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E. I. DU PONT DE NEMOURS & COMPANY
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Pyrazine Yellow Pigments

Period Covered September 1967 to September 1969 (Part Time)

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

TITLE: Pyrazine Yellow Pigments

PERIOD COVERED: September 1967 to September 1969 (Part Time)

SUBMITTED BY: G. R. Aldridge G. R. Aldridge Date Submitted: 2/8/71

APPROVED BY: E. E. Jaffe E. E. Jaffe Date Released: 4/27/71

ABSTRACT

The yellow pigment (I) from the reaction of hydrazoic acid with 10,11-diaza-trans-fluoracendione in sulfuric acid, after purification, showed poor lightfastness on Florida exposure. Its polychloro-analog (II) is a strong, intense, non-bleeding yellow pigment that is deficient in outdoor durability.

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I. Introduction

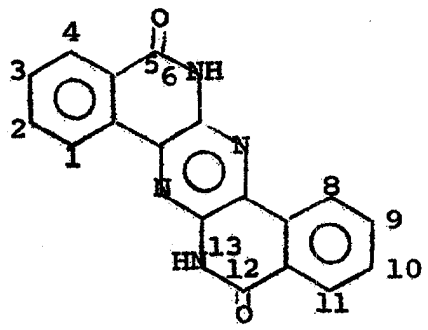
This report is a summary of the research on "diisoquinolono-pyrazine" and its polychloro-analog which were synthesized in the search for a "Monastral" yellow pigment.

II. Period Covered by Report

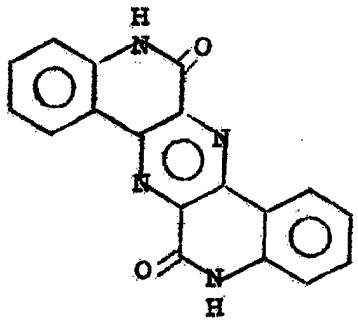
September 1967 - September 1969 (Part Time)

III. Nomenclature

The pyrazine pigment discussed in this report probably has one of the following three structures:



IA



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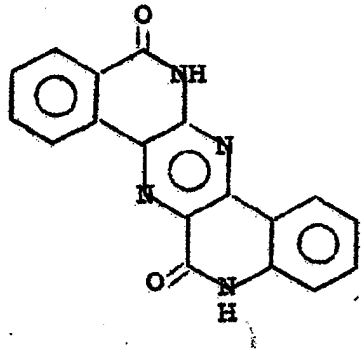


IC

The complete name of each of the three isomers follows:

IA - 5,6,12,13-tetrahydrodiisoquino-(4,3-b,4',3'-e)pyrazine-5,12-dione
B - 5,6,12,13-tetrahydro-diquino-(3,4-b,3',4'-e)pyrazine-6,13-dione
C - 5,6,12,13-tetrahydro-isoquino(4,3-b)quino(3',4'-e)pyrazine-5,13-dione

IV. Summary and Conclusions

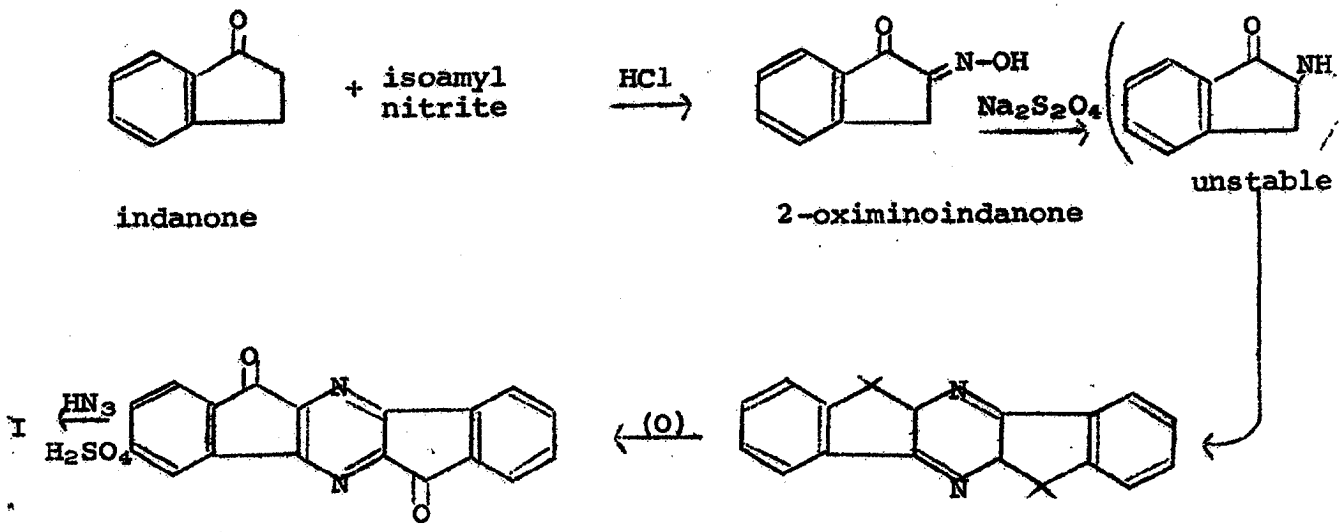
The yellow pigment (I) from the reaction of hydrazoic acid with 10,11-diaza-trans-fluorenacendione in sulfuric acid (Schmidt Reaction) probably has the IA structure, but there is insufficient evidence to rule out alternative structures IB and IC. I, after purification to remove isomeric impurities, etc., is a greenish-yellow pigment which showed poor lightfastness in thermosetting acrylic enamel (TAE-3) on Florida exposure. The polychloro-analog (II) of I is a strong, intense, non-bleeding yellow pigment that is redder in hue than I. The lightfastness of II in thermoplastic acrylic lacquer and in TAE-3 is significantly better than that of I, but II is deficient in lightfastness versus Irgazin yellow 3 RLT or Green Gold. Large particle size II is more lightfast than small particle size II, but the former is not attractive tinctorially.

V. Patent Status

CP-111, Pyrazine Yellow pigments, was submitted to the Patent Liaison Group at Newport for the preparation of a composition of matter case on I, and its polychloro-derivatives.

VI. Discussion

I was prepared from indanone as follows -



indanone

2-oximinoindanone

I

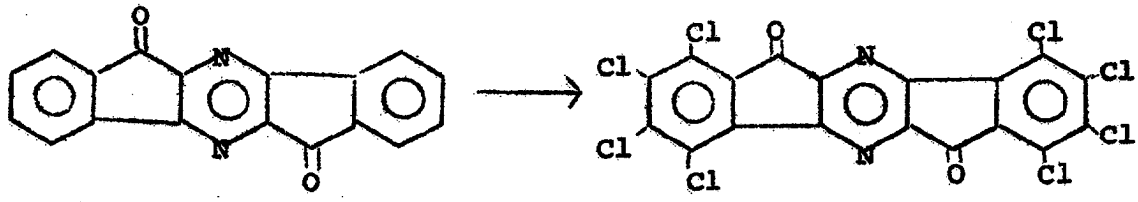
10,11-diaza-trans fluoracendione

$C_{18}H_{14}N_2$
diindenodihydropyrazine

$C_{18}H_8N_2O_2$
MW 284

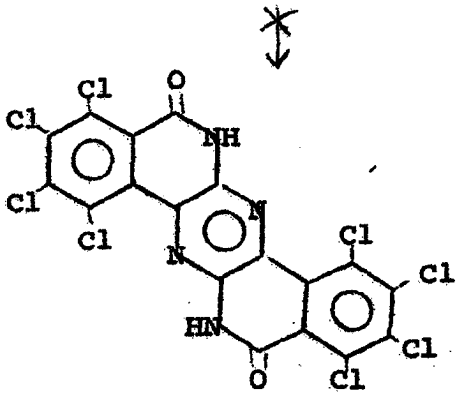
The dioxime of 10,11-diaza-trans-fluoracendione in polyphosphoric acid also gave I, probably by way of a Beckman Rearrangement. The chlorination of I in an aluminum chloride eutectic melt gave the polychloro-analog, II, probably the heptachloro-derivative. Attempts to prepare the octachloro-derivative of I from I by chlorination were unsuccessful. The preparation of the octachloro-derivative of I by the following route was also studied.

214
5
23
32



10,11-diaza-trans fluoracendione (III)

octachloro-derivative of III



The chlorination of III gave a product, presumably the octachloro-derivative of III, which did not yield the octachloro-derivative of I on treatment with hydrazoic acid in sulfuric acid.

The visible absorption spectra of I and II in dimethylformaride solution were determined. The wavelengths (λ) and molecular extinction coefficients (ε) of their absorption peaks are tabulated below.

	λ (mu)	ε
I	428	24,400
	410	21,500
II	462	25,700
	437	22,900

VII Experimental

Preparation of 2-Oximinoindanone (1871/39)

Into 100 g (0.76 mole) of 1-indanone in 1 liter of benzene anhydrous hydrogen chloride was introduced for 15 min. Isoamyl nitrite (105g, 0.90 mole) was, then, added over 110 min. while maintaining the reaction temperature at 35-40°. Benzene (50 ml) was used to rinse the

isoamyl nitrite remaining in the funnel into the reaction which was, next, heated at 35-40° for four hours. After stirring overnight (room temperature) the product was filtered, washed with ligroin, and air dried.

Yield: 109 g (90% yield) MP 189-93°

Preparation of Diindenodihydropyrazine (1871/52A) ← Step 2

Into a 5 l flask was charged
1260 ml 12.5% ammonium hydroxide,
102 g (0.63 mole) 2-oximinoindanone, and
630 ml 2B alcohol

The mixture was stirred, and treated at 28-54° (during addition) with 330 g (1.9 mole) sodium hydrosulfite. The mixture was stirred 3 days at room temperature, then refluxed 15 hrs., cooled to 30°, the solid filtered, washed with water and dried.

Yield: 76 g (93% yield) MP 223-60°

Preparation of 10,11-Diaza-Trans-Fluoracendione (1871/52B)

76 g (0.29 mole) of diindenodihydropyrazine and 1480 ml glacial acetic acid were stirred in a 5 l flask. The mixture was treated with 220 g technical sodium dichromate, and then refluxed for 14 hrs. After cooling to 30°, the solid was isolated by filtration, washed with 2B alcohol, and dried.

Yield: 67.6g (81% yield) MP. approx. 350°dec

Preparation of I (1871/29B-F)

Into a 500 ml flask was charged

8.5g (.03 mole) 10,11-diaza-trans-fluoracendione , and
170 ml (300 g) Conc'd sulfuric acid.

The mixture was stirred for 5 min. to obtain solution (red) and treated over 50 min. with 4.3g (0.066 mole) sodium azide while maintaining the reaction temperature at 28-50°. The reaction mixture was, then, heated at 40-50° for 2 hours, cooled to 30°, drowned in 2700 ml ice-water, and stirred. The solid was filtered off, washed acid free, and dried.

Yield: 8.4g

This product was purified by recrystallizing twice from concentrated sulfuric acid.

29D Yield: 5.4g (57% yield of IA or IB or IC)

Analysis Found:	C, 68.1 H, 3.01 N, 17.4	$C_{18}H_{10}N_4O_2$	C, 68.8 H, 3.18 N, 17.8

The mother liquor from the first acid crystallization was drowned in water, stirred, and filtered to isolate a second product.

Yield: 2.5g

This product was further purified by acid recrystallizing twice from concentrated sulfuric acid.

29F Yield: 1 g (11% yield of isomeric product)

Analysis	Found:		$C_{18}H_{10}N_4O_2$	
	C, 66.5			C, 68.8
	H, 3.53			H, 3.18
	N, 16.5			N, 17.8

On the melting point block both of these products were largely unchanged at 400°C.

	3200-2700 cm^{-1}	Strongest Peak	Assignment
10,11-Diaza-trans-fluoracendione	no absorption	1730	<C=O (5-membered ring)
1871/29D	broad absorption	1660	<C=O-NH-(6-membered ring)
1871/29F	broad absorption	1670	<C=O-NH-(6-membered ring)

NMR SPECTRA

1871/66A1 (essentially the same as 1871/29D) was insufficiently soluble in dimethylformamide, dimethylacetamide, dimethylsulfoxide and hexafluoroacetone deuterate for an nmr spectrum. Signal averaging for 50 passes thru a C-1024 computer of a deuterated dimethyl sulfoxide solution of 1871/66A1 gave a spectrum having a single fairly sharp line at δ=7.5 ppm. According to Dr. Harlan Foster of Central Research (Experimental Station) the structure of the main product from the hydrazoic acid reaction is more likely IA than IB or IC based on the single line at δ=7.5 ppm in the nmr spectrum.

Preparation of the Dioxime of 10,11-Diaza-trans-fluoracendione (1871/61)

To a 1 liter flask was charged
14.2 g (.05 mole) of 10,11-diaza-trans-fluoracendione
280cc pyridine. The mixture was stirred (incomplete solution) and treated with 13.7g (.2 mole) hydroxylamine hydrochloride.

The reaction mixture was refluxed 6 hrs., cooled to 30°. The solid was filtered off, washed with 2B alcohol, and then with water until the filtrate gave a negative test on Brilliant Yellow paper and was chloride ion free. After drying the yield was 12.2g MP 340-50°dec
This product was purified by extraction with hot dimethylformamide.

Analysis Found: N, 17.1

$C_{18}H_{10}N_4O_2$ (dioxime) req. N, 17.8

$C_{18}H_9N_3O_2$ (monooxime) req. N, 14.1

Rearrangement of the Dioxime of 10,11-Diazo-trans-fluoracendione (1871/63)

To a 1 liter flask was charged
6.2 (.02 mole) dioxime and
250 g polyphosphoric acid

The reaction mixture was heated at 170-80° for 1 hr., cooled to 150°, drowned in ice-water and stirred. The solid was filtered off, washed with water, and dried.

Yield: 6 g

This product was purified by recrystallizing twice from concentrated sulfuric acid

Yield: 3.1 g

The infrared spectrum and X-ray diffraction pattern of this product are identical with the spectrum and pattern of 1871/29D, respectively.

Preparation of Polychlorodiisoquinolonopyrazine (1893/2A,B)

To a 1 liter resin flask was charged
192 g anhydrous $AlCl_3$
24 g sodium chloride
3 g technical sodium fluoride.

The mixture was heated to 110-120° for 6 hrs. The reaction mixture was drowned in ice-water containing 230 cc 5N HCl, and stirred. The solid was filtered off, washed chloride ion and acid free, and dried.

Yield: 12.1 g MP > 360°C

This product was purified by recrystallizing once from concentrated sulfuric acid.

Yield (from 11 g): 9.1 g

Analysis	Calc. for $C_{18}H_2Cl_8N_4O_2$	Found	Calc. for $C_{18}H_3Cl_7N_4O_2$
C,	36.6	36.6, 36.8	38.9
H,	0.3	0.6, 0.6	0.54
N,	9.5	9.8, 9.7	10.1
Cl,	48.1	44.8, 44.9	44.7

Chlorination of 10,11-Diaza-trans-fluoracendione (1893/39A)

To a 1 liter resin flask was charged
288 g anhydrous aluminum chloride
50 g sodium chloride
22.5 g potassium chloride

The mixture was heated to 120-140° to obtain a melt.
To the melt was added
15.5 g 10,11-diaza-trans-fluoracendione

The temperature of the reaction mixture was raised to 150-60° and after stirring 10 min., chlorine was passed in at 143-67° for 6 hrs. The reaction mixture was drowned in ice-water containing 500 cc 5N HCl and stirred. The solid was filtered off, washed chloride ion and acid free, and dried.

Yield: 39 g

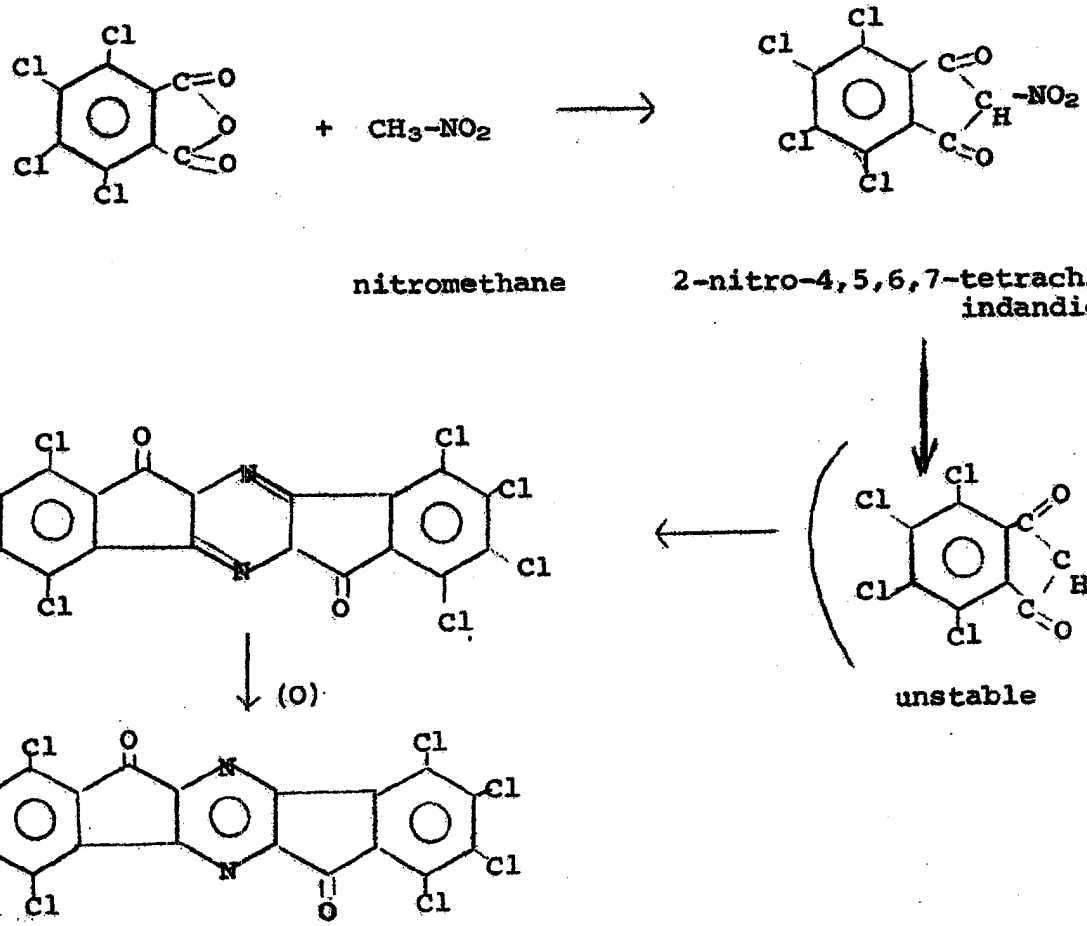
Analysis Found: Cl, 48.8 Calc. for $C_{18}Cl_8N_2O_2$: Cl, 50.6

Infrared Spectra 1730 cm^{-1} (C=O, 5-membered ring)

Attempted Rearrangement of Polychloro-10,11-diaza-trans-fluoracendione (1893/39B,C)

Under conditions that bring about the rearrangement of tetrachloro-10,11-diaza-trans-fluoracendione to the tetrachloro-derivative of I, polychloro-10,11-diaza-trans-fluoracendione does not appear to rearrange (based on the absence of a band at 1660-1670 cm^{-1} in the infrared spectrum of the product.)

Attempted Preparation of Octachlors-derivative of III from Nitromethane and Tetrachlorophthalic Anhydride



octachloro-derivative of III

In an attempt to prepare 2-nitro-4,5,6,7-tetrachloroindandione from tetrachlorophthalic anhydride and nitromethane in N,N-dimethyl-aniline, the actual product was tetrachlorophthalimide. The source of ammonia may be carbamic acid (H_2N-CO_2H) formed by a simultaneous oxidation-reduction of nitromethane by analogy to the formation of anthranilic acid from o-nitrotoluene.

VIII. Notebook References
1871
1893