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Dyes and Pigments, Vol. 37, No. 3, pp. 255–264, 1998
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Printed in Great Britain
PII: S0143-7208(97)-00062-4 0143-7208/98 $19.00 + 0.00

A Novel Synthesis of Anthraquinonoid Blue Disperse Dyes: Reaction of Primary Amines with 4,8-Dinitroanthrarufin and 4,5-Dinitrochrysazin

Y. C. Chao,* T. S. Lee & S. Y. Chang

Department of Textiles, National Taipei Institute of Technology, Taipei 10643, Taiwan

(Received 5 May 1997; accepted 11 June 1997)

ABSTRACT

Condensation of primary amines with 4,8-dinitroanthrarufin (DNAR) and 4,5-dinitrochrysazin (DNCZ) at room temperature afforded the corresponding 4-arylamino-, and 2,4(2,6)-dialkylamino-, 2,6-(2,7)-diarylamino-anthraquinone blue dyes. It is proposed that the initial enol-ketone tautomerism from DNAR and DNCZ facilitates formation of the 4-arylamino derivatives. The possibility of the formation of the reactive species 1,2,9,10-tetrahydro-1,2,9,10-tetraoxoanthracene and 1,2,5,6,9,10-hexahydro-1,2,5,6,9,10-hexaoxoanthracene(XI and XII), oxidised from ketone forms of DNAR and DNCZ (IX and X) by cupric ion and air, is also discussed. © *1998 Elsevier Science Ltd*

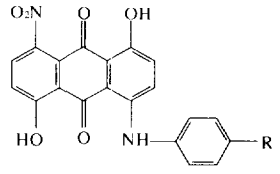
Keywords: dinitroanthrarufin, dinitrochrysazin, enol-ketone tautomerism, tetraoxoanthracene, hexaoxoanthracene, cupric ion, disperse.

1 INTRODUCTION

4,8-Dinitroanthrarufin (DNAR) and 4,5-dinitrochrysazin (DNCZ) are widely utilized in the synthesis of blue disperse dyes. Thus, the condensation of DNAR and DNCZ with alkylamines and arylamines affords the corresponding 4-alkylaminol [1, 2] 4-arylamino [3], 4-arylamino-5(8)-amino [3], and 8-(5-) amino-4-alkylamino derivatives [1, 2] and 1-alkylamino-4-arylamino-5-nitro(and-5-amino) [4], 1,5-bis(alkylamino)-4-arylamino [4], 1,4-bis(aryla-

*Corresponding author.

mino)-5-nitro (and-5-amino) [5], 1,4,5-tris(arylamino) [5], 5-alkylamino-1,4-bis(arylamino) [5], 4,8-,4,5- and 5,8- bis(arylamino) [6], 4,8(4,5)-bis(alkylamino), [1, 2] and 1,4,5,8-tetrakis(arylamino) [7, 8] derivatives. They were prepared by reaction with excess amine at high temperature (above 100°C). However, 2-substituted and 2,6- and 2,7-disubstituted derivatives can be prepared by stirring excess reagents such as thiophenol and thioglycol with DNAR and DNCZ at room temperature [9, 10]. We now report the condensation of DNAR (and DNCZ) with excess arylamines (and alkylamines) in the presence (and in the absence) of cupric acetate at room temperature to give 4-arylamino-5(8)-nitro (I and II), 2,6-(2,7)-bis(arylamino)-4,8-(4,5-) diamino (III and IV), 2,4-bis(alkyl- and aryl-amino)-8-nitro(V), and 2,6-bis(alkylamino)-4,8-dinitro(VI) derivatives, and possible mechanisms for them are discussed.



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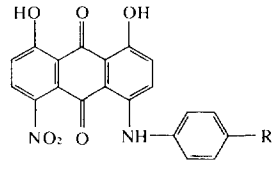

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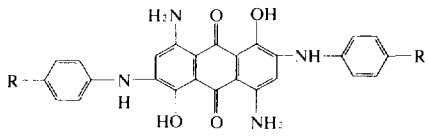

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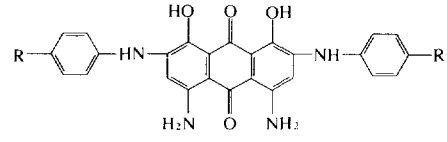

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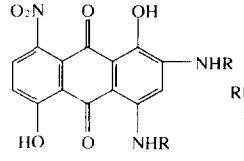

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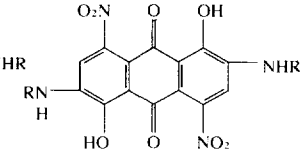

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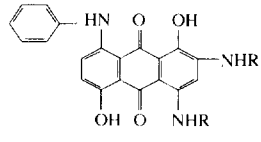

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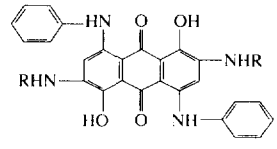


VIII

2 EXPERIMENTAL

2.1 Preparation of dyes I and II

DNAR (0.5 g) and aniline (4 g) were stirred in 20 ml *N*,*N*-dimethylformamide (DMF) at room temperature for 25 h. The mixture was stirred into 200 ml 10% aqueous hydrochloric acid. The blue solid was filtered, washed neutral with water and recrystallised from 2-methoxyethanol (0.34 g, 60%) in dark brown needles with a metallic lustre, m.p. 222°C–224°C, of 4-anilino-8-nitro-1,5-dihydroxyanthraquinone (I.1). From DNAR or DNCZ and the appropriate arylamines were similarly obtained dyes I.2, I.3 and II.1–II.3 (Table 1).

2.2 Preparation of dyes III, IV, V and VI

The above procedure (Section 2.1) was repeated in the presence of 0.33 g cupric acetate. Relevant data on yield and λ_{max} are given in Table 1.

TABLE 1
Synthesis and Characterisation Data of Dyes

Dye	*R*	*Amount of arylamines*	*Reaction time (h)*	*Weight (g) (yield,%)*	λ_{max} *(nm) in DMF*
I.1	H	4.00 g aniline	25	0.34(60)	585,620
I.2	CH_3	1.53 g *p*-toluidine	20	0.28(47)	585,621
I.3	OCH_3	1.54 g *p*-anisidine	18	0.31(50)	590,625
II.1	H	3.00 g aniline	35	0.28(50)	590,610
II.2	CH_3	1.82 g *p*-toluidine	31	0.26(44)	590,615
II.3	OCH_3	1.60 g *p*-anisidine	28	0.28(45)	595,620
III.1	H	0.60 g aniline	54	0.38(55)	595,625
III.2	CH_3	0.51 g *p*-toluidine	50	0.36(50)[a]	592,626
IV.1	CH_3	0.60 g *p*-toluidine	54	0.33(45)	600,620
V.1	*p*-CH_3-C_6H_4	0.50 g *p*-toluidine	50	0.36(50)[a]	595,642
V.2	*p*-OCH_3-C_6H_4	1.55 g *p*-anisidine	50	0.34(43)	595,642
V.3	*n*-C_4H_9	4.50 g *n*-butylamine	48	0.52(80)	587,625s
V.4	*n*-C_6H_{13}	4.50 g *n*-hexylamine	48	0.64(87)	588,634s
V.5	*n*-C_8H_{17}	4.50 g *n*-octylamine	48	0.70(85)	591,635s
VI.1	*n*-C_4H_9	4.50 g *n*-butylamine	48 (at 10°C)	0.55(78)	585,631s
VI.1	*n*-C_4H_9	20 g aniline	6	0.34(77)	605s,654
VII.2	*n*-C_6H_{13}	20 g aniline	6	0.31(70)	610s,656
VII.3	*n*-C_8H_{17}	20 g aniline	6	0.31(72)	610s,655
VIII.1	*n*-C_4H_9	20 g aniline	6	0.29(60)	570s,615

s, shoulder;
[a], purified by preparative TLC, 60% III.2 and 40% V.1.

2.3 Preparation of dyes VII and VIII

Dye V.3 (0.4g) and 20g aniline were refluxed for 6h. The liquor was cooled to room temperature, then poured into 200ml 10% aqueous hydrochloric acid and left to stand overnight. The crystalline material which separated was filtered and washed neutral with water. Recrystallization from 2-methoxyethanol gave 0.34g (77%) of 2,4-bis(*n*-butylamino)-8-anilino-1,5-dihydroxy-anthraquinone (VII.1), m.p. 280°C.

Dyes VII.2, VII.3 and VIII.1 were synthesized by a similar procedure from V.4, V.5 and VI.1, respectively, as detailed in Table 1.

2.4 General

All dyes were homogeneous on TLC (Merck, silica gel 5748) and were analytically pure; molecular weights and the absence of any higher molecular weight impurities were confirmed by mass spectrometry.

Characterisation data were obtained by mass spectrometry (Hitachi M-52), IR (Hitachi 260 - 50) and ^{1}HNMR (Varian VXR-300) (Table 2). Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in DMF (Table 1).

3 RESULTS AND DISCUSSION

Houben has pointed out that α-nitroanthraquinone undergo nucleophilic displacement in a manner analogous to that undergone by o-dinitrobenzene [11]. Locher and Fierz [12] showed that the nitro groups in nitroanthraquinones are readily replaced, in much the same way as the halogen atoms in halogenoanthraquinones, and that α-nitro groups are replaced more readily than β-groups. The 1-hydroxy group of DNAR and DNCZ could deactivate the 4-nitro group toward nucleophilic substitution because of its electron-donating power. Thus, the condensation of DNAR and DNCZ with primary amines was usually carried out under stringent conditions, e.g. refluxing in excess primary amines [13] or in water [14] and organic solvents such as 2-methoxyethanol [15], 2-ethoxyethanol [16], quinoline [15] and 1-pentanol [17]. For the more reactive primary amines, the use of reaction temperatures of 120–125°C has been concluded to give the best conditions for avoiding the formation of bis-aminated derivatives [18]. Hartke *et al.* [19] made 4-alkylamino and 2-alkylimino derivatives by stirring 1,2-naphthoquinone-4-sulfonic acid with primary aliphatic amines at room temperature. 2-Alkylaminoquinizarins have been made by addition of primary aliphatic amines to oxidised quinizarin under extremely mild conditions *via* the reactive quinone [20].

TABLE 2
Spectroscopic Data

Dye	*R*	*Mass(m/e)*	*IR[a](cm^{-1},KBr)*	*NMR[b](δ ppm,CDCl$_3$)*
I.1	H	376.2(M^+)	3400,3250,3080(Ar–NH),1650, 1590(C=O), 1545,1375(Ar–NO_2), 1565,1515, 1460(Ar ring), 1315, 1275(Car–N),1225,1160(Car–OH)	13.7381(s,1H,OH),13.3681(s,1H,OH) 11. 5665(s,1H,NH) 7.6044–7.2185(m, 9H,Ar, and Aq)
I.2	CH_3	390.1(M^+)	3420(b,Ar–NH),1600,1580(C=O), 1535,1385(Ar–NO_2),1515, 1455(Ar ring),1360(CH_3),1320, 1260(Car–N),1215,1170(Car–OH)	13.7953(s,1H,OH),13. 4131(s,1H,OH) 11.5383 (s,1H,NH), 7.5945–7.1584(m, 8H,Ar and Aq),2.4061(s,3H,CH_3)
I.3	OCH_3	406.2(M^+)	3400(b,Ar–NH),1605,1590(C=O), 1527(Ar–NO_2),1505, 1450(Ar ring), 1355(CH_3),1320(Car–N), 1245, 1020 (Ar–OCH_3), 1210, 1160(Car–OH)	13.7318(s,1H,OH),13.3386, (.s.,1H, OH),11.3978(s,1H,NH), 7.5114–6.9032(m,8H,Ar and Aq), 3.7875(s,3H,OCH_3)
II.1	H	376.2(M^+)	3370(Ar–NH),1630,1590(C=O), 1530,1365(Ar–NO_2),1492, 1460(Ar ring),1325,1250(Car–N), 1225, 1167(Car–OH)	12.8207(s,1H,OH),12.7450(s,1H,OH), 11.6726(s,1H,NH), 7.5688–7.1193(m,9H,Ar and Aq).
II.2	CH_3	390.2(M^+)	3400(Ar–NH),1630,1590 (C=O), 1535,1365(Ar–NO_2)1508, 1460(Ar ring),1375(CH_3),1250(Car–N), 1218, 1162(Car–OH)	12.9208(s,1H,OH),12.8341(s,1H,OH), 11.7251(s,1H,NH), 7.6323–7.1071(m,8H,Ar and Aq), 2.3817(s,3H,CH_3)
II.3	OCH_3	406.2(M^+)	3350(b,Ar–NH),1635,1590(C=O), 1530,1360(Ar–NO_2), 1510, 1460(Ar ring), 1310,1260(Car–N), 1242,1015(Ar–OCH_3),1220, 1170(Car–OH)	12.8292(s,1H,OH),12.7462(s,1H,OH), 11.5969(s,1H,NH), 7.5480–6.8604(m,8H,Ar and Aq), 3.7667(s,3H,OCH_3)
III.1	H	452.1(M^+)	3420(Ar–NH),1630,1590(C=O), 1500,1450(Ar ring),1305, 1265(Car–N),1215, 1165(Car–OH)	13.9420(s,2H,OH),11.4005(s,4H,NH_2), 7.7050–6.7810(m,12H,Ar and Aq)

(continued)

Table 2—*contd*

Dye	*R*	*Mass(m/e)*	*IR[a](cm^{-1},KBr)*	*NMR[b](δ ppm,CDCl$_3$)*
III.2	CH_3	480.2(M^+)	3480(Ar–NH),1640,1590(C = O), 1505,1460(Ar ring), 1375(CH3), 1260(Car–N),1170(Car–OH)	14.5330(s,1H,OH),14.3071(s,1H, O H), 13.9187(s,1H,NH_2), 13.6329(s,1H,NH_2), 13.4986(s,1H,NH_2), 13.4057(s,1H,NH_2), 7.6470–7.1914(m,10H,Ar and Aq), 2.4330(s,3H,CH_3), 2.4073 (m,3H,CH_3)
IV.1	CH_3	480.3(M^+)	3450(Ar–NH),1630,1590 (C = O), 1510,1460(Ar ring),1380(CH_3), 1260(Car–N),1170 (Car–OH)	13. 5050(s,2H,OH), 12.9500(s,2H,NH_2), 11.7600(s,2H,NH_2), 7.7000–7.2000(m,10H,Ar and Aq), 2.4500(s,3H,CH_3), 2.4000(s,3H,CH_3)
V.1	p-CH_3 –C_6H_4	495.3(M^+)	3400,3350(Ar–NH),1630,1585(C = O), 1460(Ar ring), 1370(CH_3), 1292,1245(Car–N), 12 00,1155(Car–OH)	15.0811(s,1H,OH), 14.7077(s,1H,OH), 12.0500(s,1H,NH) 7.5175–6.9520(m,12H,Ar and Aq), 2.3756(s,3H,CH_3), 2.3377(s,3H,CH_3)
V.2	p-OCH_3 –C_6H_4	527.4 (M^+)	3300(Ar–NH),1625,1580(C = O), 1505,1455(Ar ring), 1285(Car–N) 1245,1025(Ar–OCH_3),1165(Car–OH)	15.0155(s,1H,OH),14.7040(1H,OH), 11.8815(s,1H,NH), 7.5139–6.5245(m12H,Ar and Aq) 3.7569(s,3H,OCH_3), 3.7337(s,3H,OCH_3)
V.3	n-C_4H_9	427.3(M^+) 384.2(M–C_3H_7)$^+$	3400(b,Ar–OH),3350(Ar–NH),2950, 2850(C–H),1620,1560(C = O), 1550,1520,1410(Ar ring),1370(CH_3), 1160(Car–OH).	15.3000(s,1H,OH),15.2400(s,1H,OH), 10.8000(s,1H,NH), 5.8300(b,1H,β–NH), 7.1200–7.5200(m,3H,Aq), 3.4100–3.1900(m,4H,CH_2), 1.8100–0.9800(m,14H,CH_3 and CH_2)
V.4	n-C_6H_{13}	483.3(M^+)	3350(Ar–NH),2900,2850(C–H), 1620,1560(C = O),1550,1500,1460, 1410(Ar ring),1360(CH_3),1150(Car–OH)	13.4530(s,1H,OH),13.2580(s,1H,OH), 1 0.0910(s,1H,NH), 5.8700(b,1H,β–NH), 7.4900–7.1400(m,3H,Aq), 3.4300–3.2400 (m,4H,CH_2), 1.7300–0.8600 (m,22H, CH_3 and CH_2)
V.5	n-C_8H_{17}	539.4(M^+)	3400(b,OH),3350(Ar–NH),2900, 2850(C–H),1620,1560 (C = O), 1550, 1510,1460(Ar ring),1360 (CH_3), 1320,1290(Car–N),1210, 1150(Car–OH)	14.0110(s,1H,OH),13.4460(s,1H,OH), 10.1860(s,1H, NH), 7.5650–7.3020(m,3H Aq), 3.9940–3.4200(m,4H,CH_2), 2.3400–0.8600(m,30H, CH_3 and CH_2)
VI.1	n-C_4H_9	472.3(M^+) 457.2(M–CH_3)$^+$ 430.2(M–C_3H_6)$^+$	3350(b,OH and Ar–NH),2900, 2850 (C–H), 1620,1590 (C = O), 1570, 1550,1495,1410(Ar ring),1375 (CH_3), 1540,1355(NO_2), 1275(Car–N),1230,1150(Car–OH)	15.2300 (s,2H,OH), 7.5300–7.1500(m,2H,Aq), 4.0860–3.2690(m,4H,CH_2), 1.9010–0.8850(m,14H, CH_3 and CH_2)

(*continued*)

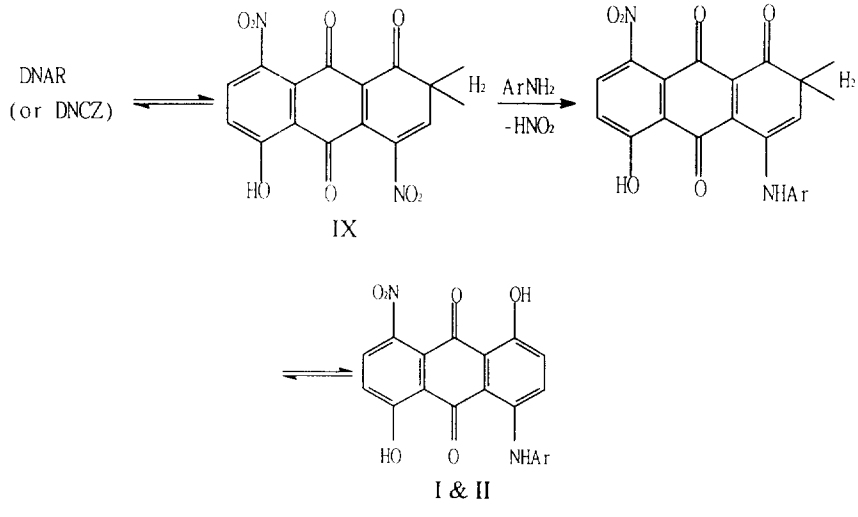
Table 2—*contd*

VII.1	n-C_4H_9	473.3(M^+) 430.2($M-C_3H_7$)$^+$	3400(b,OH),3350(Ar–NH),2950, 2900,2850(C–H), 1620, 1590(C=O),1550,1520,1500, 1470(Ar ring),1385(CH_3), 1250(Car–N), 1160(Car-OH)	15.1370(s,1H,OH), 14.7520(s,1H,OH), 11.1050(s,1H,NH),10.2700(s,1H,NH) 7.4280–7.1010(m,8H,Ar and Aq), 3.3620–3.2020 (m,4H, CH_2), 1.8010–0.8420 (m,14H, CH_3 and CH_2)
VII.2	n-C_6H_{13}	529.4(M^+) 459.3($M-C_5H_{10}$)$^+$	3400(b,OH and Ar–NH),2900, 2850(C–H),1620,1590(C=O), 1560, 1500,1460 (Ar ring),1375 (CH_3), 1300,1250, (Car–N), 1230, 1180(Car–OH)	15.0920 (s,1H,OH), 14.6210(s,1H,OH),11.0750(s,1H,NH), 10.2120 (s,1H,NH),5.4300(b,1H,β–NH) 7.4100–7.0720 (m,8H,Ar and Aq), 3.3220–3.2210(m,4H, CH_2) 1.7670–0.9810(m,22H, CH_3 and CH_2)
VII.3	n-C_8H_{17}	585.4(M^+) 557.4($M-C_2H_4$)$^+$ 458.3($M-NC_8H_{17}$)$^+$	3350(b,OH and Ar–NH),2900, 2850(C–H)1625, 1590(C=O),1550, 1495, 1460(Ar ring),1380(CH_3), 1260(Car–N), 1155(Car–OH)	15.1070 (s,1H,OH), 14.7450(s,1H,OH), 11.0800(s,1H,NH), 10.2200(s,1H,NH),7.4110–7.0770(m,8H,ArandAq) 5.4350 (b,1H,β–NH),3.3060–3.2040(m,4H, CH_2) 1.7940–0.8560(m,30H,$CH_2$and CH_3)
VIII.1	n-C_4H_9	564.4(M^+) 549.4($M-CH_3$)$^+$	3450(b,OH),3350(Ar–NH),2900, 28 50(C–H)1620, 1590(C=O), 1500,1460(Ar ring),1295(Car–N), 1250(Car–OH)	15.6500(s,2H,OH) 11.4500(s,2H,NH), 7.4600–7.1600(m,12H,Ar and Aq),5.4500(b,2H,β–NH) 3.1400–3.0400(m,4H, CH_2), 1.6310–0.9150(m,14H, CH_2 and CH_3)

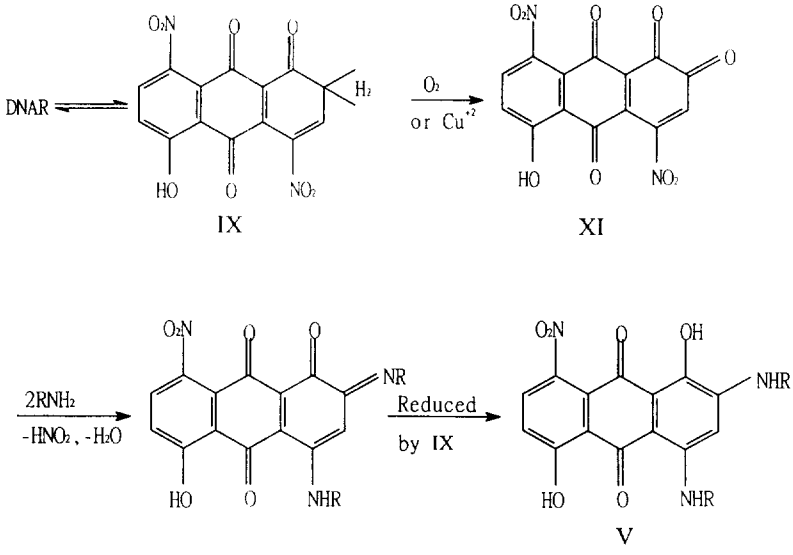
[a]Ar and ar, aromatic; b, broad.
[b] s,singlet; m, multiplet; b, broad; Ar, aromatic; Aq, anthraquinone.

Dyes III and IV, which have good order parameters, may be used in commercially viable liquid crystal devices [21].

Possible mechanisms for the reactions studied here are shown in Schemes 1, 2 and 3, in which reactive species IX and X are stabilized by forming a complex with curpric ion or cuprous ion.



Scheme 1



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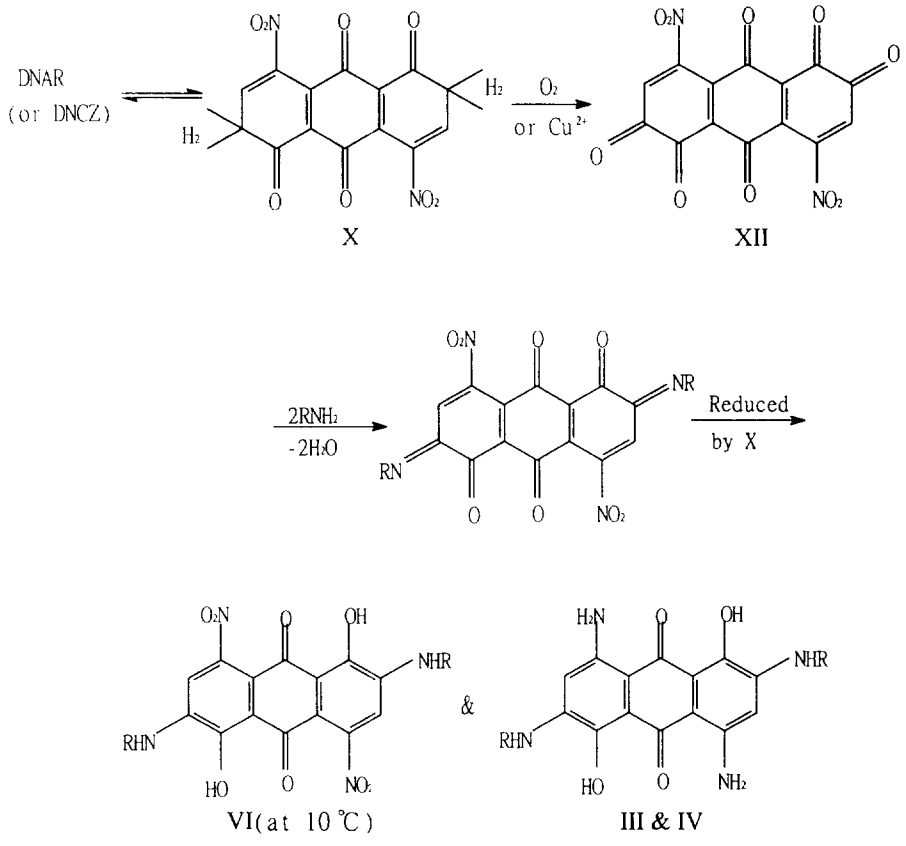

Scheme 3

ACKNOWLEDGEMENTS

The financial support of this project by the National Science Council of Taiwan is gratefully acknowledged.

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