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THE DESIGN AND SYNTHESIS OF INFRARED
FLOURESCENT COLORANTS

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American Cyanamid Company

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A full spectral examination revealed that the total fluorescence emission from Direct Blue 108, a commercial dioxazine dye with moderate near infrared fluorescence, is much greater than that from Basic Blue 3, the strongest near infrared fluorescer uncovered in a Natick investigation of commercial dyes. Molecular orbital calculations performed on twenty-one related dioxazine structures indicate that a ring system with two perylene moieties fused to the dioxazine system, the bisbenz(1,9)anthra(8,7-ab: 8',7'-lm) triphenodioxazine		

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20. system, should fluoresce near 750 nm when dyed on nylon. These calculations, coupled with literature reports of high fluorescence yield for perylene derivatives, indicate that this ring system is likely to fulfill the Natick Laboratories' requirements.

Efforts to synthesize nylon dyes containing the desired ring system have not been completed. A total of 16 new compounds prepared during the course of this effort are described and characterized. A reliable method of preparing the essential intermediate, 3-aminoperylene, (3-AMP) from commercially available starting materials in good yields was developed. Condensation of 3-AMP with a quinone to give a potential one-step precursor of the desired dioxazine ring system in moderate (20%) yield has been achieved. Several efforts to effect ring-closure of this condensation product to the desired dioxazine ring system have produced only ill-defined byproducts. Unexpected effects of degree of sulfonation of a dioxazine on spectral characteristics of product dye have been observed. Recommendations for additional research efforts are made.

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FOREWARD

The rapid proliferation in detector systems made possible by electro-optical devices necessitates a broad band approach to countersurveillance for the individual combat soldier. Such a system was devised originally by Ramsley and Walwood of Natick Laboratories through the use of colorants that can be excited by far end visible radiation and emitting non-visible IR radiation fortunately in a band which is useful. The colorants used to demonstrate feasibility of the concept are unstable in strong sunlight. The research effort reported here was undertaken to establish the possibility of obtaining more colorfast colorants by synthesis based on preliminary theoretical analysis. The work was performed under contract and was guided by Mr. A. O. Ramsley as Project Officer and Dr. Edward M. Healy as Alternate Project Officer. The program had the active support of Dr. Theodore Cooke, Director of Scientific Services, American Cyanamid Company.

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I. INTRODUCTION

For purposes of protective camouflage the Clothing and Organic Materials Division of the Natick Laboratories requires an anionic colorant suitable for application by practical, commercially useful dyeing processes to textile fibers of Nylon 66 and blends thereof. The colorant must also show fluorescence in the spectral region from 750 nm to 900 nm of an intensity at least two-thirds that of Natick's reference sample. In addition, the colorant must exhibit colorfastness to degradation by light, fastness to laundering, and be capable, upon blending with additional colorants, of achieving any of the typical camouflage colors used in field uniforms.

Although the number of anionic dyes of known structure which exhibit good fastness to light and washing when applied to nylon fibers is quite large, those which also have the property of strong near infrared fluorescence are virtually zero. The approach taken in this investigation was to evaluate the characteristics of those compounds which most closely fulfill the requirements and from this to proceed to determine the structural changes that would be required to complete those requirements. Having determined the required modifications, our goal was to then prepare new compounds having the selected structures and evaluate their performance.

II. STABILITY AND SPECTRAL EVALUATION OF COMMERCIAL DYES

A. Solution Studies

Those commercial dyes described in a Natick report¹ as having fluorescence intensity sufficient to give instrumental readings of 60 or greater were obtained, when available, from their manufacturers. The relative light stability of these dyes, together with three non-fluorescent nylon dyes considered to have good light fastness on nylon, were determined in N-butylacetamide solution. The solvent was chosen as a model for the environment of the dye when applied to nylon.

For comparative lightfastness evaluation, solutions were prepared at concentrations resulting in optical densities of 2.0 to 2.5 when measured in 1 cm. quartz cells at the wavelength of their absorption maxima. The cells were then simultaneously exposed to an artificial light source (see Experimental) approximating sunlight in wavelength distribution. The rates of disappearance of the exposed dyestuff in solution were measured periodically during the exposure. The rates were treated as first order processes with the normalized $\ln(O.D.)$ at λ_{max} of the dyes plotted against exposure time, as shown in Figure 1. The reference numbers in Figure 1 indicate the dyes as numbered in Table I. It is seen from the figure that most of the more stable dyes showed pseudo-first order decay (straight line plots) for an initial period, followed by a period of accelerated decay.

We note that samples of Direct Blue 8 from different sources have somewhat different spectral characteristics and considerably different stability characteristics. The cause of these differences was not examined since neither dye sample was sufficiently close to having the desired combination of properties.

FIGURE 1

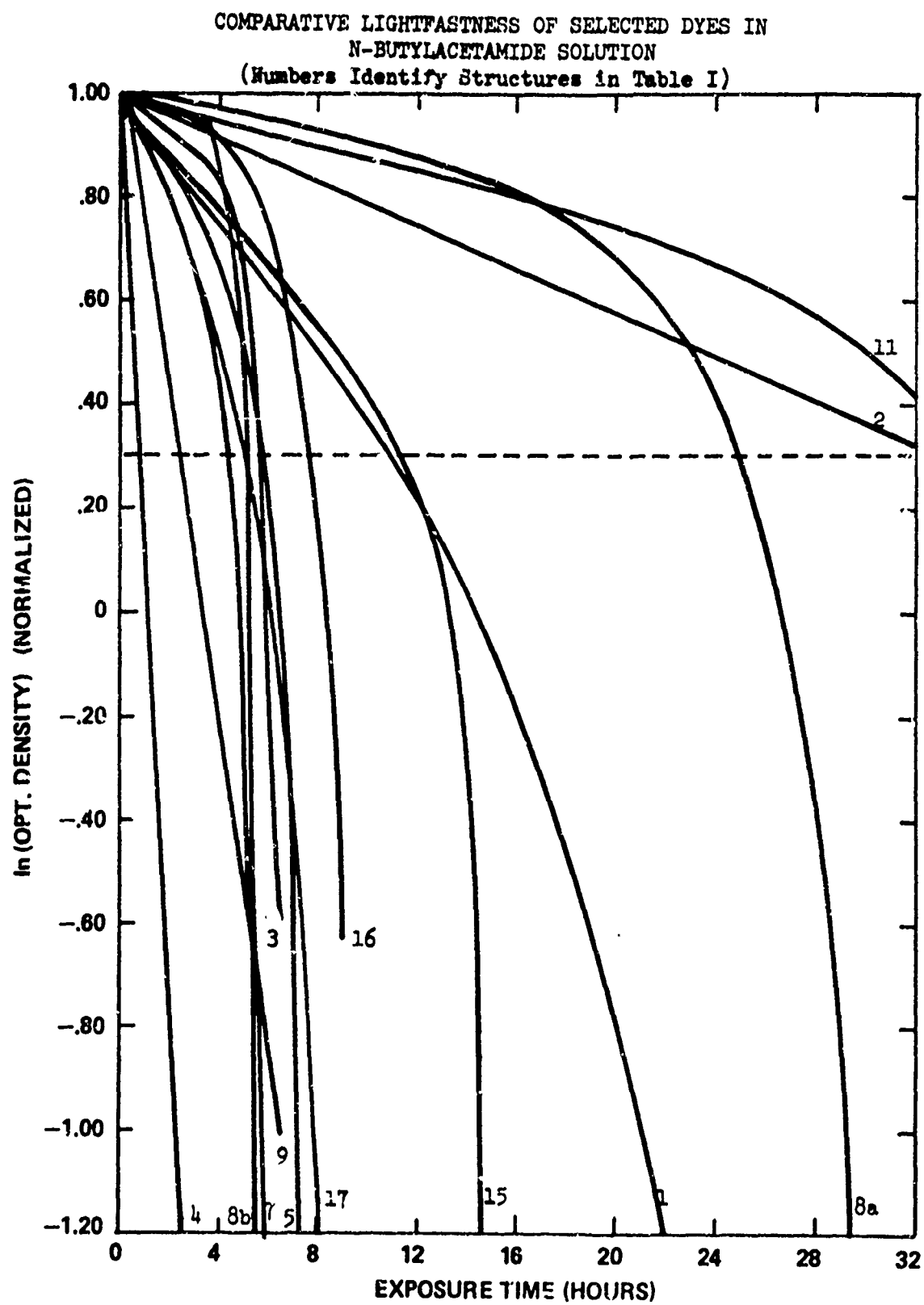


Table I.

Absorption and Fluorescence Properties
of Selected Dyes in N-Butylacetamide

Dye*	Code No.	CI No.	Absorption		Emission			Natick Reading on Nylon	Δ $\lambda_{\max}(\text{Absorpt.})$ $\lambda_{\max}(\text{Fluoresc.})$ (cm ⁻¹)
			λ_{\max}	I 1/2(hr)	λ_{\max}	Rel. Int. at λ_{\max}	Rel. Int. at 720mm		
Acid Blue 113	1	26360	590	11.0	-	0	0	-	-
Acid Green 41	2	62560	685	~33	-	0	0	-	-
Acid Blue 158	3	14880	644	5.4	-	0	0	-	-
Basic Blue 3	4	51005	648	0.8	664	720	36	7	327
Acid Blue 7	5	42080	630	5.7	658	20	1	92	675
Basic Blue 9	6	52015	657	-	677	270	30	-	450
Acid Blue 9	7	42090	625	5.0	650	32	1	90	616
Direct Blue 8	8a	24140	579	24.8	642	315	14	86	1,695
Direct Blue 8	8b	24140	582	4.3	633	324	14	86	1,385
Direct Blue 106	9	51300	626	2.4	666	108	15	88	959
Direct Blue 108	11	51320	596	~33	633	1540	54	96	980
Direct Blue 15	15	24400	602	11.2	659	240	18	95	1,437
Direct Blue 22	16	24280	598	7.6	658	150	12	50	1,524
Direct Blue 109	17	51310	657	5.0	683	47	10	72	579

* Refer to following page for a listing of structures and commercial names.

Code No.	Commercial Name	Structure
1	Calcoacid Navy Blue 3 R (Cyanamid)	
2	(e.g., Alcoquinone Brilliant Cyanine Green 5 GX, ICI)	
3	Calcofast Wool Blue 2 GW (Cyanamid)	
4	Calcozine Acrylic Turquoise 3 GW (Cyanamid)	
5	Calcoacid Blue AX conc. (Cyanamid)	
6	Calcozine Methylene Blue 2 B conc. (Cyanamid)	
7	Calcoacid Blue 2G Super conc. (Cyanamid)	
8	A: Calcomine Azurine BT conc. (Cyanamid) E: Pontamine Blue AX (DuPont)	
9	Chlorantine Fast Brill. Blue 2 GLL (Ciba-Geigy)	
11	Remastral Blue FFRL (American Hoechst)	
15	Direct Sky Blue A 300% (Young, Baltimore, Md.)	
16	Atlantic Direct Blue RW Conc. 200% (Atlantic Chem. Co.)	
17	Chlorantine Fast Blue 3 FLL (Ciba-Geigy)	

The relative half-lives of the dyes (time to reach dotted line in Figure 1) indicate that Direct Blue 108, which gave an "instrument reading" of 96 in Natick's NIR studies¹ is more photostable in solution than even the three non-fluorescent nylon lightfast dyes employed as controls. This finding will be discussed further in later sections of this report.

For comparative fluorescence studies, N-butylacetamide solutions of these dyes were prepared in 1 cm quartz cuvettes such that optical densities of 0.5 could be obtained at or near their absorption maxima. The solutions were then irradiated at the selected wavelength (in the 580-650 nm region) in the Perkin-Elmer MPF-2A Fluorescence Spectrophotometer (cf. Experimental) and the resulting emission was recorded. The wavelength of maximum emission from each dye and the relative emission intensities at the maxima are reported in Table I. Because both the source intensity for excitation and the detector response for emission show little change over the small range of wavelengths examined, these values are a fair measure of the relative fluorescence intensities from the dye solutions. The relative emission from the dyes at 720 nm is also recorded in Table I for comparative purposes.

The relatively intense fluorescence from Direct Blue 108 obtained in these studies prompted an evaluation of the properties of nylon fabric dyed with this compound.

B. Fabric Studies

A sample of nylon T-200 fabric was dyed with 1% (O.W.F.) strength commercial Direct Blue 108 (Remastral Blue FFRL) using conventional procedures (cf. Experimental). The fluorescence emission from this fabric was measured using the thin layer chromatographic (TLC) attachment to the Perkin-Elmer spectrophotometer (cf. Experimental Section). As seen in Figure 2, the emission maximum from the dyed nylon fabric was at longer wavelength (>660 nm) than from the same dye in N-butylacetamide. The emission from the infrared fluorescent polyester reference fabric containing Basic Blue 3, supplied by Natick, showed less of a red shift relative to that dye in solution. More significantly, Figure 2 shows that DB 108 dyed nylon fabric exhibits a total red emission considerably stronger than the emission from the Natick reference sample. Because the DB 108 emission is centered at shorter wavelengths, the results are (Fig. 2) consistent with the Natick report that its emission at wavelength longer than 750 nm is less intense than that of the reference sample. It should be noted that the Natick reference sample also exhibited green-yellow emission centered at ~572 nm (not shown in Fig. 2) when excited with maximum efficiency at 541 nm. The cause of this emission was not ascertained.

The lightfastness of the Direct Blue 108 dyed nylon fabric was evaluated by the standard Carbon Arc Fadeometer method. A very poor rating of only 5 hrs. was obtained by this method, which was confirmed by reflectance measurements (Table II). However, as shown in the table, the fluorescence intensity from the dyed fabric showed virtually no change even after 40 hrs. of fadeometer exposure. It is difficult to account for this unusual result. Together with the solution stability results, however, it suggests that the dioxazine may not be chemically destroyed during the photoexposure. Whatever the cause of the poor lightfastness of its color on nylon, Direct Blue 108

FIGURE 2

COMPARATIVE FLUORESCENCE SPECTRA ON FABRIC

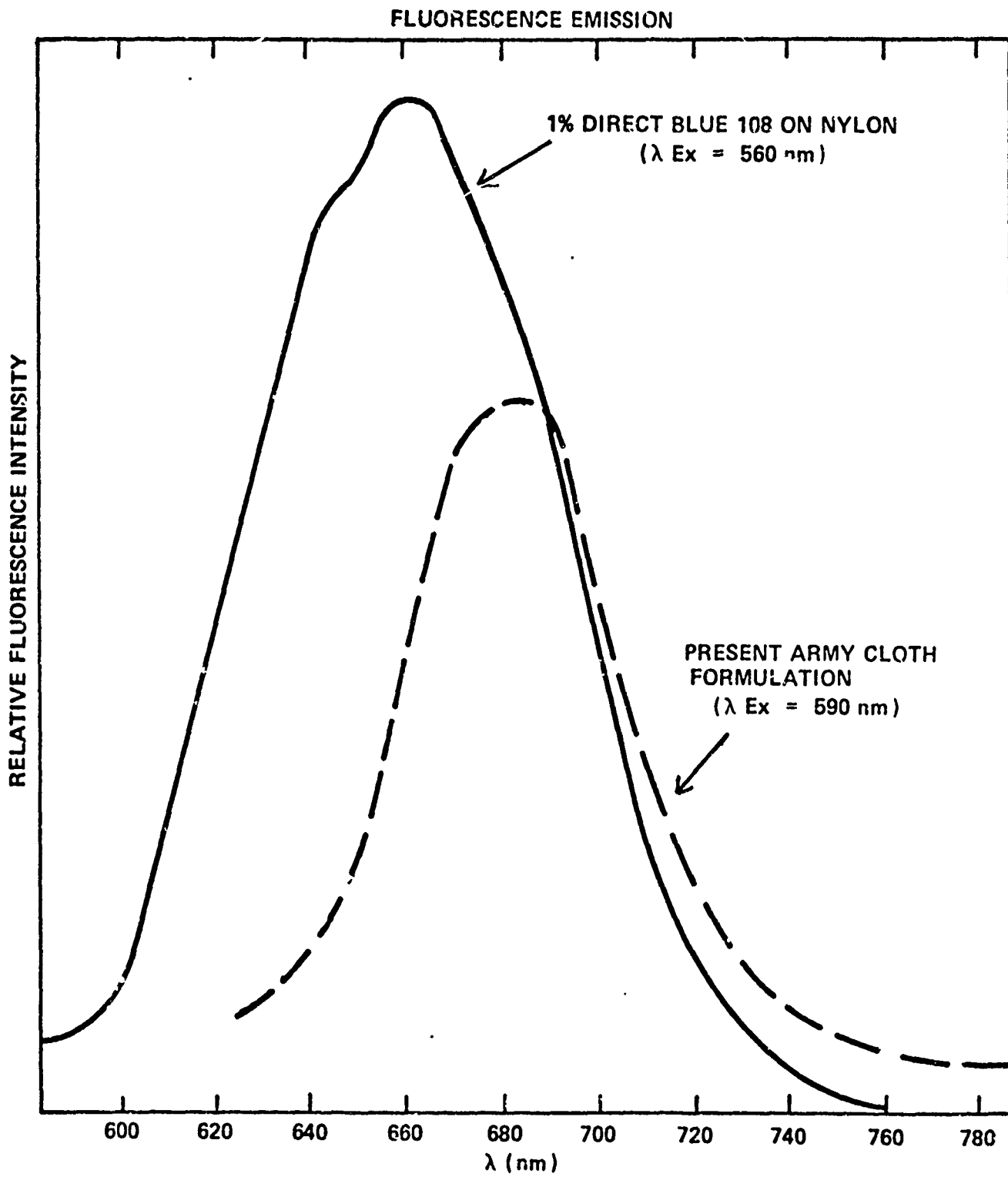


Table II

DIRECT BLUE 108

LIGHTFASTNESS ON NYLON FABRIC

Method 5660 Lightfastness Rating - 5 Hrs.

<u>Fadeometer Exposure (hrs.)</u>	<u>Total Color Difference</u>	<u>Relative Fluorescence Intensity</u>
0	--	94
5	2.1	94
10	4.1	96
20	7.3	94
40	17.6	92

might still be usable for camouflage because its emission centered at longer wavelengths is stable. Since Direct Blue 108 would only be a small component of the camouflage colorant system, the effect of its visible fading would be attenuated.

Although emission from Direct Blue 108 is centered at too short a wavelength and its lightfastness on nylon is not adequate, its combination of strong fluorescence, intrinsic photostability (as indicated by the solution studies) and dyeability on nylon are not possessed in combination to an equal extent by any other candidate molecule. Because of this, analogous dioxazine structures were sought which would have strong emission centered at longer wavelengths. Molecular orbital calculations were employed to aid in this search.

III. THEORETICAL STUDIES

A. Calculation of Wavelength of Fluorescence from Dioxazine Dyes by the Use of Molecular Orbital Theory

E. Clar established a useful classification of absorption bands which forms a consistent pattern with polycyclic benzenoid compounds.² In his classification the so-called p-bands are found to be sensitive to variations in molecular structure in a systematic way. These p-bands are the longest wavelength absorption bands. In most aromatic molecules larger than anthracene Hückel molecular orbital (HMO) theory has been able to account for, and even predict, the effects of structural modification on the energy of this p-band.³ This theory uses the carbon atomic p-orbitals in the configuration in which they appear in molecules to mathematically construct linear combinations called molecular orbitals. These molecular combinations have calculable energy values both higher or lower than that of the atomic orbitals from which they are constructed. In an extension of HMO theory, the p-band is associated with an electronic transition from the highest occupied to the lowest unoccupied molecular orbital of the molecule of concern. The accuracy with which HMO theory successfully calculates the location (energy) of the longest wavelength absorption band for aromatic hydrocarbons is demonstrated in Chapter 8 of reference 3. This chapter shows how the energy difference $\Delta \epsilon$ between the highest filled and lowest empty MO's correlates with the observed energies of the p-bands. The smaller the calculated $\Delta \epsilon$, the longer the wavelength (less energy) of the p-band as shown in Figure 3. Since there is usually a constant shift between absorption and emission (called the Stokes shift) of a molecule, $\Delta \epsilon$ should also correlate with the wavelength of emission of members in a homologous series.

Our calculations on dioxazines were performed using standard Hückel parameters for atoms and bonds significant to the pi-electronic structure of the chromophoric system.³ Structures selected for calculation included: (1) the three commercially available dioxazines, (2) several dioxazines which appeared to be readily preparable from available starting materials, and finally, (3) some dioxazines intuitively felt to be likely to have absorption and emission maxima considerably red shifted from those of DB 108. In several cases the effects of alternative positional isomerism were also examined. The structures of the selected 21 compounds calculated by this method and the $\Delta \epsilon$ values obtained are tabulated in Table III.

Figure 3

MOLECULAR ORBITAL ENERGY LEVEL SCHEMATIC

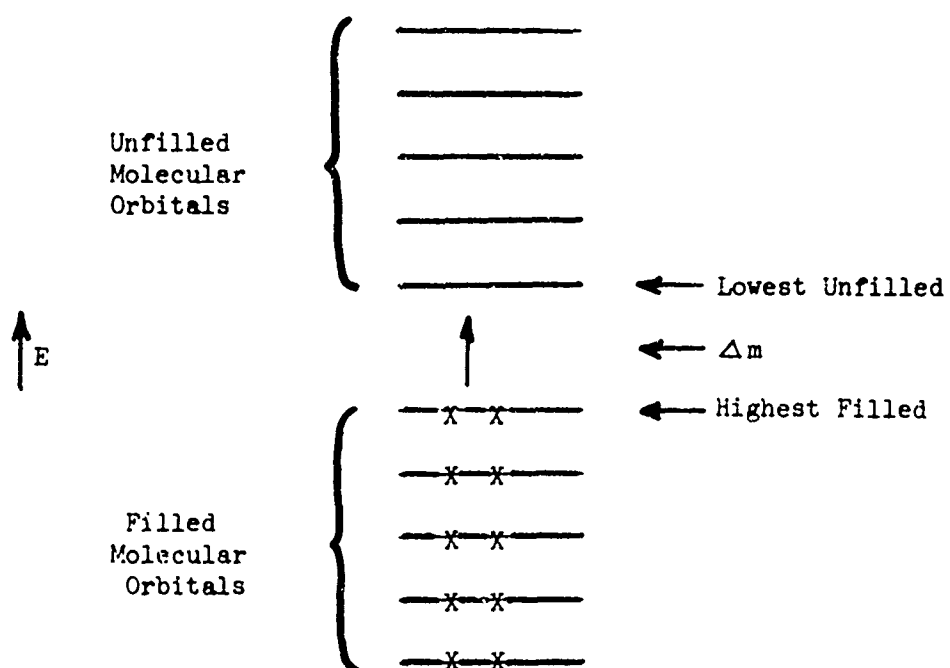


Table III.

Calculated Δm for Selected Dioxazine Structure

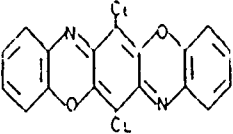
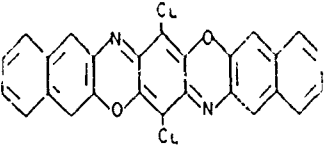
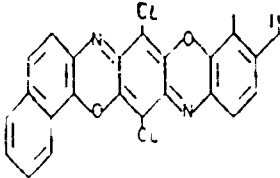
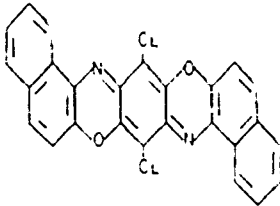
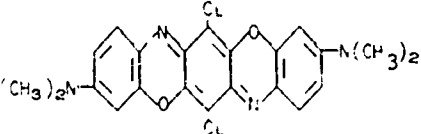
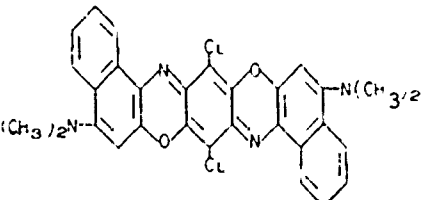
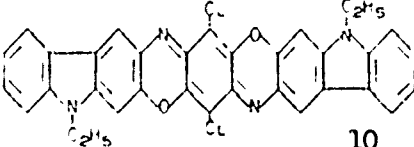
Compound Number	Structure	Comments	Δm
1		Basic dioxazine structure	0.392
2		Isomer expected from 8-naphthylamine	0.377
3		Isomer expected from 8-naphthylamine	0.357
4		Isomer expected from α -naphthylamine	0.325
5		Compound expected from N,N-dimethyl-p-phenylenediamine	0.366
6		Compound expected from 4-dimethylamino-1-naphthylamine	0.304
7		Unsulfonated Direct Blue 108	0.374

Table III (cont'd)

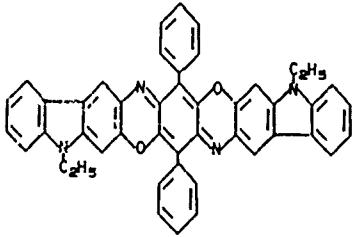
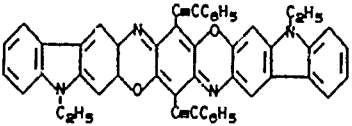
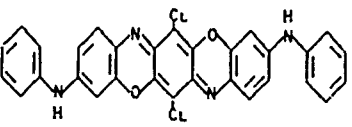
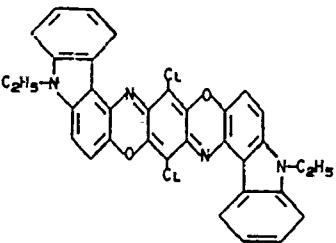
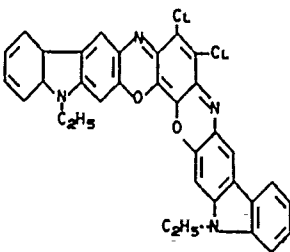
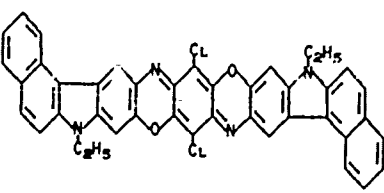
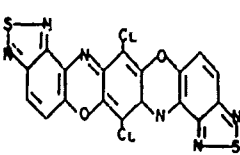
Compound Number	Structure	Comments	Δm
8		Phenyl replacement of chlorine in Direct Blue 108	0.358
9		Phenylethynyl replacement of chlorine in Direct Blue 108	0.352
10		Unsubstituted Direct Blue 106	0.364
11		Isomer of Direct Blue 108 expected from 4-amino-N-ethylcarbazole	0.350
12		Isomer of Direct Blue 108 expected from o-chloranil	0.305
13		Benzolog of Direct blue 108 expected from an aminobenzo-carbazole	0.376
14		Compound expected from available 3-aminobenzo-thiadiazole	0.306

Table III (cont'd)

Compound Number	Structure	Comments	Δm
15		Compound expected from 3-aminofluoranthene	0.294
16		Isomer expected from 8-aminofluoranthene No advantage	0.360
17		Isomer expected from 2-aminofluoranthene No advantage	0.365
18		Isomer expected from 1-aminofluoranthene Some advantage	0.275
19		Unulfonated Direct Blue 106	0.275
20		Compound expected from 3-aminoperylene	0.240
21		Isomer expected from 1-aminoperylene	0.256

Of the Δm values obtained, only those from the two dioxazines with fused perylene ring systems, compounds 20 and 21, were smaller than the value 0.275 obtained for the pyreno-fused dioxazine, compound 19, which represents the pi electronic structure of Direct Blue 109. A plot of the frequency of the emission maxima of the three commercial dioxazines as listed in Table I vs. their calculated Δm values, as shown in Figure 4, does not yield a linear relationship although a smaller Δm does consistently correlate with a lower frequency (longer wavelength) of the emission maximum. A linearization of this data with a slope approximately that found for other series of related molecules⁴ indicates a λ_{max} for compound 20 ($\Delta m = 0.240$) of 760 nm (1325 cm^{-1}). Although this estimate is obviously crude, the correlation is sufficiently good to permit the reasonable expectation that maximum emission from sulfonated compound 20 will be well above 700 nm.

B. Fluorescence Intensity

Although fluorescence intensity is not predictable by proven technique, much insight can be gained by evaluation of analogous systems. An examination of the three available dioxazine dyes shows (Table IV) an apparent relationship between the reported quantum efficiency of fluorescence of the substituents fused to the dioxazine ring system when evaluated as isolated molecules, and the intensity of emission from the corresponding sulfonated dioxazines. Thus the N-alkylcarbazole substituent is the strongest fluorescer of any of the substituents from which dioxazines have been prepared and the dioxazine containing the N-alkylcarbazole substituent is the most intense fluorescer among the dioxazines. This relationship is not unexpected, since fluorescence yield depends on the existence of alternative pathways for electronic energy deactivation (internal conversion and intersystem crossing); the fewer the alternative pathways offered by the substituent, the higher the expected fluorescence yield. This analysis would assure high fluorescence efficiency from the peryleno fused dioxazine except for the counteracting effect that as electronic transitions move to lower energy (longer wavelength) they more readily couple with vibrational transitions which increasingly provides a pathway for excitation deactivation which can compete with fluorescence emission. However, this fundamental problem is a hurdle for all organic dyes which might be near infrared fluoroscopes, and research directed to achieving the Natick camouflage objective must always contend with it. Since, of all the systems considered, the peryleno fused system has no other apparent liabilities, its synthesis and evaluation were made the next goals of this effort.

IV. SYNTHESIS

A. Introduction

Synthesis of the desired sulfonated peryleno fused dioxazine would appear to be easily accomplished by the scheme outlined in Chart 1, starting with the condensation of 3-aminoperylene, a known compound, with the commercially available p-chloranil. Problems encountered with this synthesis are of two types. The first of these is that the preparations of 3-nitroperylene (as precursor to the amine) described in the literature appeared difficult and

FIGURE 4

Δm VS. ν (MAX) EMISSION OF DIOXAZINE DYES
IN N-BUTYLACETAMIDE

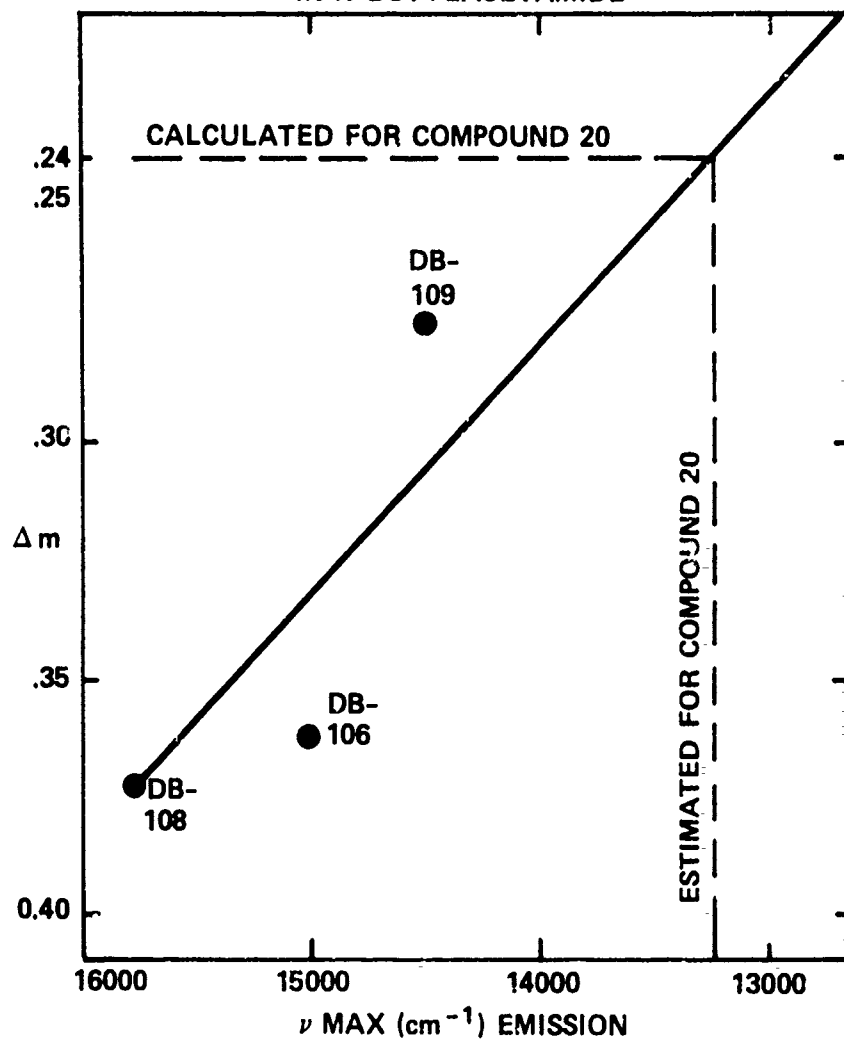


Table IV

COMPARATIVE EMISSION INTENSITIES

<u>Dioxazine Dye</u>	<u>Relative Emission at Max.</u>	<u>Substituent</u>	<u>ϕ_{FL}^a</u>
D. B. 106	108	Diphenylamine	--
Fluoranthene Subst. ^b	112	Fluoranthene	0.30
D. B. 109	47	Pyrene	0.32
D. B. 108	1540	N-alkylcarbazole	0.51
Perylene Subst.	?	Perylene	0.94

a. Values reported in reference 5 for cyclohexane solutions.

b. Prepared for this study; see Synthesis Section.

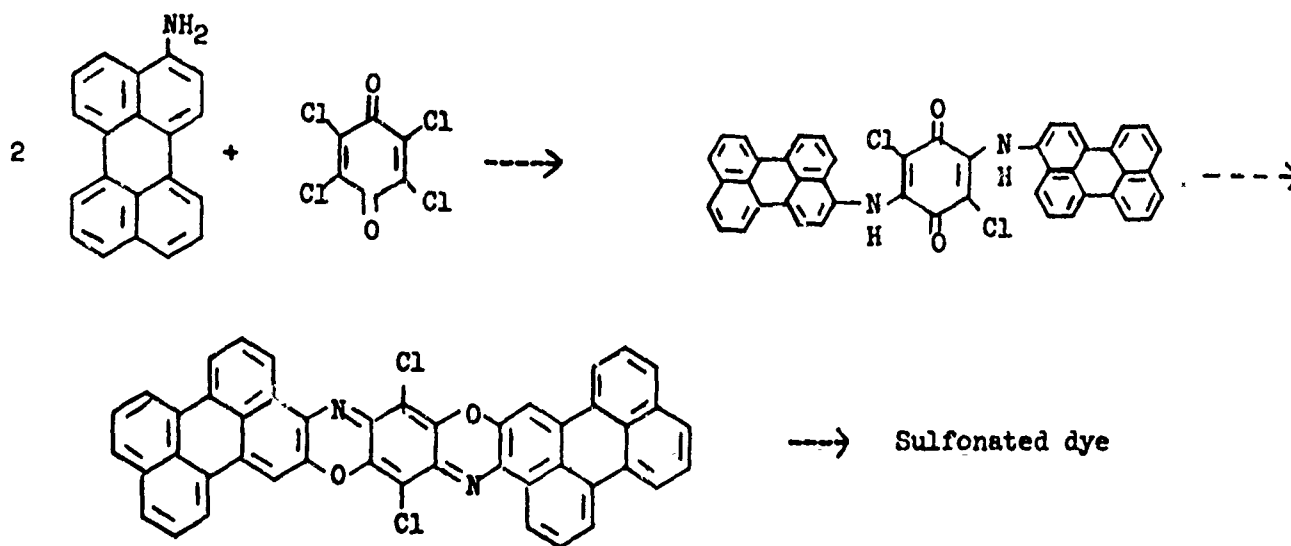


Chart 1

Proposed Synthetic Path for Sulfonated Perylene-fused Dioxazine Dye
 (Sulfonated 11, 24-Dichlorobisbenz[1,9]anthra[8,7-ab: 8',7'-lm]
 triphenodioxazine)

uncertain. The second is that methods for dioxazine synthesis could be found almost exclusively in the patent and BIOS and FIAT literature and described a bewildering variety of procedures and treatments for obtaining the desired products depending, among other things, on the arylamines and quinones used in the condensation. It was thus evident that an exploratory synthetic effort would have to be conducted in both these areas.

B. Aminoperylene Synthesis

The only method for preparing 3-aminoperylene reported in the literature is through nitration of perylene, separation of the 3-nitroperylene product, and reduction of the latter, as shown in Chart 2. Perylene is commercially available, but it is expensive.⁶ Our own studies have shown that, in suitable quantity, this need not be so. In earlier work we reproduced a synthesis⁷ of perylene in good yield from inexpensive starting materials (Chart 3) which appears to be suitable for scale-up should large quantities of this aromatic hydrocarbon be required. With this indication of availability of a key starting material, we investigated the subsequent nitration and reduction steps.

Although several publications describe conditions for nitration of perylene, these require tedious isolation of 3-nitroperylene by separation from isomers and polynitroperylenes, involving large amounts of solvents and low yields of separated product.^{8a} The mononitration of perylene by way of oxidation to its cation-radical, described in the literature⁹ (Chart 4) as a convenient procedure for making 3-nitroperylene with little by-products appeared initially to offer considerable advantages, and repetition of this procedure was attempted. Several variations of this procedure were tried. Reaction of perylene with iodine and silver nitrite, described⁹ as a preferred variation, gave us no isolable product due to side reactions resulting from nitration with NO_2I ¹⁰ formed in the reaction mixture. Electrochemical oxidation¹¹ proved inefficient. Reaction of perylene with silver perchlorate and iodine¹² followed by reaction of the precipitated perylene cation-radical salt with sodium nitrite, a procedure briefly mentioned in the literature,⁹ however, gave us a 92% yield of isolated pure 3-nitroperylene, compared with a reported 69% yield.⁹ In addition, during the chromatographic purification, we isolated and characterized from this reaction a small yield of the 1-nitroperylene isomer, m.p. 170-172°.

Although the above procedure can be used to obtain large quantities of 3-nitroperylene, the stoichiometry necessitates regeneration and separation of one equivalent of perylene for every equivalent of product. Recovery of perylene as well as the expensive silver and iodine reagents would, on a large scale, make this a very costly as well as complex process. We thus continued to examine the synthesis and developed a new convenient preparation of 3-nitroperylene in better than 65% yield. This method involves direct nitration of perylene with nitric acid in dioxane. The procedure was developed after efforts to follow another procedure for direct nitration of perylene in dioxane¹³ gave only polynitroperylene derivatives in our hands.

In contrast to the difficulties encountered in obtaining a practical procedure for 3-nitroperylene, we accomplished its reduction to 3-aminoperylene with hydrazine in ethanol, catalyzed by palladium on charcoal, in 75-92% yield according to published procedures^{8b} without incident.

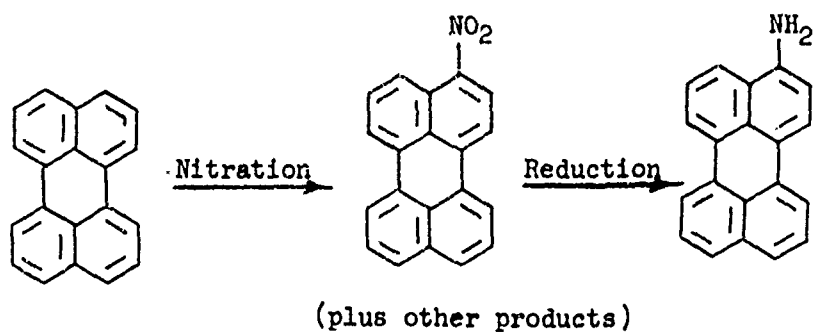


Chart 2

Generalized Scheme for Synthesis of 3-Aminoperylene

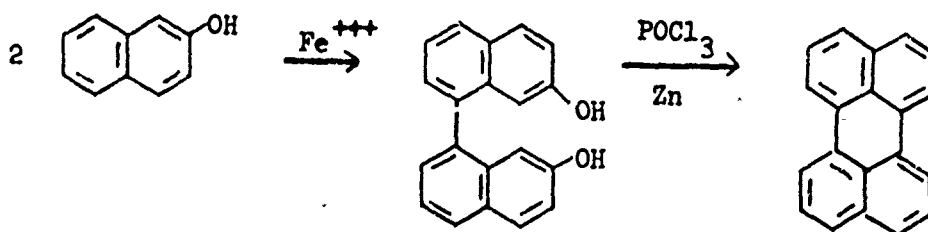


Chart 3

Scheme for Perylene Synthesis

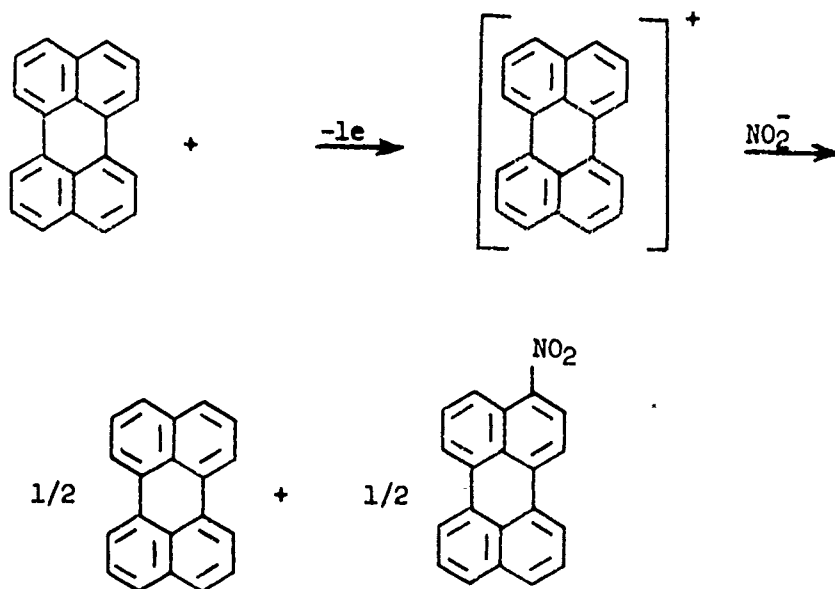


Chart 4
 Synthesis of 3-Nitroperylene through
 a Cation-Radical Intermediate

C. Dioxazine Synthesis, Sulfonation, By-Products, and Recommendations for Further Effort

The relevant FIAT¹⁴ and BIOS¹⁵ reports, and patents,^{16,17} and publications¹⁸ were consulted to assist in deciding on conditions to be used in the synthesis of the desired perylene-fused dioxazine ring system. Some of the published synthetic methods for specific dioxazine dyes are designed to go through the three steps to sulfonated dioxazine dyes (condensation, cyclization and sulfonation) from starting amine and quinone (Chart 5) without isolation of intermediates. For a new synthesis it is desirable to carry out each step separately and isolate and characterize the intermediates. Only in this way can one be assured that the desired product is formed.

The results of all our studies on the three steps involved in dioxazine dye synthesis are summarized in Tables V through IX. The main aspects of synthetic significance uncovered during the investigation are discussed below in an order which is essentially chronological.

The first reactions that were performed involved condensation of several different arylamines and quinones in order to see if procedures could be developed which would be relatively insensitive to substituents not directly involved in the reaction. Although this goal was not realized, as soon as small quantities of 3-aminoperylene (3-AMP) had been prepared, these were reacted with quinones under representative conditions. These initial efforts failed, giving insoluble products lacking the infrared spectral characteristics of either starting materials or the correct condensation products. Elemental analysis on the product showed a serious deficiency in chlorine, indicating that substitution had occurred at more than two chlorines in the p-chloranil reagent. Because of difficulties encountered in concurrent synthesis of 3-AMP (cf. previous section) further exploratory synthetic studies were made on 3-aminoanthracene (3-AMF), a commercially available compound. Condensation of this arylamine with either p-chloranil or 2,5-diphenyl-p-benzoquinone (DPBQ) proceeded readily (Chart 6) under conditions that did not work with 3-AMP. The condensation reaction of this amine with p-chloranil and subsequent synthesis of the dioxazine dye is known in the literature. Because of the too short wavelength emission maximum predicted by molecular orbital theory for dioxazines derived from 3-AMF as well as the low fluorescence efficiency of the anthracene moiety in such dioxazines (cf. Table IV), their usefulness was not expected to be better than that of Direct Blue 109 (the dioxazine with fused pyrene moieties). Although this proved to be the case, (cf. Table X) further studies on synthesis of dioxazines derived from 3-AMF provided additional understanding of the reactions of such arylamines with quinones and the competing reactions that can occur in efforts directed to preparing dioxazine dyes from such starting materials.

Condensation of 3-AMF with 2,5-DPBQ proceeded in reasonable yield (Table VII). While this reaction product is not reported in the literature, analogous reactions of other unhalogenated quinones with arylamines have been reported. A similar condensation of 2,5-DPBQ with 3-amino-N-ethylcarbazole also occurred in good yield (cf. Table VI). Cyclization of these condensation products gave dioxazines with phenyl substituents on the 11,24 positions rather than the chlorines obtained when p-chloranil is employed in the condensation reaction. By analogy with 9,10-disubstituted anthracenes, phenyl substituents

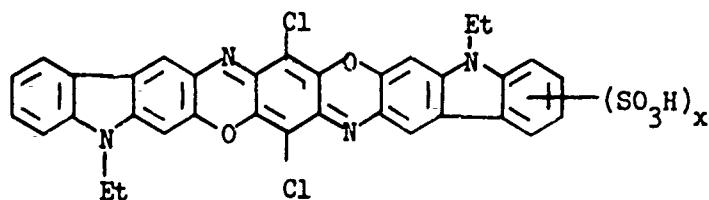
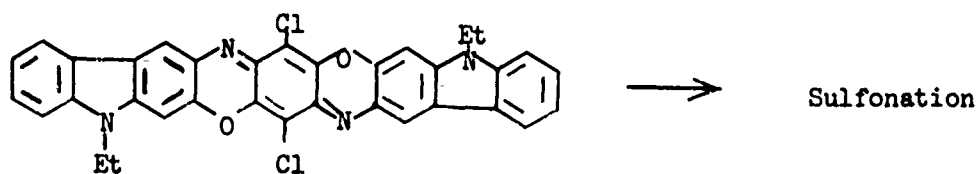
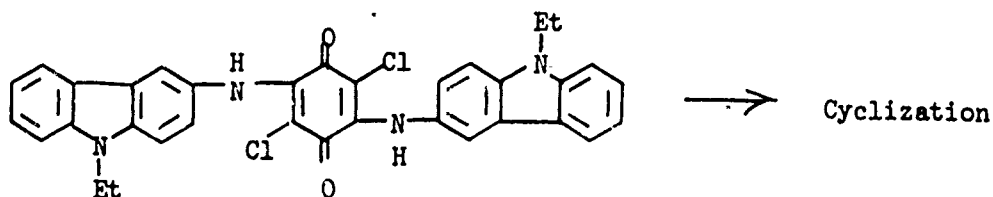
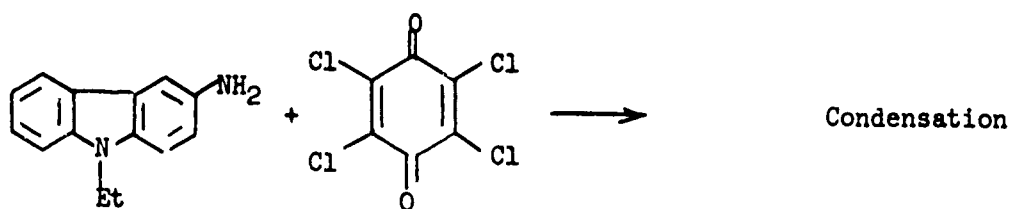

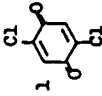
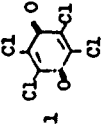
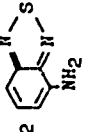
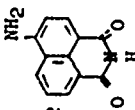
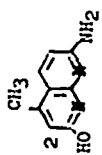


Chart 5

Typical Synthesis of Dioxazine Dye
(Direct Blue 108)

Table V

SYNTHESES OF DIOXAZINES WITH MISCELLANEOUS ARYLAMINES

Synth. #	Amine	Quinone	Condensation Step		Solvent ^a	Cyclization Step		Sulfonation	
			Time (hrs)	Temp. (°C)		Catalyst	Time (hrs)	Agent	Temp. (°C)
1			pyridine { 1 40 16	0 16					
2	"	"	EtOH	1.5 reflux	32°				
16	"	"	EtOH	3.8 reflux	15°	NB	4.5	reflux	0 (PC)
3	"		EtOH	1.5 reflux	65°				
6		"	EtOH	2.0 reflux	19				
19	"	"	EtOH	4.5 reflux	46		4.8	reflux	37
7		"	EtOH	23 reflux	0 (NR)			oleum, 20% SO ₃	3 130
11	"	"	PhCN	7 reflux	0 (IP)				
8		"	EtOH	19 reflux	0 (NR)				
12	"	"	PhCN	7 reflux	0 (IP)				

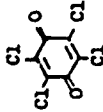
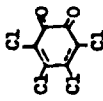
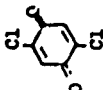
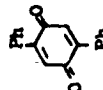
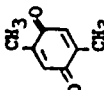


(a) Solvents: NB = nitrobenzene

(b) NR = no reaction; IP = intractable products; PC = polycondensation-type products only.

(c) Identical products obtained.

Table VI

SYNTHESIS OF DIOXAZINES WITH 3-AMINO-9-ETHYL-CARBAZOLE





Synth. #	Quinone	Amine-to- Quinone Ratio	Condensation		Solvent ^a	1 st Step		Solvent ^a	Cyclization Step		Sulfonation Agent	Sulfonation Time (hrs)	Temp. (°C)	
			Time (hrs)	Temp. (°C)		Yield ^b (% on amine)	Time (hrs)		Temp. (°C)	Yield ^b (%)				
4		2:1	EtOH	5	reflux	93 ^c	TCB	FeCl ₃	2	reflux	51			
5		2:1	EtOH	1	reflux	17(isomers?)	TCB	FeCl ₃	2	reflux	0 (PC)			
13		2:1	EtOH	2.8	reflux	35 ^c	NB	TsCl	5.5	reflux	49	100% H ₂ SO ₄	6	RT
14		2:1	EtOH	2.8	reflux	22	NB	TsCl	5.5	reflux	60	100% H ₂ SO ₄	6	RT
15		2:1	EtOH	3.8	reflux	7								
17	"	1:1	EtOH	4	reflux	15	NB	TsCl	4.8	reflux	0 (PC)			
18		1:1	EtOH	4	reflux	33	NB	TsCl	4.5	reflux	0 (PC)			
20		1:1	EtOH	4.5	reflux	0 (NR)								

(a) Solvents: NB = nitrobenzene; TCB = 1,2,4-trichlorobenzene

(b) NR = no reaction; PC = polycondensation-type products only.

(c) Identical products

Table VII
SYNTHESES OF DIOXAZINES WITH 3-AMINOFLUORANTHENE

Synth. #	Quinone	Amine-to- Quinone Ratio	Condensation Step					Cyclization Step					Sulfonation		
			Solvent ^a	Time (hrs)	Temp. (°C)	Dehydrogena- tion Agent	Yield ^b (% on amine)	Solvent ^a	Catalyst	Time (hrs)	Temp. (°C)	Yield ^b (%)	Agent	Time (hrs)	Temp. (°C)
9		2:1	EtOH	3.5	reflux	--	42	NB	TeCl	3	reflux	77	100% H ₂ SO ₄	5.5	RT
10	"	2:1	CH ₃ CN	2.5	reflux	--	38	NB	TeCl	4.5	reflux	32	100% H ₂ SO ₄	6.5	RT
23	"	2:1	NB	3	RT-125	--	--	NB	none	3	125-220	10			
24	"	2:1	NB	17	100	--	--	NB	none	6	reflux	15 ^c			
25	"	2:1	NB	17	100	--	--	NB	none	6	reflux	16 ^d			
27		1:1	NB	16.5	100	excess quinone	--	NB	none	7	reflux	20	100% H ₂ SO ₄	20	RT
28	"	2:1	NB	17	100	--	--	NB	none	6	reflux	13			
30	"	2:1	NB	16	100		--	NB	none	6	reflux	7			
31	"	2:1	TCB	16	100	"	--	TCB	none	6	reflux	3			
32	"	1:1	NB	16	100	excess quinone + Pd on C	--	NB	none	6	reflux	24			
33	"	1:1	TCB	16	100	excess quinone + Pd on C	--	TCB	none	6	reflux	13			
34	"	2:1	EtOH	18	reflux	--	0 (IP)								
35	"	2:1	EtOH	18	reflux		0 (IP)								
36	"	2:1	EtOH	18	reflux	Pd on C	0 (IP)								
37	"	1:1	NB	16	100	excess quinone	--	NB	none	6.5	reflux	12			
38	"	2:1.5	NB	15.5	150	excess quinone	--	NB	none	26	reflux	19	~100% H ₂ SO ₄	20	RT
39	"	2:1.5	NB	2	RT-200	excess quinone	--	NB	none	24	reflux	18	~100% H ₂ SO ₄	31	RT
45	"	2:1.5	EtOH	47	reflux	excess quinone	0 (IP)								

(A) Solvents: NB = nitrobenzene; TCB = 1,2,4-trichlorobenzene

(L) IP = intractable products only. When no numerical condensation yield is shown, condensation and cyclization were carried out without isolation of the intermediate condensation product. For these cases, the yields shown under cyclization are overall yields based on amine starting material.

(c) Run under stream of nitrogen.

(d) Run under stream of air.

Table VIII

SYNTHESES OF DIOXAZINES WITH 3-AMINOPERYLENE

Synth. #	Quinone	Amine-to- Quinone Ratio	Condensation Step			Cyclization Step						
			Solvent ^a	Time (hrs)	Temp. (°C)	Dehydrogena- tion Agent	Yield ^b (% on amine)	Solvent ^a	Catalyst ^c	Time (hrs)	Temp. (°C)	Yield ^b (%)
21		2:1	EtOH	4.7	reflux	--	0 (IP)					
22	"	2:1	EtOH	21	reflux	--	0 (IP)					
26	"	2:1	NB	16.5	100	--	-- ^d	NB	--	5	reflux	0 (PC)
29		1:1	NB	17	100	excess quinone	-- ^d	NB	--	6	reflux	0 (PC)
44	"	2:1.5	EtOH	70	reflux	excess quinone	25					
46	"	2:1.5	EtOH	48	reflux	excess quinone	20	NB	--	19	reflux	0 (PC)
								NB	DNP	3	reflux	0 (PC)
								CLN	TsCl	.33	270	0 (PC)

(a) Solvents: NB = nitrobenzene; CLN = 1-chloronaphthalene

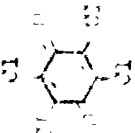
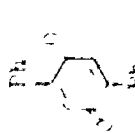
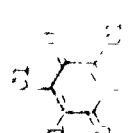
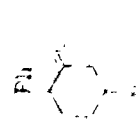
(b) IF = intractable products; PC = polycondensation-type products

(c) TsCl = p-toluenesulfonyl chloride; DNP = 2,4-dinitrophenol

(d) Not isolated, if any.

Table IX

SYNTHESES OF DIOXAZINES WITH N-DIMETHYL-p-PHENYLENEDIAMINE

Synth. #	Quinone	Amine-to- Quinone Ratio	Condensation Step			Cyclization Step						
			Solvent ^a	Time (hrs)	Temp. (°C)	Dehydrogena- tion Agent	Yield (% on amine)	Solvent ^a	Catalyst	Time (hrs)	Temp. (°C)	Yield ^b (%)
40		2:1	EtOH	4	reflux	none	46	NR	none	4	reflux	0 (PC)
								TCB	none	2	reflux	0 (PC)
								NR	none	4.5	100	0 (NR)
								TCB	none	4.5	100	0 (NR)
								TCB	none	52	100	0 (NR)
								TCB	none	16	150	0 (PC)
								TCB	FeCl ₃	27	100	0 (NR)
								NR	TsCl	27	100	0 (PC)
41		2:1.5	NR	2	RT- reflux	excess quinone	--c	NR	none	1	reflux	0 (PC)
42		2:1	EtOH	21.5	reflux	none	51					
43		2:1.5	EtOH	19	reflux	excess quinone	26					

- (a) Solvents: NR = nitrobenzene; TCB = 1,2,4-trichlorobenzene
 (b) NR = no reaction; PC = polycondensation-type products
 (c) Not isolated, if any.

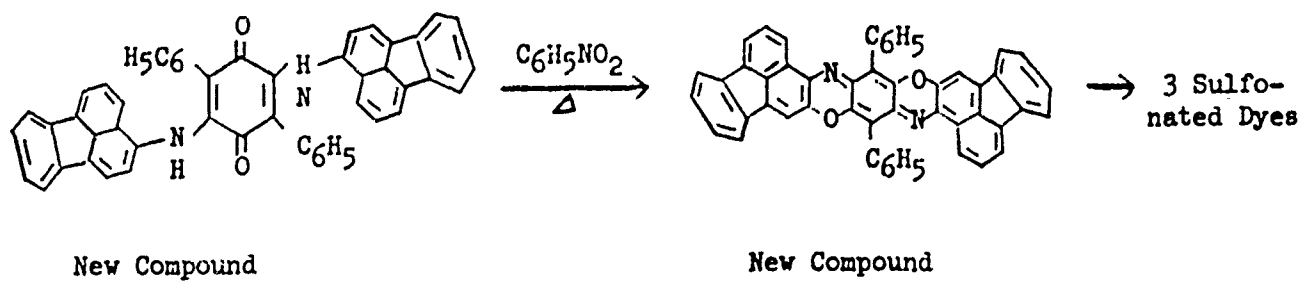
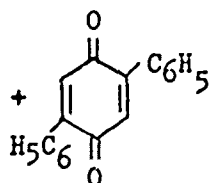
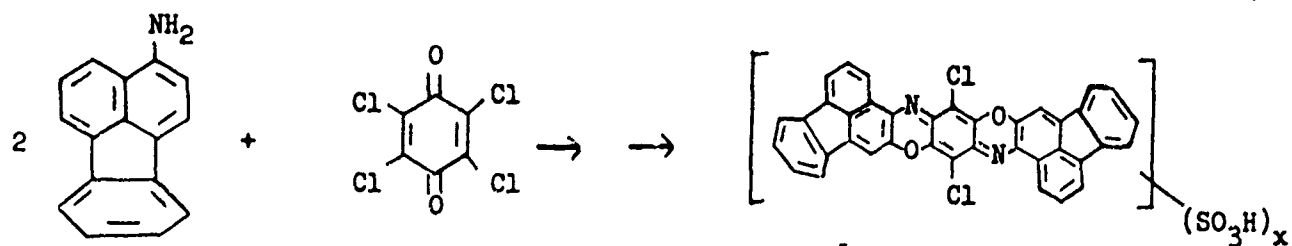
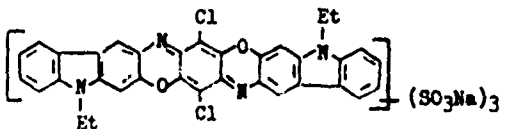
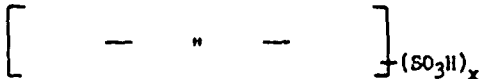
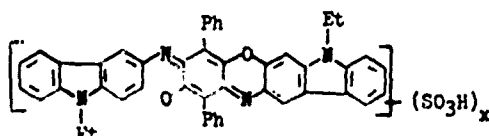
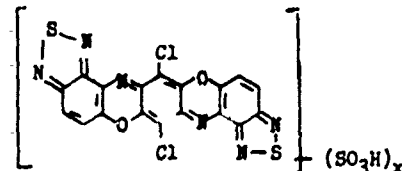
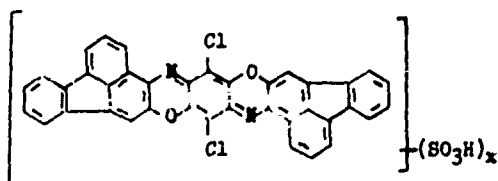
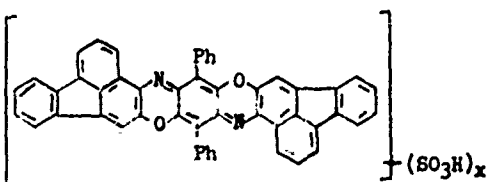


Chart 6
 , Synthesis of Dioxazines Derived from 3-Aminoanthracene

Table X

SPECTRAL DATA ON SULFONATED DIOXAZINES IN N-BUTYLACETAMIDE

Compound	Origin	λ_{max} of Absorption (nm)	λ_{max} of Emission (nm)	Relative Emission Intensity at λ_{max} of Emission (arbitrary units)
	Commercial Direct Blue 108, REMASTRAL Blue FFRL (American Hoechst)	604	635	1,540
	Synthesis #13 (see Table VI)	600	636	1,600
	Synthesis #14 (see Table VI)	587	620	1,850
	Synthesis #19 (see Table V)	574	615	107
	Synthesis #9 (see Table VII)	635	660	111
	Synthesis #27 (see Table VII)	651	670	74

on these positions are expected to increase the fluorescence efficiency of the products relative to chlorine substituents. This proved to be the case for the sulfonated dioxazine derived from 3-aminofluoranthene, but not for that derived from 3-amino-N-ethylcarbazole (Table X). Since there also appeared to be some synthetic advantage (higher yield) in not generating HCl in the reactions, the use of 2,5-DPBQ in dioxazine synthesis was examined further.

Sulfonation of the dioxazine derived from condensation of 3-AMF and 2,5-DPBQ produced a dyestuff which gave green aqueous solutions as compared to the blue color of other dioxazine solutions which we had examined. Further study revealed that the degree of sulfonation of this dioxazine is very sensitive to small changes in strength of the sulfonating reagent. This reagent is prepared by combining suitable quantities of fuming and concentrated acid. The range of SO_3 content in commercial 20-23% fuming sulfuric acid can produce a 1.6 molar percent variation in water content and this appears to affect the degree of sulfonation of the dioxazine when working in a medium of nominally 100% H_2SO_4 . Unexpectedly, we have found (Table XI) that the different sulfonated products of this dioxazine have considerably different absorption properties implying different fluorescent properties. If this observation has more general applicability, it may be found, for example, that other commercial sulfonated dyes which are weak near-infrared fluorescers actually contain small amounts of a single sulfonated species which is a strong near infrared fluorescer. Particular attention should be given to Direct Blue 109 (#17 in Table I) in this regard. Careful chromatographic separation and fluorescence analysis is recommended for this dyestuff.

Several side products were isolated during efforts to make dioxazines from 3-AMF and 2,5-DPBQ. By infrared spectroscopy, two of these (isolated from reaction mixtures of Synthesis #39 [cf. Table VII]) appeared to derive primarily from 3-AMF. One of the compounds could also be prepared by prolonged heating of 3-AMF in either nitrobenzene or 1,2,4-trichlorobenzene solvents. A small yield of well-defined brown crystals, m.p. $\sim 330^\circ$ was obtained from the latter solvent. This compound when sulfonated is strongly fluorescent ($\lambda_{\text{max}}^{\text{emission}} = 485 \text{ nm}$ in H_2O after sulfonation) and dissolves in H_2SO_4 generating a deep blue color which changes to red-violet on standing. High resolution mass spectrometry²⁰ indicates a molecular formula of $\text{C}_{32}\text{H}_{16}\text{N}_2$ ($m/e = 428$) for the unsulfonated species. This, together with its infrared spectrum, is consistent with the self-condensation product of 3-AMF shown below, containing a previously unknown polycyclic ring system.²¹

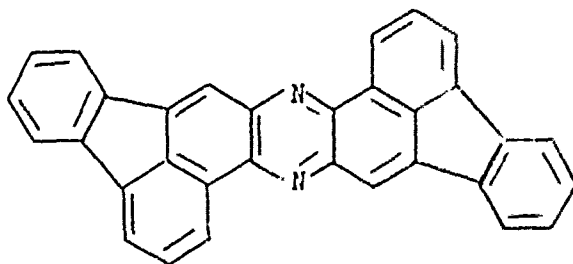


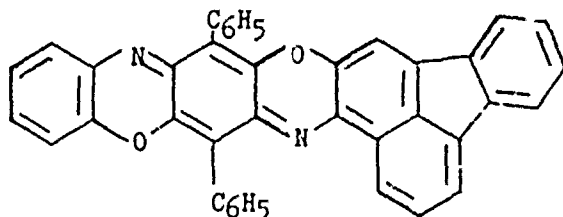
Table XI

Effect of the Degree of Sulfonation on the Spectral Properties of
Sulfonated 10,21-Diphenyl-Difluoreno [1,9-ab:9',1'-lm] Triphenodioxazine

Sulfonated Dioxazine (see Table VII)	Sulfonation Medium	Degree of Sulfonation ^a	Spectral Data		
			λ_{max} Absorption	λ_{max} Emission	Relative Emission Intensity
#27	100% H ₂ SO ₄ ^b	3.5	651 (NBA) ^d	670 (NBA) ^d	74
#38	100% H ₂ SO ₄ ^b	4.3	703 (H ₂ O) ^d (insol. in NBA)	not determined	
#39	<100% H ₂ SO ₄ ^c	not determined	646 (NBA) ^d 630 (H ₂ O)	670 (NBA) ^d none (H ₂ O)	85

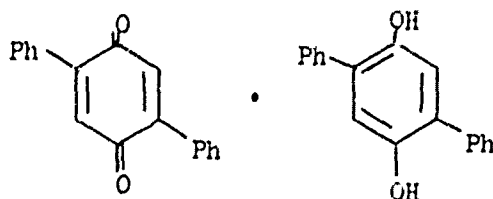
- (a) Average number of sulfonic acid groups per molecule, as determined from elemental analysis data.
 (b) Nominally equal concentrations, but prepared with different batches of fuming H₂SO₄ and therefore involving the uncertainty discussed in the text.
 (c) Containing ~2.2 to 3.6 mole % H₂O. Sulfonating action was tested in a pilot run to determine the sulfonation time required to obtain a product whose absorption spectrum would match that of #27.
 (d) NBA = N-Butylacetamide

The second by-product appears, by infrared,¹⁹ to be derived from a reaction involving 3-AMF and the nitrobenzene solvent. The physical appearance of this compound (dark purple solid with a metallic green luster) is similar to that of several dioxazines previously prepared; however, unlike those dioxazines, this compound was appreciably soluble in organic solvents such as acetone, chloroform and methylene chloride. Mass spectroscopy indicated a $C_{40}H_{22}N_2O_2$ formula for this compound ($m/e = 562$). The following unsymmetrical dioxazine structure, another new ring system,²¹ is consistent with this physical data. Its formation can be mechanistically supported, since dioxazine ring formation requires an oxidant and if the nitrobenzene solvent acts as that



oxidant, it would generate aniline which could then participate in the condensation reaction. Other mechanisms can also be envisioned.

Another side product, not derived from 3-AMF, was isolated from the reaction mixture of Synthesis #37 (cf. Table VII). A black-green solid of m.p. 224-225°, this compound exhibited an infrared spectrum entirely analogous to that of quinhydrone and consistent with the quinhydrone derived from 2,5-diphenyl-p-benzoquinone, a new compound.



Its occurrence is not unexpected since excess of 2,5-DPBQ had actually been employed to serve as hydrogen acceptor facilitating the condensation as well as the cyclization step. However, the quinhydrone was observed only under conditions where the high temperature treatment (refluxing nitrobenzene) was preceded by a prolonged reaction time at a moderate temperature (100°) intended to bring about and advance condensation before cyclization, (#37, Table VII). The previously discussed 3-AMF-derived side products arose when high temperatures were applied from the start (#39, Table VII). The phenazine derivative formed under these conditions reflects the presence of initially high concentrations of unreacted 3-AMF at high temperatures.

A number of experiments designed to prepare dioxazines and their intermediates were also carried out with commercially available *N,N*-dimethyl-*p*-phenylenediamine. Molecular orbital calculation indicated that the derived dioxazines should exhibit fluorescence red shifted from that of DB-108. Condensations of this amine with either *p*-chloranil or 2,5-DPBQ were effected

readily in refluxing ethanol; however, all attempts to cyclize the condensation product intermediate failed. Under mild reaction conditions no reaction occurred while under more forcing conditions a material was formed which from its infrared spectrum¹⁹ appears to be an aniline-black-type of condensation product. Further investigation of the requirements for the preparation of these dioxazines from the condensation products could serve as models for the synthesis of the perylene derivatives.

With these experiences in the condensation, cyclization and sulfonation steps in dioxazine synthesis and with the development of an improved synthesis of 3-AMP, efforts were redirected to the synthetic goal of preparing a dioxazine dye containing the fused perylene ring systems. Condensation of 2 moles of 3 AMP with 1 mole of 2,5 DPBQ was finally effected in 20% yield by refluxing the components in ethanol for 70 hrs. The product, a black solid, exhibited the essential infrared characteristics expected for the condensation product although parts of the spectrum lacked the sharp resolution usually seen for a pure compound. Anal: calc'd for $C_{58}H_{24}N_2O_2$: C, 88.08; H, 4.33; N, 3.54. Found: C, 83.55; H, 3.91; N, 3.87.

The bis(arylamino)quinone condensation products as well as their cyclization products (dioxazines) prepared in this study have all been found to be highly insoluble in the common organic solvents, precluding the use of recrystallization for purification. The solid products were isolated by filtration and purified by exhaustive washing with such solvents as acetone and methylene chloride until the filtrate appeared colorless or nearly so. Analytically pure products were generally obtained, but, if insoluble contaminants are present, they would, of course, not be removed. This possibility becomes more likely as the molecular weights of the materials involved (e.g., derivatives of 3-AMP) become larger.

As a concluding study in this research period, three sets of conditions were chosen for examination in an attempt to effect the cyclization of the condensation product of 3 AMP and 2,5-DPBQ. The conditions employed, described in Table VIII, Synthesis #46, are those successfully used to effect other dioxazine syntheses, cf. this work and the literature.^{15,16} Ill-defined products resulted in all three efforts. The spectral properties of these products ruled out significant dioxazine formation in all of the runs. To keep these results in proper perspective, we note that the cyclization reaction of the condensation products from N,N-dimethyl-p-phenylenediamine also could not be accomplished under conditions which worked in other dioxazine syntheses.

We conclude that properly substituted dioxazine dyes remain the most promising candidates to achieve the Natick camouflage objective with near infrared fluorescers. Their synthesis will require a further effort. Based on the experiences acquired, such an effort is believed to have a high probability of success.

V. EXPERIMENTAL

A. Spectroscopy

Unless otherwise indicated, fluorescence studies were performed on a Perkin-Elmer MPF-2A Fluorescence Spectrophotometer with a 150 watt xenon excitation source and an R-136 photomultiplier. Slit width settings of 8 nm in both the excitation and emission monochromators were employed.

Infrared spectra were recorded on a Perkin-Elmer Model 137 Sodium Chloride Spectrophotometer. Reaction products were tentatively identified on the basis of their infrared spectra. The spectra of the bis(arylamino)quinone condensation products and of the dioxazines show certain general characteristics which served to assign products to either one or the other class of compounds or to rule out their identity with either class.

Products listed in the initial section of this report bear references of belonging to either IR class I or class II. The general features of the infrared spectra are exemplified in Figures 5 and 6, which also show the spectra of the arylamines from which these products are derived. The characteristic features are described in the following:

IR Class I, Bis(Arylamino)quinones

NH stretching gives rise to a band at 3300 to 3700 cm^{-1} . A strong band is present in or near the 1500-1570 cm^{-1} region (probably due to NH bending in secondary aromatic amines). Strong bands in the 700-900 cm^{-1} region, bands associated with the adjacent hydrogen substitution patterns on aromatic rings, are similar to those seen for the arylamine starting material.

IR Class II, Dioxazines

NH stretching absorption and the strong band in or near the 1500-1570 cm^{-1} region are absent. The latter results in an easily seen (cf. Figures 5 and 6) shift towards higher frequencies of the "center of gravity" of all absorptions within the 1500-1650 cm^{-1} region. The band pattern within the 700 to 900 cm^{-1} region (adjacent hydrogens on aromatic rings) is altered more drastically from that seen for the corresponding arylamine.

B. Photoexposure Studies

The 1 cm cells containing dyes in N-butylacetamide solution were exposed to the unfiltered and uncollimated radiation from a 450 watt xenon arc at a distance (35 cm) resulting in an illuminating intensity of 1500 ft-candles (Gossen Lightmeter), corresponding to an energy flux of 42 mW/cm^2 (YSI-Kettering Model 65 Radiometer). The XBO 450 watt xenon bulb was operated at a lamp current of 27A. At intervals, the exposures were interrupted and the absorption spectra of the solutions were redetermined (P2 202 UV-VIS spectrophotometer).

Figure 5

Infrared Spectra (Nujol Mulls) of (a) 3-Amino-9-Ethyl-
carbazole, (b) its Bis-Condensation Product with p-Chloranil,
and of (c) the Corresponding Dioxazine

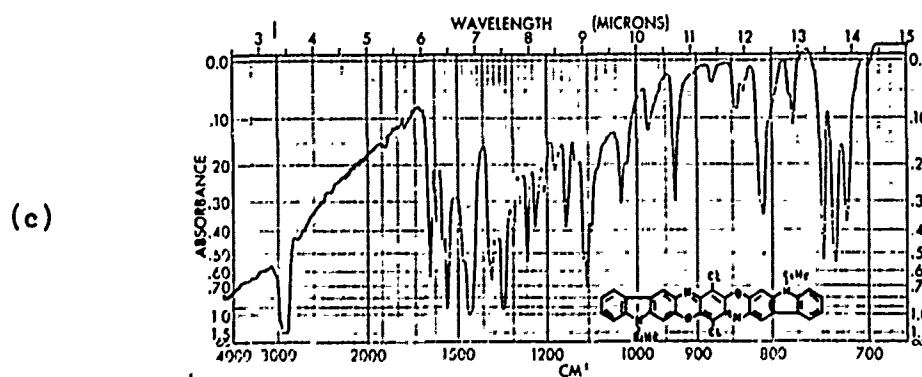
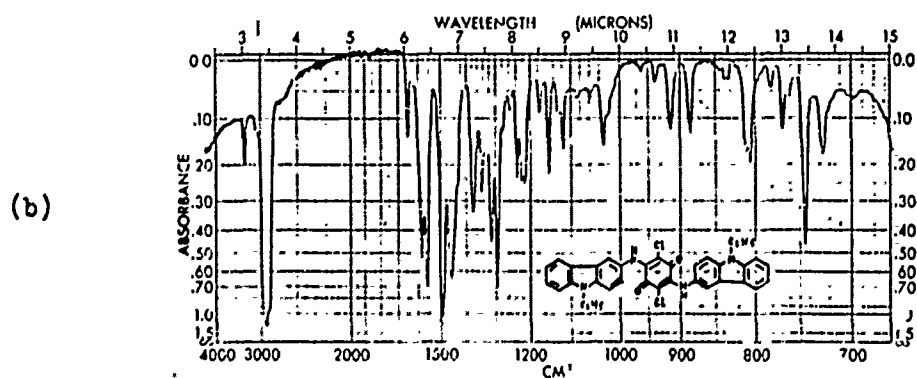
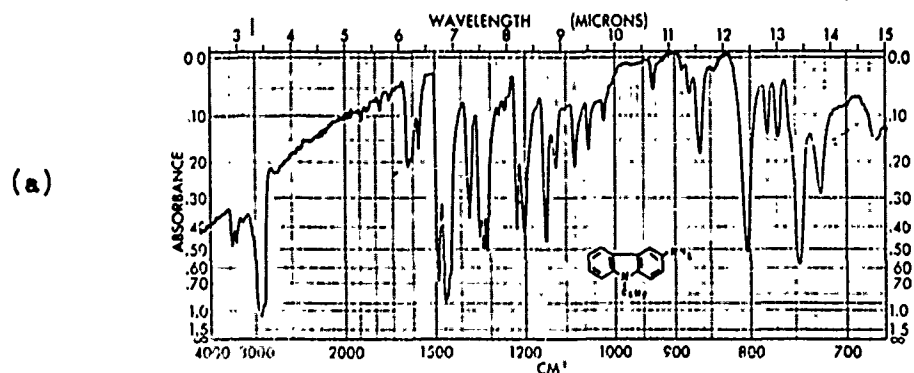
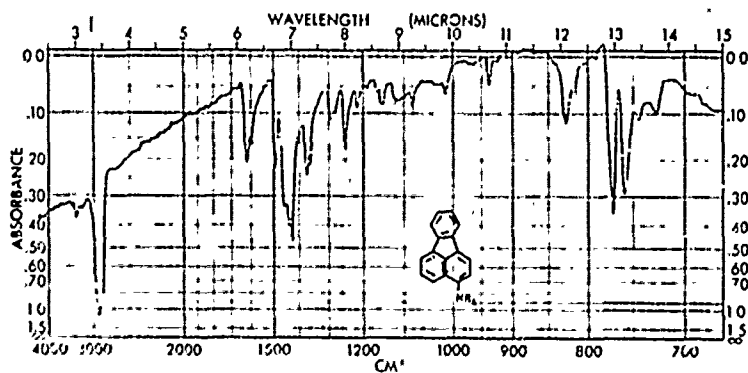


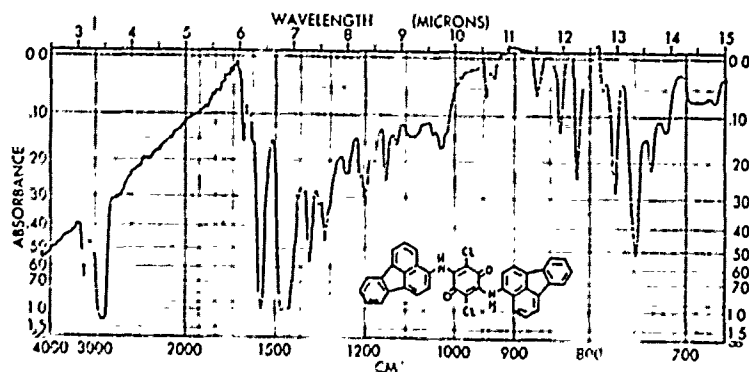
Figure 6

Infrared Spectra (Nujol Mulls) of (a) 3-Aminofluoranthene,
of (b) its Bis-Condensation Product with p-Chloranil,
and of (c) the Corresponding Dioxazine

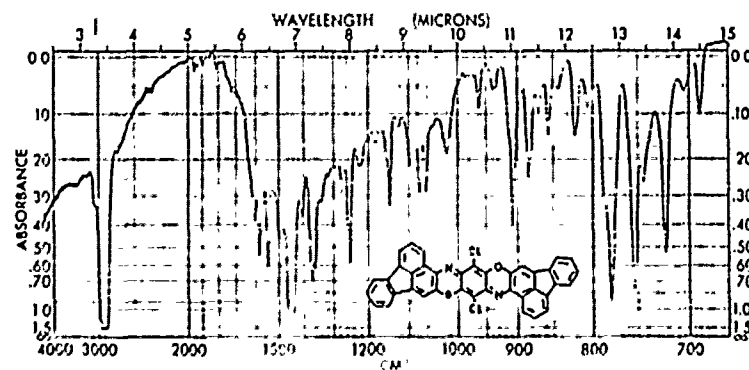
(a)



(b)



(c)



C. Fabric Dyeing Procedure

The dyeings were run for one hour at the boil with 5% on the weight of the fabric (OWF) ammonium chloride, rinsed in running warm tap water and pressed dry.

D. Synthetic Procedures

1. Mononitration of Perylene

A 500 ml. two-necked reaction flask equipped with dropping funnel, reflux condenser, and magnetic stirrer was charged with 20.74 g. (82.2 μ moles) of perylene and 250 ml. of p-dioxane. The mixture was stirred and heated on a steam bath. Nitric acid (11.1 ml. of 40% aqueous HNO_3 ; 5.56 g. real HNO_3 ; 88.3 μ moles) was added dropwise by means of the dropping funnel during a period of about 10 minutes while continuing to supply steam heat. A dark red solution formed rapidly. The mixture was heated on steam (some reflux observed) for an additional 30 minutes. After some cooling, the mixture was about to be poured into 2 liters of cold water (as called for in the original procedure from which this preparation was developed; the product was then to be isolated by filtration) when it became apparent that the nitration product had begun to crystallize directly from the reaction mixture. A sample of the crystalline material was examined and had an m.p. of 213-215° as well as the infrared spectrum of 3-nitroperylene. As some of the mixture had already been added to the water, the precipitated product was collected by centrifugation (filtration of the fine precipitate proved impractical). All product fractions were recombined and dissolved in p-dioxane for fractional crystallization, resulting in the collection of the following three product portions:

1st crop:	15.20 g. of a dark red solid, m.p. 209-211°
2nd crop:	1.06 g. dark red solid, m.p. 209-211°
	<hr/> 16.26 g. of 3-nitroperylene (IR)
	(65% of theory)
mother liquor residue:	8.72 g. dark red solid, m.p. 130°
	mixture of 1- and 3-nitroperylene
total recovered:	<hr/> 24.98 g. weight increase corresponding to a
	degree of nitration of 0.98

and indicating a practically quantitative yield of mononitration products.

It is recommended that, if this nitration is repeated, the product be crystallized directly from the reaction mixture.

The desired 3-nitroperylene can be obtained pure by chromatography on neutral alumina. The 1-isomer is eluted with benzene-cyclohexane mixtures containing 65-75 vol.% of benzene. The 3-isomer is eluted with benzene-methylene chloride mixtures containing 10 to 20 vol. % methylene chloride. The product so obtained shows a melting point of 215-216°. However, the crystallized product obtained in this preparation was found suitable as is for the conversion to 3-aminoperylene so that the chromatography, which requires rather large volumes of solvents, is not absolutely necessary.

2. Reduction of 3-Nitroperylene

The reduction of 3-nitroperylene to 3-aminoperylene was carried out following the procedure of Dewar and Mole.^{8b}

In a 5-liter three-necked RB flask (dropping funnel, reflux condenser, magnetic stirrer) were combined 4 liters of 95% ethanol, 4.04 g. (13.6 mmoles) of 3-nitroperylene (prepared as described above), 4.00 g. of 5% palladium on charcoal, and, finally, 35 ml. of 95% hydrazine. The mixture was stirred and heated on a steam bath under reflux for 15 minutes. It was permitted to cool somewhat and then filtered to remove the Pd-on-C catalyst. The filtrate was evaporated on a rotary evaporator and, after pumping off some residual hydrazine, yielded a golden orange crystalline residue of 3-aminoperylene weighing 2.7 grams (75% of theory).

Variable yields of from 75 to 90% have been obtained following this procedure. It is suspected, but has not been ascertained, that some of the product remains adsorbed on the catalyst carrier (activated charcoal) which is used in relatively large quantity (see above). Thorough washing of the filter cake may improve the yield.

The crude product can be redissolved in and recrystallized from 95% or absolute ethanol and then yields golden-orange crystals of m.p. 232-235 (apparent sublimation and decomposition to black melt). Care must be taken to proceed rapidly because in the dissolved state the amine appears to be subject to deterioration with formation of dark colored products.

3. Condensation of Arylamine with p-Benzoquinone, Cyclization to Dioxazine, and Sulfonation

Representative procedures are exemplified by the descriptions of specific reactions given below. Details of the conditions employed in specific other reactions can be found in Tables V through IX.

a. Condensation (#9 of Table VII) - Fifty ml. of absolute ethanol, 1.738 g. (8.0 mmoles) of 3-aminofluoranthene, 656 mg (8.0 mmoles) of anhydrous sodium acetate and 984 mg (4.0 mmoles) of p-chloranil were combined in a 50-ml. reaction flask. The mixture began to darken as soon as the quinone was added. The mixture was stirred (magnetic stirrer) and refluxed for 4 hours. The mixture was filtered while still warm, the collected solid then washed on the filter (medium fritted glass) as follows: (a) washed with hot ethanol; (b) with acetone; (c) with water to remove salts (NaOAc and/or NaCl); (d) with acetone to aid in the removal of water; (e) with chloroform. (The final suspension in chloroform proved difficult to filter. Methylene chloride has been used instead and without problems in many other cases.)

The washed solid (in pasty form, containing chloroform) was dried under vacuum, yielding 1.024 g. (42%) of the expected bis-condensation product in the form of hard, black pieces. Its infrared spectrum is reproduced in Figure 6.

b. Cyclization (#9 of Table VII) - In a 25 ml. RB flask (magnetic stirrer, air-cooled reflux condenser) were combined 804 mg (1.32 mmoles) of 2,5-dichloro-3,6-bis(3-fluoranthenylamino)-p-benzoquinone (the condensation product of the preceding procedure), 233 mg. (1.22 millimoles) of p-toluenesulfonyl chloride (catalyst), and 15 ml. of nitrobenzene. The mixture was stirred and heated in an oil bath and maintained at reflux temperature for 3 hours. The mixture was filtered hot (medium fritted glass), washed with hot nitrobenzene followed by exhaustive washing with acetone. The remaining solid was dried under vacuum and yielded 616 mg. (77%) of a dark solid with a metallic green luster, 10,21-dichloro-difluoreno-[1,9-ab:9'1'-lm]triphenodioxazine. Its infrared spectrum is shown in Figure 6.

c. Sulfonation (#14 of Table VI) - Five ml. of 100% sulfuric acid (prepared by combining proper quantities of concentrated and of fuming sulfuric acid) and 100 mg. of 5,15-diethyl-8,18-diphenyl-diindolo[3,2-b:3',2'-m]triphenodioxazine were combined in a 10 ml. glass-stoppered Erlenmeyer flask. A dark green solution formed. The solution was stirred for 6 hours at room temperature, then poured over ice to quench the reaction and precipitate the sulfonated product (which is insoluble in strongly acidic H₂O). The product was freed of sulfuric acid by centrifuging and decanting the supernatant, followed by three washing and centrifugation steps with 100 to 120 ml. each of aqueous sodium chloride solution prepared by combining 1 volume of saturated solution with 4 volumes of deionized water. The final wash liquor was neutral to pH paper. The precipitate was dried in vacuo over P₂O₅ in a desiccator and yielded 240 mg. of a dark, blue-grey solid of sulfonated dioxazine containing an undetermined amount of sodium chloride (about 40-60%, by experiences in other preparations) from retained wash solution.

The product was soluble in water with a deep blue color. Its violet colored solution in N-butylacetamide had its maximum absorption at 587 nm, with lesser maxima in decreasing order at 545, 505, and about 470 nm (a four-peak pattern generally observed in NBA with the sulfonated dioxazines encountered in this work).

d. One-Step Condensation-Cyclization (#39 of Table VII) - A 2 liter RB flask equipped with magnetic stirrer, thermometer, and gas inlet-exit was charged with 1.0 liter of nitrobenzene, 20.25 g. (93.2 mmoles) of 3-amino-fluoranthene, and 18.21 g. (70.0 mmoles) of 2,5-diphenyl-p-benzoquinone. The flask was immersed in an oil bath and, with stirring, heated within a period of 3.5 hours to a temperature of 205° (b.p. nitrobenzene = 211°). A very slow stream of N₂ was maintained through the flask with the purpose of sweeping water vapors (water is evolved during the reaction) from the gas space within the flask. The evolution of water began at a batch temperature of about 195°, and 1.5 ml. of H₂O were collected within an 18 hour period at 205° by means of a cold trap connected to the gas exit. The reaction was maintained for a total of 24 hours at 205°, whereupon the heating was discontinued and the black reaction mixture permitted to cool overnight.

Filtration of the reaction mixture at room temperature on a medium porosity fritted-glass filter yielded, after exhaustive washing with acetone, 5.7 grams (18%) of 10,21-diphenyl-difluoreno[1,9-ab:9',1'-lm]triphenodioxazine, a dark crystalline solid with a metallic green luster and an infrared spectrum of class II (see section V A on IR spectroscopy).

The mother liquor was treated further to possibly obtain a second crop of the desired product. The liquor was concentrated by vacuum distillation (aspirator) of 600 ml. of nitrobenzene. Filtration of the concentrate yielded 110 mg. of a dark olive green powdery solid the major constituent of which was identified as difluoreno[1,9-ab:9',1'-hi]phenazine (see List of Compounds). (This compound was also obtained merely by heating a solution of 3-aminofluoranthene in nitrobenzene (15% yield) or in 1,2,4-trichlorobenzene (4% yield) for 50 hours.)

More solids formed in the filtrate of the concentrated mother liquor upon standing overnight. Refiltration yielded 148 mg. of a dark solid with a metallic green luster. It exhibited a class II infrared spectrum (see section on spectroscopy) quite unlike that observed for the expected product. The principal component of this solid was identified as 10,17-diphenyl-fluoreno-[1,9-ab]triphenodioxazine (see List of Compounds).

In a synthesis conducted under similar conditions (Synthesis #37, Table VII), the dioxazine product was washed with methylene chloride. Isolated from the wash filtrate were, after recrystallization from benzene, 500 mg. of dark (greenish) lustrous crystals of m.p. 224-225°. This material, on the basis of its infrared spectrum, was identified as the quinhydrone derived from 2,5-diphenyl-p-benzoquinone.

4. General Remarks

Although not stated specifically in Tables V through IX, the quantities of solvents used relative to the amounts of substrates corresponded approximately to the proportions indicated in the above examples.

Anhydrous sodium acetate was used, as an HCl scavenger in all reactions in which either chloranil or 2,5-dichloro-p-benzoquinone was one of the reactants and HCl evolution could be expected (although, as it turned out for the case of the dichloroquinone the chlorine was invariably retained).

List of Compounds Prepared in this Study

Compound Name and/or Structure
Molecular Formula

Perylene cation radical perchlorate
+ silver iodide

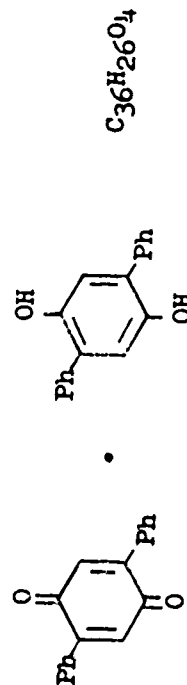
$(C_{10}H_{12})^{\bullet+}ClO_4^- + AgI$

1-Nitroperylene $C_{20}H_{11}NO_2$

3-Nitroperylene $C_{20}H_{11}NO_2$

3-Aminoperylene $C_{20}H_{11}NH_2$

* Qlnhydrone of 2,5-diphenyl-p-benzoquinone



Physical Characteristics

air stable black-green solid; insoluble or sparingly soluble in solvents such as acetonitrile methylene chloride.

red crystalline solid, m.p. 170-172. Solutions (CH_2Cl_2 , benzene) are non-fluorescent in ambient light.

Anal: calculated: C, 80.79; H, 3.73; N, 4.71
found: C, 80.79; H, 3.67; N, 4.64

dark red to brick red crystalline solid, m.p. 215-216. Solutions (CH_2Cl_2 , benzene) are highly fluorescent in ambient light.

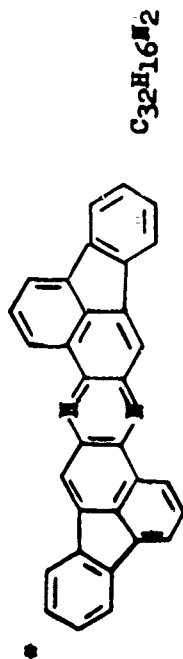
Anal: calculated: C, 80.79; H, 3.73; N, 4.71
found: C, 80.77; H, 3.67; N, 4.56

golden-orange crystalline
m.p. 232-235 (decomp.)

black-green solid, m.p. 224-225 (corrected)
somewhat soluble in methylene chloride
(green solution)

List of Compounds Prepared in this Study (continued)

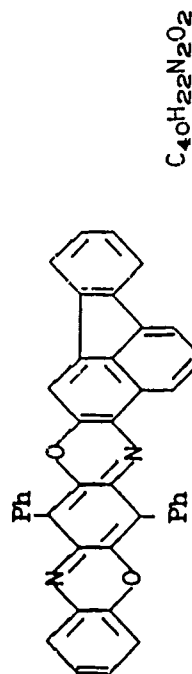
Compound Name and/or Structure
Molecular Formula



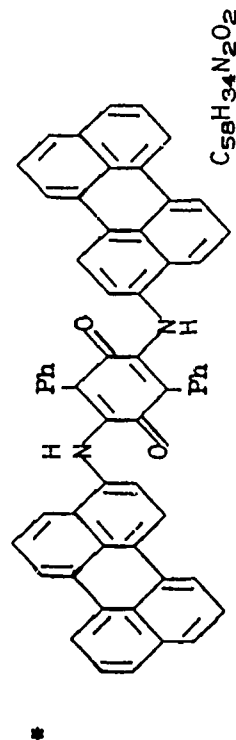
Physical Characteristics

brown crystalline solid, m.p. Δ 330
essentially insoluble in most organic solvents;
soluble in conc. H_2SO_4 with deep blue color.
H.R. Mass Spec: molecular ion at $m/e = 428$;
elemental composition $C_{32}H_{16}N_2$.
IR: no functional groups; strong bands at
719, 760, 778 cm^{-1} (adjacent and isolated
hydrogens).
Anal: calculated: C, 89.70; H, 3.76; N, 6.54
found: C, 86.16; H, 3.63; N, 5.51

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dark crystals with metallic green lustre in
reflected light; thin translucent mill is deep
violet; m.p. Δ 330. Sparingly soluble in
acetone, methylene chloride, with red violet
color.
H.R. Mass Spec: molecular ion at $m/e = 562$;
composition $C_{40}H_{22}N_2O_2$ or $C_{35}H_{22}N_4O_4$.
IR: Class II^a
Anal: calculated: C, 85.39; H, 3.94; N, 4.98
found: C, 81.95; H, 3.83; N, 4.70

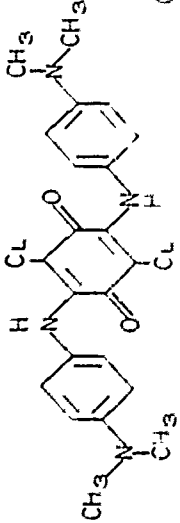
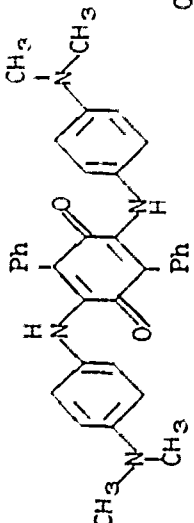
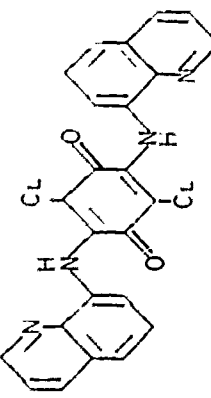
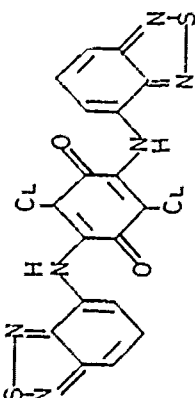


black solid insoluble in common org. solvents.
IR: Class Ia
Anal: calculated: C, 88.08; H, 4.33; N, 3.54
found: C, 83.55; H, 3.91; N, 3.87

List of Compounds Prepared in this Study (continued)

Compound Name and/or Structure
Molecular Formula

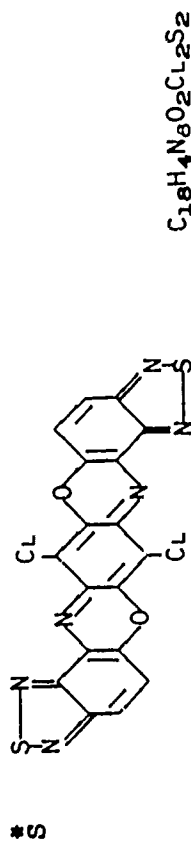
Physical Characteristics

<p>*</p>  <p><chem>C22H22N4O2Cl2</chem></p>	<p>purplish-black solid, m.p. 267-270 (decomp.) insoluble in common org. solvents. IR: Class Ia <u>Anal:</u> calculated: C, 59.33, H, 4.98; N, 12.58; Cl, 15.92 found: C, 59.24; H, 4.90; N, 12.70; Cl, 15.8</p>
<p>*</p>  <p><chem>C34H32N4O2</chem></p>	<p>purplish-black solid with metallic greenish lustre; insoluble in common org. solvents. IR: Class Ia</p>
<p>*</p>  <p><chem>C24H14N4O2Cl2</chem></p>	<p>black-brown solid, m.p. Δ 320; insoluble in common org. solvents. IR: Class Ia</p>
<p>*</p>  <p><chem>C18H8N6O2Cl2S2</chem></p>	<p>black solid insoluble in common org. solvents. IR: Class Ia</p>

List of Compounds Prepared in this Study (continued)

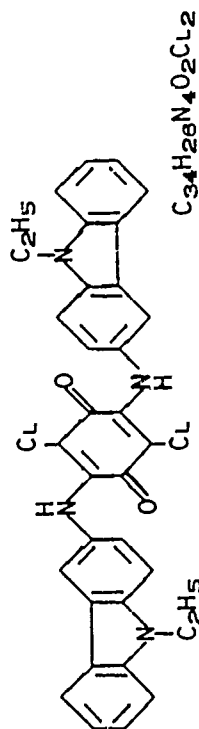
Compound Name and/or Structure
Molecular Formula

Physical Characteristics

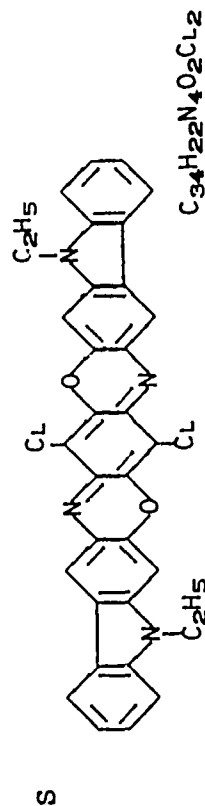


black solid insoluble in common org. solvents;
IR: Class IIa

dark purplish-brown solid insoluble in common
org. solvents.
IR: Class Ia (see Figure 5)



black solid with metallic green lustre; insoluble
in common organic solvents.
IR: Class IIa (see Figure 5)
Spectrum identical to that of an authentic
sample.

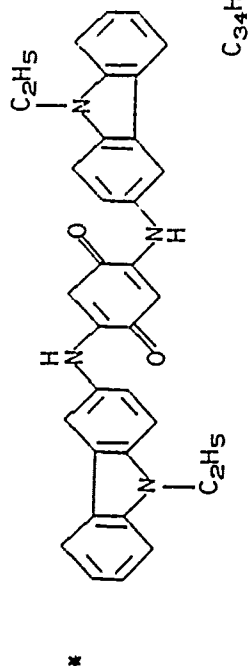


List of Compounds Prepared in this Study (continued)

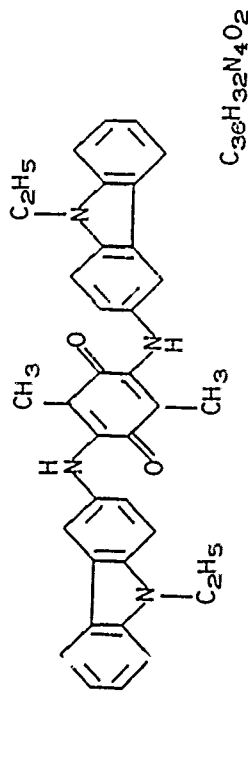
Compound Name and/or Structure
Molecular Formula

Physical Characteristics

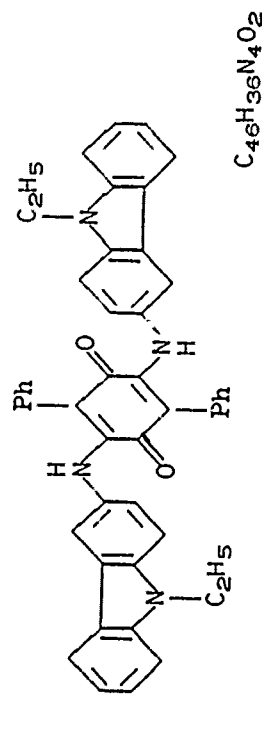
dark brown solid with metallic greenish lustre
in reflected light; insoluble in common org. solvent
IR: Class Ia



black crystalline solid insoluble in common org.
solvents.
IR: Class Ia



chocolate-brown solid insoluble in common org.
solvents; dark green solution in conc. H_2SO_4 .
IR: Class Ia

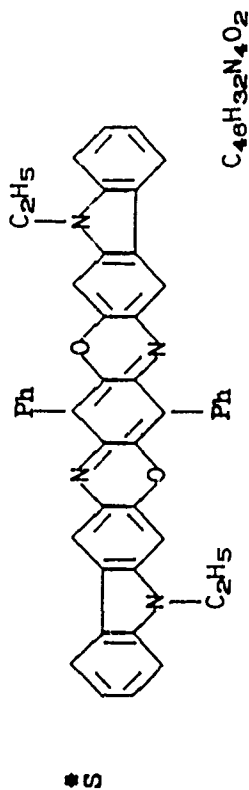


List of Compounds Prepared in this Study (continued)

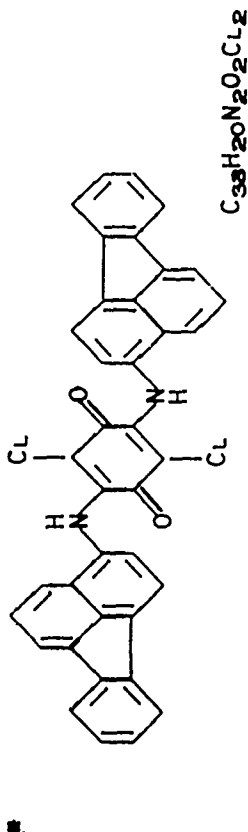
Compound Name and/or Structure
Molecular Formula

Physical Characteristics

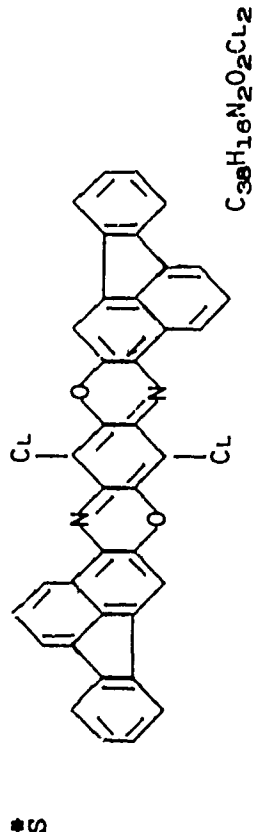
black solid with metallic green lustre in reflected light; insoluble in common org. solvents.
IR: Class IIa



black solid insoluble in common org. solvents.
IR: Class Ia (see Figure 6)

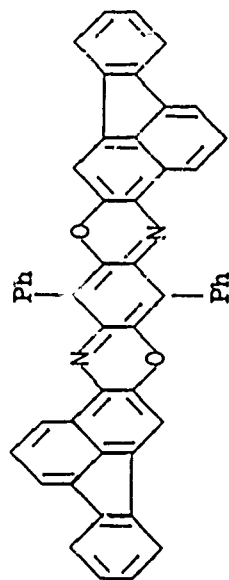


black solid with metallic greenish lustre; insoluble in common org. solvents.
IR: Class IIa (see Figure 6)



List of Compounds Prepared in this Study (continued)

Compound Name and/or Structure
Molecular Formula



$C_{50}H_{26}N_2O_2$

Physical Characteristics

dark solid with metallic green lustre; insoluble in common org. solvents.

IR: Class IIa

Anal: calculated: C, 87.44; H, 3.82; N, 4.08
found: C, 87.28; H, 3.76; N, 4.09

(*) New compound.

(S) Also prepared in sulfonated form (water-soluble dye stuff).

(a) Refer to the spectroscopy section under Experimental for an explanation and definition of Class I and Class II infrared spectra.

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17. JP 17,150 [ca 66, 47326p]; BP 892,092; FP 1,374,546; SP 408,248; FP 1,424,131; BP 892,383; SP 393,600; DBP 1,142,212; FP 1,361,268; FP 1,400,086; FP 1,280,449; FP 1,114,012; FP 1,269,107; FP 1,496,356; SP 440,508; SP 412,156; DBP 1,034,294; FPADD 80,889; FP 1,374,546; DBP 946,560; DBP 517,194; BP 850,159; BP 869,357.

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19. We thank Mr. N. B. Colthup for consultations on the interpretation of the infrared spectra described in this investigation.
20. We thank Mr. T. Mead and Mr. R. P. Welter for obtaining and interpreting the mass spectral data reported here.
21. Neither this compound nor its ring system have appeared in Chemical Abstracts through 1972.