

CHAPTER IV

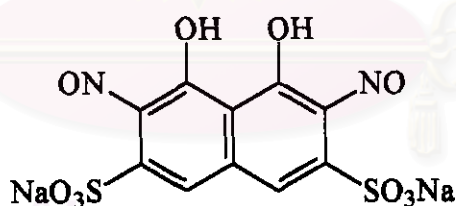
RESULTS AND DISCUSSION

4.1 Discussion on General Method for the Synthesis of

2,7-Bis(2-hydroxynitrophenylazo) Derivatives of Chromotropic Acid

2,7-Bis(2-hydroxynitrophenylazo) derivatives of chromotropic acid are conceptually synthesized by diazotizing 2-aminonitrophenol and then coupling diazonium salt with a chromotropic acid. The general reaction is shown in Figure 4.1.

It is necessary to ensure that before coupling there is no free nitrous acid present in the diazo solution. Nitrous acid can be removed by the addition of sulphamic acid to diazo solution. If nitrous acid is not destroyed, after coupling with chromotropic acid, the by-product would be obtained as nitroso compound as the following structure.



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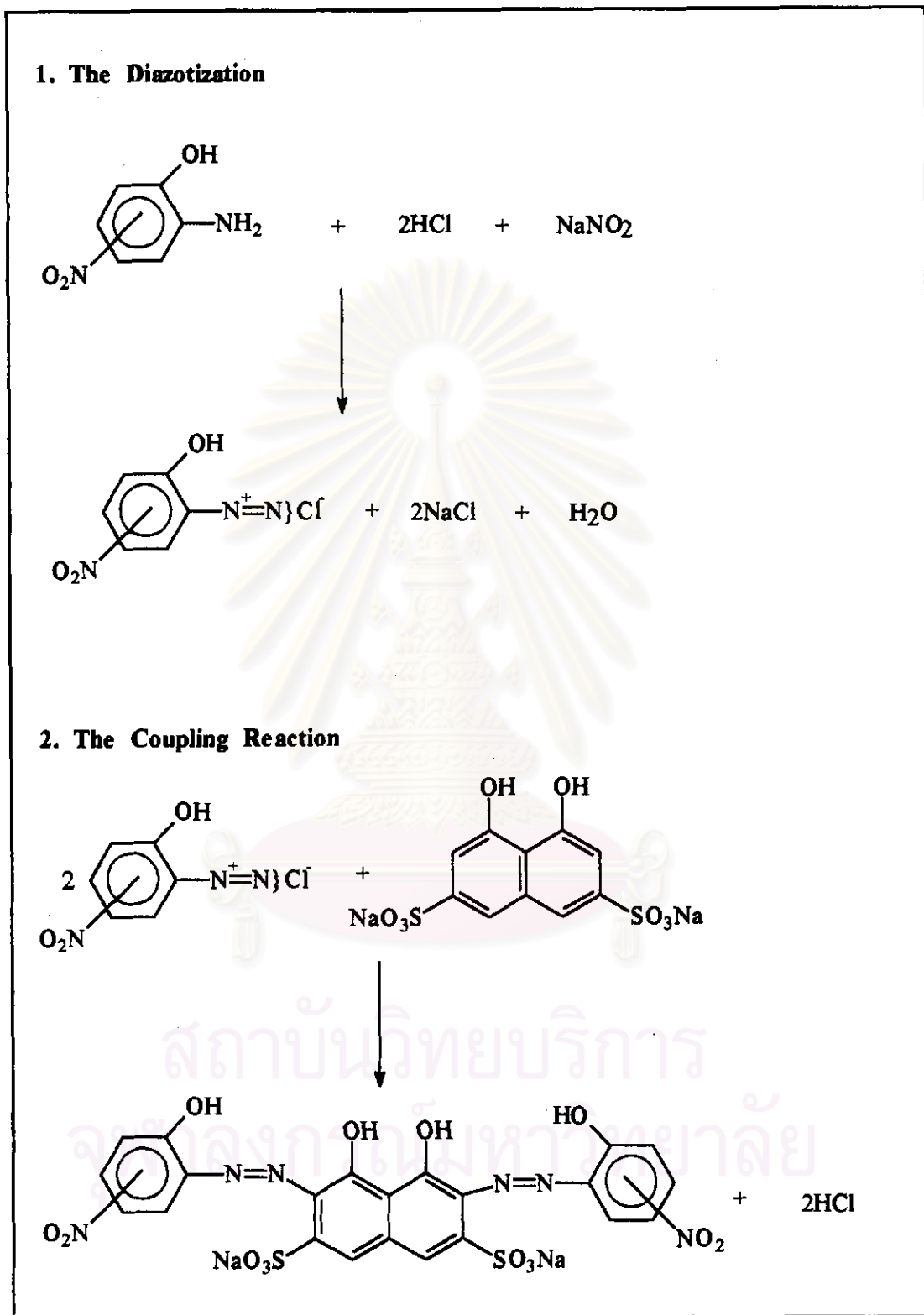
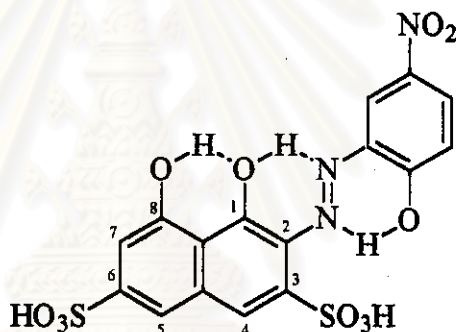


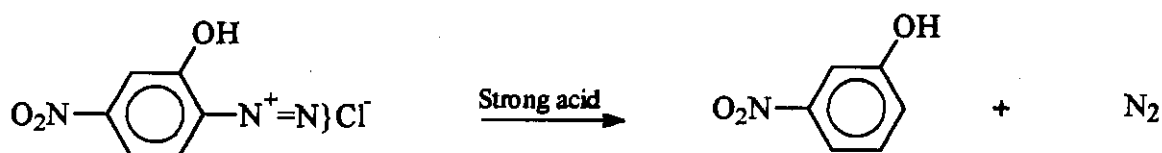
Figure 4.1 General method for the synthesis of 2,7-bis(2-hydroxynitrophenylazo) derivatives of the chromotropic acid

4.2 Discussion on the Synthesis of 2,7-Bis[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (5N-dye)

In this study, attempts to synthesize 5N-dye using methods 1,3 and 4 were carried out. In those methods, sodium hydroxide or pyridine was used in the coupling stages. It was found that bisazo compound could not be obtained, only monoazo derivatives were predominant as followed by TLC experiments (see Figures A-2 and A-3, appendix). The reason for this is that the hydrogen bonding in monoazo derivative is so strong causing a low electron density at position 7, thus preventing further reactions to be occurred at this position.



In the synthesis of 5N-dye using method 2, the diazonium salt solution was added dropwise with the alkaline sodium hydroxide chromotropic acid solution containing calcium chloride. It was found that small amount of 5N-dye was obtained (see TLC Figure A-1, appendix). During the coupling reaction, it was noticeable that considerable amount of gas bubbles occurred. This was due to the decomposition of diazonium salt given off nitrogen gas as shown in the following reaction.



For the synthesis of 5N-dye using method 5, the coupling reaction was performed in alkaline pyridine in the presence of calcium oxide. The result was not satisfactory because there were still large amounts of monoazo and diazonium salt remained (see TLC experiment in appendix Figure A-4).

The synthesis of 5N-dye using method 6 was satisfactory. Monoazo derivatives obtained by method 1 were used for coupling with chromotropic acid in the presence of lithium hydroxide. The coupling product was mainly 5N-dye with least monoazo derivative (see TLC experiment in appendix Figures A-4 and A-5). Using lithium hydroxide is probably capable to destroy hydrogen bonding of -OH at the peri-position of chromotropic acid of monoazo derivative allowing the further coupling at position 7.

In this study, elemental analysis, infrared absorption spectrometry and NMR spectroscopy were also used for the characterization of synthesized dyes.

The elemental analysis of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid and 5N-dye as shown in Table 4.1 indicated that empirical formula of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalene disulfonic acid is $C_{16}H_9N_3O_{11}S_2Na_2 \cdot 2H_2O$ and of 5N-dye is $C_{22}H_{14}N_6O_{14}S_2 \cdot 2H_2O$ corresponding to the structural formula shown below.

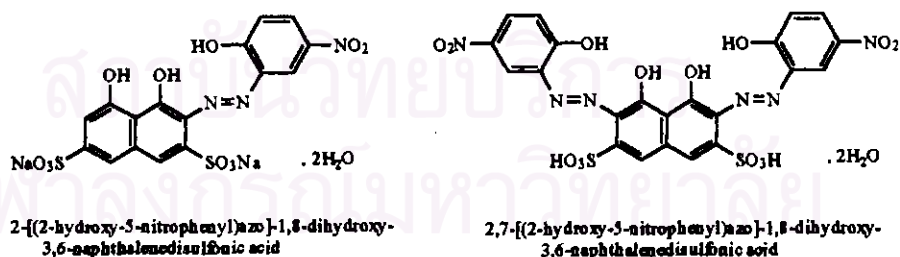


Table 4.1 Elemental analyses of the dyes

The substances	M.W.*	% C		%H		%N	
		Cal.	Found	Cal.	Found	Cal.	Found
<u>Monoazo</u>							
1) 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (C ₁₆ H ₉ N ₃ O ₁₁ S ₂ Na ₂ ·2H ₂ O)	565.41	33.99	31.76	2.32	2.31	7.43	7.06
2) 2-[(2-hydroxy-4-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (C ₁₆ H ₉ N ₃ O ₁₁ S ₂ Na ₂ ·2H ₂ O)	565.41	33.99	34.31	2.32	2.36	7.43	7.62
3) 2-[(2-hydroxy-3,5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (C ₁₆ H ₇ N ₄ O ₁₃ S ₂ Na ₃ ·3H ₂ O)	650.40	29.55	27.47	2.01	1.85	8.61	8.38
<u>Bisazo</u>							
1) 2,7-bis[2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (C ₂₂ H ₁₄ N ₆ O ₁₄ S ₂ ·2H ₂ O)	686.56	38.49	38.49	2.64	2.62	12.24	12.28

* Molecular weight calculated from summation of atomic weight, C = 12.0115, H = 1.00797, N = 14.0067, O = 15.9994, S = 32.064, and Na = 22.9898

IR spectra (KBr) of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid and of 5N-dye are shown in Tables 4.2 and 4.3 with corresponding to the spectra in Figures A-11 and A-14 in appendix (The absorption band of azo group, $-N=N-$ stretching occurs between 1575 cm^{-1} and 1630 cm^{-1} but is very weak and hence has no diagnostic value). (37)

Table 4.2 FTIR absorption characteristic of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (see appendix Figure A-11)

Absorption band (cm^{-1})	Band type	Tentative Assignment
3600-3200	b	O-H Stretching
3100	w	C-H Stretching
1622-1437	m	C=C Ring Stretching
1501	s	N=O Asymmetric Stretching
1335	s	N=O Symmetric Stretching
1200	s	S=O Asymmetric Stretching
1050	s	S=O Symmetric Stretching
982-640	m	=C-H Out of Plane Bending

Table 4.3 FTIR absorption characteristic of 2,7-bis[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (see appendix Figure A-14)

Absorption band (cm^{-1})	Band type	Tentative Assignment
3600-3150	b	O-H Stretching
3052	w	C-H Stretching
1626-1400	m	C=C Ring Stretching
1483	s	N=O Asymmetric Stretching
1342	s	N=O Symmetric Stretching
1210	s	S=O Asymmetric Stretching
1046	s	S=O Symmetric Stretching
924-637	m	=C-H Out of Plane Bending

The proton NMR spectra (DMSO- d_6) of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid and of 5N-dye as shown in Figures A-15 and A-16 in appendix indicate the signal of proton of hydroxy group at 13.05 ppm and proton of aromatic rings at 6.55, 6.70, 7.05, 7.35, 7.50, 7.90 and 8.50. For the proton NMR spectrum of 5N-dye the signal of proton of hydroxy group is at 12.30 and the proton signal of aromatic rings appear at 7.15, 7.25, 7.60, 8.15, and 8.25 ppm.

It is seen that the proton NMR spectra of 5N-dye are of symmetry and not complicated as in the case of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid. The reason for this is probably due to the tautomerize effects occurred in both molecules as shown in Figure 4.2.

Carbon-13 NMR spectra (DMSO- d_6) of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid and 5N-dye are shown in Figures A-17 and A-18 in the appendix.

Carbon-13 NMR spectra of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid give chemical shift (δ , ppm) at 181.0, 162.7, 155.1, 152.8, 142.9, 140.7, 136.5, 130.0, 129.0, 122.5, 121.9, 117.1, 116.1, 115.4, 112.3 and 112.2 (total 16 signals) and for 5N-dye the chemical shifts appear at 167.7, 155.5, 147.2, 140.4, 138.2, 133.2, 131.0, 125.3, 120.2, 117.9 and 117.8 (total 11 signals).

It is seen that Carbon-13 NMR spectrum gives an evidence that 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic which is a monoazo derivative of chromotropic acid is in the form of quinone hydrazone (II_m , Figure 4.2) whereas 5N-dye which is a bisazo derivative of chromotropic acid is in the azo form (II_b , Figure 4.2) (38) and the Table 4.4 shows the different position of carbon.

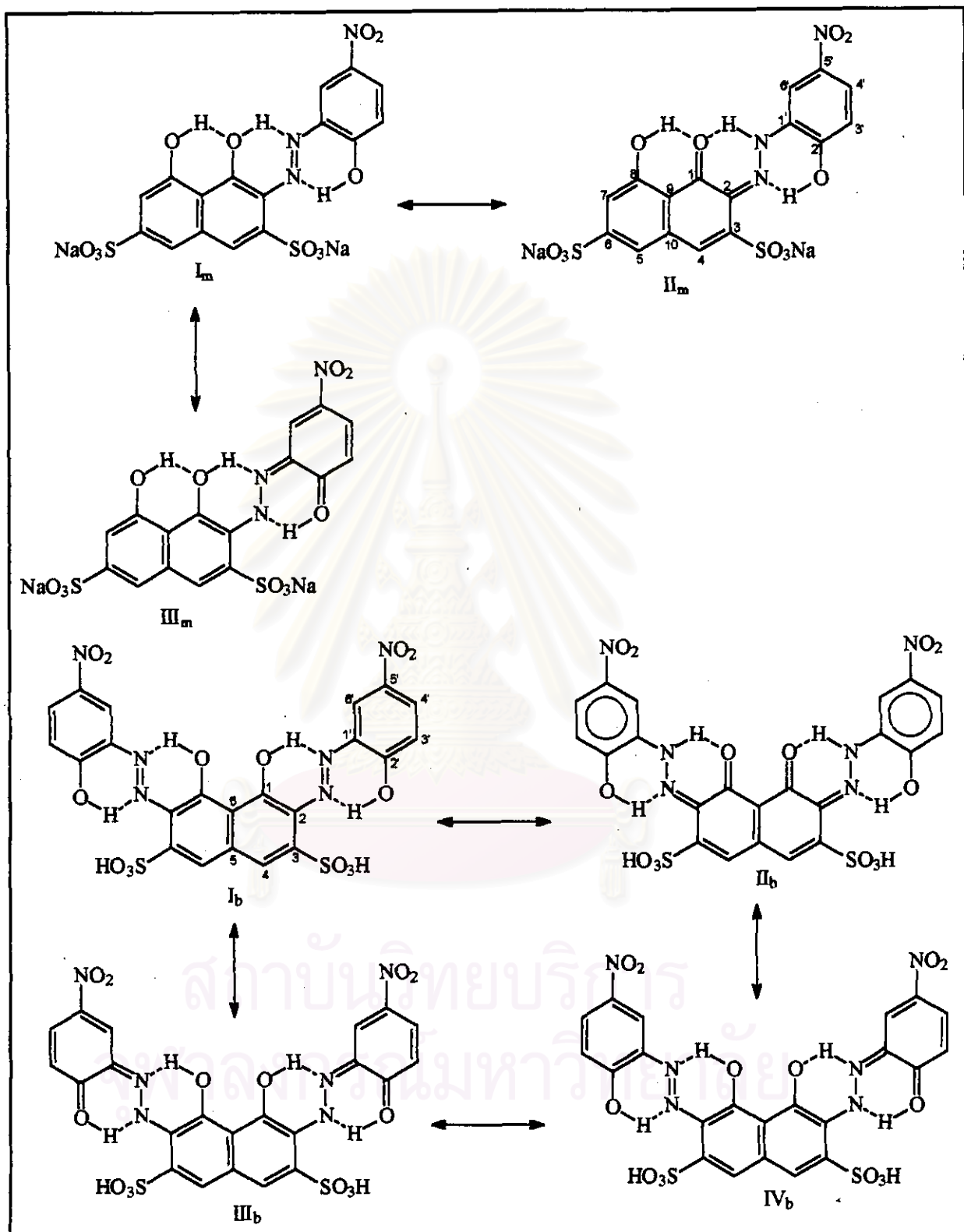


Figure 4.2 Tautomerize effects of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid and 5N-dye

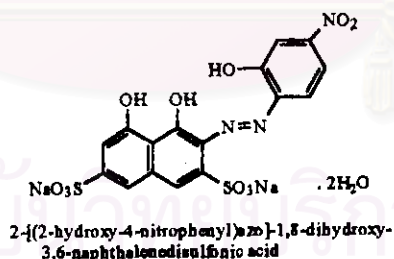
Table 4.4 Carbon position of 2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid and 2,7-bis[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid

Position	2-[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (δ , ppm)	Position	2,7-bis[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalene disulfonic acid (δ , ppm)
<u>naphthalene</u> (II_m)		<u>naphthalene</u> (I_b)	
C ₁	181.0	C ₁	167.7
C ₂	152.8	C ₂	131.0
C ₃	136.5	C ₃	138.2
C ₄	121.9	C ₄	120.2
C ₅	117.0	C ₅	147.2
C ₆	142.9	C ₆	117.8
C ₇	116.1		
C ₈	162.7		
C ₉	115.4		
C ₁₀	129.0		
<u>phenyl</u> (II_m)		<u>phenyl</u> (I_b)	
C _{1'}	130.0	C _{1'}	133.2
C _{2'}	155.1	C _{2'}	155.5
C _{3'}	122.5	C _{3'}	125.3
C _{5'}	140.7	C _{5'}	140.4
C _{4',C_{6'}}	112.2, 112.3	C _{4',C_{6'}}	117.9

4.3 Discussion on the Synthesis of 2,7-Bis[(2-hydroxy-4-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (4N-dye)

Four methods (methods 1, 2, 4 and 6) were used in the attempts to synthesize 4N-dye. Results were not satisfactory. (see TLC experiment appendix Figures A-6, A-1, A-7 and A-8). In method 2, considerable amount of bubbles occurred during coupling. This, was believed to be nitrogen gas from the decomposition of azo compound. The coupling could not happen due to the effect of nitro group which is an electron withdrawing group being at para position to the diazonium salt and causing easy and quick decomposition of diazonium compound in the presence of strong and concentrated base. It was thought that the end products contained a lot of monoazo derivatives. In order to confirm this, the product was purified and sent for elemental analysis and IR absorption spectrometry.

Results of elemental analysis as shown in Table 4.1 indicate that the empirical formula of the product is $C_{16}H_9N_3O_{11}S_2Na_2 \cdot 2H_2O$ with a possible structure as shown below.



The IR spectra (KBr) of this compound is shown in Figure A-12 in appendix and corresponding Table 4.5.

Table 4.5 FTIR absorption characteristic of 2-[(2-hydroxy-4-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (see appendix Figure A-12)

Absorption band (cm ⁻¹)	Band type	Tentative Assignment
3600-3200	b	O-H Stretching
3093	w	C-H Stretching
1626-1400	m	C=C Ring Stretching
1498	s	N=O Asymmetric Stretching
1387	s	N=O Symmetric Stretching
1218	s	S=O Asymmetric Stretching
1045	s	S=O Symmetric Stretching
932-640	m	=C-H Out of Plane Bending

4.4 Discussion on the Synthesis of 2,7-Bis[(2-hydroxy-6-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (6N-dye)

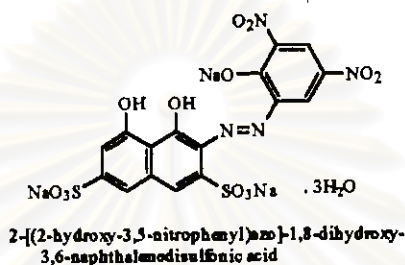
The synthesis of 6N-dye was attempted. The results were not possible due to the fact that the starting material (3NAP) could not be diazotised by the conventional acid-nitrite method. Bhagwanth (34) suggested that diazotization of 3NAP might be possible by slowly adding 3NAP into a cold of nitrosylsulphuric acid.

4.5 Discussion on the Synthesis of 2,7-Bis[(2-hydroxy-3,5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (3,5N-dye)

Methods 1 and 6 were used to synthesize 3,5N-dye. The results were not satisfactory because it seemed that at the end of coupling reaction, monoazo derivatives were obtained and a large amount of diazonium salts were still left. (see TLC experiment in appendix Figures A-9 and A-10)

In order to confirm this, a purified product was sent for elemental analysis and infrared absorption study.

Elemental analysis of the product as shown in Table 4.1 indicated that the empirical formula of the compound could be $C_{16}H_9N_3O_{11}S_2Na_3 \cdot 3H_2O$ corresponding to the structural formula shown below.



IR spectra (KBr) of the above monoazo derivative is shown in Figure A-13 in appendix with Table 4.6.

Table 4.6 FTIR absorption characteristic of 2-[(2-hydroxy-3,5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid (see appendix Figure A-13)

Absorption band (cm^{-1})	Band type	Tentative Assignment
3600-3200	b	O-H Stretching
3055	w	C-H Stretching
1626-1400	m	C=C Ring Stretching
1490	s	N=O Asymmetric Stretching
1300	s	N=O Symmetric Stretching
1212	s	S=O Asymmetric Stretching
1044	s	S=O Symmetric Stretching
932-640	m	=C-H Out of Plane Bending