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PIGMENT COLOR RESEARCH REPORT

New Pigments

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: New Pigments

PERIOD COVERED: January 1970 to December 1970

SUBMITTED BY: L. J. Pepoy DATE SUBMITTED: 1/13/71

APPROVED BY: E. E. Jaffe DATE RELEASED: 2/18/71

ABSTRACT

This report summarizes efforts directed toward the synthesis of several high strength pigments-derivatives of quinacridonequinone, triphendioxazine and fluorindine. The successful preparation of an interesting azomethine chelate is also reported.

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I. Introduction

This report is a summary of research directed toward the preparation of several high strength pigments - derivatives of quinacridonequinone, triphendioxazine and fluorindine.

II. Period Covered

January to June and June to December (Part Time) 1970

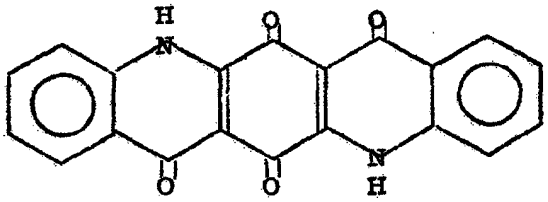
III. Patent Status

No patent application has been filed

IV. Discussion

1. Quinacridonequinone Derivative

Quinacridonequinone (QAQ), 1, is a yellow compound which is highly insoluble in organic solvents. For a compound to be useful as a pigment, it must be not only colored and quite insoluble in organic systems but also lightfast. Unfortunately, QAQ is somewhat deficient in this latter respect. Nevertheless, it was felt worthwhile to prepare compound 2 which links two QAQ molecules together by a carbon-carbon single bond and to see what characteristics such a molecule would exhibit. Based on past studies such a molecule was expected to show high tinctorial strength.



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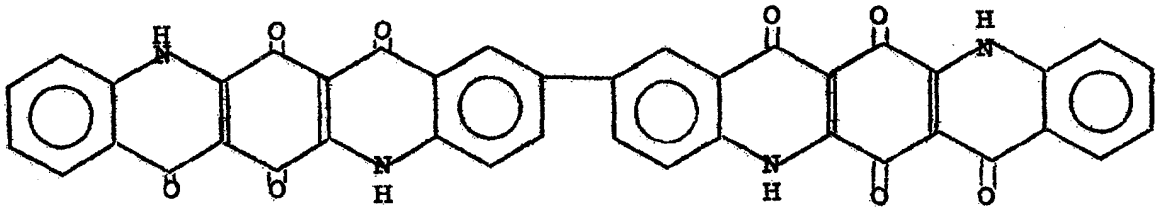

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The most attractive preparation of 2 would involve the reaction of aniline with 2,5-dicarbethoxy-3,6-dichlorobenzoquinone (DDB) to give 3 and the reaction of 3 with benzidine to give 4. Alternatively, DDB could react

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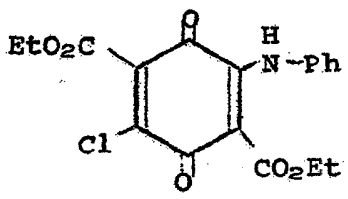

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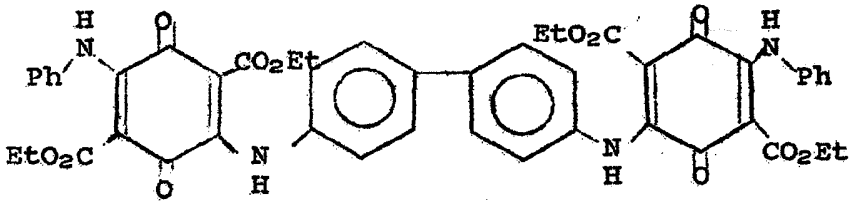
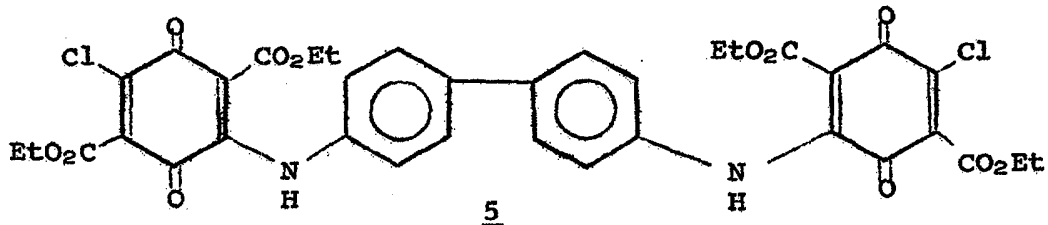


4

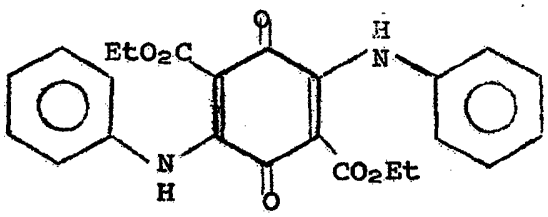
with benzidine to give 5 which in turn could be reacted with aniline to provide 4. Treatment of 4 in an inert



5

solvent at a high temperature (Conrad-Limpach reaction) could result in the fully-cyclized product, 2.

From the ambient temperature reaction (1934K-7) of aniline, DDB, and potassium carbonate in chloroform, a red-brown solid (> 90%) was isolated. A small portion of the solid was subjected to Conrad-Limpach conditions to provide a precipitate. Such behavior would be expected for the dianilino compound 6.



6

Fractional recrystallization of the solid from the aniline - DDB reaction gave the following results: 1) 48.8% of the solid was 6 (identified by ir comparison with authentic 6); 2) 14.6% as a mixture of 6 and DDB; and 3) 36.6% of DDB. If only the dianilino compound 6, were formed from the equimolar reaction of aniline and DDB, we would expect 50% of 6 and 50% of DDB. This is what we observed.

Apparently the chlorine atoms of DDB are very susceptible to nucleophilic displacement, being activated both by a carbethoxy and a keto function. Once the first anilino group has reacted with DDB, hydrogen bonding as shown in 7 might make the remaining chlorine atom even more easily displacable than the first one. Thus, the formation of 6 should be highly favored.

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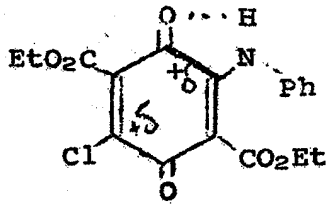
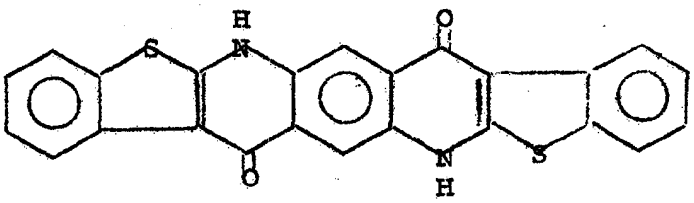


7

The alternative reaction (benzidine + DDB, 1934K-6) also gave a mixture (ir).

2. Benzthiopheno Analog of Quinacridone

Some years ago Orchem found (1) that the presence of fused benzthiopheno groups in colored compounds enhanced the strength and, in some cases, the lightfastness of these derivatives. Thus, we sought to prepare 8, an analog of quinacridone.



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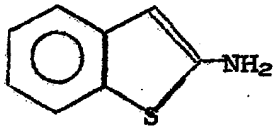
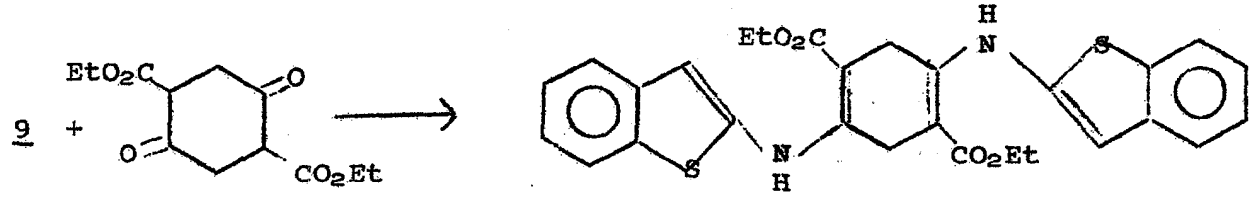


9

The necessary aromatic amine, 2-aminobenzo [b] thiophene, (9), was prepared by the recently reported (2) method of Stacy, et al.

The acid-catalyzed condensation of 9 and diethyl succinylsuccinate ester (SSE) provided (1934K-13) a low yield of material identified as the diethyl 2,5-benzthiopheneamino - 3,6-dihydroterephthalate 10. Again, the Conrad-Limpach reaction



10

was used to effect ring closure of 10 to 11, however, the

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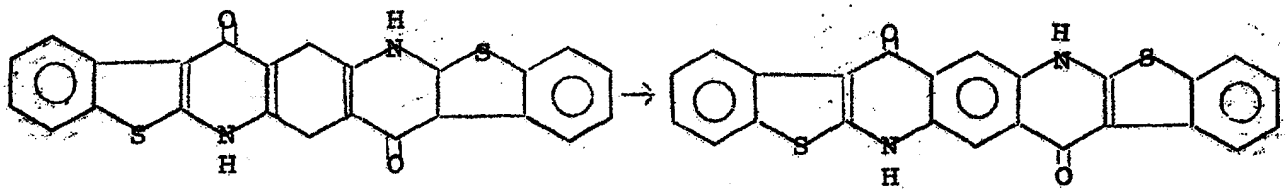
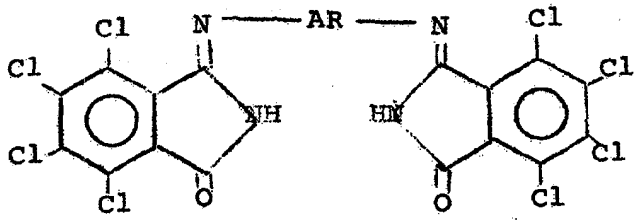


11 12

product was not analytically pure (1934-15). Attempted oxidation of 11 to 12 resulted in the recovery of 11 (identified by ir, 1934-70). Lack of sufficient material prevented further investigation. This problem should be reconsidered.

3. Chromonoxanthones

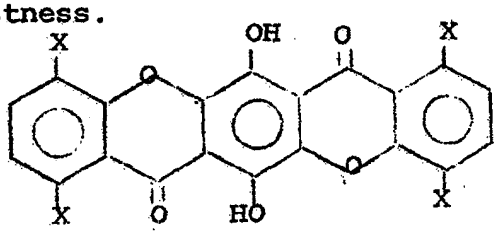
From studies to determine what structural features contribute to the durability of the Irgazin pigments, e.g.,13,



13

it was observed that the chlorines situated next to the keto and azomethine groups were necessary for good lightfastness. Just how (steric, mesomeric, or field effects) the chlorine atoms stabilize the molecule is uncertain.

We wished to prepare the chromonoxanthones 14 and 15 to see what, if any, influence the chlorine atoms would have on strength and lightfastness.



14, X=H 1902-63C

15, X=Cl 1934-24B

An unfortunate property of both 14 and 15 is that they are weak pigments and, consequently, not of much utility. Their UV and visible spectra are recorded in Table I.

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TABLE I

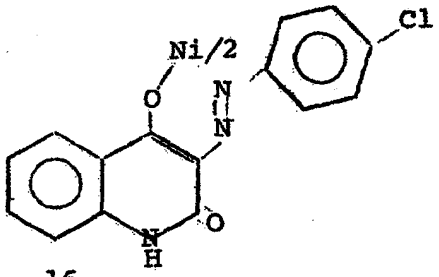
Absorption Spectra of Chromonoxanthones 14 and 15

14	λ Max. (ε)	15	λ Max. (ε)
	280(20,900)		268(19,200)
	307(14,200)		284(17,900)
	316(13,600)		297(14,500)
	490(3,100)		316(13,500)
			333(12,800)
			392(5,800)

The pigments were evaluated by rubout and Fadeometer exposure vs. YT-756-D, "Monastral" Orange. In masstone 14 showed a slight darkening while 15 faded slightly in 167 hrs. In tint both were slightly inferior to YT-756-D after the same time of exposure. However, the tetrachloro derivative, 15, was superior to the parent compound 14.

4. Azo Chelates

Green Gold, YT-714-D, 16, is a pigment possessing good lightfastness but relatively low strength (one observes the tail of a peak with its maximum in the UV region) We wished



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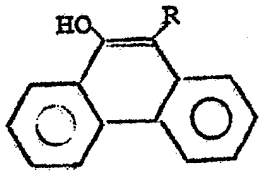
to prepared a pigment redder than Green Gold in which the position of the maximum would be in the visible region with, hopefully, a concomitant increase in strength. Thus, we prepared the following ortho hydroxyazo compounds and investigated their nickel chelates. However, none of



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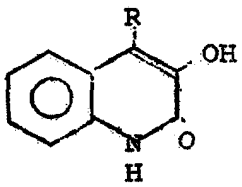

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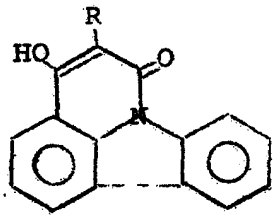

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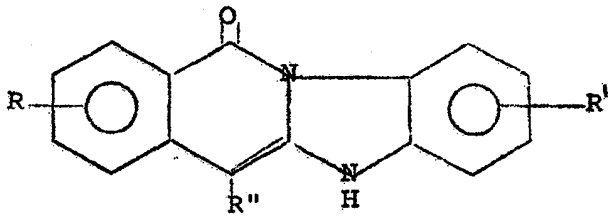
R=H		R=-N=N-⟨O⟩-Cl
17 a (1934-31),	17 b	(1934-23)
18 a (1824-65D),	18 b	(1934-30)
19 a (1934-32),	19 b	(1934-37)

the azo compounds formed an insoluble chelate in boiling DMF. In order to "push" chelate formation, the dyes were milled in acetone with nickel sulfate and ammonium hydroxide. Infrared spectra, X-ray diffraction patterns and elemental nickel analyses suggested that the chelates had been formed. Treatment of the chelates with boiling DMF effected either destruction or solution of the compounds. The instability of the chelates precludes their use as pigments. Nevertheless, the unstable chelates were evaluated vs. YT-714-D by rubout and found to fade in 72 hours.

5. Benzimidazoisoquinolone Derivatives

A report (3) in the literature concerns the preparation of azo compounds, derivatives of 11-oxo-5,11-dihydrobenzimidazo (1,2b)-isoquinolones 20 (R"=H).



20

Although the isoquinolones couple with diazonium salts, no mention was made of their forming a chelate. Thus, we prepared (1934-40) the parent compound (R=R'=R"=H) and coupled it with the diazonium salt of p-anisidine (1934-60), (R"=-N=N-⟨O⟩-OCH_3), 21. Compound 21 would not form an insoluble nickel chelate either in hot DMF or by acetone milling (1934-62,-64).

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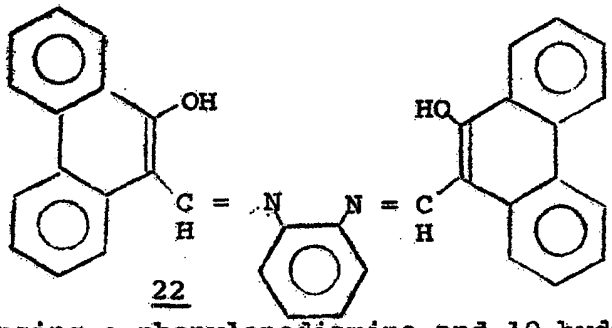
6. Azomethine Chelate

Again in the area of chelates we were interested in preparing the nickel chelate of Schiff base 22. Compound 22 was prepared (1934-61, 66)



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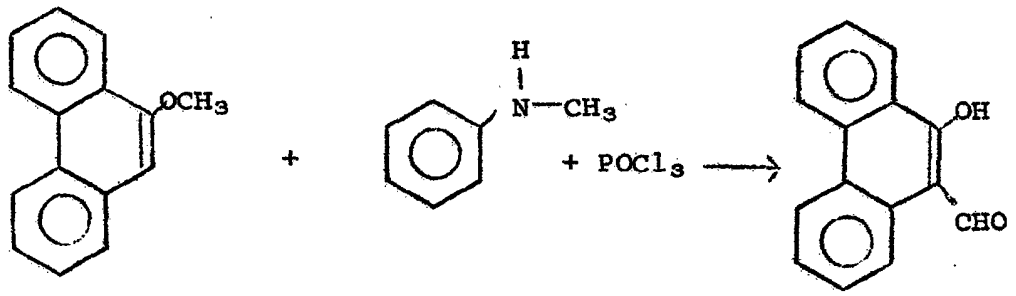
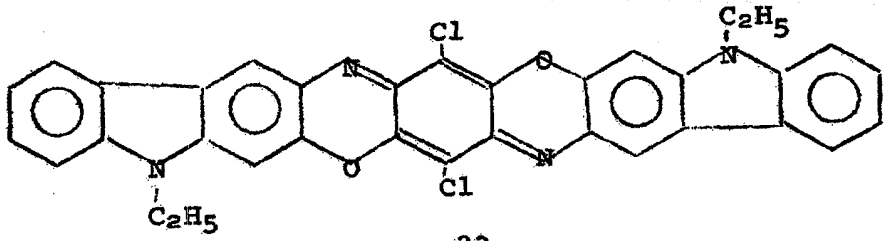
by condensing o-phenylenediamine and 10-hydroxy-9-phenanthrene-carboxaldehyde. The latter compound was prepared (1934-58) according to a published procedure (6).



The nickel chelate precipitated from a boiling DMF solution of the Schiff base and nickel acetate (1934-65). The brownish-red pigment was evaluated in the Fadeometer vs. RT-920-D, "Monastral" Maroon. In both masstone and tint the chelate was as good as RT-920-D, but only about half the strength of RT-920-D. Due to the good lightfastness of this compound this system should be investigated further.

7. Triphendioxazine Derivative

The triphendioxazines are a family of high strength but poor to fair lightfastness pigments. The only commercially available dioxazine pigment is the carbazole derivative 23



23

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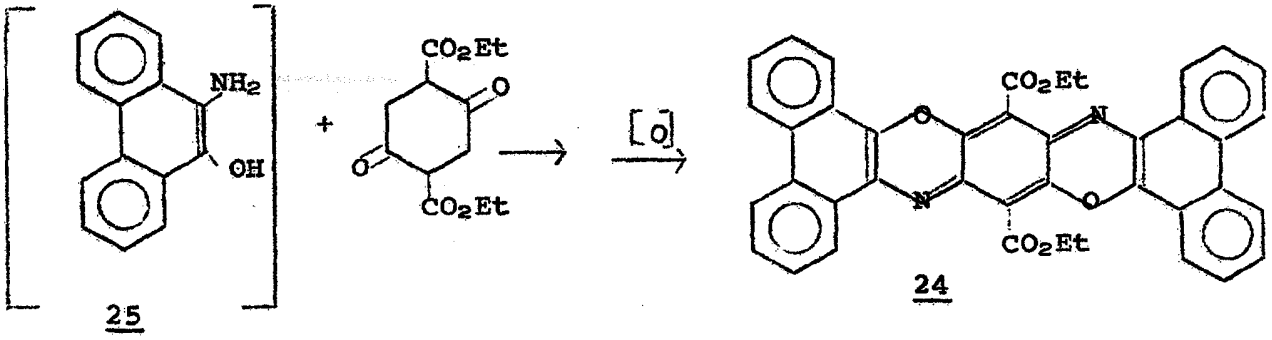
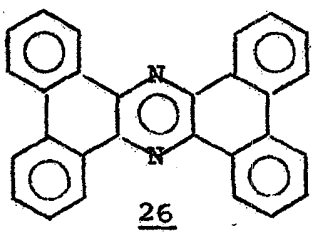
We were interested in preparing the tetrabenzo compound 24 for eventual conversion to a diamide pigmentary material.

One route to the compound involved reacting 9-amino-10-hydroxyphenanthrene, 25, and diethyl succinylsuccinate (SSE) followed by oxidative cyclization to 24.

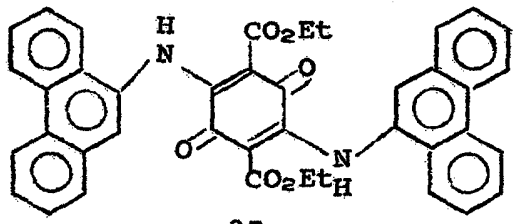


25 24

Compound 25 was prepared from the monoxime (4) of phenanthrenequinone (1934-26) which was reduced to the amine hydrochloride (1934-28) with stannous chloride in hydrochloric acid. The salt is quite stable while the free amine reacts to form the phenazine 26. In fact 26 made up the major portion of the product mixture from the reaction of 25 and SSE. Thus,



26



27

a large excess of 25 was used (1934-53), and the brown solid was extracted with o-dichlorobenzene (ODCB) (26 is insoluble) to afford a very small amount of material identified as the required intermediate diethyl 2,5-diarylamino-dihydroterephthalate. This assignment is based upon ir, elemental analysis, and a blue solution (characteristic of triphendioxazines) when the intermediate was boiled in ODCB with chloranil.

An attempt to side-step this difficulty was made by the reaction (1934-46) of 9-aminophenanthrene and DDB followed by oxidative

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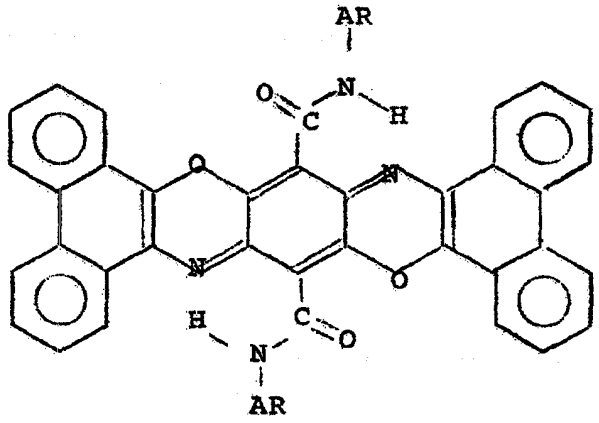
cyclization (1934-50) of the intermediate 27. The small amount of blue solid was identical to the product obtained upon cyclization of the reaction product of 25 and SSE. Further investigation of 24 was hampered by a shortage of 9-aminophenanthrene. The amine is prepared (1934-35) by the Bucherer reaction (5) of 9-phenanthrol. The phenol, in turn, can be prepared by the acid-catalyzed dehydration (1934-18) of 9,10-dihydro-9,10-dihydroxyphenanthrene or the cuprous ion catalyzed reaction (1934-31) between sodium methoxide and 9-bromophenanthrene and subsequent hydrolysis of the methyl ether.

Further work should be done on 24 to eventually prepare amides such as 28 which are capable of intramolecular hydrogen bonding. Such compounds ought to be insoluble, of high strength and possibly good durability due to steric and intramolecular hydrogen bonding factors.



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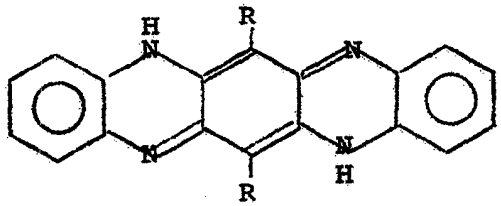
8. Fluorindine Derivative

Another system characterized by high strength but poor lightfastness is the fluorindine molecule 29(R=H).



29

We wished to prepare amides of fluorindine dicarboxylic acid analogous to the triphendioxazine 28 which would be capable of intramolecular hydrogen bonding.

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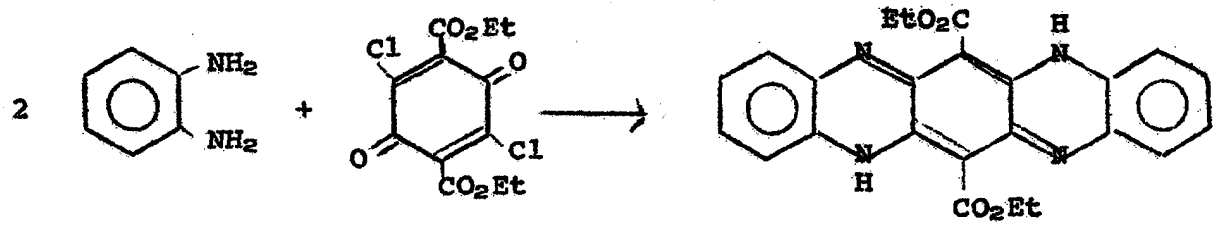
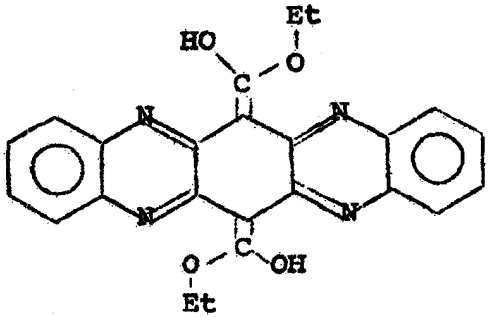
The requisite dicarbethoxy compound (30) could be prepared (1924-5) from ortho-phenylenediamine and DDB.



30

The identity of 30 was in doubt since it possessed properties not characteristic of fluorinidines, such as relatively high solubility and low extinction of its visible absorption bands. However, the compound was considered fully characterized by elemental analysis, ir, nmr, and mass spectrum. A possible explanation for the lowered e extinction might be the contribution of a form such as 31 in which the quinoid-like structure of 30 is destroyed.



31

The formation of the amides was not investigated as yet. However, 30 was condensed (1934-21) with ortho-phenylenediamine in polyphosphoric acid to yield a deep blue solid assumed to be the dibenzimidazolyl derivative. The compound behaved as an acid-base indicator and was not evaluated further.

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