410. *The Effect of Alkyl Groups on the Properties of Anthraquinone and Fluorescein Dyes.*

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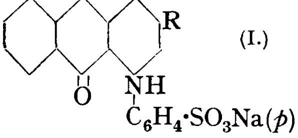
The recent use of dyes containing long alkyl chains (Report of the Progress of Applied Chemistry, 1935, **20**, 112) makes it desirable to have more knowledge of the effect of these chains on colour. It has long been known that the introduction of methyl or ethyl into amino-groups (*e.g.*, in rosaniline) shifts the colour towards the violet; the effect of alkyl groups when attached to the nucleus is known to be much smaller, but measurements on an homologous series of coloured compounds have not been available.

In this investigation three series of compounds have been studied: the red 1-amino-2-alkylanthraquinones, the blue dyes derived from these by introduction of $-NH{\cdot}C_6H_4{\cdot}SO_3Na$ into the 4-position (I), and finally some fluorescein derivatives.


(I.)

The 1-amino-2-alkylanthraquinones were carefully purified for the examination of their absorption spectra in a Hilger–Nutting spectrophotometer. All give deep red solutions in organic solvents (the crystals vary from deep red to vermilion according to the method of preparation), and at a dilution of $M/5000$ in 95% ethyl alcohol all are reddish-orange, the absorption band being in the blue (Fig. 1 and Table I).

Fig. 1.

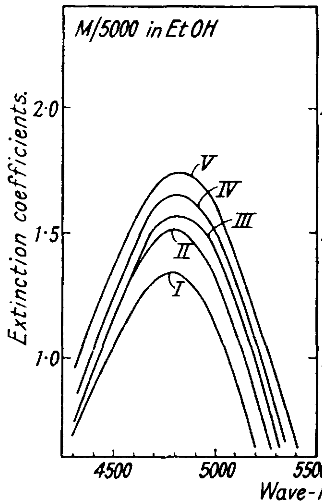


Fig. 2.

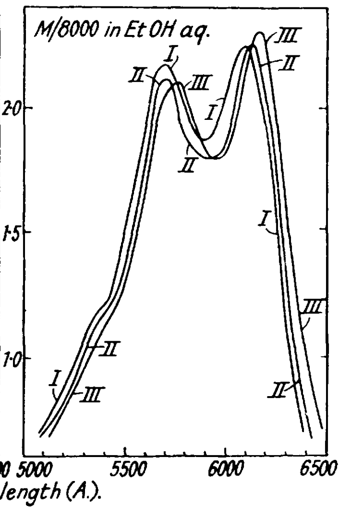


Fig. 1.

I. 1-*Aminoanthraquinone.*
II. 1-*Amino-2-methylanthraquinone.*
III. ,, -n-*butyl* ,, .
IV. ,, -n-*heptyl* ,, .
V. ,, -n-*dodecyl* ,,

Fig. 2.

I. 1-*Amino-4-anilino-2-methyl-4′-sulphonate.*
II. ,, -2-n-*heptyl-* ,, .
III. ,, -2-n-*dodecyl-* ,, .

Table I.

1-*Amino-2-alkylanthraquinones.*

Alkyl group.	M. p.	Peak of absorption band.	Extinction coefficient.	General absorption (R = H = 100).
(H)	256°, corr.	478 ± 1	1·35	100
CH_3	202, uncorr.	479	1·52	164
C_4H_9	175 ,,	480	1·56	227
C_7H_{15}	139 ,,	481	1·65	233
$C_{12}H_{25}$	135 ,,	482	1·74	238

The effect of the increasing length of the alkyl group is to cause a slight shift (which appears to be progressive) in the absorption band towards the longer wave-length, but this is insufficient to cause a change in the visible colour. At the same time there is a broadening of the absorption band and a regular increase in the extinction coefficient. In col. 5 of Table I the general absorption of light as measured in a colorimeter reaches nearly the maximum with the *n*-butyl compound.

In the blue dyes, as is shown in Tables II and III, the colour of the solution and of wool dyed with the compound shows a slight shift owing to the absorption of a longer wave-length by the higher homologues. But the changes in the extinction coefficients and in the general absorption are much smaller than with the simpler aminoanthraquinones.

TABLE II.

Wool dyes ; M/8000 *in* EtOH–H_2O (*equal vols.*).

R.	Peaks on absorption curve.	Extinction coefficients.	General absorption (R = CH_3 = 100).	Time of dyeing from dye-bath, mins.
CH_3	570, 610	2·17, 2·25	100	70
C_7H_{15}	573, 615	2·15, 2·25	103	35
$C_{12}H_{25}$	575, 618	2·07, 2·30	103	23

TABLE III.

	Colour quality of dyed wool samples.			Shade (brightness), %.	Covering power (R = CH_3 = 100).
R.	Red.	Green.	Blue.		
CH_3	12·9% or 0·226X	+ 17·8% + 0·195Y	+ 69·3% + 0·578Z	6·36	100
C_7H_{15}	12·4 or 0·223X	+ 17·8 + 0·194Y	+ 69·8 + 0·582Z	5·06	126
$C_{12}H_{25}$	12·1 or 0·222X	18·3 + 0·197Y	+ 69·6 + 0·582Z	5·16	123

The alkyl group has therefore less effect on the 1 : 4-diaminoanthraquinone than on the monoamino-compounds.

In assessing the value of a dye the covering power is an important factor, and in the above series the optical properties would suggest that equimolecular quantities of the dyes would dye wool to the same " shade " or brightness. (A dye with a *low* covering power gives a dyed sample which reflects relatively much light and has a *high* " shade " percentage.) But as is shown in Table II, and Table III (Shade), the covering power of the heptyl and the dodecyl compound is much greater than that of the first member. This increased covering power of the longer-chain compounds may be due to a greater concentration of dye near the surface of the fibre and this could be caused either by an attraction of the surface for the longer alkyl chain or by a less thorough penetration of the fibre owing to the greater speed of absorption. Parallel results have been obtained in the measurement of the covering power of other homologous series of anthraquinone dyes.

In the fluorescein dyes the effect of two *n*-hexyl chains was investigated, as it was thought that two such groups would produce a bigger effect than one dodecyl chain. The colour quality of the dyes when applied to wool and the covering power (Tables IV and V) were measured, but the results are more complex than those for the anthraquinones. On comparison of B with A (alkaline bath) a deepening of colour is evident, but in the specimen B from the alcoholic dye-bath the change is very striking. It appears that polymorphism of the dihexyl compound is responsible, and that the red instead of the usual yellow-orange form is fixed on the fibre.

C and D are very similar (from the alcoholic dye-bath), but the colour-quality (Table V) shows that the dihexyl compound *absorbs* slightly more red and less blue; the covering powers are almost identical, and it seems (on comparison with E and F) that the chlorine atoms in the phthalide nucleus hinder the action of the hexyl groups. Bromine atoms in the resorcinol nuclei do not reduce the effect of the hexyl groups : F absorbs much more red and less blue than E, and although in F the wool has taken up less than half as much

TABLE IV.

	Fluorescein derivative.	Alkaline (Shade %).	50% Alcohol (Shade %).	% of dye absorbed by the wool (alcoholic bath).
A.	Fluorescein	Lemon-yellow (48·5)	Bright yellow (52·1)	100
B.	2 : 7-*Dihexyl-*	Orange (37·6)	Red-orange (27·7)	100
C.	3′ : 6′-Dichloro-	Pale yellow (57·4)	Orange-yellow (44·3)	70
D.	3′ : 6′-Dichloro-2 : 7-dihexyl-	Orange-yellow (42·5)	Orange-yellow (44·0)	70
E.	4 : 5-Dibromo-	Pale orange	Orange (35·3)	85
F.	4 : 5-*Dibromo*-2 : 7-*dihexyl-*	Pale orange	Pink-orange (38·0)	40
(G.	3′ : 6′-Dichloro-4 : 5-dibromo-	Bright red	Deep red (16·9 ?)	100)
H.	3′ : 6′-*Dichloro*-4 : 5-*dibromo*-2 : 7-*dihexyl-*	Pale pink	Bright red (22·8)	100

TABLE V.

Fluoresceins on wool from alcoholic dye-baths.

Compound :		A.	B.	C.	D.	E.	F.	G.	H.
Colour quality (in terms of International Standard Primaries)	X	0·504	0·580	0·541	0·534	0·553	0·513	0·565	0·578
	Y	0·473	0·378	0·436	0·434	0·403	0·367	0·322	0·335
	Z	0·023	0·042	0·023	0·032	0·044	0·119	0·113	0·087

dye as in E the shade of the samples is almost equal. As in G the dye is impure, the sample cannot be compared with H.

In the two cases from which conclusions can fairly be drawn (C, D; and E, F) it appears that the hexyl groups tend to increase the absorption of red and decrease that of blue; there is also an increase in covering power.

EXPERIMENTAL.

1-*Aminoanthraquinone*.—The specimen purified by sublimation and two crystallisations from *n*-propyl alcohol melted at 256° (corr.) (Found : C, 75·5; H, 4·3. Calc. : C, 75·3; H, 4·0%). Boettger and Petersen (*Annalen*, 1873, **166**, 147) give m. p. 256° (compare Beisler and Jones, *J. Amer. Chem. Soc.*, 1922, **44**, 2296).

1-*Amino*-2-*methylanthraquinone*.—2-Methylanthraquinone was sublimed and then crystallised from *n*-propyl alcohol until the m. p. was 175°. With nitric acid (*d* 1·5, 40 hrs. at 15°) it yielded 1-nitro-2-methylanthraquinone which, crystallised from nitrobenzene, melted at 260°. The nitro-compound on reduction with sodium sulphide gave the amine, which was dissolved in hot 60% sulphuric acid, and the solution filtered and diluted. After three crystallisations from propyl alcohol the amine melted at 203°. Römer and Link (*Ber.*, 1883, **16**, 695) give m. p. 202°.

1-*Amino*-2-n-*butylanthraquinone*.—The general method of preparation is that of Scholl, Potschiwauscheg, and Lenko (*Monatsh.*, 1911, **32**, 687) for the propyl homologues, but several modifications have been made.

n-*Butylbenzene*. *n*-Butyl bromide (b. p. 102—103°; from *n*-butyl alcohol, b. p. 117·7—117·8°), bromobenzene, sodium, and toluene gave *n*-butylbenzene, b. p. 183—184°. Benzene being used instead of toluene as solvent, the yield was 28% owing to the greater ease of separation of the product. Konowalow (*J. Russ. Phys. Chem. Soc.*, 1895, **27**, 422) gives b. p. 183—184°.

2-(4′-n-*Butylbenzoyl*)*benzoic acid*. The product from *n*-butylbenzene (50 g.), phthalic anhydride (60 g.), carbon disulphide (550 c.c.), and finely powdered aluminium chloride (110 g.), crystallised from 50% acetic acid and then from alcohol, melted at 99° (Found : C, 76·4; H, 6·6. Calc. : C, 76·6; H, 6·4%). Underwood and Walsh (*J. Amer. Chem. Soc.*, 1935, **57**, 940) give m. p. 97—98°.

2-(4′-n-*Butylbenzyl*)*benzoic acid*. The Clemmensen method (*Ber.*, 1913, **46**, 1837) of reducing the keto-group gave a poor yield and was replaced by that of Scholl and co-workers (*loc. cit.*), a zinc–copper couple being employed in presence of ammonia. The product was freed from zinc by heating for several hours under reflux with concentrated hydrochloric acid; yield, 85—95%. Crystallised from alcohol, the *substance* melted at 86°; it had an irritant action on the skin (Found : C, 80·6; H, 7·4. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·4%).

2-n-*Butylanthraquinone*. The foregoing acid (20 g., finely powdered) was dissolved in sulphuric acid (220 c.c. of 97%), and the solution, after not more than 10 minutes, was poured on ice, whereupon the anthrone separated as an oil. Water was added, then sodium carbonate solution to neutralise some of the acid, and the mixture was extracted with ether. The ethereal extract yielded 11 g. (56%) of 2-*n*-butylanthrone (non-crystalline), which was used without further purification.

A solution of 2-*n*-butylanthrone (13 g.), *p*-nitrosodimethylaniline (7·3 g.), and piperidine (5 c.c.) in alcohol (165 c.c.) was refluxed for 2 hours, and the resulting purple solution of the anil poured into water (600 c.c.). Hydrolysis was effected by adding concentrated hydrochloric acid (50 c.c.) to this mixture and raising the temperature to 50° for 1 hour. 2-n-*Butylanthraquinone* separated as a green powder, which was washed with dilute hydrochloric acid, with water, and then dried. The yield was 11 g. (85%) of m. p. 72°. After two crystallisations from alcohol, the substance melted at 87·5° (Found : C, 82·1; H, 6·0. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·0%).

Conversion of the anthrone into the anthraquinone by means of bromine in acetic acid (Scholl and co-workers, *loc. cit.*; Goldmann, *Ber.*, 1887, **20**, 2436) gave a poor yield.

1-*Nitro*-2-n-*butylanthraquinone*. 2-*n*-Butylanthraquinone (1·9 g.) was dissolved at room temperature in nitric acid (13 g.; *d* 1·51, brown) and left during 40 hours. The product obtained by pouring the mixture into water had m. p. 112—117°, raised by three crystallisations from acetone to 147·5° (Found : C, 69·8; H, 4·7. $C_{18}H_{15}O_4N$ requires C, 69·9; H, 4·8%).

1-*Amino*-2-n-*butylanthraquinone*. The nitro-compound, reduced with sodium sulphide, gave 90% yields of *amine*, m. p. 160—165°. Crystallisation from *n*-propyl alcohol raised the m. p. to 174—175° (Found : C, 77·3; H, 6·0. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%).

1-*Amino*-2-n-*heptylanthraquinone*.—*Phenyl hexyl ketone*. To a mixture of heptoyl chloride (41·5 g., b. p. 81—83°/25 mm.) and A.R. benzene (110 g.), finely powdered anhydrous aluminium chloride (83 g.) was gradually added during 80 minutes. The mixture was left for 5 hours at 16° and then poured on ice. The benzene layers from several experiments were fractionally distilled, and gave a 71% yield of ketone, b. p. 140—150°/15 mm. A portion when redistilled solidified in ice-water and melted at 17°, in agreement with Krafft (*Ber.*, 1886, **19**, 2987).

Heptylbenzene. Reduction of the ketone by the original Clemmensen method (*loc. cit.*) was slow, and the yield was only 43% owing to the formation of resinous condensation products. The method of Müller and Saville (J., 1925, **127**, 599) gave the best results.

A mixture of amalgamated zinc (200 g.), phenyl hexyl ketone (69 g.), concentrated hydrochloric acid (100 c.c.), and ethyl alcohol saturated with hydrogen chloride (100 c.c.) was refluxed for ½ hour. Water (200 c.c.) was added, the mixture cooled, and about 300 c.c. of the aqueous layer removed. Again, concentrated hydrochloric acid and alcoholic hydrogen chloride (100 c.c. of each) were added, the mixture refluxed for ½ hour, and then water (200 c.c.) added. The process was carried out five times in all, and the product extracted with light petroleum (b. p. 60—80°). Distillation yielded fractions : (i) b. p. 106—110°/10 mm., 32 g.; (ii) b. p. 110—150°, 6·7 g.; (iii) b. p. > 150°, 12·3 g. By adding fraction (ii) to fresh ketone for reduction a final yield of 67% of fraction (i) was obtained. On distillation through a long column, this gave heptylbenzene, b. p. 108—111°/12 mm. Krafft (*loc. cit.*) gives b. p. 108—110°/10 mm.

2-(4′-*Heptylbenzoyl*)*benzoic acid*. The crude product containing aluminium salts was boiled with several portions of hydrochloric acid (15%), dried, and then extracted with light petroleum (b. p. 60—80°). The filtered extract, when cooled in a freezing mixture, deposited pale yellow crystals, m. p. 98—100°, and the solvent was again used for the extraction (yield 75%). Two crystallisations from light petroleum gave pale yellow crystals, m. p. 99—101° (Found : C, 77·6; H, 7·5. $C_{21}H_{24}O_3$ requires C, 77·8; H, 7·4%). The powdered *keto-acid* has an irritant action on the skin.

2-(4′-*Heptylbenzyl*)*benzoic acid*. The keto-acid was reduced in the same manner as the butyl analogue (yield 83%). A small portion, distilled (b. p. 220°/0·2 mm.) and then crystallised from light petroleum, melted at 69—71° (Found : C, 81·0; H, 8·2. $C_{21}H_{28}O_3$ requires C, 81·3; H, 8·4%).

2-n-*Heptylanthraquinone*. The foregoing acid (42 g.) was dissolved in sulphuric acid (850 c.c. of 97%) and after 10 minutes the solution was poured on ice. The anthrone was extracted with ether and obtained as a golden mass of crystals (yield 27 g., 65%). Without purification, the anthrone was condensed with *p*-nitrosodimethylaniline, and the product on hydrolysis gave a 95% yield of pale green crystals, m. p. 67—69°. Crystallised from glacial acetic acid and then from alcohol (charcoal), 2-n-*heptylanthraquinone* formed pale yellow crystals, m. p. 76° (Found : C, 82·4; H, 7·1. $C_{21}H_{22}O_2$ requires C, 82·4; H, 7·2%).

1-*Nitro*-2-n-*heptylanthraquinone*. The crude nitration *product*, m. p. 115° (yield quantitative), recrystallised from glacial acetic acid, melted at 137° (Found : N, 3·8. $C_{21}H_{21}O_4N$ requires N, 4·0%).

1-*Amino*-2-n-*heptylanthraquinone*. The nitro-compound was reduced with sodium sulphide in 95% yield to the red *amino*-compound, m. p. 121—124°. After three crystallisations from *n*-propyl alcohol, this melted at 138—139° (Found : C, 78·6; H, 7·4. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·2%).

1-*Amino*-2-n-*dodecylanthraquinone*.—A specimen supplied by Messrs. I. C. I. Ltd. (Dyestuffs Group) was distilled at a low pressure and then crystallised from *n*-propyl alcohol to constant m. p. 134—135° (Found : C, 80·0; H, 8·1. $C_{26}H_{33}O_2N$ requires C, 79·8; H, 8·4%).

Anthraquinone Wool Dyes.—1-*Amino*-4-*anilino*-2-*methylanthraquinone*. 4-Bromo-1-amino-2-methylanthraquinone (from Messrs. Imperial Chemical Industries Ltd.) was crystallised from pyridine and then melted at 246°. Eder and Manoukian (*Helv. Chim. Acta*, 1926, **9**, 53) give m. p. 245—246°. The bromo-compound (17·5 g.), potassium acetate (12 g.), copper acetate (1·0 g.), and aniline (60 c.c.) were stirred for 6 hours at 110°, and the cooled product was filtered off; when washed with alcohol, dilute hydrochloric acid, and water, it melted at 240°, and after two crystallisations from pyridine and one from benzene it melted at 245·5° (11 g. of dark blue needles). Admixture with the starting material depressed the m. p. to 215° (Found : C, 76·7; H, 5·0; N, 8·6. $C_{21}H_{16}O_2N_2$ requires C, 76·8; H, 4·9; N, 8·5%).

Sulphonation. To the amine (3 g.) in sulphuric acid (30 c.c. of 100%), oleum (6 c.c. of 20%) was added with stirring at 15—20°. As no reaction had occurred after 2 hours, a further 5 c.c. of oleum was added slowly at 25—30°, and after 30 minutes a test showed that all the product was soluble in water. The mixture was poured on ice, the dark blue solid collected, and dissolved in water, and the solution made neutral with sodium hydroxide solution. By addition of filtered brine, the *sodium* salt was precipitated, and was then crystallised from aqueous alcohol and dried at 120° (Found : S, 7·5. $C_{21}H_{15}O_5N_2SNa$ requires S, 7·4%).

The corresponding 2-heptyl and 2-dodecyl dyes were similarly prepared and purified, but the *n*-butyl compound could not be freed from disulphonation products. The *heptyl* compound (blue crystals with a bronze lustre) was moderately soluble in hot water (Found : S, 6·0. $C_{27}H_{27}O_5N_2SNa$ requires S, 6·2%), and the *dodecyl* compound was sparingly soluble in hot water (Found : S, 5·6. $C_{32}H_{37}O_5N_2SNa$ requires S, 5·5%).

Dyeing Experiments.—Squares of wool (3 × 3 inches, weighing approx. 2 g.) which had been thoroughly washed with soap and water were dried over calcium chloride and weighed. A square was then boiled for ½ hour with distilled water, for 2 minutes with ethyl alcohol, and then added to the hot (70°) dye-bath. This was made by dissolving the dye ($1·12 \times 10^{-5}$ g.-mol. per 1·0 g. of wool) in 100 c.c. of warm water and adding 25 c.c. of alcohol. After the wool had been put in, ammonium acetate solution (2 c.c. of 5%) was added and the contents of the beaker continuously stirred while the liquid was heated to boiling (hot water being added to keep the volume constant) and until almost all the dye had been absorbed. Then acetic acid (1 c.c. of 5%) was added, and stirring continued until the bath was colourless. The dyed wool was then washed several times with warm water and dried. This technique gave very evenly dyed samples. The times of exhaustion of the dye-baths were :

Dye	CH_3	C_7H_{15}	$C_{12}H_{25}$
Time (mins.)	70	35	23

Measurement of Colour Quality and Shade.—The dyed wool squares were fixed on glass plates, and measurements made on the Guild Trichromatic Colorimeter (Guild, *Trans. Optical Soc.*, 1925, **27**, 106).

Colour Quality.—The colour of the sample was then matched by adjusting the proportions of the three colour primaries of the instrument, and the result obtained in percentages; it is also expressed in terms of the colour standards X, Y, and Z recommended by the Commission Internationale de l'Eclairage (1931).

Reflecting Power (" shade " or brightness).—The covering power of dyes will be inversely proportional to the amounts of light reflected from cloth dyed in a standard manner with equimolecular quantities of the dyes. By knowing the relative amounts of luminosity contributed by the three primaries when mixed in the quantities required to match any given colour, it is possible to determine the amount of light reflected independently of the colour quality. This (the shade) is expressed as the ratio of the brightness of the specimen to the brightness of the magnesium oxide screen when both are illuminated under standard conditions. Careful regulation of the voltage on the standard lamp is essential; all samples should be tested at the same period and while the same " white light factor " holds for the instrument. Under these conditions the shade percentages are reproducible to 0·05%. The difference of 0·1% in shade between the C_7 and the C_{12} sample (see Table III) shows probably a real difference in the shade, but it is small enough to be caused by variations in the dyeing and need not represent a lower covering power of the dodecyl compound.

Fluorescein (A) and 3′ : 6′-dichlorofluorescein (C) were prepared by the method of Baeyer (*Annalen*, 1887, **239**, 357). The dichloro-compound had m. p. 285—286° (yellow plates), yellow-red in dilute sodium hydroxide solution, yellow in sulphuric acid, fluorescent. 4 : 5-Dibromofluorescein (E), obtained by bromination of fluorescein (Phillips, J., 1932, 724), was purified through the diacetate and formed red plates, m. p. 283°. It was yellow-pink (fluorescent) in sodium hydroxide solution and yellow in concentrated sulphuric acid. The 4 : 5-positions of the bromine atoms (Hewitt and Woodforde, J., 1902, **81**, 893) were confirmed by a degradation similar to that carried out by von Baeyer on eosin (*Annalen*, 1876, **183**, 47). The dibromo-compound (5 g.), heated with 50% sodium hydroxide solution (100 c.c.) at 120° for 1 hour and at 130° for 15 minutes, yielded colourless needles (from ethyl acetate and then light petroleum), m. p. 200° softening at 187°. This product was soluble in sodium carbonate solution, and behaved as the expected 2-(*3′-bromo-2′* : *4′-dihydroxybenzoyl*)*benzoic acid* (Found : C, 49·9; H, 2·8. $C_{14}H_9O_5Br$ requires C, 49·9; H, 2·7%).

2-*Bromo*-1 : 3-*dihydroxyanthraquinone*.—From the above benzoylbenzoic acid (0·2 g.), boric acid (0·8 g.), and oleum (5 c.c. of 20%) at 100° for 20 minutes, a small yield of bright yellow needles (from pyridine), m. p. 263—264°, was obtained (Found : C, 52·7; H, 2·4. $C_{14}H_7O_4Br$ requires C, 52·7; H, 2·2%). The reddish-blue solution of this 2-*bromo*-1 : 3-*dihydroxyanthraquinone* in sulphuric acid became bluer on addition of boric acid, and the substance was soluble in sodium carbonate solution (to a red colour) owing to the presence of a β-hydroxyl group.

2-*Bromoresorcinol*.—The filtrate from the degradation experiment which had already yielded the benzoylbenzoic acid was extracted repeatedly with ether. The tarry residues from the evaporation of the ethereal extracts were extracted (Soxhlet) with light petroleum. Long colourless needles were thus obtained, m. p. 100°, easily soluble in water and alcohol, less soluble in benzene and in light petroleum. With aqueous ferric chloride they gave a purple colour (Found : C, 38·3; H, 2·8. Calc. : C, 38·1; H, 2·7%). Rice (*J. Amer. Chem. Soc.*, 1926, **48**, 3126) gives the m. p. of 2-bromoresorcinol as 102·5°. Consequently, the regulated bromination of fluorescein gives 4 : 5-dibromofluorescein.

Attempts to prepare 3′ : 6′-dichloro-4 : 5-dibromofluorescein (G) by bromination of 3′ : 6′-dichlorofluorescein gave only mixtures containing di- and tetrabromo-compounds, m. p. 310—330°.

2 : 7-*Dihexylfluorescein* (B).—4-*n*-Hexylresorcinol (15 g.) (Dohme, Cox, and Miller, *J. Amer. Chem. Soc.*, 1926, **48**, 1690) and phthalic anhydride (5·5 g.) were stirred for 2 hours at 200—205°. Excess of hexylresorcinol was removed by heating in a vacuum, and the crushed residue was boiled with water and dried. Crystallisation from nitrobenzene gave yellow needles (yield 39%), which, on recrystallisation from aqueous alcohol, gave a mixture of yellow needles and red prisms, both melting at 245° (Found : C, 76·8; H, 7·5. $C_{32}H_{36}O_5$ requires C, 76·8; H, 7·2%). The crystals yield pink fluorescent solutions in sodium hydroxide and yellow faintly fluorescent solutions in concentrated sulphuric acid. Fluorescein itself is dimorphous.

4 : 5-*Dibromo*-2 : 7-*dihexylfluorescein* (F).—A solution of 2 : 7-dihexylfluorescein (2 g.) in alcohol (50 c.c.), refluxed with bromine (1·5 g.) and potassium chlorate (0·25 g.) for 2 hours, yielded yellow needles (from alcohol), m. p. 188°. These gave a red solution in sodium hydroxide and yellow in sulphuric acid; no fluorescence (Found : Br, 24·5. $C_{32}H_{34}O_5Br_2$ requires Br, 24·3%).

3′ : 6′-*Dichloro*-2 : 7-*dihexylfluorescein* (D), prepared by heating 4-hexylresorcinol (13 g.), 3 : 6-dichlorophthalic anhydride (6·5 g.), and zinc chloride (2 g.) at 200° for 45 minutes, melted at 228—229° (Found : Cl, 12·5. $C_{32}H_{34}O_5Cl_2$ requires Cl, 12·5%). The orange plates dissolved in sodium hydroxide to strongly fluorescent orange solutions; in concentrated sulphuric acid the colour was greenish-yellow, faintly fluorescent.

3′ : 6′-*Dichloro*-4 : 5-*dibromo*-2 : 7-*dihexylfluorescein* (H).—The dichlorodihexylfluorescein (2 g.), bromine (3 g.), and potassium chlorate (1 g.) in alcohol (65 c.c.), when refluxed for 2 hours, yielded pale yellow prisms, m. p. 169—170° (from glacial acetic acid). These gave a purple solution in 10% sodium hydroxide solution; the dilute solution was bluish-pink and fluorescent. The light brown solution in concentrated sulphuric acid did not fluoresce (Found : 5·89 mg. gave 5·46 mg. AgCl + AgBr. $C_{32}H_{32}O_5Cl_2Br_2$ requires 5·37 mg. AgCl + AgBr).

Dyeing with the Fluorescein Dyes.—Experiments with neutral aqueous solutions were unsuccessful owing to the sparing solubility of the hexyl compounds, and more even dyeing was obtained by addition of small amounts of sodium carbonate; but the best results were obtained with aqueous-alcoholic solutions. The dye ($2{\cdot}5 \times 10^{-5}$ g.-mol. per g. of wool) was dissolved in alcohol (50 c.c. of 95%), acetic acid (1 c.c.) and water (50 c.c.) being added. The wool, previously wetted with boiling water and then with alcohol, was introduced into the cold and stirred dye-bath in a beaker. All the samples to be compared were dyed simultaneously by placing the beakers in a trough and stirring continuously while the solutions were raised during 30 minutes to boiling, and then kept at the b. p. for 1 hour. During this period, 50 c.c. of water were added to each beaker. Even when the dye-bath was not completely exhausted, the wool was removed, rinsed and dried, the unabsorbed dye being determined colorimetrically (see Tables IV and V).

SUMMARY.

The effects of increasing length of the alkyl chain in 1-amino-2-alkylanthraquinones are: (1) A lowering of the m. p.; (2) a progressive shift and broadening of the absorption band; (3) a progressive increase in the extinction coefficient throughout the absorption band; (4) a rapid increase in general absorption up to the butyl, and very slow further increase to the dodecyl, homologue.

On the blue dyes (1-amino-4-anilino-2-alkylanthraquinone derivatives), the effects of increasing alkyl are: (1) A progressive shift in the absorption band; (2) no appreciable increase in the extinction coefficients or the general absorption; (3) an increased rate of dyeing; (4) an increase in covering power on wool, probably constant after the heptyl homologue.

Alkyl groups in fluorescein dyes cause an increased absorption of red light and an increase of covering power.

For the less soluble dyes aqueous-alcoholic dye-baths are essential for even dyeing.

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