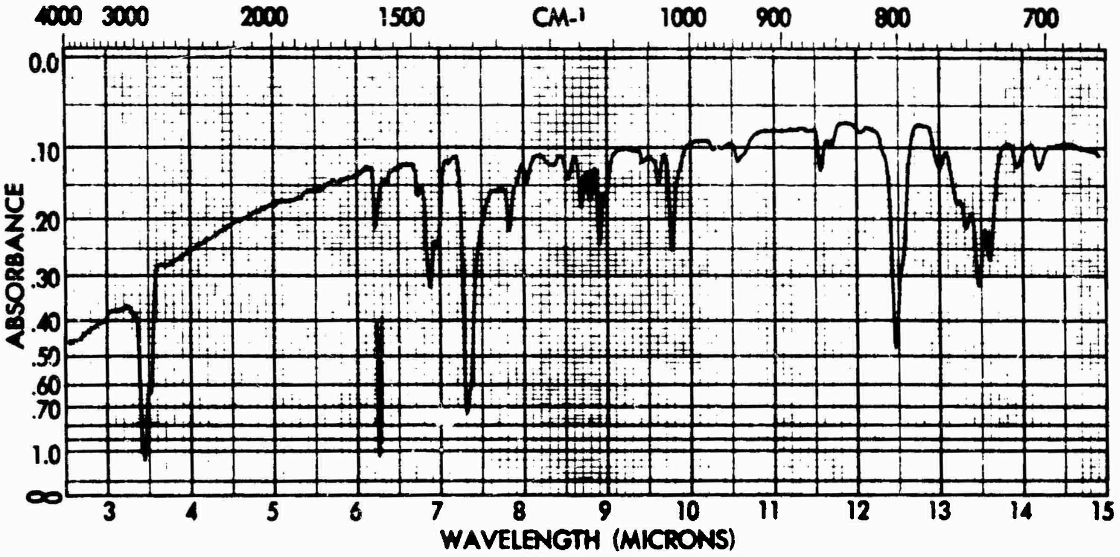
	Color	λ Max.	ε
Unirradiated	Red	580 (482)*	47.5 7,150
Irradiated		580 (482)*	47.7 7,150

Thermal Return, Half-Life:

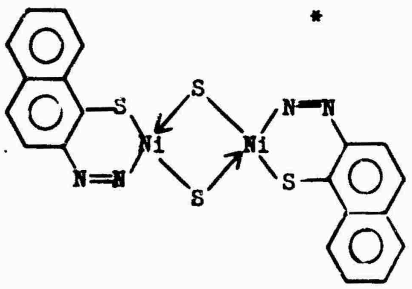
% Conversion:
(Cary 14 NIR Source)

Remarks: Not photochromic. Purification solvent: chlorobenzene.

* $\lambda_{min.}$ (mμ)



Compound No.: 97 Name: *



Mol. Wt.:* 708 M.P.: 370-371°

Appearance: Black microcrystals

Synthetic Procedure: Pg. 15 % Yield:

Analysis:	C	H	N	S	O	Ni
Found	54.9	2.87	7.81	17.6		17.1
Calc.	54.3	3.13	7.92	18.2		16.6

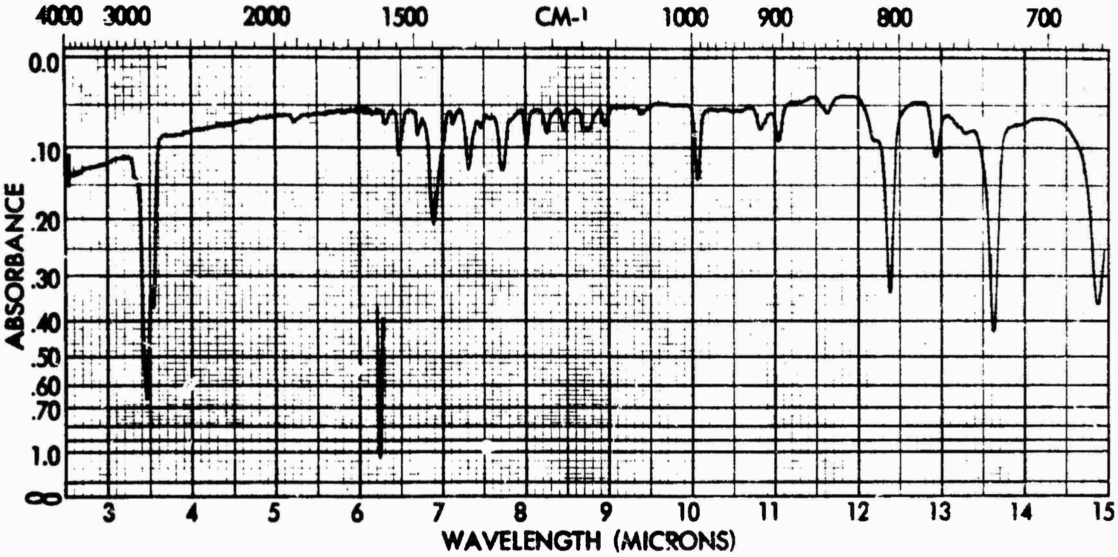
Spectral Data

	Color	λ Max.	ε
Unirradiated	Yellow-orange	482	
Irradiated			

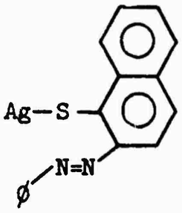
Thermal Return, Half-Life:

% Conversion:
(Cary 14 NIR Source)

Remarks: Not photochromic. Purification: recrystallization from chlorobenzene.
*This structure is proposed on the basis of the analytical data and literature analogy (see Synthesis Section); it has not been confirmed.



Compound No.: 98 **Name:** Silver 2-phenylazo-1-naphthalenethiolate



Mol. Wt.: 371 **M.P.:** 246.5-7.5°

Appearance: Red microcrystalline plates.

Synthetic Procedure: Pg. 15 **% Yield:** 50

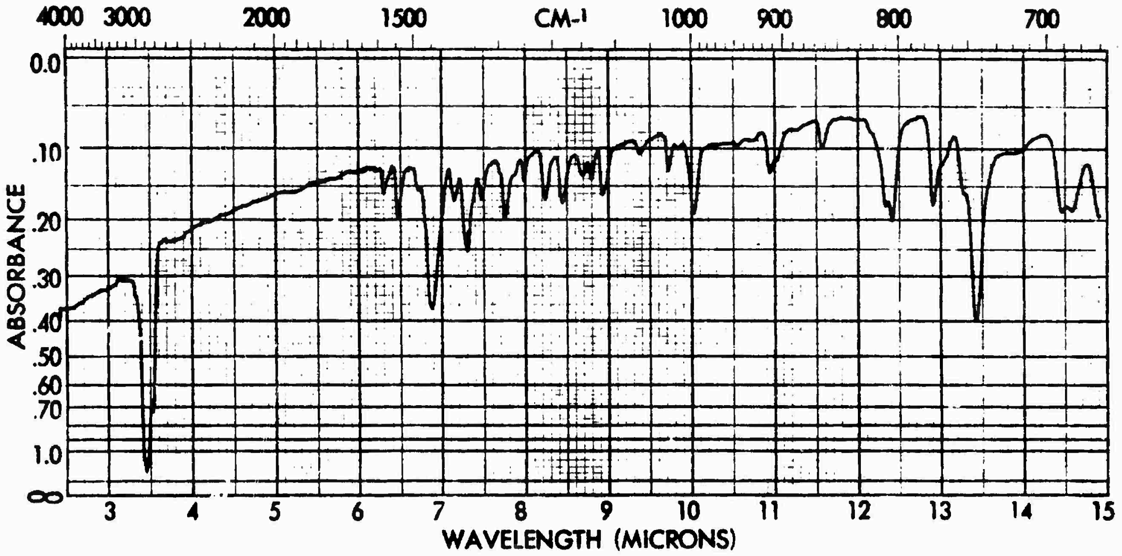
Analysis:	C	H	N	S	O	Ag
Found	51.8	2.99	7.55	9.80		29.0
Calc.	51.8	2.72	7.45	8.64		29.1

Spectral Data

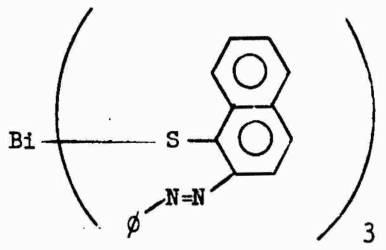
	Color	λ Max.	ε
Unirradiated	Yellow	450	4,489
Irradiated		440	3,760

Thermal Return, Half-Life: Immediate but incomplete recovery.
% Conversion:
(Cary 14 NIR Source)

Remarks: C.A. film exhibited change of intensity, but no wavelength shift.
Purification solvent: chloroform-methanol



Compound No.: 99 **Name:** Bismuth tris(2-phenylazo-1-naphthalenethiolate)



Mol. Wt.: 998 M.P.: 243-5°

Appearance: Black rods

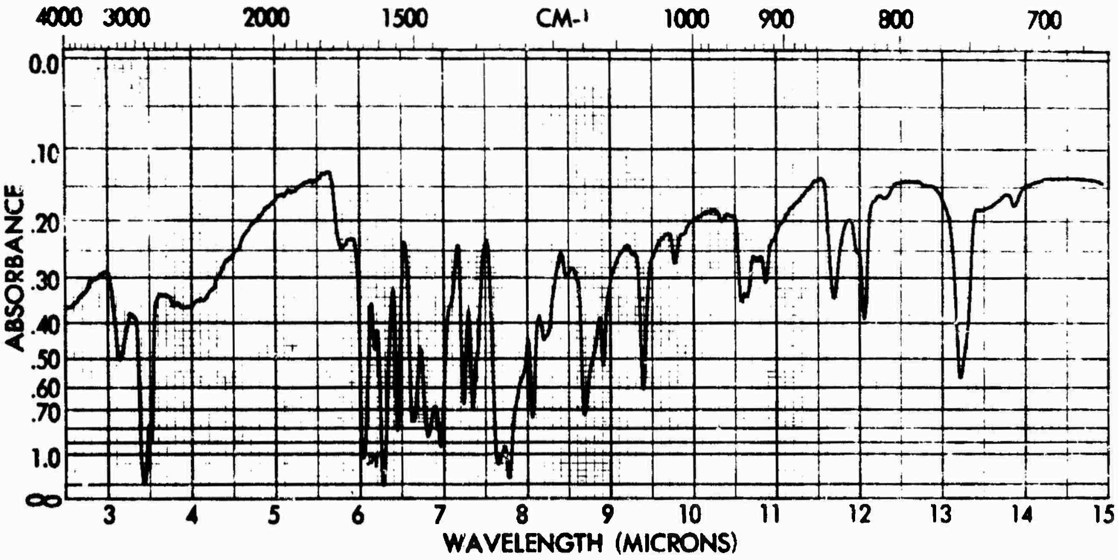
Synthetic Procedure: Pg. 15 % Yield: 46

Analysis:	C	H	N	S	O	Bi
Found	57.8	3.16	7.97	9.83		20.6
Calc.	57.7	3.33	8.42	9.63		20.9

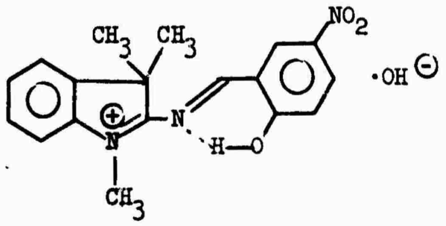
Spectral Data

	Color	λ Max.	ε	Thermal Return, Half-Life:
Unirradiated	Yellow-orange	488	13,070	**% Conversion:** **(Cary 14 NIR Sour[illegible])**
Irradiated		488	-	

Remarks: Not photochromic. Purification solvent: tetrahydrofuran-methanol.



Compound No.: 100 **Name:** 2-[(2-Hydroxy-5-nitrobenzylidene)amino]-1,3,3-trimethyl-3H-indolium hydroxide



Mol. Wt.: 341.4 M.P.: 141-142°

Appearance: Deep yellow needles

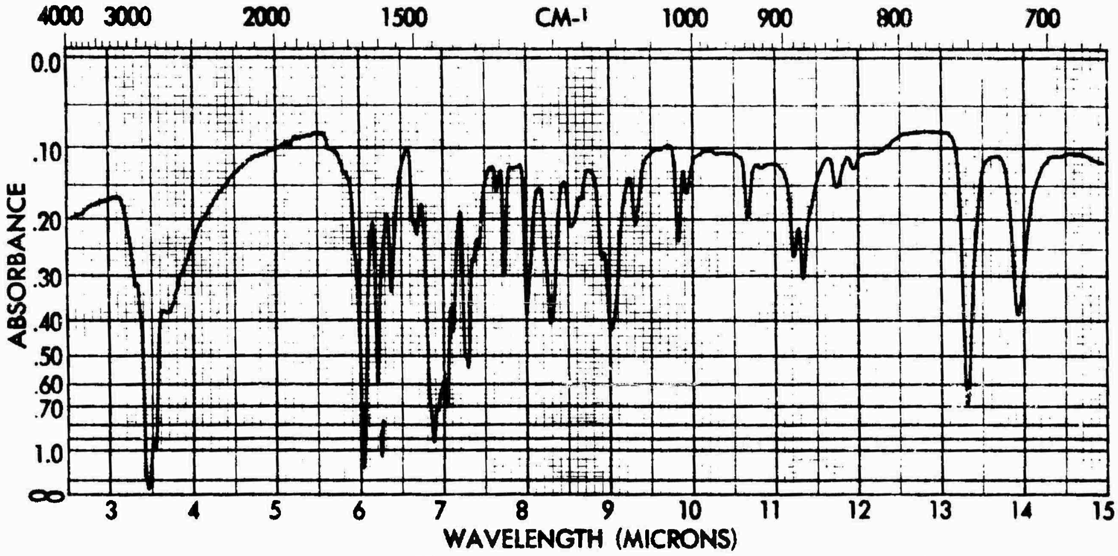
Synthetic Procedure: Pg. 20 % Yield: 67

Analysis:	C	H	N	S	O
Found	63.2	5.59	12.1		18.4
Calc.	63.3	5.61	12.3		18.7

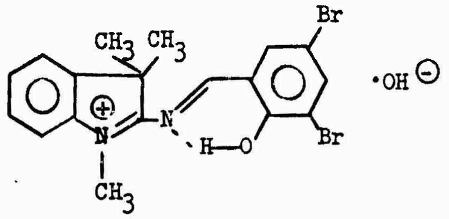
Spectral Data

	Color	λ Max.	ϵ	Thermal Return, Half-Life:
Unirradiated	Colorless	295	13,919	% Conversion: (Cary 14 NIR Source)
Irradiated	No change.			

Remarks: Not photochromic. Purification solvent: ethylacetate-hexane.



Compound No.: 101 **Name:** 2-/(3,5-dibromo-2-hydroxybenzylidene)amino/-1,3,3-trimethyl-3H-indolium hydroxide



Mol. Wt.: 454 M.P.: 143-144

Appearance: Light amber prisms

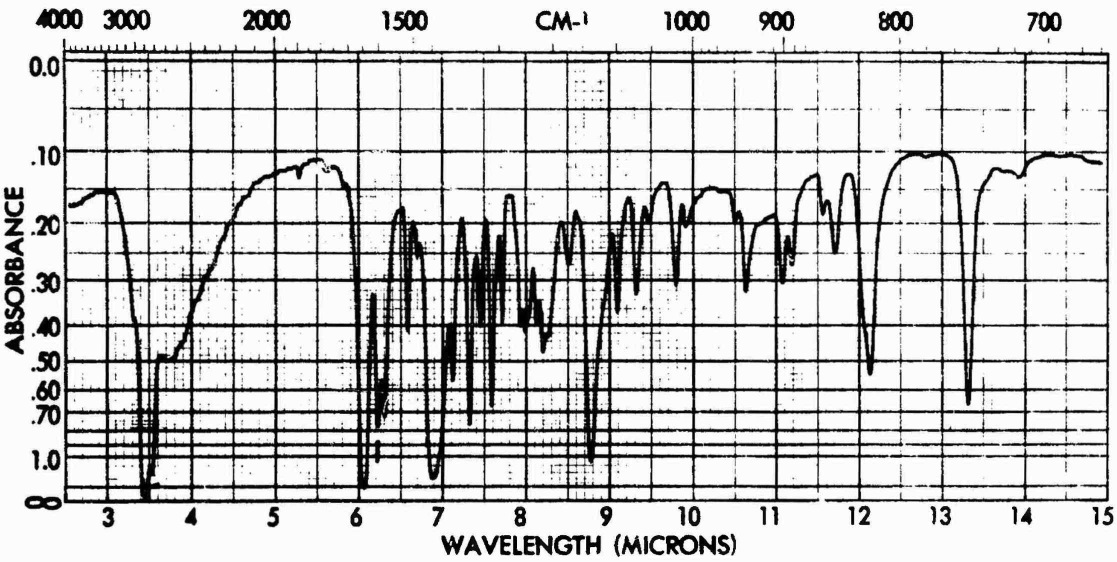
Synthetic Procedure: Pg. 20 % Yield: 66

Analysis:	C	H	N	S	O	Br
Found	47.6	3.88	6.26		7.26*	35.0
Calc.	47.6	3.99	6.17		7.05	35.2

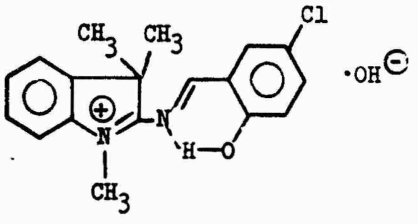
Spectral Data

	Color	λ Max.	ε	Thermal Return, Half-Life:
Unirradiated	Colorless	347	3,413	% Conversion: (Cary 14 NIR Source)
Irradiated	No change.			

Remarks: Not photochromic. Recrystallization solvent: ethyl acetate-hexane.
*By difference.



Compound No.: 102 **Name:** 2-[(5-Chloro-2-hydroxybenzylidene)amino]-1,3,3-trimethyl-3H-indolium hydroxide



Mol. Wt.: 329.9 M.P.: 100-1°

Appearance: Yellow prisms

Synthetic Procedure: Pg. 20 % Yield: 77

Analysis:	C	H	N	S	O	Cl
Found	65.5	5.88	8.49		9.65*	10.5
Calc.	65.4	5.48	8.47		9.85	10.7

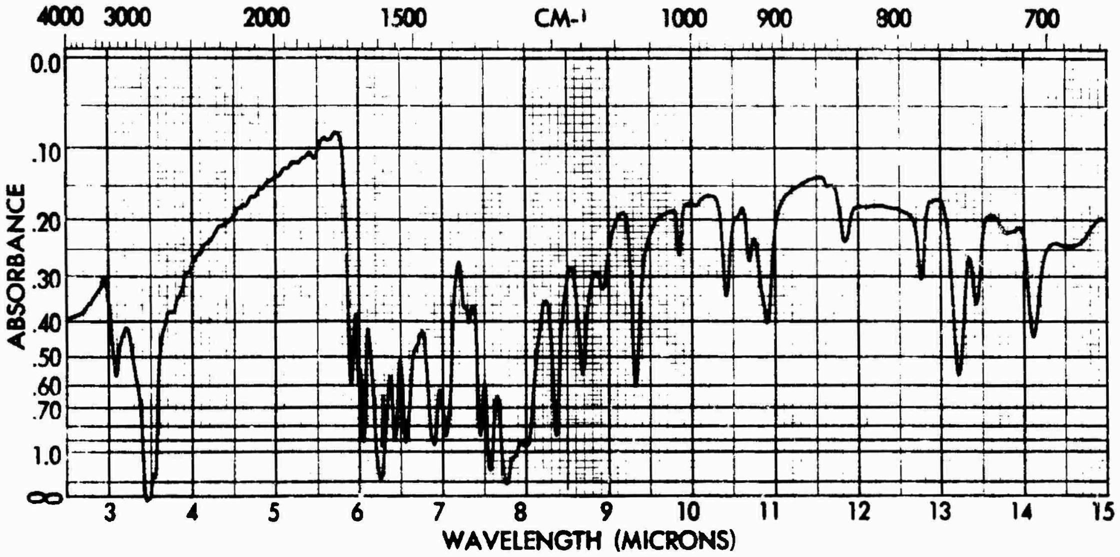
Spectral Data

	Color	λ Max.	ε
Unirradiated	Colorless	341	3,254
Irradiated	No change.		

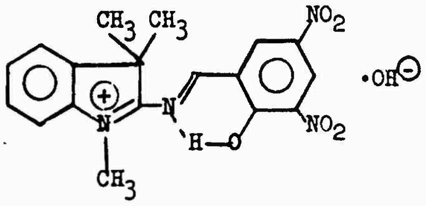
Thermal Return, Half-Life:

% Conversion:
(Cary 14 NIR Source)

Remarks: Not photochromic. Recrystallization solvent: ethyl acetate-hexane.
*By difference.



Compound No.: 103 **Name:** 2-/(3,5-Dinitro-2-hydroxybenzylidene)amino/-1,3,3-trimethyl-3H-indolium hydroxide



Mol. Wt.: 387 M.P.: 178-9°

Appearance: Orange prisms

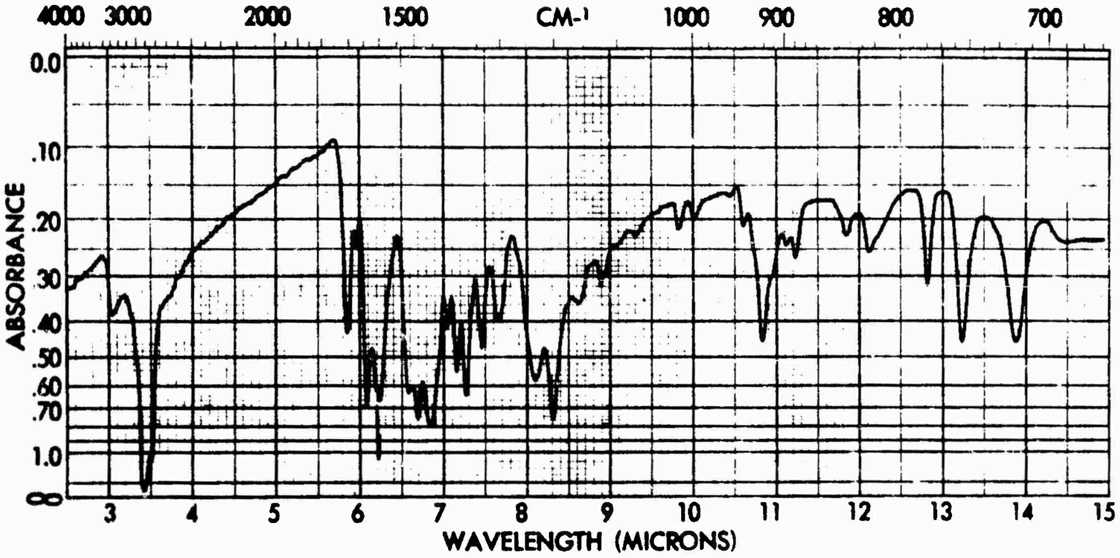
Synthetic Procedure: Pg. 20 % Yield: 66

Analysis:	C	H	N	S	O
Found	56.0	4.71	14.8		25.2
Calc.	56.0	4.70	14.5		24.9

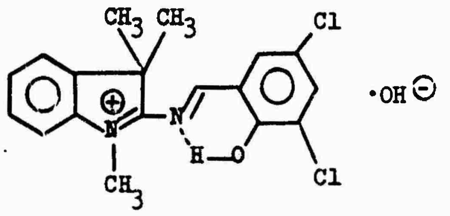
Spectral Data

	Color	λ Max.	ε	Thermal Return, Half-Life:
Unirradiated	Colorless	400 (sh) 360	8,243 15,132	% Conversion: (Cary 14 NIR Source)
Irradiated	No change			

Remarks: Not photochromic. Recrystallization solvent: ethyl acetate.



Compound No.: 104 Name: 2-/(3-Chloro-2-hydroxy-5-nitrobenzylidene)amino/-1,3,3-trimethyl-3H-indolium hydroxide



Mol. Wt.: 377 M.P.: 158-9°

Appearance: Dark orange prisms

Synthetic Procedure: Pg. 20 % Yield: 70

Analysis:	C	H	N	S	O	Cl
Found	57.2	4.79	11.3		17.3	9.45
Calc.	57.5	4.81	11.5		17.0	9.41

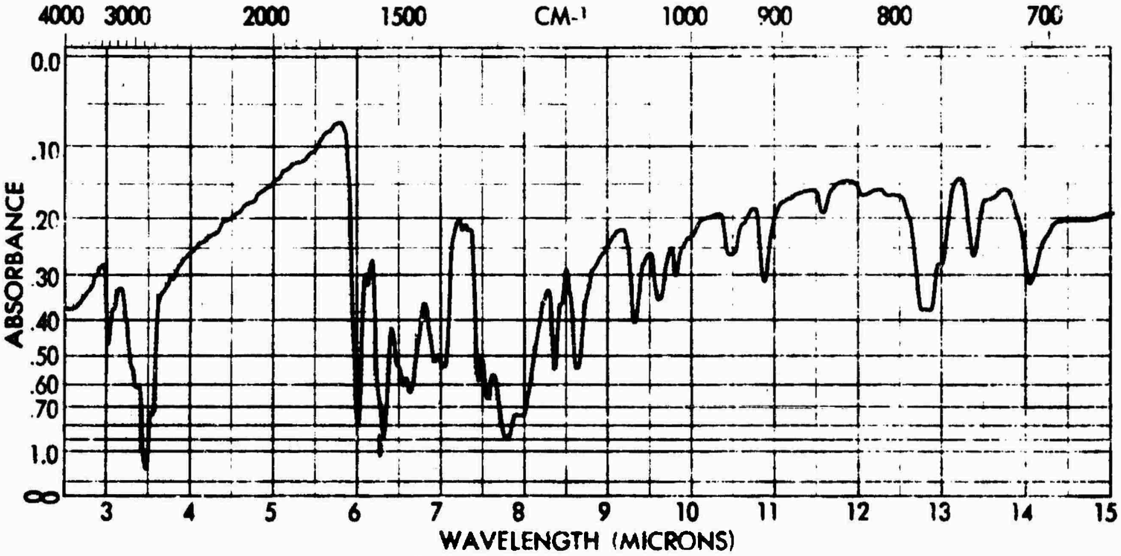
Spectral Data

	Color	λ Max.	ε
Unirradiated	Yellow	456 368	641 4,637
Irradiated	No change		

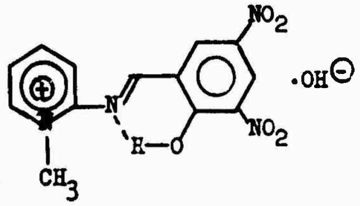
Thermal Return, Half-Life:

% Conversion:
(Cary 14 NIR Source)

Remarks: Not photochromic. Recrystallization solvent: ethylacetate-hexane



Compound No.: 105 **Name:** 2-[3,5-dinitro-2-hydroxybenzylideneamino]-1-methylpyridinium hydroxide



Mol. Wt.: 321 M.P.: 183-185°

Appearance: Orange prisms

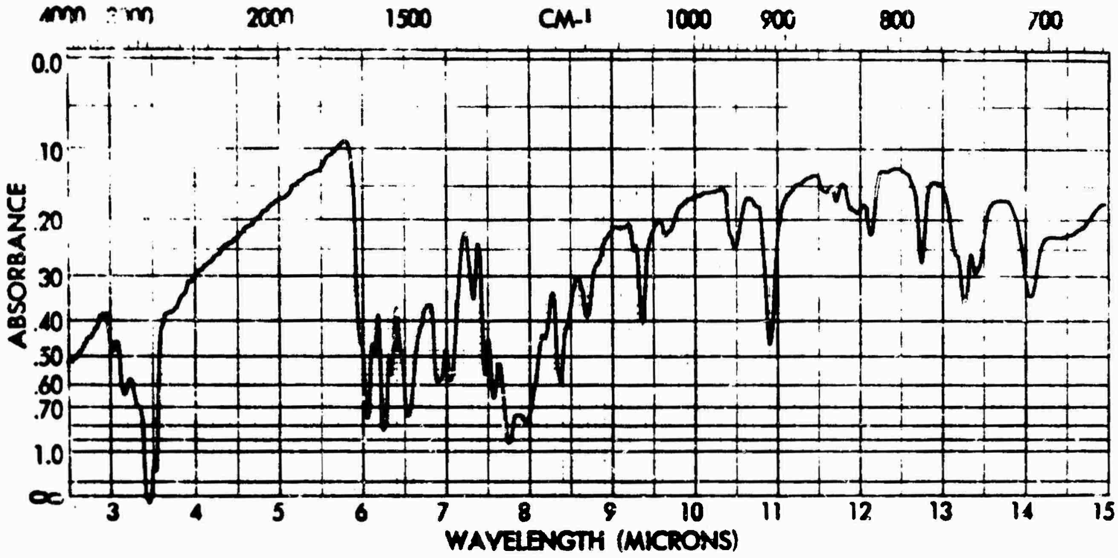
Synthetic Procedure: Pg. 12 % Yield: 50

Analysis:	C	H	N	S	O
Found	48.3	3.52	17.5		29.8
Calc.	48.8	3.78	17.5		30.0

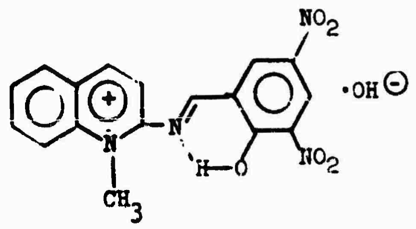
Spectral Data

	Color	λ **Max.**	ε	**Thermal Return, Half-Life:**
Unirradiated	**Colorless**	409 (sh) 364	4,586 10,025	**% Conversion:** **(Cary 14 NIR Source)**
Irradiated	**No change**			

Remarks: Not photochromic. Recrystallization solvent: nitromethane and ethanol. Thermochromic in MCB going from orange to red.



Compound No.: 106 **Name:** 2-(3,5-Dinitro-2-hydroxybenzylideneamino)-1-methylquinolinium hydroxide



Mol. Wt.: 370.3 **M.P.:** 224-225.5°

Appearance: Yellow micro needles

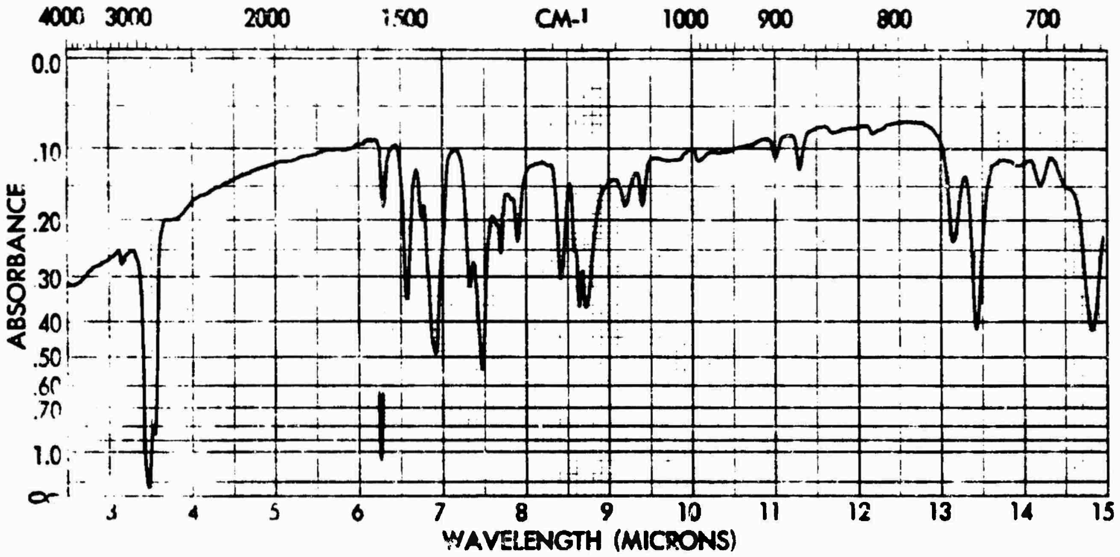
Synthetic Procedure: Pg. 20 **% Yield:** 83

Analysis:	C	H	N	S	O
Found	55.0	3.73	15.2		25.9
Calc.	55.1	3.81	15.1		25.9

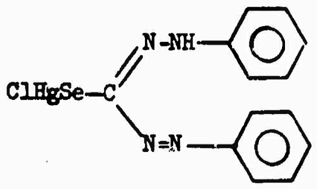
Spectral Data

	Color	λ **Max.**	ε	**Thermal Return, Half-Life:**
Unirradiated	Colorless	406 (sh)		**% Conversion:**
		356	10,175	(Cary 14 NIR Source)
		353	10,730	
Irradiated	No change.			

Remarks: Not photochromic. Thermochromic in boiling monochlorobenzene going from orange to red. Recrystallization solvent: ethyl acetate and acetonitrile.



Compound No.: 107 Name: Chloromercury 1,5-diphenylselenocarbazonate



Mol. Wt.: 538 M.P.: 187-9° (d)

Appearance: Maroon microcrystalline solid

Synthetic Procedure: Pg. 15 % Yield: 44

Analysis:	C	H	N	Se	Hg	Cl
Found	29.1	2.08	9.77	14.6	37.7	6.80*
Calc.	29.0	2.06	10.0	14.7	37.3	6.59

Spectral Data

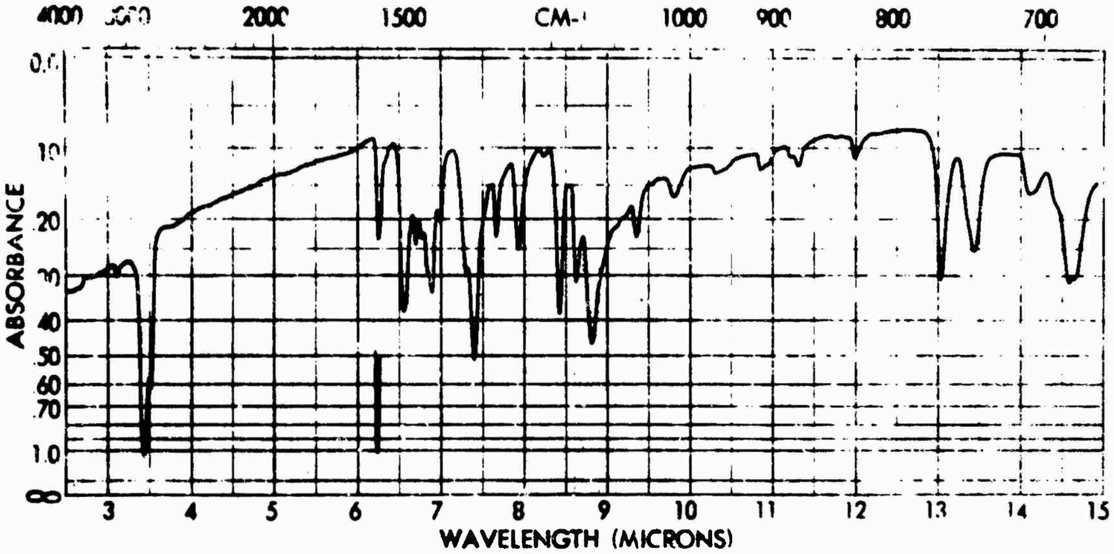
	Color	λ Max.	ε
Unirradiated	Orange	479	21,400
Irradiated	Blue	597	11,700

Thermal Return, Half-Life: 18 sec.

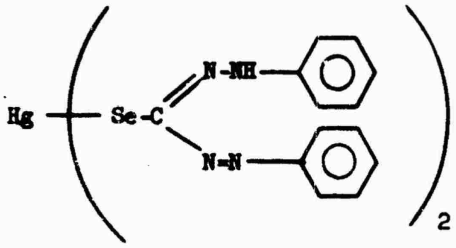
% Conversion: 98.5
(Cary 14 NIR Source)

Remarks: Forticel (cellulose propionate) films had a $t_{\frac{1}{2}}$ of 2 min. 15 sec. with ~ 85% conversion. Solution work done in toluene. Purification: chromatography and crystallization from ethylacetate-hexane.
*By difference.

GRAPHIC NOT REPRODUCIBLE



Compound No.: 108 **Name:** Mercury bis(1,5-diphenylselenocarbazonate)



Mol. Wt.: 805 **M.P.:** 196-6.5° (d)

Appearance: Maroon needles

Synthetic Procedure: Pg. 15 **% Yield:** 18

Analysis:	C	H	N	Se	Hg
Found	38.8	2.48	13.8	19.2	25.3
Calc.	38.8	2.76	13.9	19.6	24.9

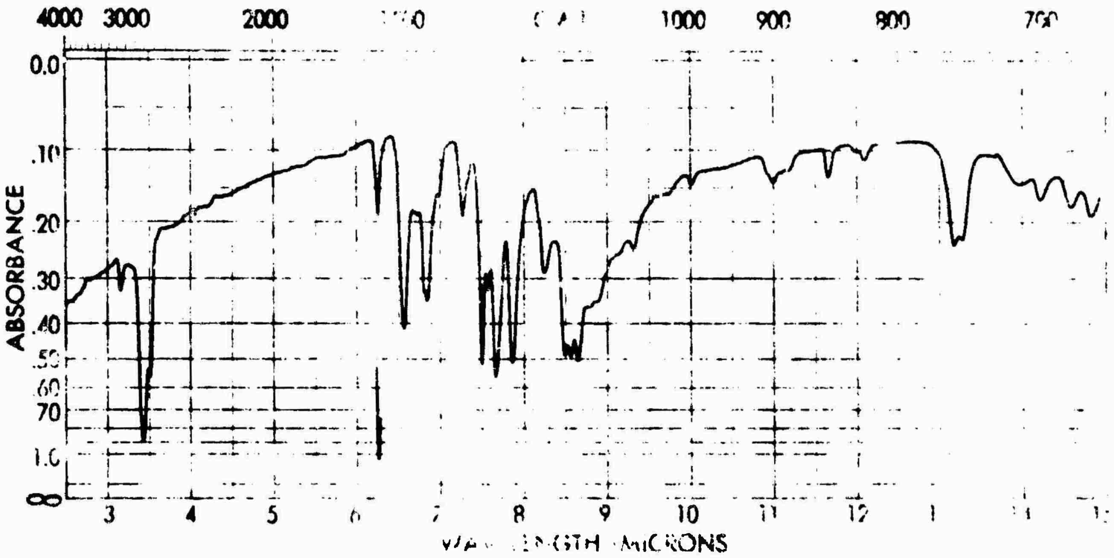
Spectral Data

	Color	λ Max.	ε
Unirradiated	**Reddish-orange**	483	50,393
Irradiated	**Greenish-blue**	600	24,150

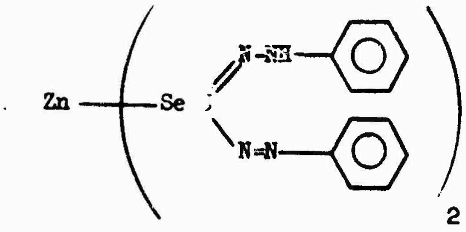
Thermal Return, Half-Life: 55 sec.

% Conversion: 91
(Cary 14 NIR Source)

Remarks: Purification: chromatography and crystallization from benzene-hexane. **Evaluations made in toluene.**



Compound No.: 109 **Name:** Zinc bis(1,5-diphenylselenocarbazonate)



Mol. Wt.: 670 M.P.: 241-2° (d)

Appearance: Iridescent green solid.

Synthetic Procedure: Pg. 15 % Yield: 37

Analysis:	C	H	N	Se	Zn
Found	46.3	3.13	16.6	23.4	9.13
Calc.	46.6	3.31	16.7	23.6	9.76

Spectral Data

	Color	λ Max.	ε
Unirradiated	Red	530 418 (sh)	71,221
Irradiated		700 418 (sh)	30,285

Thermal Return, Half-Life: Less than 15 sec.

% Conversion: 42%
(Cary 14 NIR Source)

Remarks: Purification: chromatography and crystallization from tetrahydrofuran-hexane. Evaluations made in toluene.

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Security Classification

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13. ABSTRACT

The work described in this report, which represents the final phase (~~Part~~ III) of a study of photochromic colorants potentially useful for a "chameleon" type camouflage system, has been mainly concerned with the preparation and evaluation of new and modified photochromic systems. Of the photochromic compounds prepared, only the metal derivatives of 1,5-diselenocarbazonate, an analog of dithizone (diphenylthiocarbazone), exhibit this phenomenon to a practical extent. Preliminary studies on the selenocarbazonates indicate that they may possess properties superior to those of the corresponding dithizonate compounds.

A number of thermochromic compounds prepared during the second year of this study would not function in plastic media, making them impractical for use in a chromotropic camouflage system.

The facile alkylation of o-nitrobenzyl cyanide at low temperatures, using dimethyl sulfoxide as the solvent and aqueous sodium hydroxide as the base, represents a new and mild procedure for carrying out this type of reaction. The resulting dimethyl compound, 2-methyl-2-(o-nitrophenyl)propionitrile, undergoes an interesting cyclization upon catalytic reduction to give 2-amino-3,3-dimethyl-3H-indoline 1-oxide in addition to the expected aminontrile.

A three-year project review with recommendations for future effort is included.

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Photochromism	8		10			
Thermochromism	8		10			
Thiocarbazonates	9					
Selenocarbazonates	9					
Camouflage	4		8			
Spiropyrans	9					
Dithizonates	9					
Organometallic compounds	9					
Mercury	9					
Zinc	9					
Palladium	9					
Selenium	9					
Diphenylcarbazones	9					
Naphthalenethiols	9					
Salicylaldehydes	9					
Indolines	9					
Azobispyrroles	9					
Textiles	4		9			