# 109. Studies on Heterocyclic Colouring Matters Part III[1]): 7a,14a-Diaza-7,7a,14,14a-tetrahydroquino[2,3-*b*]acridine-7,14-diones (5,7a,12,14a-Tetraaza-7,7a,14,14a-tetrahydropentacene-7,14-diones)[2])

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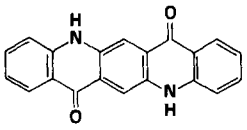
(28.XII.77)

*Summary*

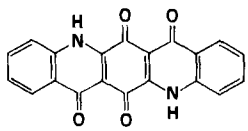
2-Aminopyridines react with diethyl 2,5-dioxo-cyclohexane-1,4-dicarboxylate (diethyl succinylsuccinate) to give 7a,14a-diaza-6,7,7a,13,14,14a-hexahydroquino-[2,3-*b*]acridine-7,14-diones (5,7a,12,14a-tetraaza-6,7,7a,13,14,14a-hexahydropentacene-7,14-diones), which are aromatized to the title compounds. Oxidation of these with a mixture of sulfuric and nitric acids results in the formation of their respective 6,13-quinones, also obtained directly from 2-aminopyridines and diethyl 2,5-dichloro-1,4-benzoquinone-3,6-dicarboxylate. The chromophore of the title compounds is compared with that of quinacridones.

**Introduction.** – Compounds structurally related to quinacridones have become of interest since the introduction of quinacridone and quinacridonequinone as commercial organic pigments. In a search for such compounds, we were interested in constructing heterocyclic analogues of these structures in which the outermost benzenoid rings contained one or more hetero atoms, preferably nitrogen. The work led to the preparation of diazaquinacridine-diones and their quinones, whose chemistry is described.

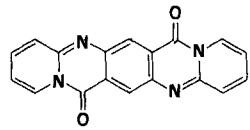
*Scheme 1*



Quinacridone



Quinacridonequinone



7a,14a-Diazaquinacridine-7,14-dione

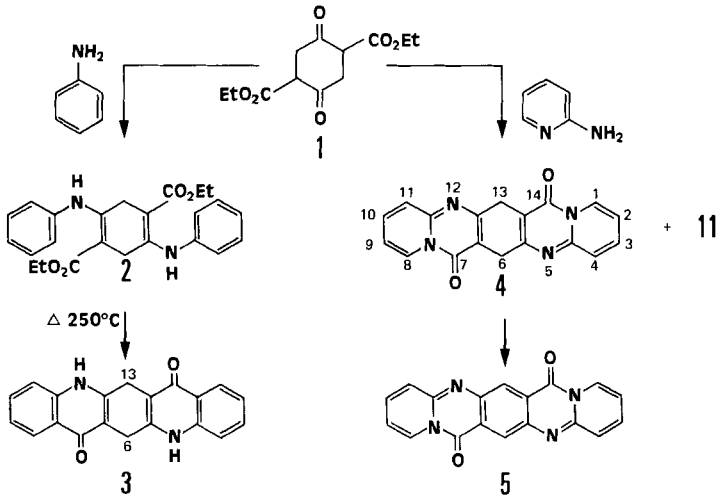
**Results and Discussion.** – Diethyl 2,5-dioxo-cyclohexane-1,4-dicarboxylate (diethyl succinylsuccinate) (**1**), when treated with aniline in acetic acid under reflux leads to

[1]) Part I, [1]. Part II, [2]. Presented at the 6th International Colour Symposium in Freudenstadt, Germany, September 27–October 1, 1976.

[2]) We use this somewhat simpler name throughout, instead of the Chemical Abstracts nomenclature: pyrido[2,1-*b*]pyrido[1′,2′:1,2]pyrimidino[4,5-*g*]quinazoline-7,15-dione.

diethyl 2,5-dianilino-3,6-dihydroterephthalate (**2**). Elevated temperatures, *e.g.* boiling Dowtherm, are required to affect the thermal cyclization of this intermediate to 6,13-dihydroquinacridone (**3**) [3]. By heating in acetic acid, however, the ester **1** reacts with 2-aminopyridine to give 7a,14a-diaza-6,7,7a,13,14,14a-hexahydroquino[2,3-*b*]acridine-7,14-dione (**4**) by simultaneous condensation and cyclization. Analogous to the oxidation of **3** to quinacridone, prolonged heating, *e.g.* in acetic acid in the presence of chloranil, aromatizes **4** to 7a,14a-diaza-7,7a,14,14a-tetrahydroquino[2,3-*b*]acridine-7,14-dione (**5**) obtained as a bright red, insoluble, high-melting solid[3] *(Scheme 2)*.

*Scheme 2*




We have made our structural assignments for the 7a,14a-diazaquinacridine-7,14-diones and their dihydro derivatives reported here on the basis of elemental analysis and mass spectroscopy. NMR. measurements could not be carried out because of the extreme insolubility of the compounds.

Since both basic centres in 2-aminopyridine are involved in its reaction with **1**, we had to distinguish between the proposed linear structure **4**, and its angular isomer **7** which would result if the initial condensation with **1** occurred at the pyridine ring nitrogen in the less likely imino form of 2-aminopyridine. Alternatively the amino tautomer could react through a conjugate acid species to give the angular product *(Scheme 3)*.

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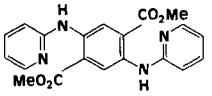
[3]) Since the completion of our work, various phases of it have been reported [4] [5]. See also [6] for a description of the reaction between 2-aminopyridine and dimethyl 2,5-dioxo-cyclohexane-1,4-dicarboxylate as giving 'dimethyl 2,5-bis(2'-pyridylamino)-3,6-dihydroterephthalate' which on subsequent oxidation led to **6**. This report is incorrect.



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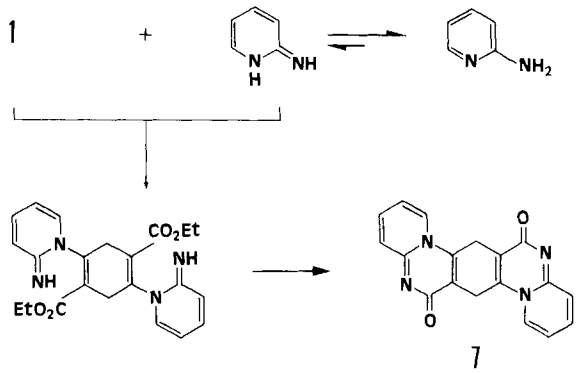
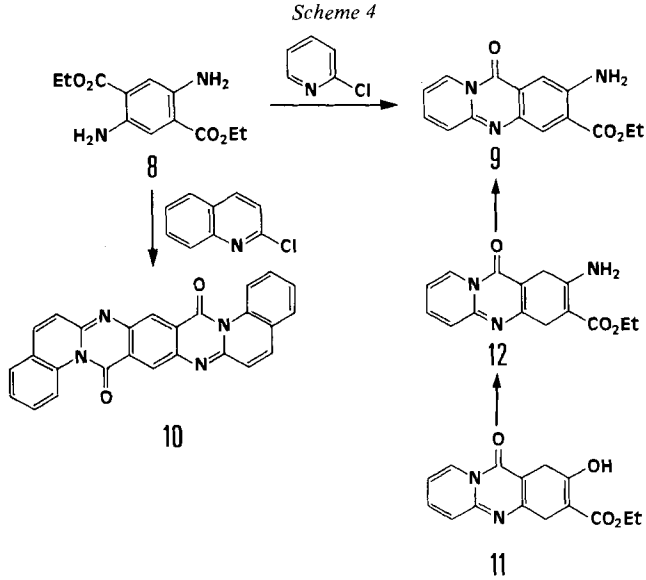
*Scheme 3*



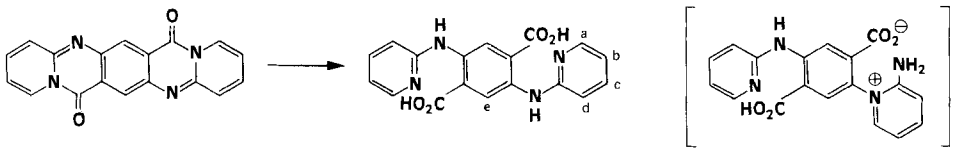
Accordingly, we attempted an unambiguous synthesis of linear 7a,14a-diazaquinacridine-dione **5** from 2-chloropyridine and diethyl 2,5-diaminoterephthalate (**8**) in a manner analogous to the preparation of the yellow dibenzo-7a,14a-diazaquinacridine-dione **10** from 2-chloroquinoline and **8**. The only isolable product from this reaction was, however, the partial reaction product, 2-amino-3-ethoxycarbonyl-8a-azaacridone (**9**) obtained as its hydrochloride in good yield. The free base was further treated with 2-chloropyridine but failed to react. This failure is attributed to the difference in reactivity between 2-chloroquinoline and 2-chloropyridine [7]. Consequently, proof was sought for the anticipated 1,4-dihydro-3-ethoxycarbonyl-2-hydroxy-8a-azaacridone (**11**), a by-product of the reaction between 2-aminopyridine and **1**. Thus, treatment of **11** with ammonium acetate resulted in the formation of its 2-amino derivative **12**. Aromatization of **12** with chloranil gave **9**, thereby providing conclusive evidence for the linearity of **11** *(Scheme 4)*.

*Scheme 4*



Although this sequence of reactions unequivocally proves the linearity of the monocyclization product in the reaction of 2-aminopyridine with **1**, it does not rule out the formation, however improbable, of an unsymmetrical linear/angular structure by further reaction with 2-aminopyridine. Final proof for the complete linearity of the diazaquinacridine-diones was ultimately obtained from results of alkaline hydrolysis *(Scheme 5)*. Treatment of **5** with aqueous potassium hydroxide resulted in ring cleavage to give a quantitative yield of a product whose NMR. is consistent with the symmetrical 2,5-bis(2′-pyridylamino)terephthalic acid (**13**). The equivalence of the carbocyclic protons is clearly shown by the presence of a singlet at 8.46 ppm *(Figure)*. This product can only be derived from the completely linear and hence symmetrical diazaquinacridine-dione **5**. Hydrolysis of a linear/angular structure would undoubtedly lead to the unsymmetrical species **14**, which would show nonequivalence of both carbocyclic and pyridine ring protons. These results further rule out the formation of diazaquinacridone by cyclization at carbon instead of nitrogen, since the hydrolysis conditions employed were singularly mild to cause ring opening of such a product.

*Scheme 5*




5 13 14

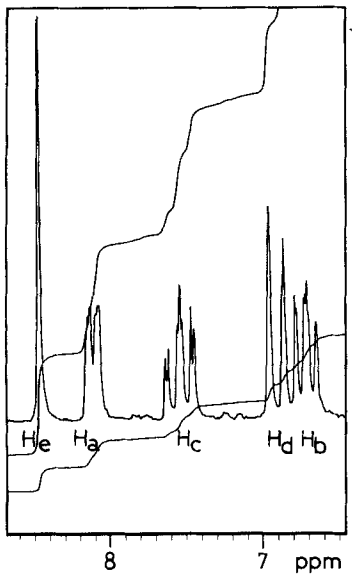
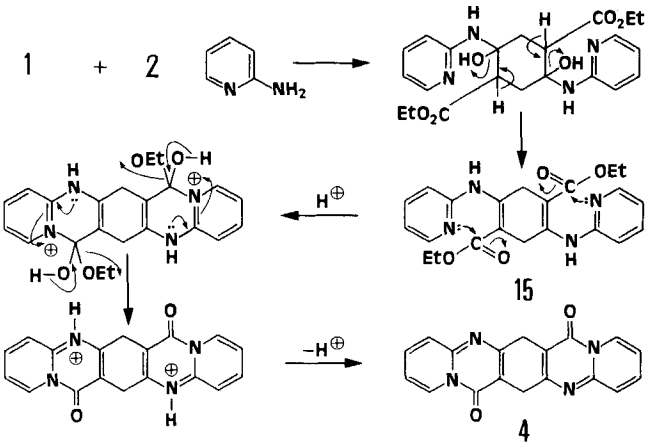



Fig. $^1H$-*NMR. spectrum of* **13** *in* $(CD_3)_2SO$

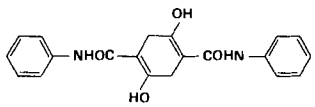
A possible mechanism for the formation of 7a,14a-diaza-6,7,7a,13,14,14a-hexahydroquinacridine-7,14-dione (**4**) is shown in *Scheme 6*. Diethyl 2,5-dioxo-cyclohexane-1,4-dicarboxylate (**1**) and 2 eq. of 2-aminopyridine react by a nucleophilic addition-elimination mechanism either in a synchronous step as shown or stepwise, to form the bis(enamine) **15** irreversibly which is usually not isolated and undergoes spontaneous cyclization to give the final product **4**. The basicity of the pyridine nitrogen is responsible for the facile cyclization.

*Scheme 6*




In the initial step of the reaction, the amino nitrogen is depicted as the nucleophile, although the pyridine nitrogen is known to be more basic. Consequently it is conceivable that reaction at this more basic pyridine nitrogen atom occurs initially, perforce with the ester group of **1** (since reaction with the keto group would lead to the formation of the angular product **7**), as is the case with a number of reactions of 2-aminopyridines [8]. However, since there is no precedent for the reaction of **1** with nucleophiles where the ester group reacts preferentially, this alternative is ruled out[4]). It is also possible that only 1 mol of 2-aminopyridine reacts with a keto group in **1**. The resulting monocondensation product **17** would then cyclize to give **11**, prior to reaction of a second mol of 2-aminopyridine. Evidence for this alternative is provided by the fact that in the reaction of 2-aminopyridine, 2-amino-5-methylpyridine and 2-aminobenzimidazole with **1**, **11**, **19** and **20** are formed respectively, presumably *via* the intermediates **17**, **18** and **21**, in the first two cases as minor products and in the last as the only isolable major product (74%) *(Scheme 7)*.

[4]) However, the condensation of aniline with **1** in the melt at 190° is reported to give 2,5-dihydroxy-3,6-dihydroterephthaldianilide (**16**) [9]. We have been unable to reproduce this reaction.

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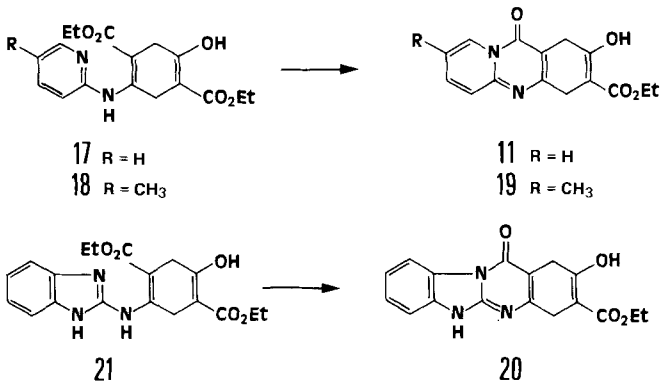
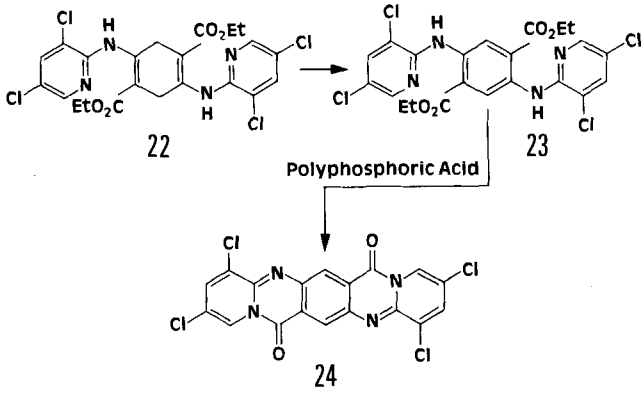
*Scheme 7*




Finally, in the case of 2-amino-3,5-dichloropyridine, the chloro groups sufficiently lower the basicity of the pyridine nitrogen such that cyclization does not occur under the conditions used. The intermediate dihydro ester **22** isolated, after oxidation to the fully aromatic **23**, can be cyclized with polyphosphoric acid (PPA), to give the desired tetrachloro-diazaquinacridine-dione **24** *(Scheme 8).*

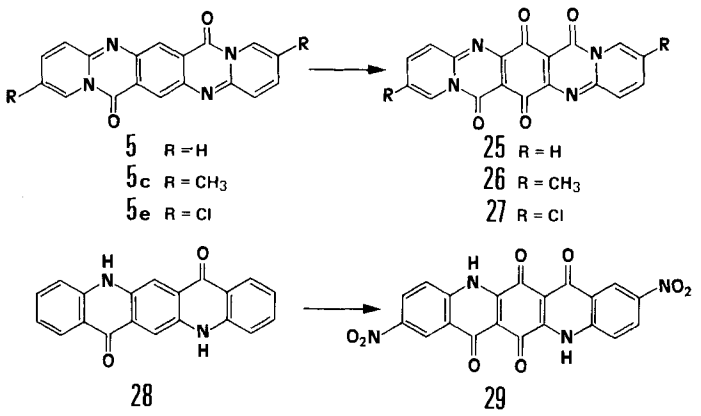
*Scheme 8*



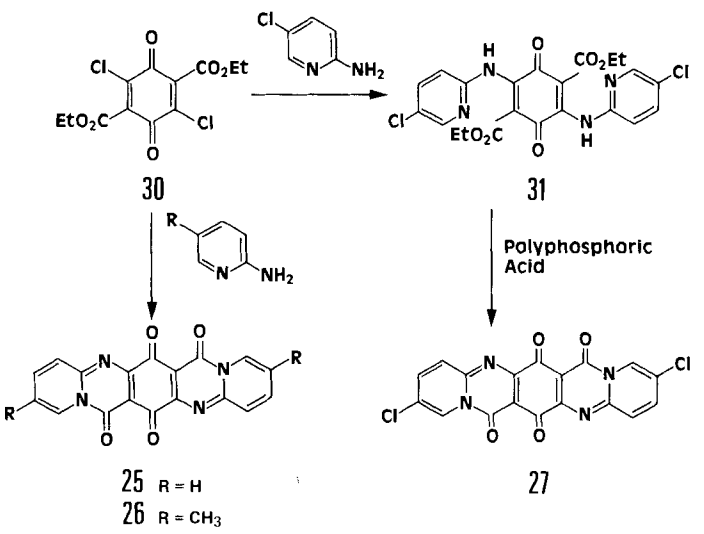

Treatment of the diazaquinacridine-diones **5**, **5c** and **5e** with a mixture of nitric and sulfuric acids resulted in the oxidation of the carbocyclic ring to give the novel, high-melting, insoluble, yellow quinones **25**, **26** and **27** respectively [10]. Similar treatment of quinacridone (**28**) results in simultaneous oxidation and nitration to give 2,9-dinitroquinacridonequinone (**29**). The absence of nitration in the case of the diazaquinacridine-diones is presumably due to deactivation of the pyridine rings in **5**, **5c** and **5e** to electrophilic aromatic substitutions.

The structure of the quinones was verified by their IR. spectra and by their unambiguous preparation from 2-aminopyridines and diethyl 2,5-dichloro-1,4-benzoquinone-3,6-dicarboxylate (**30**) *(Scheme 10).* While 2-aminopyridine and 2-amino-5-methylpyridine gave their respective quinones **25** and **26** in one step, only the initially formed benzoquinone ester **31** could be isolated from 2-amino-

*Scheme 9*




*Scheme 10*




5-chloropyridine; cyclization of **31** in PPA gave the desired quinone **27**. Evidently the chloro group in 2-amino-5-chloropyridine also reduces the basicity of the pyridine nitrogen such that **27** is not formed under the mild conditions used. The identity of the quinones obtained by each route was verified by their superimposable IR. spectra.

It is interesting to note that the colour of the diazaquinacridine-diones differs substantially from those of the corresponding quinacridones as reflected in their respective absorption spectra. The orange to red diazaquinacridine-diones absorb at shorter wavelength than the bluish red to violet quinacridones. This difference may be correlated with the presence of the two additional nitrogen atoms in the chromophore of diazaquinacridine-diones. Thus while there is present one donor group for each acceptor in quinacridone (**28**), there are two donors for each acceptor

in **5** *(Scheme 11)*. This added bridgehead nitrogen donor in turn would exert an electron flow towards the carbonyl group, intercepting the conjugation of the main donor nitrogen and hence a hypsochromic shift would result. This approach has been successfully applied by *Kaul* [2], to interpret the colour difference between thioindigo (**32**) and benzothiazine indigo (**33**) which also contains an added donor. Moreover, the fact that the electron flow in **28** can occur additionally through the outer rings whereas this effect is blocked in the case of **5**, may also be a contributing factor. Support for this view is provided by the observation that, in contrast to quinacridones, the effect of substitution in the diazaquinacridine-diones on the $\lambda_{max}$ values is practically negligible since the substituent is in fact isolated from the chromophore. *Table 1* shows the longest wavelength absorption in DMSO solution for a number of quinacridones and their respective diazaquinacridine-diones. For comparison, the values for acridone and 8a-azaacridone are also given.

*Scheme 11*

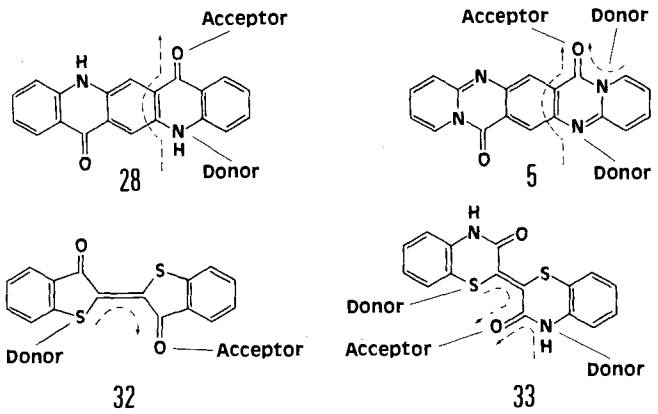



Table 1. *The longest wavelength absorption* (in DMSO) *for a number of quinacridones and their respective 7a,14a-diazaquinacridine-7,14-diones*

| | Substituent | |
|---|---|---|
| 521<br>532<br>592 | —<br>2.9 -Dimethyl<br>4.11-Dimethyl<br>2.9 -Dichloro | 414<br>420<br>412<br>418 |
| 400 (in MeOH)[1] | — | 357 (in EtOH)[2] |

$\lambda_{MAX.}$ (nm)

[1]) Taken from [11]. [2]) Taken from [12].

## Experimental Part

*General.* The melting points (m.p.) were determined on a *Kofler* block and are uncorrected. The IR. spectra were recorded on a *Perkin-Elmer* model 21 spectrophotometer, the UV./VIS. on a *Beckmann* DK-2, and the NMR. on a *Brucker* 90 MHz spectrometer. The mass spectra were measured by the direct insertion technique with a CEC 21-110 B instrument (70 eV).

*Starting Materials.* Diethyl 2,5-diaminoterephthalate (**8**) was prepared from its 3,6-dihydro derivative [13]. The latter was obtained (72.7%) by passing ammonia through a 15.5% solution of **1** in butanol containing 2% $NH_4Cl$ at reflux temperature for 3.5 h and isolating the product from the cooled reaction mixture (*cf.* [14]). Diethyl 2,5-dichloro-1,4-benzoquinone-3,6-dicarboxylate (**30**) was prepared by chlorination of **1** as described by *Hantzsch & Zechendorf* [15].

*7a,14a-Diaza-6,7,7a,13,14,14a-hexahydroquino*[2,3-b]*acridine-7,14-diones* **4** *and* **4b–4e** *(Table 2).* A mixture of **1**, 2.6–3.1 times its mol-weight of the appropriate 2-aminopyridine and approximately 5 times its weight of glacial acetic acid was stirred at 110° for 12 h under $N_2$. The precipitated crystalline product was filtered off at RT., washed with glacial acetic acid and ethanol and dried.

*Table 2*

| 2-Amino-pyridine | Product[a]) Substituent | Appearance (Yield %) | Formula (Mol-Wt.) | | Analysis % C | H | Cl | N | O |
|---|---|---|---|---|---|---|---|---|---|
| Unsubstituted | **4** | pale orange | $C_{18}H_{12}N_4O_2$ | Calc. | 68.3 | 3.8 | – | 17.7 | 10.1 |
| | – | (51.3) | (316.320) | Found | 67.7 | 3.9 | – | 18.3 | 11.4 |
| 4-$CH_3$ | **4b** | pale pink | $C_{20}H_{16}N_4O_2$ | Calc. | 69.8 | 4.6 | – | 16.3 | 9.3 |
| | 3,10-di-$CH_3$ | (16.8) | (344.374) | Found | 69.4 | 4.7 | – | 16.2 | 9.7 |
| 5-$CH_3$ | **4c** | pale pink | $C_{20}H_{16}N_4O_2$ | Calc. | 69.8 | 4.6 | – | 16.3 | 9.3 |
| | 2,9-di-$CH_3$ | (51.0) | (344.374) | Found | 69.4 | 4.4 | – | 16.1 | 9.4 |
| 6-$CH_3$ | **4d** | pale pink | $C_{20}H_{16}N_4O_2$ | Calc. | 69.8 | 4.6 | – | 16.3 | 9.3 |
| | 1,8-di-$CH_3$ | (trace) | (344.374) | Found | 69.6 | 4.2 | – | 16.1 | 9.6 |
| 5-Cl | **4e** | pale yellow | $C_{18}H_{10}Cl_2N_4O_2$ | Calc. | 56.1 | 2.6 | 18.4 | 14.5 | 8.3 |
| | 2,9-di-Cl | (85.2) | (385.210) | Found | 55.9 | 2.6 | 18.7 | 14.2 | 8.7 |

[a]) None of the products melted below 360°.

*Diethyl 2,5-bis(3',5'-dichloro-2'-pyridylamino)-3,6-dihydroterephthalate* (**22**). Using 2-amino-3,5-dichloropyridine, and proceeding as above, **22** was isolated (45.0%).

$C_{22}H_{20}Cl_4N_4O_4$ (546.238) Calc. Cl 26.0 N 10.3 O 11.7% Found Cl 26.3 N 10.5 O 11.8%

*1,4-Dihydro-3-ethoxycarbonyl-2-hydroxy-8a-azaacridones* **11** *and* **19**. Addition of water to the mother liquors of **4** and **4c** precipitated **11** and **19** respectively which were purified by 2 recrystallizations from ethanol, and obtained as cream coloured crystals. **11**: m.p. 204–207°.

| | | | | | |
|---|---|---|---|---|---|
| $C_{15}H_{14}N_2O_4$ | Calc. | C 62.9 | H 4.9 | N 9.8 | O 22.4% |
| (286.287) | Found | „ 62.5 | „ 4.9 | „ 9.6 | „ 22.1% |

**19**. m.p. 195–198°.

| | | | | | |
|---|---|---|---|---|---|
| $C_{16}H_{16}N_2O_4$ | Calc. | C 64.0 | H 5.3 | N 9.3 | O 21.9% |
| (300.314) | Found | „ 63.9 | „ 5.6 | „ 9.2 | „ 21.4% |

*7a,14a-Diaza-7,7a,14,14a-tetrahydroquino*[2,3-b]*acridine-7,14-diones* **5–5c**, **5e** *and* **24** *(Table 3).* A mixture of equimolar amounts of the appropriate **4** and chloranil was stirred in approximately 10 times their combined weight of glacial acetic acid at 110–115° for 1.5–2 h. The red precipitate which gradually formed was filtered off at 90°, washed with glacial acetic acid and ethanol. It was taken up in boiling water, filtered off and washed well with water. Purification was carried out by

*Table 3*

| Product[a]) Substituent | Appearance (Yield %) | Formula (Mol-Wt.) | | Analysis % C | H | Cl | N | O |
|---|---|---|---|---|---|---|---|---|
| **5** | red | $C_{18}H_{10}N_4O_2$ | Calc. | 68.8 | 3.2 | – | 17.8 | 10.2 |
| – | (88.4) | (314.304) | Found | 68.9 | 3.4 | – | 17.8 | 10.0 |
| **5a**[b]) | red | $C_{20}H_{14}N_4O_2$ | Calc. | 70.2 | 4.1 | – | 16.4 | 9.3 |
| 4,11-di-$CH_3$ | (79.0) | (342.358) | Found | 69.8 | 4.2 | – | 16.1 | 9.8 |
| **5b** | red | $C_{20}H_{14}N_4O_2$ | Calc. | 70.2 | 4.1 | – | 16.4 | 9.3 |
| 3,10-di-$CH_3$ | (87.5) | (342.358) | Found | 69.7 | 4.4 | – | 15.8 | 8.8 |
| **5c** | red | $C_{20}H_{14}N_4O_2$ | Calc. | 70.2 | 4.1 | – | 16.4 | 9.3 |
| 2,9-di-$CH_3$ | (90.5) | (342.358) | Found | 69.9 | 4.1 | – | 16.2 | 9.6 |
| **5e** | orange | $C_{18}H_8Cl_2N_4O_2$ | Calc. | 56.4 | 2.1 | 18.5 | 14.6 | 8.4 |
| 2,9-di-Cl | (93.5) | (383.194) | Found | 56.3 | 2.4 | 18.6 | 14.4 | 8.7 |
| **24**[c]) | red | $C_{18}H_6Cl_4N_4O_2$ | Calc. | 47.8 | 1.3 | 31.4 | 12.4 | 7.1 |
| – | (43.3)[d]) | (452.084) | Found | 47.6 | 1.7 | 30.3 | 12.2 | 7.5 |

[a]) None of the products melted below 360°.
[b]) Obtained from crude **4a** not listed in *Table 2.*
[c]) Prepared by PPA cyclization (150°, 1 h) of the intermediate **23**, obtained from **22** by the above procedure.
[d]) Overall yield.

stirring the product for 1 h in dimethylformamide (DMF) at reflux temperature, filtering the mixture hot and washing the solid with DMF and ethanol.

*2-Amino-3-ethoxycarbonyl-8a-azaacridone* (**9**). – *Method A.* An intimate mixture of 2.5 g (0.01 mol) of diethyl 2,5-diaminoterephthalate (**8**) and 5 g of 2-chloropyridine was heated slowly to 160° with intermittent stirring, an orange-red precipitate separating from the melt. The reaction mixture was kept at 160° for 3 h and after cooling, triturated with acetone to give a quantitative yield of the hydrochloride of **9** which was converted to the free base **9** by treating it with aqueous $Na_2CO_3$ solution, m.p., 244–245°.

| | | | | | |
|---|---|---|---|---|---|
| $C_{15}H_{13}N_3O_3$ | Calc. | C 63.6 | H 4.6 | N 14.8 | O 17.0% |
| (283.287) | Found | „ 63.6 | „ 4.4 | „ 14.8 | „ 16.7% |

*Method B.* An intimate mixture of 0.5 g (0.00175 mol) of **11** and 5 g of ammonium acetate was heated slowly to 160° and kept at that temperature for 1 h with intermittent stirring. The product was isolated by treatment of the reaction mixture at 80° with water, filtering off the solid and washing it with water and ethanol. The yield of *2-amino-3-ethoxycarbonyl-1,4-dihydro-8a-azaacridone* (**12**) was 0.38 g (76.0%), m.p., 290–300°.

| | | | | | |
|---|---|---|---|---|---|
| $C_{15}H_{15}N_3O_3$ | Calc. | C 63.2 | H 5.2 | N 14.7 | O 16.8% |
| (285.303) | Found | „ 63.3 | „ 5.2 | „ 14.5 | „ 16.4% |

A mixture of 0.38 g (0.0013 mol) of **12**, 0.32 g (0.0013 mol) of chloranil was stirred in 15–20 ml of *n*-pentanol at 135° for 1 h. Upon cooling to RT., a thick orange precipitate of the hydrochloride of **9** separated from the greenish-brown fluorescent solution which was filtered off and washed with *n*-pentanol and ethanol. It was converted to the free base **9** by treatment with aqueous $Na_2CO_3$, m.p., 245–246°. The product is spectroscopically (IR.) identical to that obtained by *Method A.*

| | | | | | |
|---|---|---|---|---|---|
| $C_{15}H_{13}N_3O_3$ | Calc. | C 63.6 | H 4.6 | N 14.8 | O 17.0% |
| (283.287) | Found | „ 63.2 | „ 4.7 | „ 14.4 | „ 16.9% |

*1,2,8,9-Dibenzo-7a,14a-diaza-7,7a,14,14a-tetrahydroquino[2,3-*b*]acridine-9,18-dione* (**10**). A mixture of 2.5 g (0.01 mol) of diethyl 2,5-diaminoterephthalate (**8**) and 5.0 g of 2-chloroquinoline was heated

slowly to 165° and kept at that temperature for 4 h with intermittent stirring. Trituration of the cooled semisolid with acetone gave a quantitative yield of the yellow **10** which was purified through DMF extraction as described above for **5**, m.p., > 300°.

| | | | | | |
|---|---|---|---|---|---|
| $C_{26}H_{14}N_4O_2$ | Calc. | C 75.4 | H 3.4 | N 13.5 | O 7.7% |
| (414.424) | Found | „ 75.2 | „ 3.4 | „ 13.5 | „ 7.6% |

*2,5-Bis(2'-pyridylamino)terephthalic acid* (**13**). A suspension of 0.5 g (0.0016 mol) of **5** in *ca.* 10 ml of 10% aqueous KOH and 10 ml ethanol was refluxed and more alcohol added until almost complete dissolution. Acidification of the clear solution with dilute acetic acid gave a yellow precipitate of **13** which was filtered off, washed with water and dried. Yield of **13**, 0.5 g (89.7%), m.p., decomposes slowly with cyclization to **5**.

| | | | | | |
|---|---|---|---|---|---|
| $C_{18}H_{14}N_4O_4$ | Calc. | C 61.7 | H 4.0 | N 16.0 | O 18.3% |
| (350.334) | Found | „ 61.5 | „ 4.0 | „ 16.3 | „ 18.1% |

*3-Ethoxycarbonyl-2-hydroxy-12-oxo-1*H*-benzimidazolo[2,3-*b*]-1,4-dihydroquinazoline* (**20**). An intimate mixture of 2.5 g (0.01 mol) of **1** and 2.6 g (0.02 mol) of 2-aminobenzimidazole was heated to 160° with intermittent stirring, and kept at that temperature for 2 h. The warm (120°) reaction mixture was triturated with glacial acetic acid, the yellow solid filtered off, washed with glacial acetic acid and acetone to give 2.4 g (74.0%) of crude **20**. A sample recrystallized from DMF gave pale yellow crystals, m.p. > 340°.

| | | | | | |
|---|---|---|---|---|---|
| $C_{17}H_{15}N_3O_4$ | Calc. | C 62.8 | H 4.6 | N 12.9 | O 19.7% |
| (325.324) | Found | „ 62.5 | „ 4.6 | „ 12.8 | „ 19.5% |

*7a,14a-Diaza-6,7,7a,13,14,14a-hexahydroquino[2,3-*b*]acridine-6,7,13,14-tetrones* **25**, **26** *and* **27** *(Table 4). – Method A.* To a solution of 2 g of the appropriate **5** in 20 ml of concentrated sulfuric acid was added dropwise with stirring a mixture of 15 ml of nitric acid (d = 1.4) and 55 ml of concentrated sulfuric acid, and the whole heated at 60° for 2 h. The cooled reaction mixture was poured onto crushed ice and the resulting yellow precipitate filtered off, washed with water and dried. Purification was carried out through DMF extraction as described above for **5**.

*Method B. – Compounds* **25** *and* **26**. A mixture of 0.02 mol of the appropriate amine (2-aminopyridine for **25**, 2-amino-5-methylpyridine for **26**), 3.21 g (0.01 mol) of **30**, 1.6 g (0.02 mol) of anhydrous sodium acetate and 50 ml of ethanol was heated at reflux temperature for 2 h. The resulting precipitate was filtered off at RT., washed with ethanol and water and dried. Purification through DMF extraction as described above for **5**, gave **25** and **26** which were analytically and spectroscopically (IR.) identical with those prepared according to *Method A*.

*Compound* **27**. Using 2-amino-5-chloropyridine, and proceeding as above, gave the uncyclized product, *2,5-bis(5'-chloro-2'-pyridylamino)-3,6-diethoxycarbonyl-1,4-benzoquinone* (**31**).

| | | | | | | |
|---|---|---|---|---|---|---|
| $C_{22}H_{18}Cl_2N_4O_6$ | Calc. | C 52.3 | H 3.6 | Cl 14.1 | N 11.1 | O 19.0% |
| (505.314) | Found | „ 51.7 | „ 3.5 | „ 13.9 | „ 11.0 | „ 20.0% |

*Table 4*

| Starting material | Product[a]) | Yield % | Formula (Mol-Wt.) | | Analysis % C | H | Cl | N | O |
|---|---|---|---|---|---|---|---|---|---|
| **5** | **25** | 77.3 | $C_{18}H_8N_4O_4$ | Calc. | 62.8 | 2.3 | – | 16.3 | 18.6 |
| | | | (344.286) | Found | 62.3 | 2.5 | – | 16.1 | 17.8 |
| **5c** | **26** | 72.1 | $C_{20}H_{12}N_4O_4$ | Calc. | 64.5 | 3.2 | – | 15.1 | 17.2 |
| | | | (372.340) | Found | 64.6 | 3.4 | – | 15.1 | 16.8 |
| **5e** | **27** | 80.8 | $C_{18}H_6Cl_2N_4O_4$ | Calc. | 52.3 | 1.5 | 17.2 | 13.6 | 15.5 |
| | | | (413.176) | Found | 52.1 | 1.5 | 16.9 | 13.6 | 15.4 |

[a]) None of the products melted below 360°.

Cyclization of **31** in PPA (120°, 2 h), gave **27** which was analytically and spectroscopically (IR.) identical with that prepared according to *Method A*.

*2,9-Dinitroquinacridonequinone* (**29**). Treating 5 g of quinacridone (**28**) as described in *Method A* gave **29**.

$C_{20}H_8N_4O_8$ (432.304) Calc. N 13.0 O 29.6% Found N 13.4 O 29.8%

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