578. N-*Methyl Derivatives of Phthaloylacridones.*

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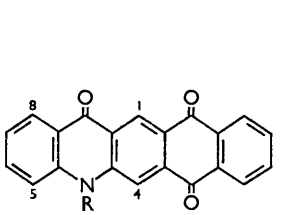
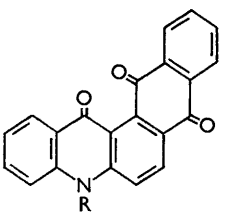
A series of phthaloylacridones and their substitution products has been prepared and the influence of structure has been traced on melting point, solubility and light-absorption. *N*-Methylation modifies these properties. The results indicate steric restriction of the normal effect of the *N*-methyl group.

The phthaloylacridones form a class of crystalline coloured compounds of high melting point and low solubility in organic media which exist in three isomeric amide-type forms [1] with characteristic differences in chemical properties.

2,3-Phthaloylacridone (I; R = H) is an orange-yellow compound,[2] which is almost insoluble in chlorobenzene. It forms a green derivative with methanolic potassium hydroxide in dry pyridine.[3] On being heated with methyl toluene-*p*-sulphonate and potassium carbonate in trichlorobenzene it forms an *N*-methyl derivative (I; R = Me) of lower melting point which is identical with the compound prepared by reaction of ethyl 2-chloroanthraquinone-3-carboxylate with *N*-methylaniline and cyclisation of the product. The *N*-methyl derivative shows no reaction with the potassium hydroxide–pyridine reagent and is notably more soluble in organic solvents. It absorbs at the same wavelength as 2,3-phthaloylacridone itself, though the intensity is increased. These properties suggest the occurrence of intermolecular hydrogen-bonding between –NH– and C=O groups in two or more molecules of the parent acridone, a property which is lost on *N*-methylation.



(I)



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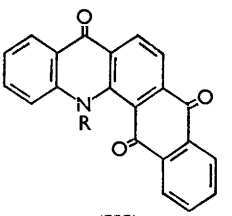


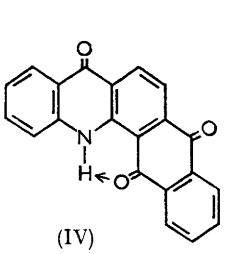
(III)

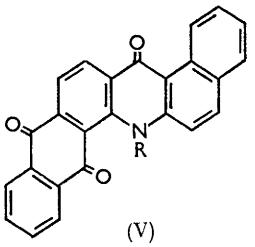
1,2-Phthaloylacridone [4] (II; R = H) resembles the 2,3-isomer closely in melting point, solubility, and light absorption. It is a relatively strong acid which dissolves in alcoholic potassium hydroxide with a violet colour. The *N*-methyl derivative is non-acidic, more soluble in organic media, and lower-melting than the parent acridone, the properties of which are probably the result of intermolecular hydrogen-bonding.

3,4-Phthaloylacridone [5] (III; R = H) is similar to 1-anilinoanthraquinone in its red-violet colour, which indicates that it is a true acridone, not a hydroxyacridone. It is lower-melting and more soluble in organic solvents than its isomers, suggesting the occurrence of intramolecular hydrogen-bonding (IV). The effect of nuclear substitution on these properties is recorded in Tables 1 and 2. Electron-releasing substituents (Me, Pr, MeO, and EtO) displace $\lambda_{max.}$ towards higher values, whilst electron-attracting groups (Cl, Br, NO_2) have the reverse effect, in agreement with the known influence of substituents on the availability of the unshared electrons of nitrogen. With *all* substituents the 1-derivative absorbs at shorter wavelengths than the 3-isomer, an indication that interaction of the nitrogen with the nucleus is reduced in the 1-series, and suggesting that a

[1] Mason, *J.*, 1957, 4874, 5010.
[2] Ullmann and Das Gupta, *Ber.*, 1914, **47**, 563.
[3] Bradley, *J. Soc. Dyers and Colourists*, 1942, **58**, 2.
[4] Ullmann and Sone, *Annalen*, 1911, **380**, 340.
[5] Ullmann and Ochsner, *Annalen*, 1911, **381**, 6.

1-substituent has the additional steric effect of inhibiting movement of the –NH– hydrogen atom into the plane of the acridone ring. To test this view a corresponding series of *N*-methyl derivatives has been studied. (Tables 3 and 4.)


(IV)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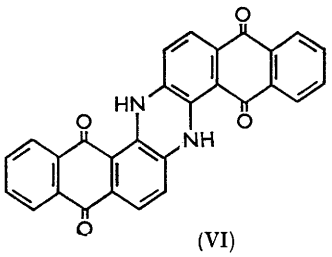
(VI)

N-Methylation of 3,4-phthaloylacridone displaces $\lambda_{max.}$ towards shorter wavelengths and *N*-ethylation has a slightly larger effect in the same sense. The result differs from that observed in the monomethylation of 1-aminoanthraquinone,[6] where the displacement is towards longer wavelengths owing to unrestricted electron-release by the methyl group and must be due to the inability of the *N*-methyl group to move into the plane of the acridone ring. Lack of planarity should be more pronounced with the *N*-Me than with the *N*-H derivative and the *N*-methylated compounds would be expected, as found, to absorb at shorter wavelengths, notwithstanding the electron-releasing effect of the methyl group. Again all the 1- and 3-substituted *N*-methyl-3,4-phthaloylacridones examined absorbed at shorter wavelengths than the corresponding unmethylated compounds, the effect of a substituent being almost the same whether the 1- or 3-position was occupied. The effect of *N*-methylation was least with the 3-nitro-derivative which already absorbed at a lower wavelength than any of the other compounds examined.

It is worthy of note that the main absorption maxima were the same throughout the series whether the medium was *o*-dichlorobenzene or pyridine. Displacement of $\lambda_{max.}$ towards shorter values was also found on *N*-methylation of 5,6-phthaloyl-1,2-benzacridone (V) (Table 5).

In every example *N*-methylation reduces the extinction coefficient, a result which follows diminished resonance due to steric factors.[7] The solubility of 3,4-phthaloylacridone in *o*-dichlorobenzene was increased by every substituent investigated, the largest effect being in the 1-position. The t-butyl group caused the largest enhancement. Again *N*-methylation increased the solubility throughout the whole series. The lack of a specific effect of substituents suggests that whether they are attached to nitrogen or to the nucleus they enhance solubility by hindering the association of phthaloylacridone molecules. A similar result is seen in 3,3-di-t-butylflavanthrone which is readily soluble in benzene [8] whilst flavanthrone itself is very sparingly soluble in any organic solvent.

N-Methylation of the phthaloylacridones notably reduces the cotton affinity of the parent compounds. It thus appears that the vat-dyeing property of the phthaloylacridones is due in the main to the formation of hydrogen bonds between their NH groups and oxygen of cellulose.

The light absorption, solubility, and cotton-affinity relationships of the phthaloylacridones are parallel to those observed with indanthrone.[9] The parent compound (VI) has marked affinity for cellulose and is sparingly soluble in organic media, but the solubility increases progressively with mono- and di-methylation; at the same time $\lambda_{max.}$ is displaced towards shorter values and the affinity for cellulosic fibres is reduced.

N-Methyl-3,4-phthaloylacridone and its substitution products also sublime more readily than the unmethylated derivatives.

[6] Peters and Sumner, *J.*, 1953, 2105.
[7] Crombie, *Quart. Rev.*, 1952, Vol. VI, p. 115.
[8] Bradley and Nursten, *J.*, 1951, 2170.
[9] Bradley and Leete, *J.*, 1951, 2129

Several of the phthaloylacridones examined had been prepared already. The remainder were made by established methods, a derivative of aniline being brought into reaction with methyl 1-chloroanthraquinone-2-carboxylate, or a derivative of anthranilic acid being condensed with 1-chloroanthraquinone, the products so obtained being then cyclised to form derivatives of acridone. The following derivatives of 3,4-phthaloylacridone are new or are known compounds for which additional data are given: 5-methyl-, 7-methyl-, 5-t-butyl-, 7-t-butyl-, 5-methoxy-, 5-ethoxy-, 7-ethoxy-, 5-chloro-, 7-chloro-, 5-bromo, 7-bromo-, 7-nitro-. The last was identical with the mononitro-derivative of 3,4-phthaloylacridone prepared by direct nitration,[5] and the 7-bromo-derivative with the product of direct bromination.[5]

Experimental

Cyclisation to the *acridones* of Table 1 was by heating with concentrated sulphuric acid in three cases. Under these conditions 1-*p*-tolylaminoanthraquinone-2-carboxylic acid gave a sulphonic acid, but cyclisation succeeded when the carboxylic acid (5 g.), acetyl chloride (5 g.), and nitrobenzene (40 c.c.) were stirred at 130° for 30 min. and then at the b. p. of the mixture for a few min. This method was also used for the preparation of 5-methyl-3,4-phthaloylacridone.

Table 1. *Derivatives of* 3,4-*phthaloylacridone.*

			Found (%)				Required (%)			
Subst.	M. p.	Compn.	C	H	N	Cl/Br	C	H	N	Cl/Br
7-Me [10]	326—327°	$C_{22}H_{13}O_3N$	77·8	3·8	4·1	—	77·8	3·8	4·1	—
5-Me	340—341	$C_{22}H_{13}O_3N$	77·5	4·1	4·3	—	77·8	3·8	4·1	—
7-Bu^t	300—301	$C_{29}H_{19}O_3N$	78·6	4·9	3·6	—	78·7	4·9	3·7	—
5-Bu^t	299—300	$C_{29}H_{19}O_3N$	78·3	5·0	3·4	—	78·7	4·9	3·7	—
5-OMe	338—339	$C_{22}H_{13}O_4N$	74·0	3·5	4·0	—	74·4	3·7	4·0	—
7-OEt	378—380	$C_{23}H_{15}O_4N$	74·7	4·0	3·8	—	74·8	4·0	3·8	—
5-OEt	334—335	$C_{23}H_{15}O_4N$	74·5	3·9	3·9	—	74·8	4·0	3·8	—
7-Cl [10]	355—356	$C_{21}H_{10}O_3NCl$	70·0	2·6	4·1	10·1	70·2	2·8	3·9	9·9
5-Cl [11]	317—318	$C_{21}H_{10}O_3NCl$	69·9	3·0	4·2	10·1	70·2	2·8	3·9	9·9
7-Br [5]	341—342	$C_{21}H_{10}O_3NBr$	63·0	2·9	3·4	19·5	63·3	2·5	3·5	19·8
5-Br	311—312	$C_{21}H_{10}O_3NBr$	63·3	2·4	3·6	19·8	63·3	2·5	3·5	19·8
7-NO_2 [5]	357—358	$C_{21}H_{10}O_5N_2$	68·3	2·7	7·3	—	68·6	2·7	7·6	—

Table 2. *Derivatives of* 3,4-*phthaloylacridone.*

Subst.	$\lambda_{max.}$ (mμ) (in *o*-$C_6H_4Cl_2$)		$\lambda_{max.}$ (mμ) (in pyridine)		Solubility in *o*-$C_6H_4Cl_2$ at 20° (g./100 c.c.)	Subst.	$\lambda_{max.}$ (mμ) (in *o*-$C_6H_4Cl_2$)		$\lambda_{max.}$ (mμ) (in pyridine)		Solubility in *o*-$C_6H_4Cl_2$ at 20° (g./100 c.c.)
Unsubst.	516	(0·80)	516	(0·80)	0·013	7-NO_2 ...	485	(0·78)	—		0·060
7-Me	526	(0·74)	526	(0·76)	0·076	5-Me	520	(0·75)	520	(0·76)	0·082
7-Bu^t	520	(0·75)	520	(0·75)	0·230	5-Bu^t ...	516	(0·74)	516	(0·74)	1·100
7-OMe ...	540	(0·56)	540	(0·57)	0·055	5-OMe ...	530	(0·67)	530	(0·68)	0·062
7-OEt ...	540	(0·60)	—		0·014	5-OEt ...	532	(0·66)	—		0·018
7-Cl	512	(0·78)	512	(0·78)	0·020	5-Cl	505	(0·76)	505	(0·78)	0·024
7-Br	512	(0·74)	512	(0·74)	0·052	5-Br	504	(0·76)	504	(0·78)	0·140

1-*p*-t-Butylanilinoanthraquinone-2-carboxylic acid was cyclised by heating 0·005 mol. of it with phosphorus pentachloride (0·006 mol.) until the chloride was formed, then cooling, adding anhydrous aluminium chloride (0·02 mol.), and heating the whole at 60° until formation of the *acridone* was complete. The same procedure was used in the preparation of 5-t-butyl-, 5-methoxy-, 7-methoxy-, 5-ethoxy-, 7-ethoxy, 5-bromo-, and 7-bromo-3,4-phthaloylacridone. All the derivatives crystallised readily from nitrobenzene and sublimed as red to violet needles of leaflets, with the exception of 7-nitro-3,4-phthaloylacridone which was orange-red. Each gave a vivid grass green colour when a drop of concentrated methanolic potassium hydroxide was added to its solution in dry pyridine.

N-*Methyl*-3,4-*phthaloylacridone.*—Finely powdered 3,4-phthaloylacridone (0·005 mol.) was heated in an open flask with anhydrous potassium carbonate (0·05 mol.) and 1,2,4-trichlorobenzene (300 c.c.) until moisture had been expelled. Methyl toluene-*p*-sulphonate (0·05 mol.) was

[10] *Friedländer*, 1910, **10**, 708.
[11] D.R.-P. 551,885; *Friedländer*, 1934, **19**, 2078.

TABLE 3. *Derivatives of* N-*methyl*-3,4-*phthaloylacridone.*

Subst.	M. p.	Yield (%)	Compn.	Found (%) C	H	N	Cl/Br	Required (%) C	H	N	Cl/Br
7-Me ...	288—289°	42	$C_{23}H_{15}O_3N$	77·8	4·4	4·0	—	78·2	4·2	4·0	—
5-Me ...	250—251	25	$C_{23}H_{15}O_3N$	78·1	4·5	4·0	—	78·2	4·2	4·0	—
7-Bu^t ...	250—251	39	$C_{26}H_{21}O_3N$	78·9	5·3	3·9	—	79·0	5·3	3·6	—
7-OMe ...	300—301	39	$C_{23}H_{15}O_4N$	74·6	3·9	3·9	—	74·8	4·0	3·8	—
5-OMe ...	247—248	28	$C_{23}H_{15}O_4N$	74·5	4·4	3·8	—	74·8	4·0	3·8	—
7-OEt ...	267—268	41	$C_{24}H_{17}O_4N$	75·0	4·5	3·6	—	75·1	4·4	3·7	—
5-OEt ...	227—228	28	$C_{24}H_{17}O_4N$	75·0	4·5	3·6	—	75·1	4·4	3·7	—
7-Cl	346—347	50	$C_{22}H_{12}O_3NCl$	70·4	3·3	3·9	9·8	70·6	3·2	3·7	9·5
5-Cl	258—259	43	$C_{22}H_{12}O_3NCl$	70·9	3·5	3·6	9·1	70·6	3·2	3·7	9·5
7-Br	329—330	49	$C_{22}H_{12}O_3NBr$	63·5	2·8	3·3	19·0	63·4	2·9	3·4	19·3
5-Br	289—290	26	$C_{22}H_{12}O_3NBr$	63·6	3·1	3·1	19·2	63·4	2·9	3·4	19·3
7-NO_2 ...	330—331	55	$C_{22}H_{12}O_5N_2$	68·5	2·8	6·9	—	68·8	3·1	7·3	—

TABLE 4. *Derivatives of* N-*methyl*-3,4-*phthaloylacridone.*

Subst.	$\lambda_{max.}$ (mμ) (in *o*-$C_6H_4Cl_2$)	$\lambda_{max.}$ (mμ) (in pyridine)	Solubility in *o*-$C_6H_4Cl_2$ at 20° (g./100 c.c.)	Subst.	$\lambda_{max.}$ (mμ) (in *o*-$C_6H_4Cl_2$)	$\lambda_{max.}$ (mμ) (in pyridine)	Solubility in *o*-$C_6H_4Cl_2$ at 20° (g./100 c.c.)
Unsubst.	504 (0·62)	504 (0·62)	0·110	7-NO_2 ...	480 (0·70)	—	0·300
7-Me	512 (0·68)	512 (0·68)	0·133	5-Me	506 (0·60)	506 (0·61)	0·435
7-Bu^t	512 (0·67)	512 (0·67)	0·340	5-OMe ...	516 (0·56)	516 (0·56)	0·320
7-OMe ...	525 (0·53)	525 (0·53)	0·328	5-OEt ...	515 (0·55)	—	0·551
7-OEt.....	522 (0·56)	—	0·135	5-Cl	495 (0·48)	495 (0·50)	0·230
7-Cl	498 (0·56)	498 (0·60)	0·125	5-Br	495 (0·60)	495 (0·64)	0·240
7-Br	502 (0·68)	502 (0·69)	0·092				

then added and the reaction continued with stirring under reflux for 48 hr. The suspension was then filtered, the residue was extracted with fresh hot solvent (200 c.c.), and the combined filtrate and extract were filtered, cooled, mixed with benzene (150 c.c.), and chromatographed on alumina. Three zones were formed and were developed with benzene. The lowest band was red; the adsorbed derivative was eluted with hot ethyl acetate (500 c.c.) and recovered after concentration as red needles (0·745 g., 44%), m. p. 317—318°. Further crystallisation from *o*-dichlorobenzene gave N-*methyl*-3,4-*phthaloylacridone*, m. p. 320—321° (Found: C, 77·8; H, 4·0; N, 4·2. $C_{22}H_{13}O_3N$ requires C, 77·9; H, 3·8; N, 4·1%). This was the method used, with small variations, in all the preparations recorded in Table 3. Each derivative was purified by chromatography on alumina and was present in the most mobile of the bands on the column. None showed any colour change when methanolic potassium hydroxide was added to its solution in dry pyridine.

Yields were generally lower with the 5-derivatives; 5-t-butyl-3,4-phthaloylacridone could not be converted into an *N*-methyl derivative.

When the period of heating was 8 hr. the yield of *N*-methyl-3,4-phthaloylacridone was 10%. The same derivative was formed under the following conditions. (*a*) 3,4-Phthaloylacridone (1·62 g.) was heated for 5 min. at 130° with powdered potassium hydroxide (2·8 g.) and methanol (1 c.c.). The resulting dark mass was powdered and then heated with methyl iodide (19·8 g.) at 150° for 48 hr. The cooled product was extracted with 1,2,4-trichlorobenzene (500 c.c.), and the filtered extract was mixed with benzene (250 c.c.) and chromatographed on alumina. The most mobile band gave *N*-methyl-3,4-phthaloylacridone (24%), m. p. 320—321° (Found: C, 77·8; H, 4·0; N, 4·2%). (*b*) Repetition of experiment (*a*) but with methyl sulphate (12·8 g.) gave the same *N*-methyl derivative (30%).

N-*Ethyl*-3,4-*phthaloylacridone* was formed when 3,4-phthaloylacridone (1·62 g.) was refluxed for 48 hr. with ethyl toluene-*p*-sulphonate (10 g.) and anhydrous potassium carbonate (6·9 g.) in 1,2,4-trichlorobenzene (300 c.c.). The derivative (43%) crystallised from *o*-dichlorobenzene as dark red needles, m. p. 368—369° (Found: C, 78·1; H, 3·8; N, 4·0. $C_{23}H_{15}O_3N$ requires C, 78·2; H, 4·2; N, 4·0%).

N-*Methyl*-2,3-*phthaloylacridone*.—This *derivative* was formed in 95% yield by 5 hours' refluxing and stirring of 2,3-phthaloylacridone (1·62 g.) with anhydrous potassium carbonate (6·9 g.) and methyl toluene-*p*-sulphonate (18·6 g.) in 1,2,4-trichlorobenzene (200 c.c.). It crystallised from *o*-dichlorobenzene as yellow needles, m. p. 349—350° (Found: C, 77·8; H, 3·9; N, 3·7. $C_{22}H_{13}O_3N$ requires C, 77·9; H, 3·8; N, 4·1%).

N-*Methyl*-1,2-*phthaloylacridone*, prepared similarly from 1,2-phthaloylacridone in 94% yield, crystallised from *o*-dichlorobenzene as yellow needles, m. p. 351—352° (Found: C, 77·3; H, 4·2; N, 4·1. $C_{22}H_{13}O_3N$ requires C, 77·9; H, 3·8; N, 4·1%).

N-*Methyl*-5,6-*phthaloyl*-1,2-*benzacridone* was obtained in 40% yield by applying the standard conditions of methylation to 5,6-phthaloyl-1,2-benzacridone. After purification by chromatography it crystallised from *o*-dichlorobenzene as red needles, m. p. 366—367° (Found: C, 80·0; H, 3·8; N, 3·7. $C_{26}H_{15}O_3N$ requires C, 80·2; H, 3·9; N, 3·6%).

The following new compounds were made in the course of preparing the acridones and their *N*-methyl derivatives.

1-p-*t-Butylanilinoanthraquinone* was formed by 8 hours' refluxing of 1-chloroanthraquinone (5 g.), *p*-t-butylaniline (6 g.), anhydrous potassium carbonate (2·8 g.), cupric acetate (0·3 g.), and copper bronze (0·1 g.) in 1,2,4-trichlorobenzene (100 c.c.). After crystallisation from ethanol the derivative was obtained as deep purple plates (5·0 g.), m. p. 147·5° (Found: C, 81·0; H, 5·9; N, 4·2. $C_{24}H_{21}O_2N$ requires C, 81·2; H, 5·9; N, 3·9%).

Methyl p-*t-butylanilinoanthraquinone*-2-*carboxylate*, prepared by refluxing for 12 hr. in pentyl alcohol (65 c.c.) a mixture of methyl 1-chloroanthraquinone-2-carboxylate (3 g.), *p*-t-butylaniline (3 g.), anhydrous calcium carbonate (2 g.), cupric acetate (0·1 g.), and copper bronze (0·1 g.), crystallised from ethanol as red plates (3·6 g.), m. p. 133—134° (Found: N, 3·0. $C_{26}H_{23}O_4N$ requires N, 3·4%). 1-p-*t-Butylanilinoanthraquinone*-2-*carboxylic acid*, prepared from this ester by hydrolysis with alcoholic potassium hydroxide, crystallised from acetic acid as violet needles, m. p. 265—266° (Found: C, 74·9; H, 5·4; N, 3·6. $C_{25}H_{21}O_4N$ requires C, 75·2; H, 5·2; N, 3·5%).

TABLE 5.

Substance	$\lambda_{max.}$ (mμ) (in *o*-$C_6H_4Cl_2$)		$\lambda_{max.}$ (mμ) (in pyridine)		Solubility in *o*-$C_6H_4Cl_2$ at 20° (g./100 c.c.)
N-Ethyl-3,4-phthaloylacridone	510	(0·75)	—		0·88
2,3-Phthaloylacridone	—		400	(1·04)	Very small
N-Methyl-2,3-phthaloylacridone	—		400	(1·22)	0·090
1,2-Phthaloylacridone	—		400	(1·13)	Very small
N-Methyl-1,2-phthaloylacridone	—		400	(1·28)	0·104
5,6-Phthaloyl-1,2-benzacridone (IV)	515	(0·90)	—		0·041
N-Methyl-5,6-phthaloyl-1,2-benzacridone	505	(0·66)			0·092

Numbers in parentheses are values of $10^{-4}\varepsilon$. Each compound shows absorption in the 315—370 mμ region in addition to the bands recorded in the Tables.

Methyl o-*t-butylanilinoanthraquinone*-2-*carboxylate*, prepared similarly, crystallised from acetone as red plates, m. p. 130—131° (Found: N, 3·4. $C_{26}H_{23}O_4N$ requires N, 3·4%). The *acid* crystallised from acetic acid as red needles, m. p. 258—259° (Found: C, 75·6; H, 5·2; N, 3·6. $C_{25}H_{21}O_4N$ requires C, 75·2; H, 5·2; N, 3·5%).

Methyl 1-o-*chloroanilinoanthraquinone*-2-*carboxylate* crystallised from ethanol as red leaflets, m. p. 222—224° (Found: C, 67·2; H, 3·6; N, 3·5; Cl, 9·2. $C_{22}H_{14}O_4NCl$ requires C, 67·5; H, 3·5; N, 3·5; Cl, 8·9%). The p-*isomer* crystallised from acetone as red needles, m. p. 184—185° (Found: C, 67·7; H, 3·2; N, 3·4; Cl, 8·6. $C_{22}H_{14}O_4NCl$ requires C, 67·5; H, 3·5; N, 3·5; Cl, 8·9%). 1-*p*-Chloroanilinoanthraquinone-2-carboxylic acid crystallised from acetic acid as red plates, m. p. 307—308° (Found: C, 66·2; H, 3·3; N, 3·6; Cl, 9·7. Calc. for $C_{21}H_{12}O_4NCl$: C, 66·5; H, 3·1; N, 3·7; Cl, 9·4%) (cf. D.R.-P. 237,236 [10]). *Methyl* 1-o-*bromoanilinoanthraquinone*-2-*carboxylate* was obtained from ethanol as bright red needles, m. p. 163—164° (Found: C, 60·2; H, 2·9; N, 3·6; Br, 18·0. $C_{22}H_{14}O_4NBr$ requires C, 60·5; H, 3·2; N, 3·2; Br, 18·3%); the derived *acid* separated from acetic acid as red needles, m. p. 233—234° (Found: C, 60·0; H, 3·0; N, 3·1; Br, 18·9. $C_{21}H_{12}O_4NBr$ requires C, 60·0; H, 2·8; N, 3·3; Br, 19·0%). The p-*bromoanilino-ester* crystallised from acetone as wine-red needles, m. p. 190—191° (Found: C, 60·6; H, 3·4; N, 3·6; Br, 17·9. $C_{22}H_{14}O_4NBr$ requires C, 60·5; H, 3·2; N, 3·2; Br, 18·3%), and its *acid* as wine-red needles (from acetic acid), m. p. 306—307° (Found: C, 59·9; H, 2·8; N, 3·6; Br, 18·6. $C_{21}H_{12}O_4NBr$ requires C, 60·0; H, 2·8; N, 3·3; Br, 19·0%). *Methyl* 1-o-*nitroanilinoanthraquinone*-2-*carboxylate* was obtained in only 40% yield; it crystallised from acetic acid as orange-red needles, m. p. 245—246° (Found: C, 65·4; H, 3·4; N, 7·2. $C_{22}H_{14}O_6N_2$ requires C, 65·7; H, 3·5; N, 7·0%). The p-*nitroanilino-ester*, formed in 50% yield, crystallised from acetone as orange-red needles, m. p. 276—277° (Found: C, 65·3; H, 3·6; N, 7·2%).

1-o-*Ethoxyanilinoanthraquinone*-2-*carboxylic acid* was prepared directly by 5 hours' refluxing of 1-chloroanthraquinone-2-carboxylic acid (5·73 g.), *o*-phenetidine (5·48 g.), dry calcium carbonate (4 g.), cupric acetate (0·2 g.), and copper bronze (0·1 g.) in pentyl alcohol (120 c.c.). It was obtained from acetic acid as purple needles, m. p. 237—238° (Found: C, 71·0; H, 4·1; N, 3·3. $C_{23}H_{17}O_5N$ requires C, 71·3; H, 4·4; N, 3·6%). The p-*ethoxyanilino-acid* formed violet needles, m. p. 245—246° (Found: C, 70·9; H, 4·2; N, 3·3%). The o-*methoxyanilino-acid* crystallised from acetic acid as red-violet needles, m. p. 220—220·5° (Found: C, 70·8; H, 3·7; N, 3·5. $C_{22}H_{15}O_5N$ requires C, 70·8; H, 4·0; N, 3·8%) and the p-*methoxy-isomer* had m. p. 288—289° (Found: C, 70·5; H, 4·2; N, 3·5%).

2-*Anilino*-1-*cyanoanthraquinone*.—2-Bromo-1-cyanoanthraquinone (6·24 g.), aniline (62·4 g.), dry calcium carbonate (6 g.), cupric acetate (0·2 g.), and copper bronze (0·1 g.) were refluxed for 30 min. The resulting deep purple solution was distilled in steam, and the residue extracted with dilute hydrochloric acid. The insoluble product crystallised from acetic acid as dark red needles (85%), m. p. 309—310° (Found: C, 77·1; H, 3·7; N, 8·9. $C_{21}H_{12}O_2N_2$ requires C, 77·5; H, 3·7; N, 8·6%). It dissolved in pyridine, forming an orange-red solution which was changed to deep green on the addition of methanolic potassium hydroxide. The green colour (potassium salt) was fairly stable towards dilution with methanol or benzene though ultimately the original orange-red colour was restored.

N-*Methyl*-p-*nitroanilinoanthraquinone*.—Finely divided 1-*p*-nitroanilinoanthraquinone (1·72 g.) was heated in an open flask with dry potassium carbonate (6·9 g.) and 1,2,4-trichlorobenzene (200 c.c.) until moisture had been expelled. A solution of methyl toluene-*p*-sulphonate (9·3 g.) in trichlorobenzene (150 c.c.) was then added during 1 hr. to the suspension which was heated under reflux. After 3 hr. the suspension was filtered, the residue washed with the solvent, and the combined filtrates were evaporated to 500 c.c., then cooled, mixed with benzene (200 c.c.), and chromatographed on alumina. Two zones formed. The more mobile, red zone was eluted with trichlorobenzene and N-*methyl*-p-*nitroanilinoanthraquinone* obtained (22%) as bright red plates, m. p. 233—234° (Found: C, 70·1; H, 4·2; N, 7·4. $C_{21}H_{14}O_4N_2$ requires C, 70·4; H, 3·9; N, 7·8%), which showed no change in colour when methanolic potassium hydroxide was added to its solution in pyridine. In the same test the original unmethylated derivative changed in colour from red to purple.

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