Vat Dyes of Acenaphthene Series. VI. Derivatives of Acenaphthene Violet[1]

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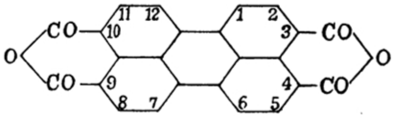
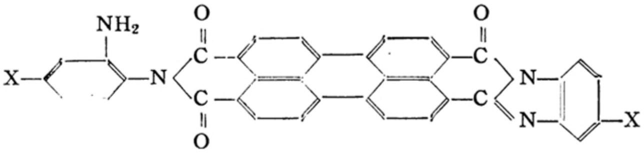
The formation of Acenaphthene Violet (II), a new, deep violet vat dye of maximum fastness, from 3,4,9,10-perylene-tetracarboxylic anhydride (I) and *o*-phenylenediamine was reported in our previous paper[2].

We have now prepared *p,p'*-dichloro derivative of Acenaphthene Violet (III), a brilliant violet vat dye, by condensation of 4-chloro-1,2-phenylenediamine (VII) with (I) at 170°, and also a violet blue dibenzo derivative (V) from (I) and 1,2-naphthylenediamine (VIII) at 150°. As 4-methoxy-1,2-phenylenediamine has been found to be unstable, di(*p*-methoxy-*o*-nitro)phenyl-diimide (VI) was synthesized by condensing 4-methoxy-2-nitroaniline (IX) and (I) at 200°, and *p,p'*-dimethoxy Acenaphthene Violet (IV) was obtained by its reduction with sodium sulfide via the corresponding diamino-dimethoxyl compound.

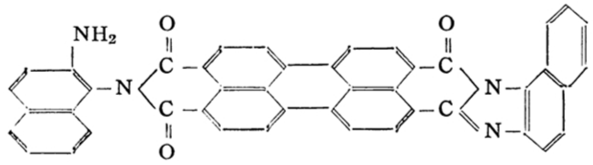
The fastness of the cotton dyeings of these vat dyes are excellent and among them the unsubstituted Acenaphthene Violet has the maximum light fastness, while the violet shade of the dichloro compound is most brilliant.



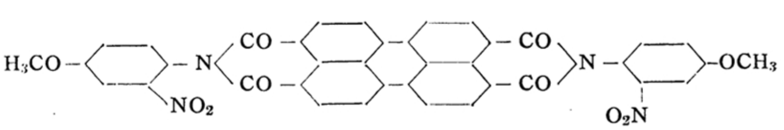
(I)



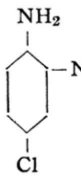
(II) X=H
(III) X=Cl
(IV) X=OCH₃



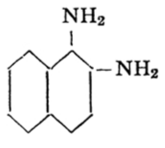
(V)



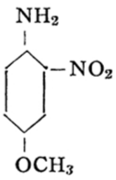
(VI)



(VII)



(VIII)



(IX)

	Cotton dyeings		
	Shade	Light fastness	Yield of the theory (%)
Acenaphthene Violet (II)	Violet	8	60.6
Dichloro Derivative (III)	Brilliant violet	7~8	66.3
Dimethoxyl Derivative (IV)	Reddish violet	6~7	49.6
Dibenzo Derivative (V)	Violet blue	7	33.5

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[1] Read before the 7th Annual Meeting of the Chemical Society of Japan on April 3, 1954.

[2] This Bulletin, **25**, 411 (1952).

Constitution		(II)	(III)	(IV)	(V)
Trichromatic coefficient	x	0.2712	0.2632	0.2794	0.2463
	y	0.1963	0.1796	0.2093	0.2074
Brightness Y (%)		6.49	6.55	8.21	7.88
Dominant wavelength (mμ)		564.0c	564.6c	562.8c	461
Color purity (%)		40.8	46.2	37.4	38.1

More accurate comparison of the shades of Acenaphthene Violet and its derivatives were carried out using G.E. recording spectrophotometer with 1% cotton dyeings (IW method) and the obtained reflectance curves (Fig. 1) were analysed according to the I.C.I. system.

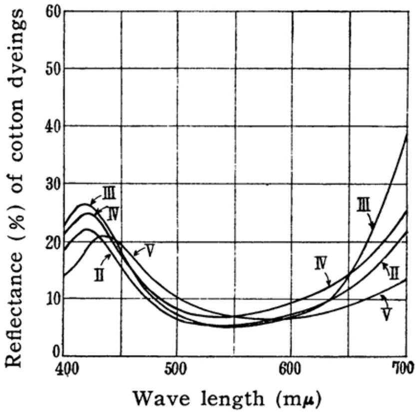
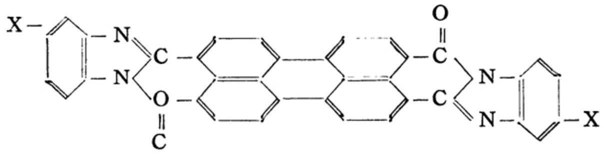


Fig. 1.

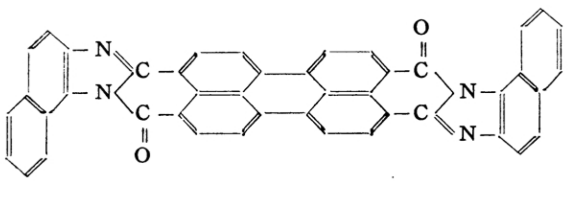
These vat dyes of the mono-imidazole type (II–V) are easily soluble in alkaline hydrosulfite and also soluble in 85∼90% sulfuric acid. The straight and short conjugation between the two upper (3,10–) carbonyls is considered as the cause of the easy vattability. The associated bis-imidazoles (X–XI), violet blue or blue pigments of highest stability, are the ultimate reaction products and insoluble in alkaline hydrosulfite. Theoretically both *cis*- and *trans*-isomers of the bis-imidazoles may be possible as in the case of 1,4,5,8-naphthalene-tetracarboxylic acid. In the present case, however, the structure of the bis-imidazoles must be *trans*-forms (X–XI) of long and crooked conjugation between the two carbonyls (3,9–) owing to their perfect insolubility against alkaline hydrosulfite. The associated *o,o'*-diamino compounds, the initial condensation products, are insoluble in 85–90% sulfuric acid and have weak dyeing properties of low value.

Experimental Part

Dichloro Derivative of Acenaphthene Violet (III).—Perylene-tetracarboxylic anhydride (1, 31 g., 1 mol. ratio) was heated with an excess of 4-chloro-1,2-phenylenediamine[3] (4.8 g., 10 mol. ratio) and 1.0 g. (5 mol. ratio) of glacial acetic acid in an oil bath under reflux at 170° (bath temperature) for 1 hour. The product was heated up with 20 cc. of alcohol, the hot solution was filtered and washed with more alcohol until the filtrate became colorless. The collected precipitate was then treated with 200 cc. of hot aqueous 1% sodium hydroxide. The amount of the unchanged tetracarboxylic acid (alkali soluble) was only a trace. The yield of the crude condensation product was 1.92 g. The crude product was finely powdered, kept with 4 g. of sodium hydroxide, 4 g. of sodium hydrosulfite and 200 cc. of water at 50° for 15 minutes, filtered, and the insoluble part was further treated with 2 g. of sodium hydroxide and 2 g. of sodium hydrosulfite and 100 cc. of water. The part insoluble in the alkaline hydrosulfite, 0.26 g. or 12.9% of the theory, is the blue violet bis-imidazole pigment (X,X=Cl)



(X)



(XI)

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[3] *p*-Chloroaniline was acetylated with acetic anhydride in benzene to *p*-chloroacetoanilide, m.p. 179.5—180.5° (corr.), in 94.7% yield, converted then into 4-chloro-2-nitroaniline, m.p. 116.4—116.9°, by nitration in conc. sulfuric acid, hydrolysis with 70% sulfuric acid and recrystallisation from water. Yield was 62.9%. The latter was reduced with zinc dust using alcohol and 20% sodium hydroxide and after recrystallisation from water 4-chloro-1,2-phenylenediamine, m.p. 75.0°, was obtained in 50.3% yield. See also Bruyn, *Rec. trav. chim.*, **36**, 127 (1916); Ullmann, Manthner, *Ber.*, **36**, 4027 (1903); *Org., Synth.*, **19**, 70 (1939).

The combined vat filtrate was oxidized by a current of air, the collected precipitate, as a dry powder, dissolved in 42 g. of 99.2% sulfuric acid and 4.3 cc. of water was dropped in under ice cooling to produce 90% sulfuric acid. The insoluble, 0.08 g. or 3.7% of the theory, is the *o,o'*-diamino compound, which dyes cotton in weak, dull violet red of low value from a violet red vat (IW).

The part soluble in 90% sulfuric acid is the main dye, dichloro Acenaphthene Violet (III), the yield was 1.38 g. or 66.3% of the theory. The dichloro compound (III) is a black violet powder, soluble in conc. sulfuric acid and the solution shows blue (thin layer) and violet blue (thick layer) dichroism with weak red fluorescence. Violet precipitate resulted from the conc. sulfuric acid solution by the addition of water. Hydrosulfite vat (IW) is red violet and dyes cotton in brilliant violet of powerful intensity with 1∼2% dye, a little more bluish than the chlorine free Acenaphthene Violet (II). The light fastness of the cotton dyeings were found to be 7—8 grade. Found Cl, 10.91; calcd. for $C_{36}H_{16}O_3N_4Cl_2$ (III): Cl, 11.37%.

Dimethoxyl Derivative of Acenaphthene Violet.—A mixture of 1.31 g. (1 mol. ratio) of perylene-tetracarboxylic anhydride and 7.8 g. (14 mol. ratio) of 4-methyoxy-2-nitroaniline (m.p. 124.5—125°, corr.)[4] was heated with 1.0 g. (5 mol. ratio) of glacial acetic acid in an oil bath under reflux at 200° (bath temperature) for 7 hours. The unchanged components were removed with 100 cc. of alcohol and 500 cc. of 1% sodium hydroxide as above. The yield of the dinitro compound (VI) was 1.60 g. or 69.3% of the theory. It is a dark brownish red crystalline powder with a pink streak, soluble in conc. sulfuric acid with violet blue (thin layer) and violet red (thick layer) dichroism without fluorescence. Pink precipitate is formed from the conc. sulfuric acid solution by the addition of water. It dyes cotton in a weak, dull violet red shade of diamino compound from a violet red vat (IW). The vat shows weak orange fluorescence. The powder is a little soluble in boiling nitrobenzene with red-orange color and strong green-yellow fluorescence.

The dinitro compound (1.30 g., 1 mol. ratio) was dissolved in 50 g. of ice cold conc. sulfuric acid and poured into 1,000 cc. of ice cold water. The filtered and neutral washed paste was reduced with 1.1 g. of 55% sodium sulfide (4 mol. ratio) and 15 cc. of water by treating 1 hour at room temperature and 3 hours at 60°. It was then made up to 100 cc. with warm water (60°), the collected precipitate washed neutral and dried at 110° for 5 hours. The yield of the crude product was 1.20 g.

The crude reduction product was treated with 4 g. of sodium hydroxide, 4 g. of sodium hydrosulfite and 200 cc. of water at 50° for 15 minutes. The amount of the hydrosulfite insoluble (dimethoxy bis-imidazole) was only a trace. The soluble part was, after air oxidation, separated with 55.6 parts of 85% sulfuric acid. The part insoluble in 85% sulfuric acid corresponds to the diamino compound (0.24 g. or 20.2% of the theory). It dissolves in conc. sulfuric acid with blue color (without dichroism) and weak red fluorescence, and red violet precipitate is produced from the solution by the addition of water. Hydrosulfite vat (IW) is violet red with weak orange fluorescence and dyes cotton in weak, dull violet red of low value.

The part soluble in 85% sulfuric acid is the main dye, dimethoxy Acenaphthene Violet (IV). It was precipitated by pouring the sulfuric acid filtrate into ice water. The yield was 0.83 g. or 71.6% of the theory (49.6% of the theory from 4-methoxy-2-nitroaniline). It is a dark violet powder with a violet streak. The conc. sulfuric acid solution is blue (without dichroism) with weak red fluorescence, from which a red violet precipitate is formed by water. It is very easily soluble in alkaline hydrosulfite (IW) giving red violet vat with weak orange fluorescence and dyes cotton in a deep reddish violet shade. The grade of the light fastness of its dyeings is 6—7. The substance is a little soluble in boiling nitrobenzene with violet red color and green yellow fluorescence. Found: N, 8.93; calcd. for $C_{38}H_{22}O_5N_4$ (IV): N, 9.12%.

It is interesting that in the case of this methoxyl compound the imidazolization of one of the *o*-amino groups occurs readily at the same time with sodium sulfide reduction even at 60°. When the reduction was carried out at 100° for 3 hours the imidazolization proceeded further, giving 36% of the bis-imidazole pigment (X, $X = OCH_3$), 16% of the *o,o'*-diamino compound and only 32% of the mono-imidazole dye (IV). The drying temperatures of the products, when they were not higher than 110°, had practically no influence upon the rate of imidazolization.

Dibenzo Derivative of Acenaphthene Violet (V).—Perylene-tetracarboxylic anhydride (1.31 g., 1 mol. ratio) was heated with 5.2 g. (10 mol. ratio) of 1,2-naphthylenediamine (m.p. 95—96°, uncorr.)[5] and 1.0 g. (5 mol. ratio) of glacial acetic acid in an oil bath at 150° (bath temperature) for 1 hour and the unchanged components were removed with alcohol and 1% sodium hydroxide as in the above experiments. The weight of the crude condensation product was 2.10 g. It was then treated twice with 4 g. of sodium hydroxide, 4 g. of hydrosulfite and 200 cc. of water at 50° for 15 minutes and filtered. The amount of the hydrosulfite insoluble was 1.16 g. or 55.3% of the crude product. The part soluble in hydrosulfite was treated, after air oxidation as a dry powder, with 90% sulfuric acid. The amount of the sulfuric

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[4] *Org. Synth.*, **25**, 78 (1945); 4-Methoxy-2-nitroacetanilide, m.p. 118.7—119.2° (corr.) was obtained in 73.5% yield from *p*-anisidine and then saponified with potassium hydroxide in methanol to 4-methoxy-2-nitroaniline. The yield was 99.3%.

[5] Diazotized aniline was coupled with *β*-naphthylamine in alcoholic solution to 1-benzene-azo-2-naphthylamine, m.p. 102.5—103° in 90.8% yield of the theory. It was then reduced with zinc dust in aqueous acetic acid. The yield of pure 1,2-naphthylenediamine was 53.2%. See Bamberger, Schieffelin, *Ber.*, **22**, 1376 (1889); Yokote et al., *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 476 (1951).

acid insoluble was a trace and the soluble part was the main vat dye, dibenzo Acenaphthene Violet (V), which was collected after pouring the sulfuric acid filtrate into ice water. The yield was 0.74 g. or 33.5% of the theory[6]. It is a black violet powder of violet streak, hardly soluble in organic solvents, soluble in conc. sulfuric acid blue without dichroism and fluorescence and a violet precipitate is formed from the solution by the addition of water. The hydrosulfite vat (IW) is red violet, from which cotton is dyed in a violet blue (navy blue) shade of excellent light fastness (grade 7). Found: N, 8.24; calcd. for $C_{44}H_{22}O_3N_4$ (V): N, 8.56%.

The *o,o'*-diamino compounds of the benzene series (N,N'-diphenyldiimide type) were soluble in alkaline hydrosulfite, but the hydrosulfite insoluble of the above 150°-condensation product of 1,2-naphthylenediamine was found to be mainly *o,o'*-diamino compound by the actual estimation of the nitrogen evolution from the corresponding diazo compound. The di(*o*-amino)naphthyl-diimide is soluble in conc. sulfuric acid in blue color without dichroism and fluorescence and is a violet substance in the precipitated state. The hydrosulfite insoluble of 120°-condensation was also the *o,o'*-diamino compound. On the other hand, however, the hydrosulfite insoluble of 170°-condensation was mainly the bis-naphthoimidazole, which had analytically no more free $-NH_2$ groups. The bis-naphthoimidazole (XI) is a blue pigment and its blue conc. sulfuric acid solution shows neither dichroism nor fluorescence.

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[6] By 170°-condensation the yield of the main vat dye (V) was 17.4% and at 120° 16.5% of the theory.