Vat Dyes of Pyrazoloanthrone Series. IV. Constitution and Properties of N-alkyl Derivatives of Pyrazoloanthrone Yellow(1)

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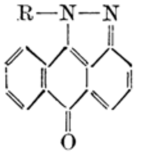
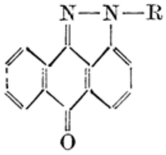
The actual existence of the two isomers of N-alkyl derivatives of pyrazoloanthrone, 9-N-alkyl form (I) and 1-N-alkyl isomer (II), was shown in our previous report.(2) We have then pointed out the tautomerism of Pyrazoloanthrone Yellow (2, 2'-dipyrazoloanthronyl) (III $\rightleftarrows$ IV, R=H)

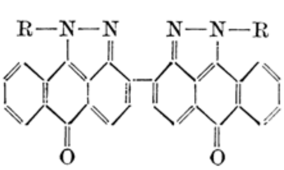


(I)

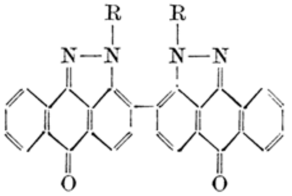


(II)

and established the constitution of the two isomers of its N, N'-dialkyl derivatives. Thus, 9-N, 9'-N'-dialkyl formula (III) has been given to the rubine red dyes and 1-N, 1'-N'-dialkyl structure (IV) to the orange isomers.(3)



(III)



(IV)

The methyl ($R=CH_3$) and ethyl ($R=CH_2\cdot CH_3$) compounds were already described in our preceding report.(3) We have now prepared hitherto unknown N, N'-di-n-propyl (III, IV, $R=CH_2\cdot CH_2\cdot CH_3$) and N, N'-di-n-butyl (III, IV, $R=CH_2\cdot CH_2\cdot CH_2\cdot CH_3$) derivatives by the alkylation of Pyrazoloanthrone Yellow with the corresponding alkyl *p*-toluenesulfonate. In all cases rubine red vat dyes (III) of higher light fastness and orange isomers (IV) of lower light fastness were simultaneously produced, and the former dyes were the principal products (72~75% of the theory). The rubine red dyes are nearly insoluble in organic solvents, while the orange isomers so very easily soluble, that the quantitative separation of the two isomers can simply be carried out using *o*-dichlorobenzene.

	Yield (% of the theory)	
	Rubine red dyes (III)	Orange isomers (IV)
$R=CH_3$	75.1%	21.4%
$R=CH_2\cdot CH_3$	74.9	23.8
$R=CH_2\cdot CH_2\cdot CH_3$	72.6	26.8
$R=CH_2\cdot CH_2\cdot CH_2\cdot CH_3$	72.3	27.3

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(1) Read before the 5 th Annual Meeting of the Chemical Society of Japan on April 5, 1952.

(2) T. Maki and T. Akamatsu, *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 281 (1951).

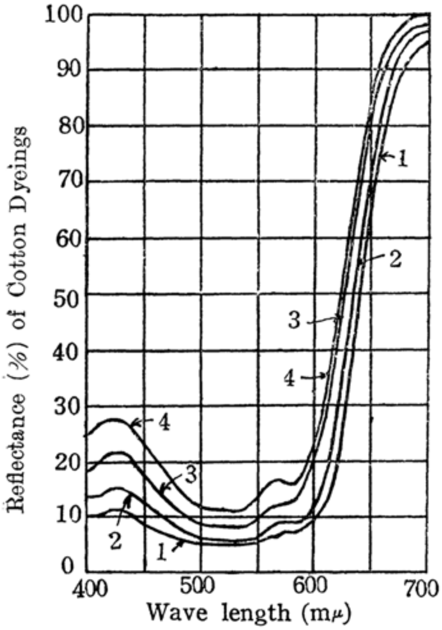
(3) T. Maki and T. Akamatsu, *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 326 (1951); See also *J. C. S.*, **1952**, 1631, 1637~8.

Various coloring properties of the four principal rubine red vat dyes are compared.

Constitution (III)	Streak	Conc. H_2SO_4	Vat	On cotton	
				Shade	Light fastness
$R=CH_3$	Purple red	Red orange	Blue (A)	Rubine red	5∼6(B)
$R=C_2H_5$(4)	Purple red	Red orange	Blue (A)	Rubine red	6 (A)
$R=n\text{-}C_3H_7$	Purple red	Red orange	Blue (C)	Rubine red	5∼6(C)
$R=n\text{-}C_4H_9$	Purple red	Red orange	Blue (B)	Rubine red	5∼6(D)

In the column of vat, (A) means easily soluble, (B) and (C) soluble with some difficulty. Under the light fastness, (A), (B), (C) and (D) denote the order of fastness. (A) is the highest among the four compounds.

More accurate comparison of the four rubine red dyeings were carried out using self recording G. E. spectrophotometer with 1% cotton dyeings (IN method) and the obtained reflectance curves (Fig. 1) were analysed according to the I. C. I. system.(5)



1…………… (III), $R=CH_3$
2…………… (III), $R=C_2H_5$
3…………… (III), $R=n\text{-}C_4H_9$
4…………… (III), $R=n\text{-}C_3H_7$

Fig. 1

Constitution (III)	R= CH_3	R= C_2H_5	R= $n\text{-}C_3H_7$	R= $n\text{-}C_4H_9$
Trichromatic coefficient x	0.4352	0.4252	0.3894	0.4137
Trichromatic coefficient y	0.2725	0.2609	0.2625	0.2650
Brightness Y(%)	9.16	11.47	19.46	16.07
Dominant wave-length (mμ)	495.1c	496.9c	499.2c	497.0c
Color purity (%)	41	44	36.2	40

Comparing the dominant wave-lengths it is known that the shade of the N, N'-dimethyl derivative is most reddish and that of the N, N'-di-n-propyl derivative most bluish although their differences are not very remarkable. It was unexpected that the n-butyl is less bluish than the n-propyl homologue. The shade of the N, N'-diethyl compound shows the highest color purity (i. e. most monochromatic) among the four, while lower brightness (Y) of the N, N'-dimethyl and diethyl compounds is shown due principally to their stronger dyeing powers. The order of the cotton dyeing powers is: methyl>ethyl>n-butyl>n-propyl.

Vinylon(6) fibres and cloths, to which most vat dyes are not satisfactorily applicable, can be dyed in rubine red shades by a modified IN method with these N, N'-dialkylated Pyrazoloanthrone Yellow, in which the N, N'-di-n-propyl compound gives the most clear and strong red dyeings of sufficient intensity. The washing fastness of vinylon dyeings of the *n*-propyl derivative was excellent, light fastness about 5 grade, their fastness to rubbing, however, was not very high (nearly 3 grade). The order of the vinylon dyeing powers is: n-propyl>ethyl>n-butyl>methyl.

Experimental Part

N, N'-Di-*n*-propyl Derivatives of Pyrazoloanthrone Yellow.—1.32 g. (1 mol. ratio) of Pyrazoloanthrone Yellow(3) was converted into nearly 20% paste by the usual method, heated on a water bath with 4 g. of 90% sodium hydroxide and 4 cc. of water, diluted with 62 cc. of cold water, the N, N'-disodium salt thus formed was filtered and without washing perfectly dried in vacuum at room temperature. This was then finely powdered and boiled under reflux with stirring in 26 g. of *o*-dichlorobenzene with 1.93g. (3 mol. ratio) of n-propyl p-toluenesulfonate (b. p. 4 mm. 145±3°) for 6 hours. When the hot solution was filtered and washed with alcohol and hot water the rubine red compound (III, $R=CH_2{\cdot}CH_2{\cdot}CH_3$) was obtained as an insoluble

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(4) According to our studies this must be the true constitution of Indanthren Rubine R. See reference (3).

(5) A. C. Hardy, Handbook of Colorimetry.

(6) Polymerized vinyl alcohol partially acetallized (ca. 35%) with formaldehyde.

crystalline powder. Yield was 1.14 g. (72.61% of the theory). From the *o*-dichlorobenzene filtrate crude orange isomer (IV, $R=CH_2{\cdot}CH_2{\cdot}CH_3$) was collected after steam distillation. Yield was 0.42 g. (26.75% of the theory), the total yield corresponds to 99.36% of the theory.

The insoluble rubine red compound is a brown red powder, having a purple red streak, dissolves in conc. sulfuric acid with red orange color, from which by gradual addition of water successively resulted yellow-orange solution, yellow solution, yellow precipitate and at last purple red precipitate. Hydrosulfite vat, which is a little less easily soluble than other three N, N'-dialkyl derivatives, is blue, and cotton is dyed in clear purple-red shade by IN method (2% dye). When the substance was dissolved in 20 parts of 98.5% sulfuric acid and 8.2 cc. of water added dropwise with external cooling to produce 70% sulfuric acid the insoluble part (92%) was the rubine red dye of highest purity. Found: N, 10.68; Calculated for $C_{34}H_{26}O_2N_4$ (III, $R=n\text{-}C_3H_7$): N, 10.72 %.

The crude orange isomer, which had been obtained by steam distillation from the *o*-dichlorobenzene filtrate, was further purified by dissolving in monochlorobenzene, shaking with active coal, filtering and adding alcohol to the concentrated filtrate. It is an orange brown crystalline powder with an orange streak. Conc. sulfuric acid solution is red orange, from which orange precipitate resulted by the addition of water. From a blue hydrosulfite vat (IN) it dyes cotton red-orange of lower light fastness than the rubine red isomer. Found: N, 10.62; Calculated for $C_{34}H_{26}O_2N_4$ (IV, $R=n\text{-}C_3H_7$): N, 10.72%.

Vinylon fibres can be dyed by a modified IN method using dye paste. The dye bath consisted of 120 cc. of water, 3 cc. of 25% sodium hydroxide, 0.8 g. of hydrosulfite and 0.4 cc. of turkey red oil and vatted at 60° for 15 min. The fibres were dyed at 50° for 90 min. and after air oxidation, washing and acidification treated with soap solution (0.2:100) at 60° for 30 min. Sufficient intensity is obtained with 2% dye.

N, N'-Di-*n*-butyl Derivatives of Pyrazoloanthrone Yellow.—2.19 g. (1 mol. ratio) of Pyrazoloanthrone Yellow was converted into N, N'-disodium salt using 8 g. of 90% sodium hydroxide as in the case of the above n-propyl compounds. This was then as a dry, fine powder boiled with 44 g. of o-dichlorobenzene and 3.42 g. (3 mol. ratio) of n-butyl *p*-toluenesulfonate (b. p. 3.5 mm. 140~145°) for 6 hours and filtered hot. The yield of insoluble crystalline powder of the rubine red compound (III, $R=CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$) was 1.96 g. (72.33% of the theory), while the amount of the soluble orange isomer (IV, $R=CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$) was 0.74 g. (27.31% of the theory). The total yield was 99.64% of the theory. Their color reactions and dyeing properties are on the whole similar to those of the corresponding n-propyl derivatives. The comparison of the homologous rubine red dyes are given in the general part of this paper. The rubine red n-butyl compound of the highest purity remained insoluble (93%) by the treatment with 70% sulfuric acid. Found: N, 10.17; Calculated for $C_{36}H_{30}O_2N_4$ (III, $R=n\text{-}C_4H_9$): N, 10.18%.

The orange isomer was purified a in the case of the n-propyl compound with monochlorobenzene, active coal and alcohol and the orange brown crystalline powder thus obtained was analysed. Found: N, 10.11; Calculated for $C_{36}H_{30}O_2N_4$ (IV, $R=n\text{-}C_4H_9$): N, 10.18%.

Measurement of Reflectance Curves of the Cotton Dyeings.—1% IN cotton dyeings were carefully prepared using the rubine red vat dyes purified with 70% sulfuric acid. The dyes were converted into paste form before dyeing. The reflectance (%) of the cotton dyeings was measured by self recording G. E. spectrophotometer taking a similarly treated, undyed cotton cloth as the standard in order to cancel the absorption effect of the latter. The light source C of the I. C. I. system was used.

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