CHEMICAL REVIEWS

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QUINACRIDONES

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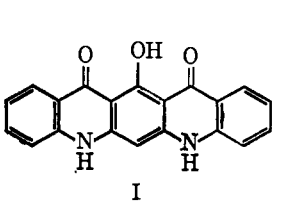
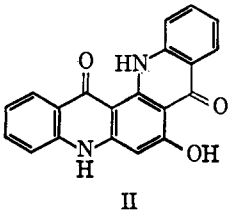
I. INTRODUCTION

The name quinacridone was coined by Niementowski in 1896 when he attributed it to a mixture of I and II prepared by heating phloroglucinol and anthranilic acid or anthranilic aldehyde (147, 148). These structures were considered to be formed from fusion of the quinoline and acridine residues. The mixture was later shown to consist of at least 95% of the angular compound II (13, 105). In 1906 Ullmann and Maag cyclized III in sulfuric acid and obtained yellow needles, mp 394°, to which they ascribed linear structure IV (114, 184). Their product has recently been proven to be the angular compound V (14).



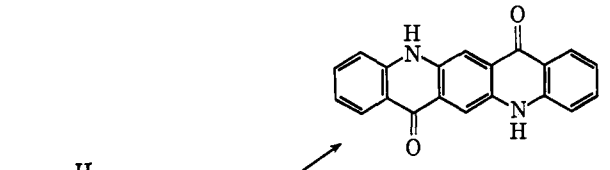
I



II

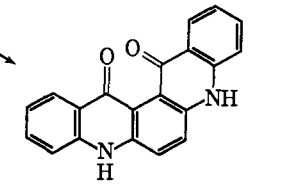
The first example of the synthesis of the basic linear quinacridone ring system was the quinacridonequinone VI prepared by Sharvin in 1915 (167). The preparation of the first linear-*cis*-quinacridone VII was described by Eckert and Seidel in 1921 (62). The linear-*trans*-quinacridone system remained unknown until 1926 when Lesnianski and Czerski synthesized VIII (123).

A procedure for the preparation of another class of

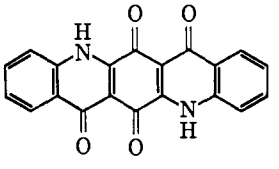


III

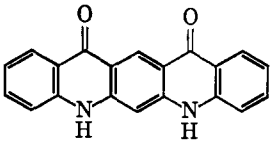
IV



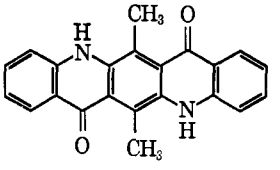
V



VI

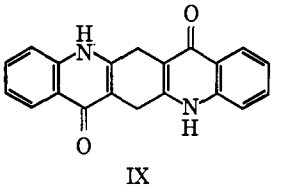


VII



VIII

compounds in this series, the dihydroquinacridones, of general structure IX, was claimed by Pendse and Dutt in 1932 (150). However, the unsubstituted linear-*trans*-quinacridone IV, a red-violet powder, was not synthesized by an unambiguous route until 1935 (129).



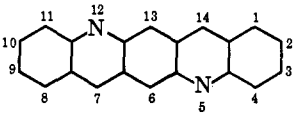
IX

The quinacridones attracted no particular attention until 1955, when Du Pont chemists discovered methods of preparing some linear-*trans*-quinacridones in a useful pigmentary form (172). A number of quinacridone pigments are now marketed: Monastral Red B, Monastral Red Y, Monastral Violet R, Monastral Scarlet, Monastral Maroon B, Monastral Orange, Newport Gold, Hostaperm Pink E, Quindo Magenta, and Quindo Violet (7, 8, 48, 91, 145).

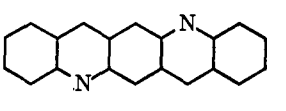
The growing commercial interest in these compounds is evidenced by the extensive number of patents issued in recent years to various chemical companies. Further, derivatives of quinacridone IV have been described as useful for an electrophotographic process (183).

II. NOMENCLATURE

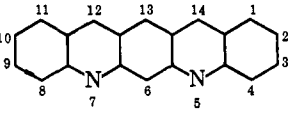
Quinacridones are diketo derivatives of quinacridines. The following skeletal structures for quinacridines have been identified (149).



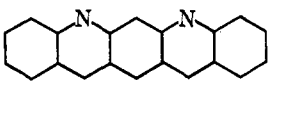
Xa
(RRI 6261)



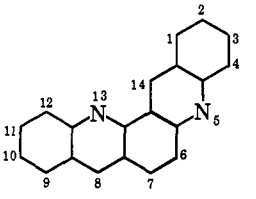
Xb



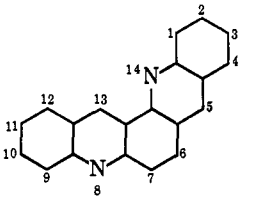
XIa
(RRI 6260)



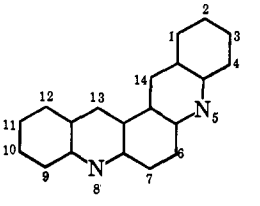
XIb



XIIa
(RRI 6265)

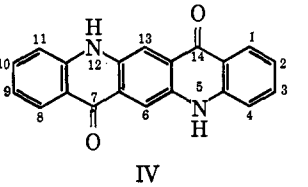


XIIb



XIII
(RRI 6262)

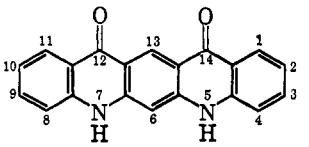
The name linear-*trans*-quinacridone is commonly used for the 7,14-diketo derivatives of Xa. Prior to the year 1916, these compounds were described as 5,12-(7,14)-quinacridinediones and were written in the orientation Xb. They were known as 5,12(7,14)-α-quinacridinediones or simply α-quinacridinediones between 1917 and 1926. Later the orientation was changed to the currently used Xa, and the more systematic name of quin[2,3-*b*]acridine-7,14(5,12)-diones was given to them. Since 1947, the diketo derivatives of Xa have been abstracted under quino[2,3-*b*]acridine-5,12-dihydro-7,14-dione. In the patent literature, compound IV is commonly known as a linear-*trans*-quinacridone (29, 55). Other names for IV include linear *p*-N,N′-quinacridone (188), linear quinacridone (86, 173), and 7,14-dioxo-5,7,12,14-tetrahydroquinolino[2,3-*b*]acridine.



IV

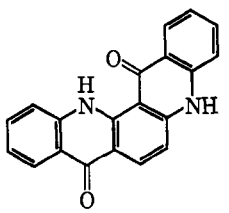
The diketo derivative of XIb was known as 12,14-(5,7)-γ-quinacridinedione before 1926, after which it was changed to quino[3,2-*b*]acridine-12,14(5H,7H)-

dione and written in the orientation VII. It is presently denoted as quino[3,2-*b*]acridine-5,7-dihydro-12,14-dione in *Chemical Abstracts*. In the patent literature, VII is known as linear-*cis*-quinacridone (19) or isoquinacridone (49).

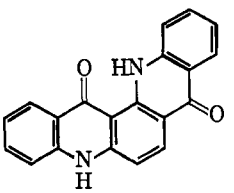


VII

The diketo derivative of XIIb was known as 5,13-(8,14)-β-quinacridinedione and written as XIVb before 1926; after that date it was changed to quin[2,3-*c*]-acridine-5,13-dione. From 1937 through 1946 the diketo derivative of XIIa, written in the orientation XIVa, was known as quin[2,3-*a*]acridine-5,13-dihydro-8,14-dione or β-quinacridone. The name dibenzo-



XIVa



XIVb

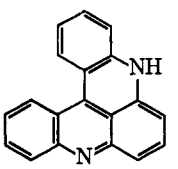
[*b*,*j*][1,7]phenanthroline-5,13-dihydro-8,14-dione is currently used for XIVa.

The quinacridone V has been known as quino[3,2-*a*]-acridine-5,8-dihydro-13,14-dione. It is now listed as dibenzo[*b*,*j*][4,7]phenanthroline-5,8-dihydro-13,14-dione in *Chemical Abstracts*.

For the purpose of this review, IV will be called a linear-*trans*-quinacridone; VI will be called linear-*trans*-quinacridonequinone. Quinacridone VII will be designated as linear-*cis*-quinacridone and IX as 6,13-dihydro-linear-*trans*-quinacridone.

III. Scope

This review covers linear-*trans*-quinacridones, 6,13-dihydro-linear-*trans*-quinacridones, linear-*cis*-quinacridones, and linear-*trans*-quinacridonequinones. Literature appearing in *Chemical Abstracts* up to the end of 1965 has been covered. An attempt has been made to cover other likely sources of information on the subject up to the end of 1965. Quinacridones V and XIV have not received sufficient attention in the literature during recent years to warrant their inclusion in this review, and readers are referred to other sources (2, 121, 175, 185, 188). Quinacridines lacking the two keto groups and derivatives of *peri*-quinacridine (XV) are not included in the subject matter of this review (189).



XV

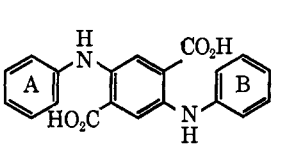
IV. Linear-*trans*-quinacridones

A. Methods of Preparation

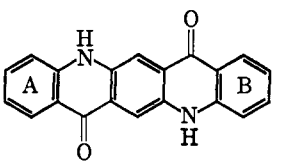
Linear-*trans*-quinacridones are prepared by the following three general methods.

1. *Cyclization of 2,5-Diarylaminoterephthalic Acids*

Cyclization of 2,5-diarylaminoterephthalic acids (XVI) or their esters to linear-*trans*-quinacridones XVII, in which rings A and B may carry substituents, can be carried out under a variety of conditions using almost any Friedel–Craft catalyst. The major research efforts on the process of cyclization have been aimed at the development of conditions under which the quinacridone obtained possesses a particle size and crystal structure useful as a pigment without further treatment.



XVI



XVII

The following condensing agents have been used for the conversion of 2,5-diarylaminoterephthalic acids (XVI) to quinacridones XVII.

a. Polyphosphoric Acid

Polyphosphoric acid of 83% phosphorus pentoxide content is an excellent condensing agent (151, 152). When diarylaminoterephthalic acids are heated with about 20 parts of polyphosphoric acid at 150–160°, almost quantitative yields of quinacridones are obtained in about 0.5 hr (156). Use of the esters and of the sodium or potassium salts of XVI as starting materials has been described (85). If polyphosphoric acid of lower concentration is used, the reaction may be carried out at higher temperatures. Phosphorus pentoxide has been used for cyclization with tetrahydronaphthalene or cymene as the solvent (31, 129).

b. Benzoyl Chloride

Cyclization of 2,5-diarylaminoterephthalic acids can be achieved by heating them with benzoyl chloride in an inert solvent of high boiling point (44, 171). Thus, 2,5-dianilinoterephthalic acid, when heated with benzoyl chloride in nitrobenzene, gives an almost quantitative yield of linear-*trans*-quinacridone IV (163). Benzoyl chloride may be replaced by *p*-chlorobenzoyl chloride or phosgene, and trichlorobenzene has been used as a solvent in place of nitrobenzene (160, 171).

An interesting example describes the use of benzoyl chloride in a mixture of nitrobenzene and pyridine. Linear-*trans*-quinacridone IV can be obtained in α- or β-crystal modification depending upon the amount of pyridine used, the larger amount used being favorable for producing β crystals (46).

c. Phosphorus Halides

Ring closure of 2,5-diarylaminoterephthalic acid derivatives can be carried out in nitrobenzene at 205° using phosphorus oxychloride, phosphorus trichloride, or phosphorus pentachloride. The reaction is usually complete in less than 1 hr (124, 157).

d. Aluminum Chloride and Titanium Chloride

Conversion of 2,5-diarylaminoterephthalic acids or esters to quinacridones XVII can be affected in about 70% yield by heating them with aluminum chloride or titanium chloride in inert high-boiling solvents, such as trichlorobenzene or dimethylformamide (80, 86). Low-melting mixtures of aluminum chloride with sodium chloride, potassium chloride, or urea have been used to carry out reactions at lower temperatures (4, 39, 159, 198).

Linear-*trans*-quinacridone IV in the β-crystal form can be obtained in 90% yield by heating 2,5-dianilinoterephthalic acid with aluminum chloride and an excess of phosphorus oxychloride (10).

e. Sulfuric Acid and Its Derivatives

Ring closure of 2,5-diarylaminoterephthalic acids in concentrated sulfuric acid is accompanied by extensive sulfonation. However, water-soluble quinacridonesulfonic acids can be salted out and desulfonated by heating them with dilute sulfuric acid under pressure (41). When 70% sulfuric acid is used, quinacridones are obtained in less than 40% yield (57). However, a 92% yield of 2,9-dimethyl-linear-*trans*-quinacridone has been obtained by cyclization of 2,5-di-*p*-toluidinoterephthalic acid in 83% sulfuric acid at 150° (45).

Sulfonation of quinacridones can be avoided by carrying out the reaction in fuming sulfuric acid in the presence of an aromatic compound such as naphthalene, which can be sulfonated (56).

Linear-*trans*-quinacridones are obtained in excellent yields when the reaction is carried out in monochloroacetic acid or ethylene glycol containing a small amount of sulfuric acid (25). The use of methanesulfonic acid as condensing agent has also been described (33). Dry mixtures of 2,5-diarylaminoterephthalic acids and sodium bisulfate, when heated at 250°, yield about 40% of quinacridones XVII (49).

f. Hydrofluoric Acid

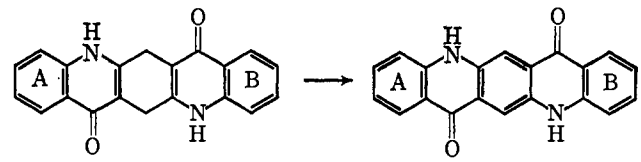
Moderate yields of linear-*trans*-quinacridones are obtained by heating 2,5-diarylaminoterephthalic acids or their esters with anhydrous hydrofluoric acid at 150° in an autoclave (79, 88). Hydrogen bromide in glacial acetic acid solution has been used with a resulting poor yield (129).

g. Boric Acid

Boric acid possesses historical importance in that it was used for the first synthesis of linear-*trans*-quinacridone IV. When 2,5-dianilinoterephthalic acid is heated with boric acid above 300°, IV is obtained in 87% yield (129).

2. *Oxidation of Dihydroquinacridones*

Quinacridones XVII are easily obtained by the oxidation of 6,13-dihydro-linear-*trans*-quinacridones (XVIII) (68). The following examples of dehydrogenating agents have been described.



XVIII XVII

a. Aromatic Nitro Compounds

Dihydroquinacridones XVIII when heated with *m*-nitrobenzenesulfonic acid in ethanol or ethylene glycol containing aqueous sodium hydroxide are converted to quinacridones XVII in excellent yields (34, 36, 73, 172). A product of greater tinctorial strength is obtained using nitrobenzene in ethylene glycol monoethyl ether in the presence of powdered sodium hydroxide (43). Dehydrogenation of XVIII can also be achieved by refluxing in an excess of nitrobenzene (34). If the oxidation is carried out in an aqueous solution of pH 13 using *m*-nitrobenzenesulfonic acid, dihydroquinacridone IX is converted to a mixture of quinacridone IV and quinacridonequinone VI (64).

b. Chloroanil

Excellent yields of quinacridones XVII can be obtained by heating dihydroquinacridones XVIII with chloroanil in chlorobenzene (34). About 90% yields of quinacridones XVII have been obtained through a one-step process in which the dihydroquinacridones XVIII are prepared by cyclization of 2,5-diarylamino-3,6-dihydroterephthalic acids in polyphosphoric acid. Subsequent dehydrogenation with chloranil is carried out on the crude reaction mixture without isolation of XVIII (51).

c. Anthraquinone-2,7-disulfonic Acid

Dehydrogenation of XVIII with disodium anthraquinone-2,7-disulfonate in alkaline aqueous ethanol produces quinacridones (XVII) in 80 to 96% yields (40).

d. Halogens

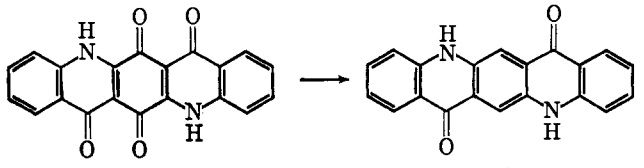
The use of halogens for oxidation of dihydroquinacridones XVIII has not been investigated. However, 6,13-dihydro-linear-*trans*-quinacridone (IX) is converted to dibromo-linear-*trans*-quinacridone by simultaneous dehydrogenation and bromination (119,120). The positions of the bromine atoms have not been established. Dehalogenation of 6,13-dihaloquinacridones can be accomplished with zinc dust in acetic acid (140).

e. Electrolytic Oxidation

An interesting electrolytic method is described for anodic oxidation of dihydroquinacridone IX to linear-*trans*-quinacridone IV. Electrolysis is carried out in alkaline aqueous methanol with simultaneous cathodic reduction of azoxyanisole to hydrazoanisole (3).

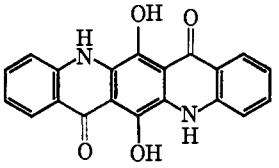
3. Reduction of Quinacridonequinones

Linear-*trans*-quinacridonequinone VI is reduced to linear-*trans*-quinacridone IV with zinc, iron, or copper under various conditions. A suspension of quinacridonequinone VI heated with zinc dust in 70% sulfuric acid gives a good yield of linear-*trans*-quinacridone IV



VI IV

(17). If reduction is carried out at higher concentrations of sulfuric acid, dihydroquinacridone IX is the major product. Use of copper powder in 70% sulfuric acid leads to 6,13-dihydroxyquinacridone (XIX) in 70% yield (26).



XIX

By heating with zinc dust in phosphoric acid, quinacridonequinone VI is converted to quinacridone IV in 85% yield (27). Zinc in molten aluminum chloride reduces VI to a mixture of quinacridone IV and dihydroquinacridone IX (143). However, if the reduction is carried out at lower temperatures in mixtures of aluminum chloride with sodium chloride, potassium chloride, urea, or acetamide, excellent yields of quinacridone IV are obtained (26, 28, 30). Reduction of quinacridonequinone VI with zinc and sodium hydroxide in an aqueous alcoholic medium at 200° under pressure yields a mixture of quinacridone IV and dihydroquinacridone IX (29). A number of substituted linear-*trans*-quinacridones described in the literature are listed in Table I.

4. Synthesis of 2,5-Diarylaminoterephthalic Acid

The two general methods available for the preparation of diarylaminoterephthalic acids use 2,5-dihaloterephthalic acids or 2,5-diarylamino-3,6-dihydroterephthalic acids as starting materials.

a. From 2,5-Dihaloterephthalic Acids

Moderate yields of 2,5-diarylaminoterephthalic acids are obtained by reacting an excess of aromatic amines with 2,5-dichloroterephthalic acid or its diesters (75). The components are heated in buffered aqueous ethylene glycol in the presence of copper acetate and potassium iodide (62, 155). However, better yields are obtained by using 2,5-dibromoterephthalic acid or its diesters. For example, 2,5-dibromoterephthalic acid and aniline heated in dimethylformamide in the presence of cuprous chloride and copper powder yield 70% of 2,5-dianilinoterephthalic acid (98). The preparation of 2,5-diarylaminoterephthalic acids with two different arylamino substituents, desirable for the preparation of unsymmetrically substituted linear-*trans*-quinacridones, is accomplished through a two-step reaction sequence. The copper salt of 2,5-dichloroterephthalic acid is heated with aniline in a buffer medium using potassium fluoride as catalyst. The product, 2-chloro-5-anilinoterephthalic acid, is purified by fractional precipitation from alkaline solution and then made to react with the second arylamine (155).

Terephthalic acid can be halogenated in 30–50% oleum solution to yield 2,5-dihaloterephthalic acids (194). Alternatively, 2,5-dihaloterephthalic acids may be prepared by nitric acid oxidation of 2,5-dihalo-*p*-xylene (125, 164). A process for the production of 2,5-dichloroterephthalic acid based on the hydrolysis of 2,5-dichloro-1,4-bis(trichloromethyl)benzene has been described (186).

b. By Dehydrogenation of 2,5-Diarylamino-3,6-dihydroterephthalic Acids

Dehydrogenation of 2,5-diarylamino-3,6-dihydroterephthalic acids or their esters may be carried out by using any of the dehydrogenating agents described for the oxidation of dihydroquinacridones (42, 50). In addition, iodine converts 2,5-diarylamino-3,6-dihydroterephthalic esters to the corresponding 2,5-diarylaminoterephthalic esters in very good yields (100, 127, 128).

B. PROPERTIES

1. Pigmentary Qualities

Linear-*trans*-quinacridones are high melting or infusible, deeply colored solids ranging from orange to

TABLE I
LINEAR-*trans*-QUINACRIDONES

Substituents	Color	Method[a]	% yield	Ref
None	Red	2a	99	71
	Red	1a	92	72
	Red	1b	85	161
	Bluish red	1d	94	4
	Bluish red	3	96	28
	Red-violet	1e	..	158
	Red-violet	2a	93	34
2-Methyl	Red-violet	1c	98	157
3-Methyl	Red	1a	..	192
4-Methyl	Red-violet	1c	..	157
3-Ethyl	Red	1a	..	21
6-Hydroxy	Red-violet	3	80	28
2-Methoxy	Blue-violet	1a	..	21
3-Methoxy	Red	1a	..	21
4-Methoxy	Red-violet	1a	..	21
3-Ethoxy	Red	1a	..	81
2-Fluoro	Red-violet	1a	..	21
3-Fluoro	Red	1a	..	21
4-Fluoro	Orange	1a	..	21
2-Chloro	Red	1a, e	..	192, 158
3-Chloro	Red	1c	..	157
4-Chloro	Bright red	1a	..	192
2-Bromo	Red	1a	..	21
3-Bromo	Red	1a	..	21
4-Bromo	Orange	1a	..	21
3-Nitro	Red	1a	..	21
4-Nitro	Red-violet	1a	..	21
2,9-Dimethyl	Bluish red	1a	94	5
	Red-violet	1d	92	11
	Red-violet	2a	97	172
	Red-violet	2c	..	43
	Violet	1e	92	49
2,11-Dimethyl	Red-violet	1a	..	21
3,10-Dimethyl	Scarlet	1a	..	78
4,11-Dimethyl	Yellowish red	1a	88	5
	Bluish red	1b, d, f	..	171, 86, 88
3-Methyl-9-ethyl	Red	1a	..	21
4,11-Diisopropyl	Bluish red	1b	..	171
2,9-Dicyclohexyl	Bluish red	1b	..	171
3,10-Bis(triphenylmethyl)	Bluish violet	1a	..	191
2,9-Diphenyl	Violet	2a, c	88	34, 40
	Blue-violet	1a	..	191
2,9-Dimethoxy	Red-violet	1a	68	72
	Red-violet	1d	90	11
	Red-violet	2a	97	172
3,10-Dimethoxy	Orange	1b	..	171
3,11-Dimethoxy	Red	1a	..	21
4,11-Dimethoxy	Red	1a	..	39
	Bordeaux	1f	..	88
	Red	2a	82	34
4-Methyl-10-methoxy	Red	1a	..	21
3-Methoxy-10-ethoxy	Red	1a	..	21
2,9-Diethoxy	Blue	1b	..	171
2,9-Diphenoxy	Bluish violet	1a	..	85
	Bluish violet	2a	83	34
4,11-Diphenoxy	Red-violet	2a	88	34
2,9-Difluoro	Red-violet	2a	45	
	Red-violet	1a, e	..	85, 49
3,10-Difluoro	Red	1a	..	192
4,11-Difluoro	Orange	1b	..	38
1,2-Dichloro	Red	1a	..	156
1,4-Dichloro	Red	1a	..	21
2,3-Dichloro	Violet-red	1a	..	156
2,4-Dichloro	Red	1a	..	21

TABLE I (*Continued*)

Substituents	Color	Method[a]	% yield	Ref
2,9-Dichloro	Bluish red	1a	92	191
	Bluish red	2a	90	172
	Red-violet	2a	..	43
	Red-violet	1b	91	162
	Violet	1d, f	..	86, 88
3,4-Dichloro	Red	1a	..	21
3,10-Dichloro	Red	1a	..	78
	Red	1e	98	158
3,11-Dichloro	Orange	1a	..	21
4,11-Dichloro	Orange	2a	84	43
	Red-orange	1a	88	72
	Red	1a, e	60	85, 49
4-Chloro-11-bromo	Orange	1a	..	21
6,13-Dichloro	Red	3	85	139
2,9-Dibromo	Brown	1a	..	76
3,10-Dibromo	Bluish red	1a	..	78
4,11-Dibromo	Red-orange	1a	88	67
2,9-Diiodo		1a	..	72
2-Chloro-4-methyl	Red	1a	..	156
2,9-Dianilino	Blue-violet	1a	..	191
4,11-Dipyridyl	Bluish red	1a	..	191
3,10-Dinitro	Red-violet	1a	..	156
4,11-Dinitro	Red	1a	..	21
6,13-Dihydroxy	Red-violet	3	70	26
2,9-Disulfonic	Dark brown	1e	..	41
2,9-Disulfonilamide	Bluish red	..	..	183
1:2-Benzo	Red	1a	..	192
2,9-Bis(diethylamino)	Grayish blue	1b	..	171
3,10-Bis(benzoylamino)	Bluish red	1a	..	76
3,10-Bis(*m*-chlorobenzoylamino)	Red	1a	..	76
3,10-Bis(trifluoromethyl)	Bluish red	1a	..	191
2,9,11-Trimethyl	Red-violet	1a	..	21
2,9,11-Trimethoxy	Violet	1a	..	21
1,2,4-Trichloro	Red	1a	..	21
1,4,11-Trichloro	Orange	1a	..	21
2,3,11-Trichloro	Red	1a	..	21
2,4,11-Trichloro	Red	1a	..	21
3,4,11-Trichloro	Red	1a	..	21
1,4-Dibromo-11-chloro	Orange	1a	..	21
2,4-Dibromo-11-chloro	Red	1a	..	21
2-Chloro-8:9-benzo	Brown-red	1a	..	192
1:2,8:9-Dibenzo	Orange-red	1b	..	129
	Orange	2a	..	43
2:3,9:10-Dibenzo	...	1a	..	72
3:4,10:11-Dibenzo	Orange	2a	87	43
	Orange	1a	83	5
1:2,8:9-Dinaphtho	Orange-yellow	1b	..	38
3:4,10:11-Dinaphtho	Orange	1b	..	38
1,3,8,10-Tetramethyl	Bluish red	1a, f	..	76, 88
	Orange-red	1b	..	38
1,4,8,11-Tetramethyl	Orange	1d	..	198
2,4,9,11-Tetramethyl	Yellowish red	1d	..	4
	Red	1a	..	31
	Bluish red	1b	..	38
4,11-Dimethyl-2,9-dimethoxy	Red-violet	2a	81	34
2,9-Dimethyl-4,11-diethoxy	Red	1b	..	171
1,8-Dimethyl-3,10-dichloro	Scarlet	1a	..	78
2,9-Dimethyl-3,10-dichloro	Bluish red	1a	90	78
2,9-Dimethyl-4,11-dichloro	Bluish red	1a	..	78
4,11-Dimethyl-11,8-dichloro	Brownish red	1a	..	78
4,11-Dimethyl-2,9-dichloro	Red	1a	..	156
	Bluish red	1d	..	198
4,11-Dimethyl-3,10-dichloro	Scarlet	1a, b	..	78, 171
1,4,8,11-Tetrafluoro	Orange	2a	..	173
2,4,9,11-Tetrafluoro	Orange	2a	..	173

TABLE I (*Continued*)

Substituents	Color	Method[a]	% yield	Ref
1,2,8,9-Tetrachloro	Red	2a	..	173
1,3,8,10-Tetrachloro	Orange-red	2a	..	173
1,4,8,11-Tetrachloro	Yellowish red	1d, 2a	..	198, 173
2,3,9,10-Tetrachloro	Red-violet	1d	88	11
	Red	2a	..	173
2,4,9,11-Tetrachloro	Orange-red	1a, e	..	31, 41
	Orange-red	2a, c	..	173, 400
2,4,10,11-Tetrachloro	Red	1a	..	221
3,4,10,11-Tetrachloro	Orange-red	2a	..	173
	Orange	1d	93	11
1,4,8,11-Tetrabromo	Orange	2a	..	173
2,3,9,10-Tetrabromo	Red	2a	..	173
2,4,9,11-Tetrabromo	Orange	2a	..	173
2,4,9,11-Tetraiodo	Orange	2a	..	173
1,2,4,8,9,11-Hexachloro	Red	1a	..	21
1,4,8,11-Tetramethoxy-2,9-bis-(benzoylamino)	Violet	1b	..	38
Decachloro	Brown	...	..	129
Dodecachloro	Brown	...	..	129
5,12-Dimethyl	Orange	1e	..	129
5,12-Diphenyl	Orange	1e	..	129
1:2,8:9-Dibenzo-5,12-diphenyl	Orange	1e	..	129
4,11-Diphenyl-6,13-dihydroxy	Blue-violet	...	90	153
4,11-Dimethoxy-6-13-dihydroxy	Violet	...	66	153
4,11-Diphenoxy-6,13-dihydroxy	Violet	...	48	153
4,11-bis(2'-methyl-phenoxy)-6,13-dihydroxy	Violet	...	67	153
1:2,8:9-Dibenzo-6,13-dihydroxy	Violet	...	48	153

violet. They are insoluble in all the common organic solvents. However, the 5,12-disubstituted derivatives are weakly colored and are soluble in alcohol and pyridine. Not all of the compounds are obtained in a pigmentary form. Much effort has been expended in finding methods to prepare derivatives of linear-*trans*-quinacridone in a uniform, finely divided state.

The tinctorial power of linear-*trans*-quinacridone IV is enhanced by ball-milling with anhydrous aluminum chloride. The resulting dark blue complex is decomposed with dilute acids (110). The particle size of IV is also reduced by dry ball-milling (137) or grinding with sodium chloride (154, 179) or aluminum sulfate (109). A pigment of soft texture and good coloring power has been obtained by grinding quinacridone IV with small amounts of organic solvents (37, 131). The light stability of quinacridone pigments may be increased by the addition of small amounts of manganese salts (63).

Polyvinyl chloride containing quinacridone pigments has been pressed into films resistant to light and heat (138). For bright pink to deep bluish red coloration of linear polyamides, 2,9-dimethyl-linear-*trans*-quinacridone has been described as an outstanding pigment (6). The ductility of polypropylene is increased without change in melt index, hardness, and elasticity by the addition of approximately 20 ppm of quinacridone IV (59). However, when present in the extent of 2%, quinacridone IV promotes crystallization of molten isotactic polystyrene (115).

Aqueous dispersions of quinacridone IV containing certain surfactants dye polyolefin fibers to yellowish pink shades (23). A derivative of linear-*trans*-quinacridone IV which does not flocculate or crystallize in nonaqueous media has been described (107). Thus far, no commercial application of soluble dyes derived from linear-*trans*-quinacridones has been made (117).

2. *Spectral Properties*

The visible absorption spectra of linear-*trans*-quinacridones have been described only in a few cases. Because of the great insolubility of these compounds in common organic solvents, the spectra are usually recorded in sulfuric acid solutions. There are three absorption peaks between 480 and 640 mμ and strong absorption below 400 mμ. The visible spectra of linear-*trans*-quinacridones in solvents like 1-chloronaphthalene and *t*-butylformamide show only two peaks above 480 mμ. Figure 1 shows the visible absorption spectra of linear-*trans*-quinacridone (IV) in concentrated sulfuric acid and *t*-butylformamide (118). The data for the visible spectra of derivatives of linear-*trans*-quinacridones in concentrated sulfuric acid are summarized in Table II. The position of the longest wavelength absorption maxima has been recorded by Hashizume for several compounds (100).

In sulfuric acid solution, linear-*trans*-quinacridones show strong absorption (log ϵ 5) in the ultraviolet region as shown in Figure 2 (118). The position of the absorption maxima for some of the compounds is listed in Table III (100).

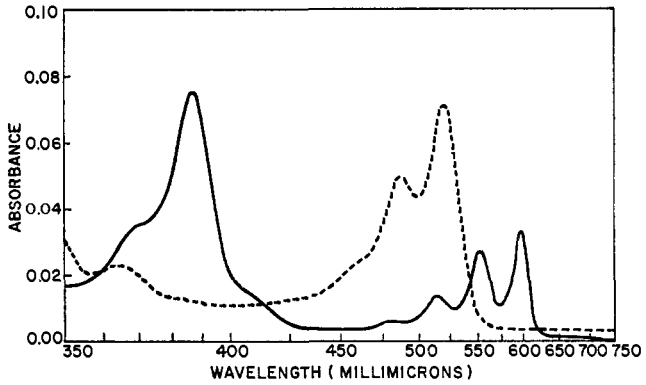


Figure 1. Visible spectra of linear-*trans*-quinacridone IV (solid line in concentrated H_2SO_4; dashed line in *t*-butylformamide).

TABLE II
VISIBLE SPECTRA OF LINEAR-*trans*-QUINACRIDONES

Substituents	Absorption maxima, mμ λ_1	λ_2	λ_3	λ_4
None	597	551	514	387
3-Methyl	593	550	514	390
2-Chloro	603	557	519	398
4-Chloro	604	558	520	385
2,9-Dimethyl	605	560	519	393
2,9-Dimethoxy	610	568	530	
2,9-Difluoro	604	557	517	388
2,9-Dichloro	610	564	522	397
3,10-Dimethyl	610	570	530	
4,11-Dimethyl	605	560	520	
3,10-Dimethoxy	560	520	486	
3,10-Dichloro	605	559	522	
2,3-Dichloro	606	559	520	
4,11-Dichloro	605	567	528	
4,11-Dimethoxy	635	588	540	
2-Chloro-4-methyl	606	559	521	392
1:2-Benzo	577	536	460	402
2-Chloro-8:9-benzo	569	529	490	436
2,9-Dichloro-4,11-dimethyl	618	569	529	

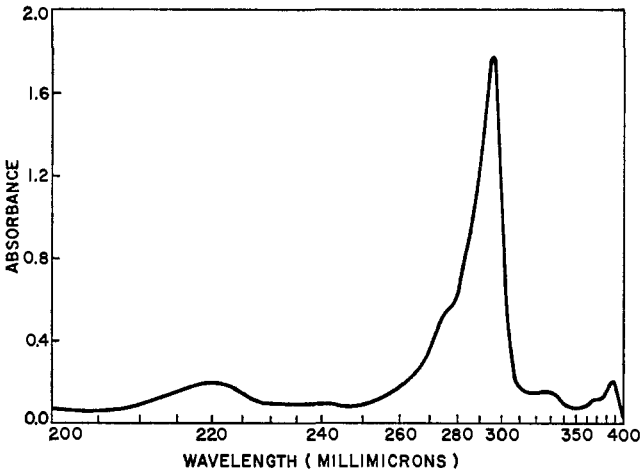
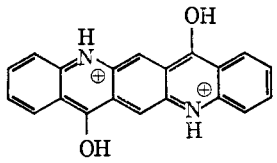


Figure 2. Ultraviolet spectrum of linear-*trans*-quinacridone IV in concentrated H_2SO_4.

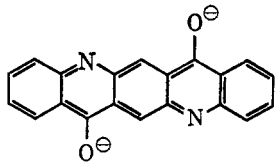
The visible spectrum of quinacridone IV in concentrated sulfuric acid shows remarkable similarity to the visible spectrum of pentacene. This, of course, is to be expected from structure IVa. Three peaks above 500 mμ correspond to the ^1L_a band of pentacene. Absorptions at 387 and 297 mμ will then correspond to the ^1L_b and ^1B_b transitions of pentacene. Simple HMO calculations identify the lowest energy band (597 mμ) as the transition from the highest occupied (B_g) point group (C_{2h}) level to the lowest empty (A_u) level. The band in the ultraviolet region at 387 mμ originates from transitions between the second highest occupied (A_u) and the second lowest unoccupied (B_g) levels. The absorption at 297 mμ corresponds to transitions between the highest occupied (B_g) and the third lowest unoccupied (A_u) levels (118). The visible spectra of quinacridone IV in strong alkali are very similar to that in concentrated sulfuric acid with the exception that all the absorption bands are shifted to longer wavelengths. These spectra are indicative of the completely aromatic structure IVb (118).

TABLE III
ULTRAVIOLET SPECTRA
OF LINEAR-*trans*-QUINACRIDONES

Substituents	λ_{max}, mμ
None	297
2,9-Dimethyl	303
2,9-Dimethoxy	308
2,9-Difluoro	297
2,9-Dichloro	305
3,10-Dimethyl	302
3,10-Dimethoxy	296
3,10-Dichloro	303
4,11-Dimethyl	299
4,11-Dimethoxy	308
4,11-Dichloro	302

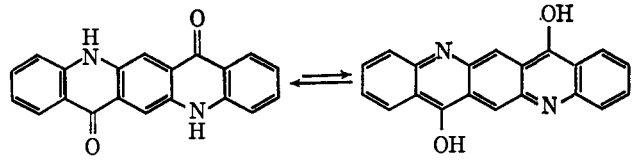


IVa



IVb

The visible spectrum of quinacridone IV in *t*-butylformamide suggests that this compound exists in the ketonic form IV and not in the enolic form IVc. This



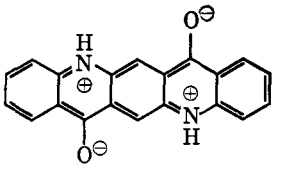
IV IVc

TABLE IV
X-RAY DIFFRACTION PATTERN OF LINEAR-*trans*-QUINACRIDONE IV[a]

α phase	β phase	γ phase	γ′ phase	δ phase	
14.24 (s)	15.23 (s)	13.58 (s)	13.58 (s)	15.1 (w)	3.34 (s)
7.13 (m)	7.55 (m)	6.70 (m)	6.75 (m)	13.6 (m)	3.28 (w)
6.32 (m)	5.47 (m)	6.41 (s)	6.65 (m)	6.63 (m)	3.247 (w)
5.30 (m)	4.06 (m)	5.24 (m)	6.46 (s)	6.41 (s)	3.184 (w–m)
4.27 (w)	3.31 (s)	4.33 (s)	5.21 (m)	5.23 (w)	3.119 (w)
3.46 (s)		3.74 (m)	4.33 (w)	4.36 (w)	2.948 (w)
3.19 (s)		3.37 (s)	3.74 (m)	4.11 (w)	2.915 (w)
			3.56 (w)	4.00 (w)	2.813 (w)
			3.37 (s)	3.74 (m)	2.413 (w)
				3.64 (w)	2.0208 (m)
				3.55 (m)	2.179 (w)
				3.37 (s)	

[a] Interplanar spacings in angstrom units: w = weak, m = medium, s = strong.

view is supported by the fact that the spectrum is unchanged when the two hydrogen atoms are replaced by methyl groups as in 5,12-dimethylquinacridone. The carbonyl absorption at 1625 cm^{-1} in the infrared spectrum is consistent with ketonic structure IV and also indicates that resonance form IVd is of less importance.



IVd

3. *Polymorphism*

Linear-*trans*-quinacridones XVII exist in polymorphic forms (134). Three distinct crystal phases for 2,9-dichloro-linear-*trans*-quinacridone (22, 57, 142) and two for 2,9-dimethoxy-linear-*trans*-quinacridone (47) have been described. The five different crystal modifications of linear-*trans*-quinacridone IV range in color from yellowish red to violet. The characteristic X-ray diffraction patterns of these crystal modifications of IV are listed in Table IV.

X-Ray diffraction data have been obtained on powder samples and are used only to distinguish one crystal phase from another. Detailed study of these polymorphic forms has not been described. Information about the number of molecules in a unit cell and the stacking and interaction of molecules in the different crystal forms is not available. Crystallographic evidence about the planarity of the quinacridone molecule has not been given. Molecular models, however, show that quinacridone IV is planar.

a. α-Crystal Form of Linear-*trans*-quinacridone

In the α form linear-*trans*-quinacridone IV is bluish red. In this crystalline state quinacridone IV is not useful as a pigment.

A variety of condensing agents cyclize 2,5-dianilinoterephthalic acid to linear-*trans*-quinacridone IV in the α-crystal form (43). This α modification is the sole product obtained by precipitation from sulfuric acid solution, or upon its being heated with aqueous potassium hydroxide (180). The other forms of IV are converted to the α form when dry ball-milled with sodium chloride (154, 179).

b. β-Crystal Form of Linear-*trans*-quinacridone

In the β-crystal modification, linear-*trans*-quinacridone IV is valued as a brilliant violet pigment (176).

Other crystal forms of IV are converted to the β modification when ball-milled with sodium chloride in the presence of a small amount of a chlorinated aromatic hydrocarbon (179). Precipitation from polyphosphoric acid solution by the addition of acetone (5) or methanol (92), or from methylsulfuric acid solution by the addition of water (12), yields quinacridone IV in the β-crystal phase. Methods for conversion of the α to β form by heating with sodium hydroxide under pressure have been described (83, 89). Linear-*trans*-quinacridone IV is precipitated in the β-crystal form from alcoholic sodium hydroxide solution by water or dilute acid (87).

c. γ-Crystal Form of Linear-*trans*-quinacridone

Quinacridone IV in the γ-crystal form possesses a red color with blue undertone (77). Since it is stable to light and organic solvents, it is a valuable pigment (132), especially in the form of a rosinated lake (69).

The γ-crystal modification of IV is prepared by dehydrogenation of 6,13-dihydroquinacridone using sodium *m*-nitrobenzenesulfonate in the presence of pyridine (70, 94). When quinacridone IV is ball-milled with sodium chloride in the presence of dimethylformamide, it is converted to the γ form (179). If the other crystal modifications of quinacridone IV are heated with organic solvents, such as quinoline (82), xylene (53, 54, 101), *p*-cresol (181), or dimethyl sul-

foxide (22, 182), the γ form results. When dimethyl sulfoxide is used, the addition of a small amount of boric acid helps to prevent pyrolysis of the solvent (199). The γ modification is obtained by heating the α form in aqueous ethanol under pressure (90) or in alcoholic potassium hydroxide (43, 84). However, it is interesting to note that aqueous potassium hydroxide converts the γ form to the α form (180).

A different γ modification of linear-*trans*-quinacridone is obtained when the α-crystal form is heated with N-methylpyrrolidone (15, 55). Cyclization of 2,5-dianilinoterephthalic acid with benzoyl chloride in the presence of N-methylpyrrolidone also yields this new γ form (161). The new modification, a yellowish red pigment, is described as one which possesses good fastness, high purity of shade, superior hiding power, and intense brilliance (55). The new γ form, in contrast to the earlier γ form, shows no absorption at 13.35 μ in the infrared spectrum (58, 161).

d. δ-Crystal Form of Linear-*trans*-quinacridone

Linear-*trans*-quinacridone IV in its δ-crystal modification is prepared by sublimation under vacuum at temperatures above 400°. It possesses a pure red color much like that of the second γ-crystal form of IV. The X-ray diffraction pattern shows some resemblances to that of the γ-crystal forms (165, 166).

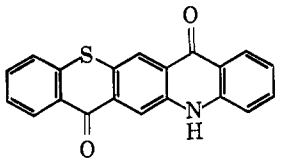
4. Solid Solutions

In attempts to obtain pigments of various shades possessing the fastness and brilliance of linear-*trans*-quinacridones, their solid solutions with other colored compounds have been investigated. The color resulting from simple physical mixtures of components is predictable. However, solid solutions give rise to unpredictable tinctorial values. Solid solutions are also characterized by the fact that the X-ray diffraction pattern differs from the sum of the X-ray diffraction patterns of the constituents (108). The components of the solid solution become coinhabitors of the same crystal lattice, often the lattice of one of the individual components.

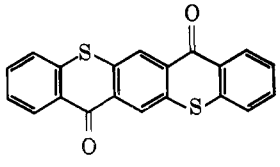
Solid solutions of two or more quinacridones are prepared by precipitation of a mixture of the components from solution in sulfuric acid or polyphosphoric acid followed by heating in an organic solvent, such as dimethylformamide (74). Alternatively, the components can be intimately mixed by ball-milling with aluminum sulfate, then washed free of the salt before heating with an organic solvent (74). A simultaneous preparation of the two quinacridones leading to a solid solution is accomplished by beginning with a mixture of the appropriate aromatic amines in any of the synthetic methods for linear-*trans*-quinacridones (192, 195).

Not only have solid solutions been prepared from mixtures of various linear-*trans*-quinacridones but also from the quinacridones and quinacridonequinones, linear-*cis*-quinacridones, or dihydroquinacridones to yield pigmentary products with enhanced light fastness or a particularly desired shade (65).

In particular, solid solutions of orange shades containing linear-*trans*-quinacridone and thiachromono-[2,3-*b*]acridones (XX) (193, 196, 197) and benzobisthiachromones (XXI) are described (32, 190, 196). A solid solution of 2,9-dichloro-linear-*trans*-quinacridone and 2,9-dichlorothiachromonoacridone is an excellent red pigment (106).



XX



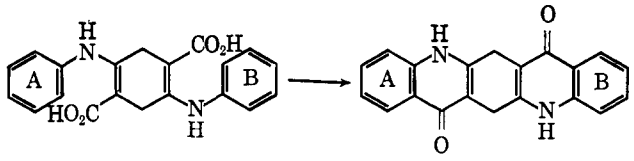
XXI

V. 6,13-Dihydro-linear-*trans*-quinacridones

Derivatives of 6,13-dihydro-linear-*trans*-quinacridone (IX) are important intermediates in the preparation of linear-*trans*-quinacridones.

A. Methods of Preparation

Dihydroquinacridones XVIII are prepared by the cyclization of 2,5-diarylamino-3,6-dihydroterephthalic acids (XXII) under various conditions.

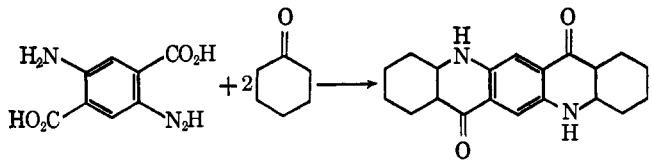


XXII XVIII

This cyclization is achieved by heating XXII in inert high-boiling solvents (66). A mixture of 76.5% diphenyl oxide and 23.5% biphenyl, commerically known as Dowtherm A (130), is especially useful for this purpose, and it gives 60–75% yields of XVIII, the derivatives of IX with substituents in rings A and B (133, 172). Polyphosphoric acid is also a useful agent for cyclization of 2,5-diarylamino-3,6-dihydroterephthalic esters to dihydroquinacridones in almost quantitative yields (34, 51).

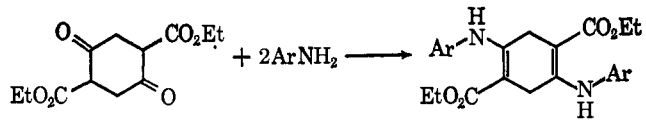
A one-step process for the manufacture of dihydroquinacridone IX by condensing aniline with diethyl succinylsuccinate in polyphosphoric acid has been described (36). Diethyl 2,5-diarylamino-3,6-dihydroterephthalates, when heated with anhydrous hydrofluoric acid at 145° under pressure, give dihydroquinacridones in yields greater than 80% (35). A melt of aluminum chloride and sodium chloride in a 4:1 ratio at 180° has also been used in the cyclization of XXII to XVIII (39).

An example of 1,2,3,4,8,9,10,11-octahydro-linear-*trans*-quinacridone (XXIII) has been described. The octahydro derivative XXIII is prepared by treating 2 moles of cyclohexanone with 2,5-diaminoterephthalic acid in concentrated sulfuric acid (146).



XXIII

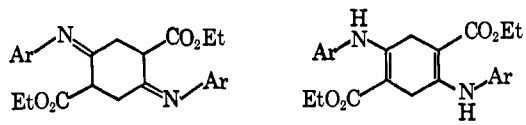
Various 2,5 - diarylamino - 3,6 - dihydroterephthalic acids (XXII) are easily prepared from diethyl cyclohexane-1,4-dione-2,5-dicarboxylate (XXIV) (99). In the literature XXIV has been described as diethyl succinylsuccinate or ethyl succinosuccinate (18, 60, 61, 102, 103). Diethyl succinylsuccinate (XXIV) can be prepared from diethyl succinate (18, 169, 170, 178) or diketone (99).



XXIV XXII

The condensation of XXIV with aromatic amines is effected in boiling alcohol containing glacial acetic acid or hydrochloric acid under a nitrogen atmosphere (127, 135, 136, 150). This condensation can also be carried out in Dowtherm A using *p*-toluenesulfonic acid (95) or an arylamine hydrochloride as catalyst (174).

There has been some controversy about the existence of two tautomeric forms of the esters of 2,5-diarylaminoterephthalic acids (XXII). A colored form XXIIa and a colorless form XXIIb have been proposed (20, 93, 127). It was later shown that the 2,5-diarylamino-3,6-dihydroterephthalic esters exist only in one form, namely XXIIb, and are practically colorless.



XXIIa XXIIb

The color which is observed in some instances for XXII arises from the oxidation of these compounds by atmospheric oxygen to form the highly colored 2,5-diarylaminoterephthalic esters XVI (116).

B. PROPERTIES

Dihydroquinacridone IX and its substituted derivatives are light tan or salmon to brown colored solids. These compounds are insoluble in ethanol, acetone, benzene, and in aqueous alkalies. However, they dissolve in concentrated sulfuric acid and in alcoholic alkalies giving reddish yellow solutions. Dihydroquinacridones are stable to heat up to 400° but are readily oxidized to intensely colored quinacridones when heated in air (133).

As do linear-*trans*-quinacridones, 6,13-dihydro-linear-*trans*-quinacridones show polymorphism. Two different crystal forms, designated α and β, are described for dihydroquinacridone IX.

Dihydroquinacridone IX in the α-crystal form is characterized by an X-ray diffraction pattern consisting of five strong lines corresponding to interplanar spacings of 3.32, 3.50, 6.41, 7.01, and 14.01 A. Cyclization of 2,5-dianilino-3,6-dihydroterephthalic acid in nonpolar, inert, high-boiling liquids yields dihydroquinacridone IX in its α form. Alternatively, IX can be obtained in the α-crystal phase by precipitation from sulfuric acid solution upon addition of water (177).

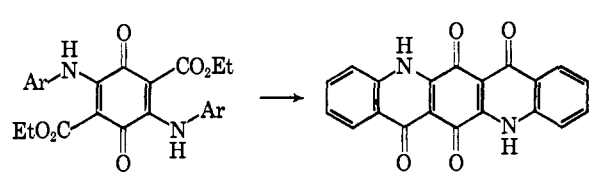
Dihydroquinacridone IX in the β-crystal form shows eight lines in its X-ray diffraction pattern. The strongest of these lines correspond to interplanar spacing of 11.77 A. Lines of medium intensity are seen at 3.23, 3.67, 5.68, and 5.96 A, and three weak lines corresponding to interplanar spacings of 3.83, 4.28, and 6.32 A. Cyclization of 2,5-dianilino-3,6-dihydroterephthalic acid in polar solvents such as tetramethyl sulfone yields dihydroquinacridone IX in the β-crystal form. α crystals of IX are converted to the β-crystal phase by refluxing with dimethylformamide or by the action of strong aqueous alkalies.

VI. LINEAR-*trans*-QUINACRIDONEQUINONES

A. METHODS OF PREPARATION

1. Cyclization of 2,5-Diarylamino-3,6-dicarbethoxy-1,4-benzoquinone

Derivatives of linear-*trans*-quinacridonequinone VI are obtained in good yields by cyclization of 2,5-diarylamino-3,6-dicarbethoxy-1,4-benzoquinone (XXV), carried out by heating in organic solvents usually at tem-

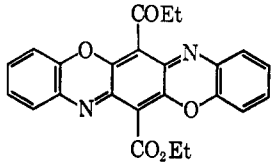


XXV VI

peratures from 230 to 270°. The aromatic amino residues may be mono-, di-, or trisubstituted with a large variety of substituents leading to the appropriately substituted linear-*trans*-quinacridonequinones (9, 111).

Although this method is quite general, possessing the advantages of readily attainable starting materials, relatively good yields, and pure products, some difficulties arise from a side reaction leading through cycliza-

tion to triphenodioxazine-9,10-dicarboxylate (XXVI). The formation of XXVI represents only a few per cent yield in some instances; however, in others XXVI is the major product obtained (52).

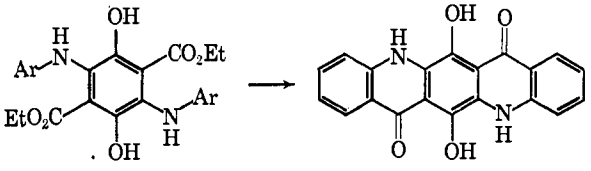


XXVI

The side reaction is favored by the presence of an active hydrogen or an ether function in the position *ortho* to the amino group. Acids catalyze the formation of side product XXVI, and temperatures of cyclization below 200° also favor XXVI (153).

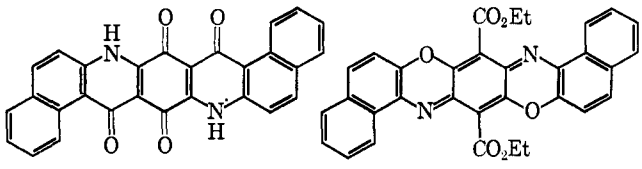
2. *Oxidation of 6,13-Dihydroxy-linear-trans-quinacridones*

In an attempt to overcome the difficulties associated with the side reaction leading to the formation of XXVI, the 2,5-diarylamino-3,6-dicarbethoxy-1,4-benzoquinones (XXV) are reduced in alcoholic solution or suspension by adding an excess of bisulfite or sodium metal to the corresponding dihydroxy compounds



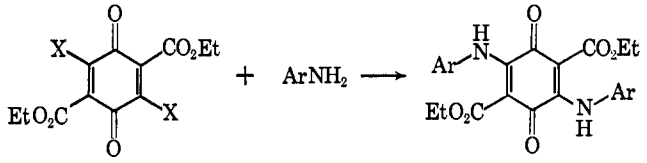
XXVII XIX

XXVII. Cyclization of XXVII by heating in inert organic solvents at 230–270° yields the 6,13-dihydroxy-linear-*trans*-quinacridones (XIX). The dihydroxy compounds XIX are more intensely colored than derivatives of linear-*trans*-quinacridonequinone VI. Oxidation of compound XIX is accomplished by refluxing with nitrobenzene, chloranil, nitric acid, or chromic acid to produce linear-*trans*-quinacridonequinones in good yields. Not only does this multistep preparation lead to linear-*trans*-quinacridonequinones with better pigmentary quality, but it also permits or favors the preparation of some substituted VI, otherwise difficult or impossible to obtain (113). For example, 1:2,8:9-dibenzo-linear-*trans*-quinacridonequinone (XXVIII) is formed in moderate yields by method 2, while method 1 largely produces the corresponding triphenodioxazine-3,6-dicarboxylate (XXIX) (153).



XXVIII XXIX

The starting material, 2,5-diarylamino-3,6-dicarbethoxy-1,4-benzoquinone (XXV), for both methods discussed thus far, is prepared by condensing 2 moles of primary aromatic amine with 1 mole of 2,5-dichloro- or 2,5-dibromo-3,6-dicarbethoxy-1,4-benzoquinone (XXX) in ethanol (9, 52, 96, 97).

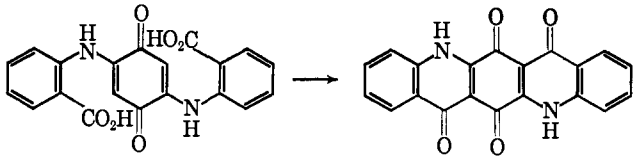


XXX XXV

X = Cl or Br

3. *Cyclization of 2,5-Bis(2′-carboxyanilino)-1,4-benzoquinone*

The classic method (and until 1962 only known method) for the preparation of linear-*trans*-quinacridonequinones consisted of cyclization of 2,5-bis(2′-carboxyanilino)-1,4-benzoquinone (XXXI) and its substituted analogs (167). Heating XXXI for periods of 30 min to several hours in concentrated sulfuric acid at temperatures between 150 and 200° yields VI (122, 126, 167). Polyphosphoric acid has also been used for this cyclization (16).



XXXI VI

The starting material, 2,5-bis(2′-carboxyanilino)-1,4-benzoquinone, is obtained by the addition to 1,4-benzoquinone of anthranilic acid or substituted anthranilic acids (187). A variety of methods can be employed for the condensation of anthranilic acid and benzoquinone. In one of them, the two components are heated in ethanol (1). Benzoquinone and anthranilic acid can also be condensed in acetic acid (141, 144) or in an aqueous acidic medium (pH 2–5) using vanadium pentoxide as catalyst and sodium chlorate as oxidizing agent (112). The cyclization of 2,5-bis(2′-carboxyanilino)-1,4-benzoquinone (XXXI) suffers from the disadvantage that the substituted anthranilic acids are much more difficult to obtain than the primary simple or substituted aromatic amines used in the preparation of 2,5-diarylamino-3,6-dicarbethoxy-1,4-benzoquinones (XXV).

Linear-*trans*-quinacridonequinones made by these methods are listed in Table V.

B. PROPERTIES

Linear-*trans*-quinacridonequinones are highly colored yellow to red compounds, practically insoluble in the

TABLE V
LINEAR-*trans*-QUINACRIDONEQUINONES

Substituents	Color	Method	% yield	Ref
None	Brownish yellow	1	83	153
	Brownish yellow	2	...	113
	Brownish yellow	3	83	112
3,10-Dimethyl	Yellow	1	86	111
4,11-Dimethyl	...	3	...	112
2,9-Dimethoxy	Maroon	1	97	111
	Brown	3	...	126
2,9-Dihydroxy	Brown	3	...	126
4,11-Dimethoxy	Dark red	1	86	9
2,9-Diphenyl	Red-orange	1	...	9
4,11-Diphenyl	Orange	1	86	153
2,9-Diphenoxy	Brown	1	93	153
4,11-Diphenoxy	Brown	1	15	153
2,9-Dimethylamino	Violet	1	80	111
2,9-Difluoro	Reddish yellow	1	100	111
2,9-Dichloro	Orange	1	100	111
3,10-Dichloro	Yellow	1	98	111
4,11-Dichloro	Brown-yellow	2	...	113
2,9-Dicarbethoxy	Yellow	1	...	9
2,9-Dinitro	Brownish yellow	1	95	153
3,10-Dinitro	Brown-yellow	1	88	153
1,2:8,9-Dibenzo	Brown-orange	2	90	153
3:4,10:11-Dibenzo	Bluish red	1	...	9
	Orange	2	...	113
3:4,10:11-Diphthaloyl	Greenish brown	1	...	9
2,9-Bis(2-anthraquinonyl)	Violet-brown	1	...	9
1,8-Dichloro-4,11-dimethoxy	Brown-violet	1	77	153
1,8-Dibenzoyl-4,11-dimethoxy	Brown-yellow	1	61	153
2,4,9,11-Tetraphenylthio	Brown-violet	1	80	153
2,4,9,11-Tetrabromo	Brown	3	40	168
1,8-Dichloro-2,9-bis(benzoyl-amino)-4,11-dimethoxy	Red	1	45	153

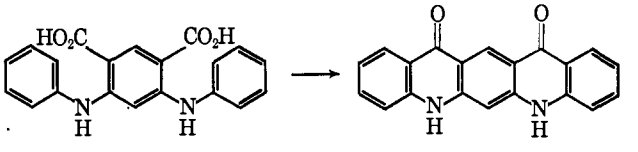
usual organic solvents, possessing high decomposition temperatures rather than melting points. They dissolve in concentrated sulfuric acid to yield colored solutions (153). Commercially, quinacridonequinone VI is used as a pigment for plastics and resins because it is quite stable to heat and light (113).

It has been claimed that formation of the metal chelates of linear-*trans*-quinacridonequinones leads to improved light fastness compared to the parent compounds. Nickel, copper, or zinc chelates were prepared by refluxing the quinacridonequinone in dimethylformamide with a salt of the metal (104). The products obtained were not specific compounds but mixtures of chelates. These ranged from 6.8 to 18.6% in metal content according to the length of reflux time and the particular metal used. Colors varied from yellow to brown and red or reddish violet (104).

VII. LINEAR-*cis*-QUINACRIDONES

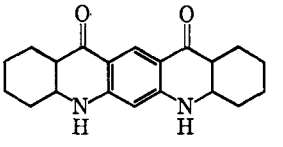
A. METHODS OF PREPARATION

Linear-*cis*-quinacridone VII is prepared by the cyclization of 4,6-dianilinoisophthalic acid (XXXII). This cyclization is carried out by heating the acid XXXII in polyphosphoric acid at 120–160° or in monochloracetic acid containing a small amount of



XXXII VII

concentrated sulfuric acid at about 180° (24). Benzoyl chloride (19), phosphorus pentachloride, and aluminum chloride (62) have also been used for this cyclization with good results. Heating 4,6-dianilinoisophthalic acid with sodium bisulfate at 250° for 2 hr gives a good yield of quinacridone VII (49). The octahydro derivative XXXIII of quinacridone VII is obtained by condensing 4,6-diaminoisophthalic acid with cyclohexanone in an acidic medium (146).



XXXIII

B. PROPERTIES

Linear-*cis*-quinacridone VII exists in three different crystal forms designated as α, β, and γ. Only β- and γ-crystal modifications of VII are useful as pigments,

which impart clear yellow shades to synthetic resins and printing inks. Linear-*cis*-quinacridones are less stable and more soluble than linear-*trans*-quinacridones (19). Powder X-ray diffraction patterns of these forms of linear-*cis*-quinacridone VII are described in Table VI.

TABLE VI
X-RAY DIFFRACTION PATTERNS OF LINEAR-*cis*-QUINACRIDONE VII (19)[a]

α phase	β phase	γ phase
14.2 (s)	14.97 (s)	13.80 (s)
7.19 (s)	13.18 (w)	6.91 (m)
6.32 (m)	11.94 (w)	6.51 (m)
5.47 (w)	7.56 (m)	6.06 (w)
3.47 (m)	6.60 (w)	5.433 (w)
3.21 (m)	5.535 (w)	4.267 (w)
	4.924 (w)	3.735 (w)
	4.092 (w)	3.601 (w)
	3.767 (w)	3.386 (m)
	3.312 (w)	3.324 (w)
	3.005 (w)	3.151 (w)

[a] Interplanar spacing in angstrom units.

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