

## NOTES

## The Cyclisation of Anthrimides to Carbazoles. IV.\* The Cyclisation of 4, 4'-Dibenzamido Dianthrimides

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Indanthrene Corinth RK (C. I. No. 65020), containing only one benzamido group in the 4th position, does not cyclise to a carbazole, but hydrolyses with sulphuric acid at 100°C.<sup>1)</sup> The cyclisation of a dianthrimide to a carbazole with sulphuric acid is successful only when two benzamido groups are present in 4, 4'- or 4, 5'- or 5, 5'-positions. E.g., Indanthrene Gray K, 4, 4'-dibenzamido-1, 1'-dianthrimide, cyclises to the corresponding carbazole, Indanthrene Olive R.

In order to confirm this observation and to compare the reactivity of 1, 1'- and 1, 2'-dianthrimides, 4, 4'-dibenzamido-1, 2'-dianthrimide was prepared by the condensation of 1-benzamido-3-bromoanthraquinone with 1-amino-4-benzamidoanthraquinone. The product exhibited  $\lambda_{max}$  values at 290, 325–330 and 455 m $\mu$ . When treated with sulphuric acid at 26–30°C for about three hours while being stirred, it changed to another compound which exhibited  $\lambda_{max}$  values at 280, 360–380, 570 m $\mu$ . Indanthrene Gray K exhibits  $\lambda_{max}$  values at 250–260, 335–340 and 435 m $\mu$ . Indanthrene Olive R exhibits  $\lambda_{max}$  values at 225, 260–270, 360–380, 548, and 580 m $\mu$ . From these changes it is evident that 4, 4'-dibenzamido-1, 2'-dianthrimide cyclises to a carbazole under this treatment.

The spectral study of the rates of cyclisation with sulphuric acid (see attached graphs) of 4, 4'-dibenzamido-1, 1'-dianthrimide and 4, 4'-dibenzamido-1, 2'-dianthrimide indicated that the former compound cyclised readily in almost 50 min., while the latter compound cyclised very slowly (in about three hours) in an unstirred, 1 cm. long cell on a recording spectrophotometer (C  $\phi$ -C 10). Therefore, 1, 1'-dianthrimide derivative cyclises more readily than the corresponding 1, 2'-dianthrimide derivative.

One point to be noted is that dianthrimides without benzamido groups exhibit  $\lambda_{max}$  values at 360 m $\mu$ , those with a benzamido group in the

4-position exhibit  $\lambda_{max}$  values at 390–405 m $\mu$ ,<sup>1)</sup> and those with two benzamido groups in the 4, 4'-positions exhibit  $\lambda_{max}$  values at 435–455 m $\mu$ . The corresponding carbazoles containing benzamido group in the 4 or 4, 4'-positions exhibit  $\lambda_{max}$  values at 360–380 m $\mu$ .<sup>1)</sup> This does not apply to carbazoles containing benzamido groups in 4, 5'- or 5, 5'-positions. Indanthrene Brown FFR or R, obtained by the cyclisation of 4, 5'-dibenzamido-1, 1'-dianthrimide, exhibits  $\lambda_{max}$  values at 343, 560 and 605 m $\mu$ .<sup>2)</sup> Indanthrene Golden Orange 3G, obtained by the cyclisation of 5, 5'-dibenzamido-1, 1'-dianthrimide, exhibits  $\lambda_{max}$  values at 323 and 640 m $\mu$ .<sup>2)</sup>

### Experimental

Ultraviolet and visible spectra were taken on a Carl-Zeiss spectrophotometer, while the rate of cyclisation was studied on a Recording Spectrophotometer (C  $\phi$ -C 10). Analar sulphuric acid was used.

**The Purification of Indanthrene Gray K.**—The commercial dye (4 g.), after water and alcohol solubles had been removed, crystallised from nitrobenzene as blue needles; these needles gave a green color when dissolved in concentrated sulphuric acid. UV:  $\lambda_{H_2SO_4}^{max}$  m $\mu$ : 250–260, 335–340, 430–440.

Found: C, 75.5; H, 3.9; N, 6.6. Calcd. for C<sub>42</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>: C, 75.6; H, 3.8; N, 6.8%.

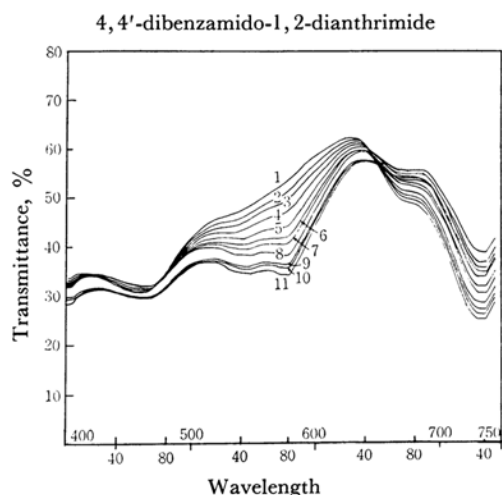
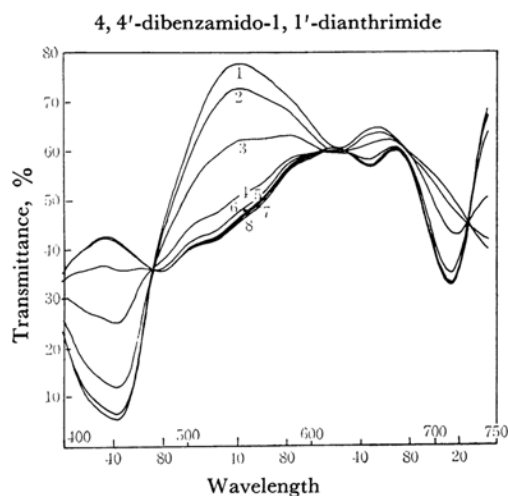
**The Cyclisation of Indanthrene Gray K.**—The above dye (1.2 g.) was stirred with concentrated sulphuric acid (8 g. of 96%) for two hours at 26–28°C. The olive dye which precipitated when the solution was then poured on ice was collected. It crystallized from nitrobenzene as microcrystals. UV:  $\lambda_{H_2SO_4}^{max}$  m $\mu$  262, 360–375, 538–545, and 580. In 50 min. Indanthrene Gray K was cyclised to Indanthrene Olive R by "Analar" sulphuric acid at 23°C; this was indicated by the recording spectrophotometer (see attached graph).

**The Purification of Commercial Indanthrene Olive R.**—The commercial dye (2 g.), after water and alcohol solubles had been removed, crystallised from nitrobenzene as microcrystals which gave a red color

\* Part III: K. S. Nair and K. H. Shah, This Bulletin, **39**, 2023 (1966).

1) K. H. Shah and K. M. Shah, *Indian J. Chem.*, **1965**, 273.

2) W. Bradley and J. V. Butcher, *J. Chem. Soc.*, **1954**, 2317.



when dissolved in concentrated sulphuric acid. UV:  $\lambda_{max}^{H_2SO_4}$   $m\mu$ : 225, 260—270, 360—380, 548, 580.

**4, 4'-Dibenzamido-1, 2'-dianthrimide.**—1-Benzamido-3-bromoanthraquinone.—A mixture of crystallised 1-amino-3-bromoanthraquinone<sup>3)</sup> (1.5 g.), benzoyl chloride (2 ml.), and *o*-dichlorobenzene (13 ml.) was refluxed while being stirred for two hours. The product was then collected; it crystallised from benzene as yellowish-green needles.

Found: N, 3.9. Calcd. for  $C_{21}H_{12}BrNO_3$ : N, 3.5%.

**4, 4'-Dibenzamido-1, 2'-dianthrimide.**—A mixture of crystallised 1-amino-4-benzamido anthraquinone (0.6 g.), 1-benzamido-3-bromoanthraquinone (0.75 g.), sodium acetate (0.2 g.), soda-ash (0.2 g.), copper powder (0.07 g.), copper acetate (0.01 g.) and naphthalene (8.0 g.) was refluxed while being stirred for eight hours. The product (1.1 g.) was collected after steam distillation. It separated from nitrobenzene as blackish-gray microcrystals; these gave a greenish-yellow colour when dis-

solved in concentrated sulphuric acid. UV:  $\lambda_{max}^{H_2SO_4}$   $m\mu$ : 290, 325—330, 455.

Found: C, 74.0; H, 3.7; N, 5.6. Calcd. for  $C_{42}H_{25}N_3O_6 \cdot 0.5H_2O$ : C, 74.5; H, 3.8; N, 6.2%.

**The Cyclisation of 4, 4'-dibenzamido-1, 2'-dianthrimide.**—The above dye (0.6 g.) was stirred with concentrated sulphuric acid (8 ml.) for 3.5 hr. at 25—30°C. The black compound which precipitated when the solution was then poured on ice crystallised from nitrobenzene as black needles; when dissolved in concentrated sulphuric acid, these needles gave a reddish-violet colour. UV:  $\lambda_{max}^{H_2SO_4}$   $m\mu$  280, 360—380, 570.

Found: C, 74.4; H, 3.7. Calcd. for  $C_{42}H_{23}N_3O_6 \cdot 0.5H_2O$ : C, 74.8; H, 3.6%.

4, 4'-Dibenzamido-1, 2'-dianthrimide was cyclised in three hours by "Analar" sulphuric acid at 23°C, as was indicated by a recording spectrophotometer (see attached graph).

Recording Spectrophotometer (C  $\phi$ -C 10)  
Temperature 23°C

Rate of cyclisation of Indanthrene Gray K  
(4, 4'-Dibenzamido-1, 1'-dianthrimide)

Indanthrene Gray K	0.0132 g./l.
Graph No.	Time interval
	min. sec.
1	6 15
2	13 45
3	22 00
4	27 15
5	29 40
6	34 55
7	42 10
8	50 45

Rate of cyclisation of 4, 4'-dibenzamido-1, 2'-dianthrimide; concentration, 0.0132 g./l.

Graph No.	Time interval
	hr. min. sec.
1	10 15
2	18 30
3	26 45
4	39 00
5	58 15
6	1 15 30
7	1 32 45
8	1 55 00
9	2 6 15
10	2 28 30
11	3 15 45

### Summary

Cyclisation of a dianthrimide to a carbazole with sulphuric acid is successful only when two benzamido groups are present. The spectral study of rates of cyclisation with sulphuric acid indicates that 4, 4'-dibenzamido-1, 1'-dianthrimide cyclises more readily than 4, 4'-dibenzamido-1, 2'-dianthrimide.

3) F. Ullmann and O. Eiser, *Chem. Ber.*, **49**, 2156 (1916).