

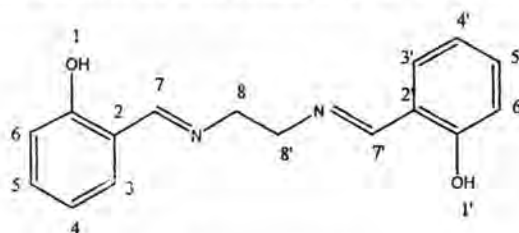
CHAPTER IV

RESULT AND DISCUSSION

4.1 Characterization of synthetic imines [2,20,25]

4.1.1 Bis (salicylaldehyde) N, N'-ethylenediimine [1]

Bis (salicylaldehyde) N, N'-ethylenediimine was synthesized from the reaction of salicylaldehyde and ethylenediamine, to yield a yellow solid, m.p. 120-121°C: with 91% (24.29 g) yield. The structure of compound 1 is as follows:



Compound 1

The infrared spectrum (Fig. 1a) revealed the absorption peaks at 3,417 cm^{-1} (O-H stretching of phenol), 3,053 cm^{-1} and 3,005 cm^{-1} (=C-H stretching of aromatic), 1,635 cm^{-1} (C=N stretching of imine), 1,610 cm^{-1} and 1,496 cm^{-1} (C=C ring stretching of aromatic), 1,456 cm^{-1} (C-H stretching of aromatic), and 1,149 cm^{-1} (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 2a) revealed the presence of a benzene ring at δ_{H} 7.19 (4H, *m*, position 3, 3', 6 and 6'), and 6.96 (4H, *m*, position 4, 4', 5 and 5'). Protons at the positions 7, 7', 8, 8' were indicated at δ_{H} 8.34 (2H, *s*), and 3.92 (4H, *t*, 9.0 Hz), respectively. The $^1\text{H-NMR}$ spectrum also revealed the prominence of a hydroxy group at δ_{H} 13.20 (2H, *s br*, position 1 and 1'). The assignments are concluded in Table 4-1.

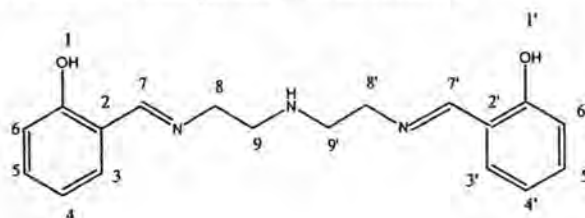
Table 4-1: The ^1H -NMR spectral data of Compound 1

Position	δ_{H} , multiplicity, J (Hz)
1, 1'	13.20, <i>s br</i>
3, 3', 6, 6'	7.19, <i>m</i>
4, 4', 5, 5'	6.96, <i>m</i>
7, 7'	8.34, <i>s</i>
8, 8'	3.92, <i>t</i> , 9.0

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 3a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.0 ppm and 166.5 ppm, respectively. The ^{13}C shifts of the benzene ring carbons appeared at 116.9-118.7 ppm. From the spectrum, it indicated that the carbons signal at δ_{C} 59.7 was attributed to $-\text{CH}_2$ carbons at position 8 and 8'.

4.1.2 Bis (salicylaldehyde) N, N'-diethylenetriimine [2]

Bis (salicylaldehyde) N, N'-diethylenetriimine was synthesized from the reaction of salicylaldehyde and diethylenetriamine, to yield a yellow liquid: with 86 % (26.76 g) yield. The structure of compound 2 is as follows:

Compound 2

The infrared spectrum (Fig. 4a) revealed the absorption peaks at $3,055\text{ cm}^{-1}$ (N-H stretching of amine), $3,006\text{ cm}^{-1}$, and $2,844\text{ cm}^{-1}$ ($=\text{C}-\text{H}$ stretching of aromatic), $1,631\text{ cm}^{-1}$ ($\text{C}=\text{N}$ stretching of imine), $1,581\text{ cm}^{-1}$, and $1,462\text{ cm}^{-1}$ ($\text{C}=\text{C}$ ring stretching of aliphatic), $1,490\text{ cm}^{-1}$ ($\text{C}-\text{H}$ stretching of amine), and $1,151\text{ cm}^{-1}$ ($\text{C}-\text{O}$ stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 5a) revealed the presence of a benzene ring at δ_{H} 7.16 (4H, m, position 4, 4', 5 and 5'), and 6.82 (4H, m, position 3, 3' 6, and 6'). Protons at the positions 7, 7', 8, 8', 9, and 9' appeared at δ_{H} 8.31 (2H, s), 3.67 (4H, t, 6.0 Hz) and 2.95 (4H, t, 6.0 Hz), respectively. The $^1\text{H-NMR}$ spectrum was also revealed the prominence of hydroxy group at δ_{H} 13.27 (2H, s *br*, position 1 and 1'). The assignments are concluded in Table 4-2.

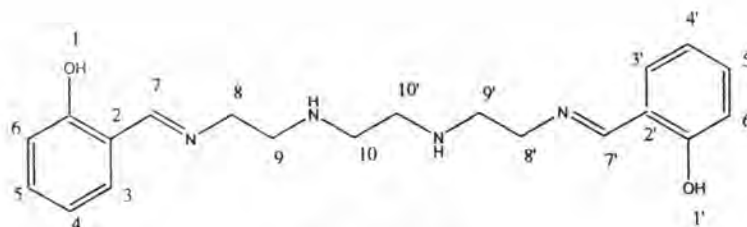
Table 4-2: The $^1\text{H-NMR}$ spectral data of Compound 2

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
1, 1'	13.27, s <i>br</i>
3, 3', 6, 6'	6.82, m
4, 4', 5, 5'	7.16, m
7, 7'	8.31, s
8, 8'	3.67, t, 6.0
9, 9'	2.95, t, 6.0

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) (Fig. 6a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.1 ppm and 166.1 ppm, respectively. The ^{13}C shifts of the benzene ring carbons appeared at 117.0-132.3 ppm. From the spectrum, it indicated that the signals at δ_{C} 49.7, and 59.5 were attributed to $-\text{CH}_2$ carbons at position 8, 8', 9, and 9'.

4.1.3 Bis (salicylaldehyde) N, N'-triethylenetetrimine [3]

Bis (salicylaldehyde) N, N'-triethylenetetrimine was synthesized from the reaction of salicylaldehyde and triethylenetetrimine, to yield a yellowish-orange solid, m.p. 166-167°C; with 73.5% (25.77 g) yield. The structure of compound 3 is as follows:

Compound 3

The infrared spectrum (Fig. 7a) revealed the absorption peaks at $3,431\text{ cm}^{-1}$ (N-H stretching of amine), $3,051\text{ cm}^{-1}$ (=C-H stretching of aromatic), $2,947\text{ cm}^{-1}$ and $2,821\text{ cm}^{-1}$ (=C-H stretching of aliphatic), $1,635\text{ cm}^{-1}$ (C=N stretching of imine), $1,609\text{ cm}^{-1}$ and $1,456\text{ cm}^{-1}$ (C=C ring stretching of aromatic), and $1,282\text{ cm}^{-1}$ (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 8a) revealed the presence of a benzene ring at $\delta_{\text{H}} 7.28$ (4H, *m*, position 4, 4', 5 and 5'), and 6.89 (4H, *m*, position 3, 3', 6 and 6'). Protons at the positions 7, 7', 8, 8', 9, 9' 10 and 10' were indicated at $\delta_{\text{H}} 8.33$ (2H, *s br*), 3.71 (4H, *t*, 6.5 Hz), 2.76 (4H, *t*, 8.5 Hz) and 2.56 (4H, *s*), respectively. The $^1\text{H-NMR}$ spectrum also revealed the prominence of a hydroxy group at $\delta_{\text{H}} 13.42$ (2H, *s br*, position 1 and 1'). The assignments are concluded in Table 4-3.

Table 4-3: The $^1\text{H-NMR}$ spectral data of Compound 3

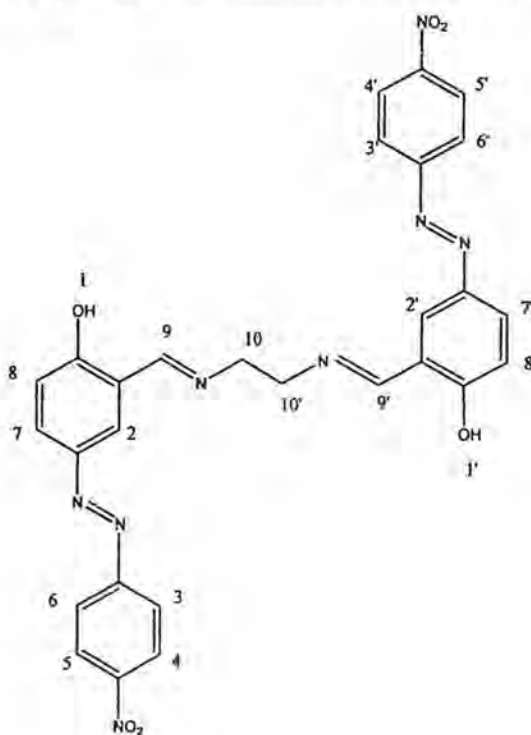
Position	δ_{H} , multiplicity, <i>J</i> (Hz)
1, 1'	13.42, <i>s br</i>
3, 3', 6, 6'	6.89, <i>m</i>
4, 4', 5, 5'	7.28, <i>m</i>
7, 7'	8.33, <i>s br</i>
8, 8'	3.71, <i>t</i> , 8.5
9, 9'	2.76, <i>t</i> , 8.5
10, 10'	2.56, <i>s</i>

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 9a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.2 ppm and 165.6 ppm, respectively. The ^{13}C shifts of the benzene ring carbons appeared at 117.0-132.2 ppm. From the spectrum, it indicated that the signals at δ_{C} 53.4, 57.0, and 58.6 were attributed to $-\text{CH}_2$ carbons at position 8, 8', 9, 9', 10, and 10'.

4.2 Characterization of synthetic azo dyes

4.2.1 Bis (salicylaldehyde) N, N'-ethylene diimine-*p*-nitrophenyl azo or Dye 1

Bis (salicylaldehyde) N, N'-ethylene diimine-*p*-nitrophenyl azo was synthesized from the reaction of *p*-nitroaniline and diphenolate diimine ion, to yield brown solid, m.p. 151-152°C: with 82.5% (3.44 g) yield. The structure of Dye 1 is as follows:



Dye 1

The infrared spectrum (Fig. 10a) revealed the absorption peaks at $3,408\text{ cm}^{-1}$ (O-H stretching of phenol), $1,666\text{ cm}^{-1}$ (C=N stretching of imine), $1,520\text{ cm}^{-1}$ and $1,344\text{ cm}^{-1}$ (N=O stretching of nitro group), $1,485\text{ cm}^{-1}$ (C=C stretching of aromatic), and $1,101\text{ cm}^{-1}$ (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 11a) revealed the presence of a substituted benzene ring at δ_{H} 7.01 (4H, *m*, position 3, 3', 6 and 6'), and 8.34 (4H, *dd*, 3.0 and 5.0 Hz, position 4, 4', 5 and 5'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 8, 8', 9, and 9' occurred at 7.23 (4H, *m*). Positions 2, 2', 7 and 7' revealed at 8.00 (4H, *dd*, 2.5 and 6.0 Hz), and positions 10 and 10' occurred at 3.98 (4H, *t*, 12.0 Hz), respectively. The $^1\text{H-NMR}$ spectrum also revealed the prominence of a hydroxy group at δ_{H} 13.49 (2H, *s br*, position 1 and 1'). The assignments are concluded in Table 4-4.

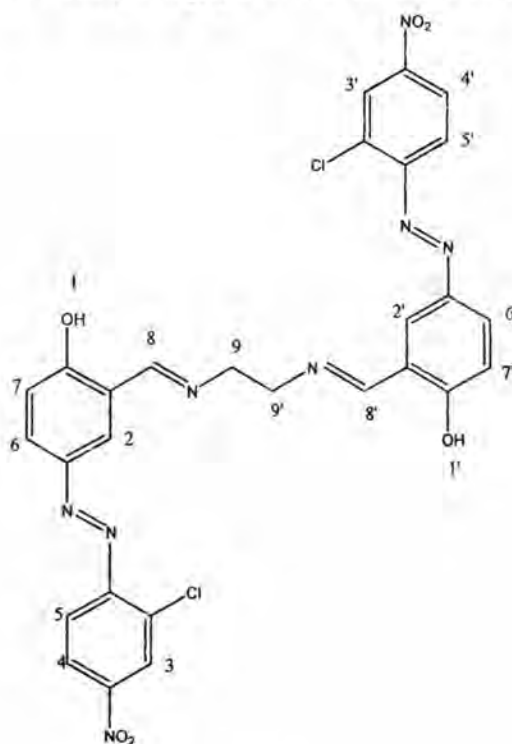
Table 4-4: The $^1\text{H-NMR}$ spectral data of Dye 1

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
1, 1'	13.49, <i>s br</i>
2, 2', 7, 7'	8.00, <i>dd</i> , 2.5 and 6.0
3, 3', 6, 6'	7.01, <i>m</i>
4, 4', 5, 5'	8.34, <i>dd</i> , 3.0 and 4.0
8, 8', 9, 9'	7.23, <i>m</i>
10, 10'	3.98, <i>t</i> , 12.0

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) (Fig. 12a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.1 ppm and 166.5 ppm, respectively. The ^{13}C shifts of the benzene ring carbons occurred at 116.9-132.4 ppm. From the spectrum, it indicated the prominence at δ_{C} 59.5 attributed to $-\text{CH}_2$ carbon at position 10 and 10'. Two $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 145.2 and 161.0, respectively.

4.2.2 Bis (salicylaldehyde) N, N'-ethylenediimine--2-chloro-4-nitrophenyl azo [Dye 2]

Bis (salicylaldehyde) N, N'-ethylenediimine-2-chloro-4-nitrophenyl azo was synthesized from the reaction of 2-chloro-4-nitroaniline and diphenolate diimine ion, to yield a brown solid: with 79.0% (3.57 g) yield. The structure of Dye 2 is as follows:



Dye 2

The infrared spectrum (Fig. 16a) revealed the absorption peaks at $3,404\text{ cm}^{-1}$ (O-H stretching of phenol), $1,651\text{ cm}^{-1}$ (C=N stretching of imine), $1,590\text{ cm}^{-1}$, and $1,481\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,516\text{ cm}^{-1}$ and $1,342\text{ cm}^{-1}$ (N-O stretching of nitro group), $1,481\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,176\text{ cm}^{-1}$ (C-O stretching of phenol), and $1,049\text{ cm}^{-1}$ (C-Cl stretching of chloro group).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 17a) revealed the presence of a substituted benzene ring at δ_{H} 8.43 (2H, *d*, 2.5 Hz, position 3 and 3'), 8.37 (2H, *d*, 2.5 Hz, position 4 and 4') and 8.32 (2H, *d*, 2.5 Hz, position 5 and 5'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 2, 2', 6, 6', 7 and 7' appeared at 8.26 (2H, *d*, 2.5 Hz), 8.22 (2H, *d*, 2.5 Hz), and 8.17 (2H, *d*, 2.5 Hz), respectively. Protons at the positions 8 and 8' were assigned at δ_{H} 7.80 (2H, *dd*, 6.5 and

3.0 Hz). The $^1\text{H-NMR}$ spectrum also showed prominently a hydroxy group at δ_{H} 11.51 (2H, s, position 1 and 1'). The assignments are concluded in Table 4-5.

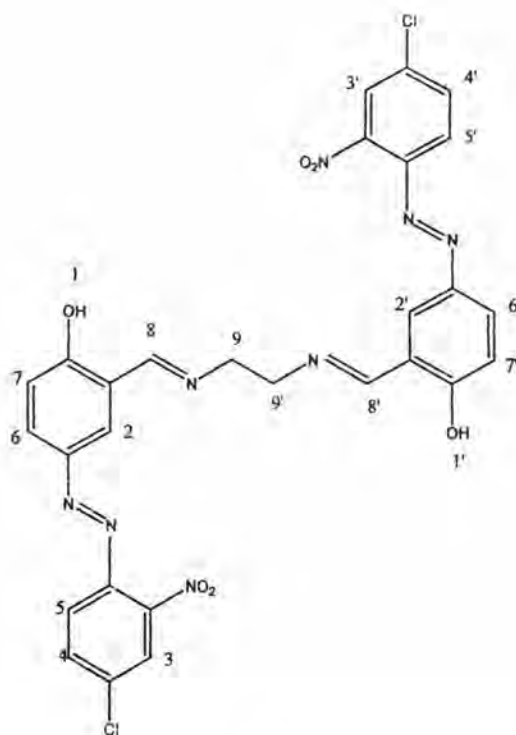
Table 4-5: The $^1\text{H-NMR}$ spectral data of Dye 2

Position	δ_{H} , multiplicity, J (Hz)
1, 1'	11.51, s
2, 2'	8.26, d, 2.5
3, 3'	8.43, d, 2.5
4, 4'	8.37, d, 2.5
5, 5'	8.32, d, 2.5
6, 6'	8.22, d, 2.32
7, 7'	8.17, d, 2.5
8, 8'	7.80, dd. 6.5 and 3.0

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) (Fig. 18a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.0 ppm and 166.0 ppm, respectively. The ^{13}C shifts of the benzene ring carbons appeared at 117.6-137.0 ppm. From the spectrum, it indicated that the signal at δ_{C} 59.1 was attributed to $-\text{CH}_2$ carbons at position 9 and 9'. Both $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 146.8.

4.2.3 Bis (salicylaldehyde) N, N'-ethylenediimine-4-chloro-2-nitrophenyl azo [Dye 3]

Bis(salicylaldehyde) N, N'-ethylenediimine-4-chloro-2-nitrophenyl azo was synthesized from the reaction of 4-chloro-2-nitroaniline and diphenolate diimine ion, to yield a brown liquid: with 77.3% (3.49 g) yield. The structure of Dye 3 is as follows:



Dye 3

The infrared spectrum (Fig. 22a) revealed the absorption peaks at $3,381\text{ cm}^{-1}$ (O-H stretching of phenol), $3,093\text{ cm}^{-1}$, and $2,862\text{ cm}^{-1}$ (C-H stretching of aliphatic), $1,660\text{ cm}^{-1}$ (C=N stretching of imine), $1,614\text{ cm}^{-1}$, and $1,471\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,537\text{ cm}^{-1}$ and $1,350\text{ cm}^{-1}$ (N=O stretching of nitro group), $1,284\text{ cm}^{-1}$ (C-O stretching of phenol), and $1,105\text{ cm}^{-1}$ (C-Cl stretching of chloro group).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 23a) revealed the presence of a substituted benzene ring at $\delta_{\text{H}} 8.19$ (2H, *m*, position 4, 4', 5 and 5'), and 7.67 (2H, *m*, position 2, 2', 3 and 3'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 6, 6', 7 and 7' revealed at 7.11 (2H, *d*, 9.0 Hz). Protons at the positions 8 and 8' were assigned at $\delta_{\text{H}} 7.70$ (2H, *d*, 2.0 Hz), and 9, 9' at 4.02 (4H, *t*, 7.0 Hz). The $^1\text{H-NMR}$ spectrum also revealed the signal of a hydroxy group at $\delta_{\text{H}} 11.46$ (2H, *s*, position 1 and 1'). The assignments are concluded in Table 4-6.

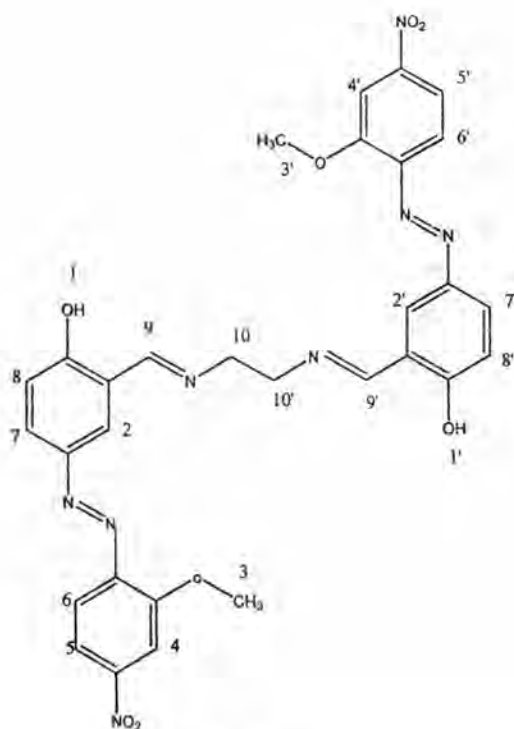
Table 4-6: The ^1H -NMR spectral data of Dye 3

Position	δ_{H} , multiplicity, J (Hz)
1, 1'	11.46, s
2, 2', 3, 3'	7.67, m
4, 4', 5, 5'	8.19, m
6, 6', 7, 7'	7.11, d, 9.0
8, 8'	7.70, d, 2.0
9, 9'	4.02, t, 7.0

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 24a) revealed the presence of phenoxy carbon and imino carbon signals at δ_{C} 161.6 ppm and 163.0 ppm, respectively. The ^{13}C shifts of the benzene ring carbons were at 117.5-137.0 ppm. From the spectrum, it indicated that the signal at δ_{C} 59.6 was attributed to $-\text{CH}_2$ carbon at position 9 and 9'. Both $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 145.8.

4.2.4 Bis (salicylaldehyde) N, N'-ethylenediimine-2-methoxy-4-nitrophenyl azo [Dye 4]

Bis (salicylaldehyde) N, N'-ethylenediimine-2-methoxy-4-nitrophenyl azo was synthesized from the reaction of 2-methoxy-4-nitroaniline and diphenolate diimine ion, to yield a brownish-orange solid: with 78.5% (3.51 g) yield. The structure of Dye 4 is as follows:



Dye 4

The infrared spectrum (Fig. 28a) revealed the absorption peaks at $3,327\text{ cm}^{-1}$ (O-H stretching of phenol), $1,653\text{ cm}^{-1}$ (C=N stretching of imine), $1,593\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,516\text{ cm}^{-1}$ and $1,342\text{ cm}^{-1}$ (N=O stretching of nitro group), and $1,178\text{ cm}^{-1}$ (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 29a) revealed the presence of a substituted benzene ring at δ_{H} 8.42 (2H, *m*, position 5, 5', 6 and 6'), 8.26 (2H, *d*, 5.0 Hz, position 2, 2', 4 and 4'), and 4.06 (6H, *s*, position 3 and 3'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 7, 7', 8 and 8' appeared at 7.81 (4H, *d*, 6.5 Hz). Positions 10 and 10' occurred at 3.95 (4H, *t*, 9.0 Hz). The $^1\text{H-NMR}$ spectrum also revealed the prominence of a hydroxy group at δ_{H} 11.50 (2H, *s br*, position 1 and 1'). The assignments are concluded in Table 4-7.

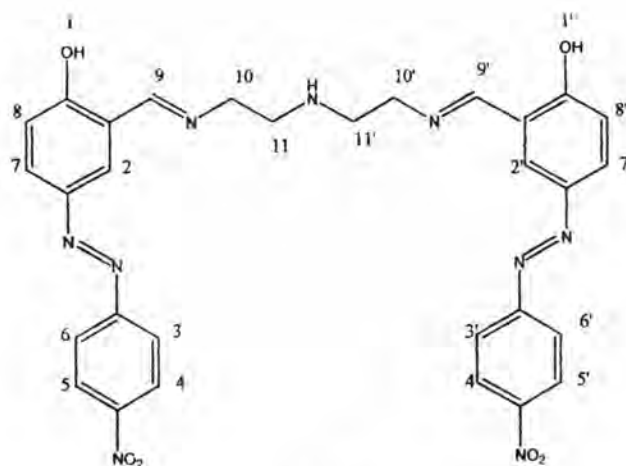
Table 4-7: The ^1H -NMR spectral data of Dye 4

Position	δ_{H} , multiplicity, J (Hz)
1, 1'	11.50, <i>s br</i>
2, 2', 4, 4'	8.26, <i>d, 5.0</i>
3, 3'	4.06, <i>s</i>
5, 5', 6, 6'	8.42, <i>m</i>
7, 7', 8, 8'	7.81, <i>d, 6.5</i>
10, 10'	3.95, <i>t, 9.0</i>

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 30a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.7 ppm and 166.6 ppm, respectively. The ^{13}C shifts of the benzene ring carbons appeared at 107.8-137.0 ppm. From the spectrum, it indicated that the signals of at δ_{C} 56.7, 58.1, and 59.7 were attributed to $-\text{CH}_2$ carbons at position 3, 3', 9, 9', 10, 10'. Both $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 145.7.

4.2.5 Bis (salicylaldehyde) N, N'-diethylenetriimine-*p*-nitrophenyl azo [Dye 5]

Bis (salicylaldehyde) N, N'-diethylenetriimine-*p*-nitrophenyl azo was synthesized from the reaction of *p*-nitroaniline and diphenolate diimine ion, to yield a reddish-brown solid: with 78.0% (3.59 g) yield, m.p. 183-184 °C. The structure of Dye 5 is as follows:

Dye 5

The infrared spectrum (Fig. 34a) revealed the absorption peaks at $1,645\text{ cm}^{-1}$ (C=N stretching of imine), $1,518\text{ cm}^{-1}$ and $1,329\text{ cm}^{-1}$ (N=O stretching of nitro group).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 35a) revealed the presence of a substituted benzene ring at δ_{H} 8.39 (4H, m, position 5, 5', 6 and 6'), and 8.01 (4H, d, 9.0 Hz, position 3, 3', 4 and 4'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 7, 7', 8 and 8' were assigned at 7.01 (4H, t, 7.5 Hz). Position 2 and 2' appeared at 7.55 (2H, d, 7.0 Hz). The $^1\text{H-NMR}$ spectrum also revealed the prominence of a hydroxy group at δ_{H} 11.45 (2H, s, position 1 and 1'). The assignments are concluded in Table 4-8.

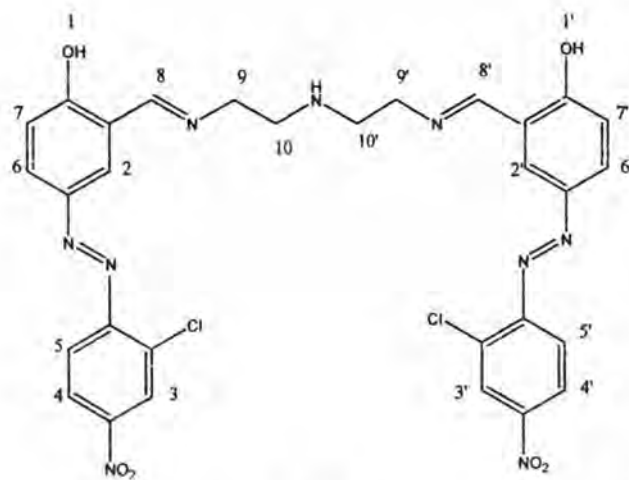
Table 4-8: The $^1\text{H-NMR}$ spectral data of Dye 5

Position	δ_{H} , multiplicity, J (Hz)
1, 1'	11.45, s
2, 2'	7.55, d, 7.0
3, 3', 4, 4'	8.01, d, 9.0
5, 5', 6, 6'	8.39, m
7, 7', 8, 8'	7.01, t, 7.5
10, 10'	4.14, t, 6.0
11, 11'	3.90, d, 5.5

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 36a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.6 ppm and 166.0 ppm, respectively. The ^{13}C shifts of the benzene ring carbons occurred at 114.2-137.6 ppm. From the spectrum, it indicated that the prominence at δ_{C} 49.3, and 59.1 ppm were attributed to $-\text{CH}_2$ carbon at position 10, 10', 11, and 11', respectively. Both $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 145.8.

4.2.6 Bis (salicylaldehyde) N, N'-diethylenetriimine-2-chloro-4-nitrophenyl azo [Dye 6]

Bis (salicylaldehyde) N, N'-diethylenetriimine-2-chloro-4-nitrophenyl azo was synthesized from the reaction of 2-chloro-4-nitroaniline and diphenolate diimine ion, to yield a brownish-orange solid: with 73.6% (3.64 g) yield. The structure of Dye 6 is as follows:



Dye 6

The infrared spectrum (Fig. 40a) revealed the absorption peaks at $1,658\text{ cm}^{-1}$ ($\text{C}=\text{N}$ stretching of imine), $1,581\text{ cm}^{-1}$ ($\text{C}=\text{C}$ stretching of aromatic), $1,520\text{ cm}^{-1}$ and $1,346\text{ cm}^{-1}$ ($\text{N}=\text{O}$ stretching of nitro group), and $1,182\text{ cm}^{-1}$ ($\text{C}-\text{O}$ stretching of phenol).

The ^1H -NMR spectrum (CDCl_3) (Fig. 41a) revealed the presence of a substituted benzene ring at δ_{H} 7.55 (4H, *m*, position 4, 4', 5 and 5'), and 7.46 (2H, *d*, 2.0 Hz, position 3 and 3'). This spectrum also revealed the existence of a coupled diimine in the marker

dye, whose δ_{H} at the positions 6, 6', 7 and 7' were at 7.03 (4H, *d*, 1.0 Hz). Positions 2 and 2' revealed at 7.00 (2H, *m*). In addition, protons at the positions 9 and 9' were assigned at δ_{H} 4.03 (4H, *t*, 6.0 Hz), and position 10 and 10' appeared at 3.94 (4H, *t*, 6.0 Hz). The assignments are concluded in Table 4-9.

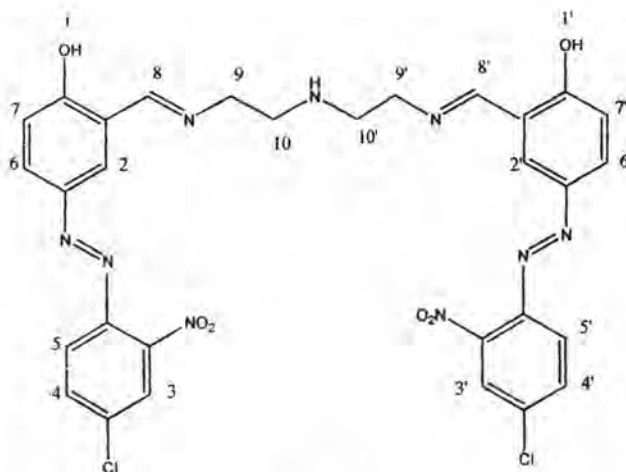
Table 4-9: The ^1H -NMR spectral data of Dye 6

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
2, 2'	7.00, <i>m</i>
3, 3'	7.46, <i>d</i> , 2.0
4, 4', 5, 5'	7.55, <i>m</i>
6, 6', 7, 7'	7.03, <i>d</i> , 1.0
9, 9'	4.03, <i>t</i> , 6.0
10, 10'	3.94, <i>t</i> , 6.0

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 42a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.6 ppm and 165.8 ppm, respectively. The ^{13}C shifts of the benzene ring carbons showed at 113.7-137.0 ppm. From the spectrum, it indicated that the signals at δ_{C} 49.2, and 59.3 were attributed to $-\text{CH}_2$ carbon at position 9, 9', 10 and 10', respectively. Two $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 146.6 ppm.

4.2.7 Bis (salicylaldehyde) N, N'-diethylenetriimine-4-chloro-2-nitrophenyl azo [Dye 7]

Bis (salicylaldehyde) N, N'-diethylenetriimine-4-chloro-2-nitrophenyl azo was synthesized from the reaction of 4-chloro-2-nitroaniline and diphenolated diimine ion, to yield a brown liquid: with 72.4% (3.58 g) yield. The structure of Dye 7 is as follows:

Dye 7

The infrared spectrum (Fig. 46a) revealed the absorption peaks at $3,420\text{ cm}^{-1}$ (O-H stretching of phenol), $1,631\text{ cm}^{-1}$ (C=N stretching of imine).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 47a) revealed the presence of a substituted benzene ring at $\delta_{\text{H}} 8.04$ (4H, *d*, 2.5 Hz, position 4, 4', 5 and 5'). Protons at the positions 9 and 9' were assigned at $\delta_{\text{H}} 4.10$ (4H, *t*, 5.5 Hz), position 10 and 10' appeared at 3.90 (4H, *t*, 6.0 Hz). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 2 and 2' were attributed at 7.51 (2H, *s*). The $^1\text{H-NMR}$ spectrum also revealed that the signals of a hydroxy group at $\delta_{\text{H}} 6.18$ (2H, *s br*, position 1 and 1'). The assignments are concluded in Table 4-10.

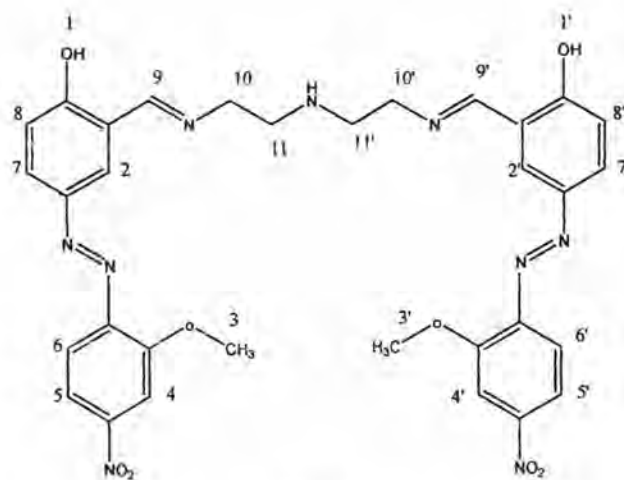
Table 4-10: The $^1\text{H-NMR}$ spectral data of Dye 7

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
1, 1'	6.18, s br
2, 2'	7.51, s
4, 4', 5, 5'	8.04, d, 2.5
9, 9'	4.10, t, 5.5
10, 10'	3.90, t, 6.0

The ^{13}C -NMR spectrum (CDCl_3) (Fig. 48a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.6 ppm and 167.0 ppm, respectively. The ^{13}C shifts of the benzene ring carbons revealed at 116.9-137.0 ppm. From the spectrum, it indicated that the signals at δ_{C} 56.9, and 59.7 were attributed to $-\text{CH}_2$ carbons at position 9, 9', 10 and 10', respectively. Both $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 143.4 ppm.

4.2.8 Bis (salicylaldehyde) N, N'-diethylenetriimine-2-methoxy-4-nitrophenyl azo [Dye 8]

Bis (salicylaldehyde) N, N'-diethylenetriimine-2-methoxy-4-nitrophenyl azo was synthesized from the reaction of 2-methoxy-4-nitroaniline and diphenolate diimine ion, to yield a brown liquid: with 70.6% (3.46 g) yield. The structure of Dye 8 is as follows:



Dye 8

The infrared spectrum (Fig. 52a) revealed the absorption peaks at $3,383\text{ cm}^{-1}$ (N-H stretching of amine), $1,658\text{ cm}^{-1}$ (C=N stretching of imine), $1,581\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,520\text{ cm}^{-1}$ and $1,346\text{ cm}^{-1}$ (N=O stretching of nitro group), and $1,119\text{ cm}^{-1}$ (C-O stretching of phenol).

The ^1H -NMR spectrum (CDCl_3) (Fig. 53a) revealed the presence of a substituted benzene ring at δ_{H} 7.54 (2H, *d*, 2.5 Hz, position 6, 6'), and 7.49 (2H, *d*, 2.5 Hz, position 5,

5'). Protons at the positions 11 and 11' were assigned at δ_H 3.93 (4H, *d*, 4.0 Hz), position 10 and 10' at 4.10 (4H, *t*, 5.5 Hz). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_H at the positions 2, 2', 8, and 8' were assigned at 7.45 (2H, *d*, 2.0 Hz), and 7.02 (2H, *s*), respectively. The 1H -NMR spectrum also revealed the prominence of a hydroxy group at δ_H 6.94 (2H, *d*, 2.5 Hz, position 1 and 1'). The assignments are concluded in Table 4-11.

Table 4-11: The 1H -NMR spectral data of Dye 8

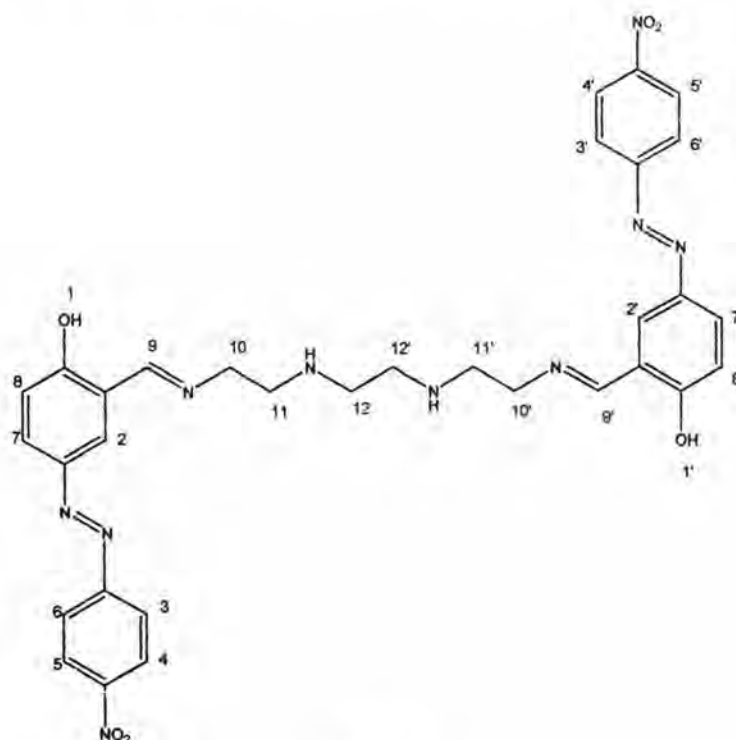
Position	δ_H , multiplicity, <i>J</i> (Hz)
1, 1'	6.94, <i>d</i> , 2.5
2, 2'	7.45, <i>d</i> , 2.0
3, 3'	3.87, <i>s</i>
5, 5'	7.49, <i>d</i> , 2.5
6, 6'	7.54, <i>d</i> , 2.5
8, 8'	7.02, <i>s</i>
10, 10'	4.10, <i>t</i> , 5.5
11, 11'	3.93, <i>d</i> , 4.0

The ^{13}C -NMR spectrum ($CDCl_3$) (Fig. 54a) revealed the presence of phenoxy carbon and imino carbon signals at δ_C 161.5 ppm and 167.0 ppm, respectively. The ^{13}C shifts of the benzene ring carbons appeared at 107.2-137.0 ppm. From the spectra, it indicated that the signals at δ_C 55.8, 56.7, and 56.3 were attributed to $-CH_2$ carbons at position 3, 3', 10, 10', 11 and 11', respectively. Both $-CH$ atoms adjacent to the azo of a coupled aromatic were apparent at 145.2 ppm.

4.2.9 Bis (salicylaldehyde) N, N'-triethylenetetrimine-*p*-nitrophenyl azo [Dye 9]

Bis (salicylaldehyde) N, N'-triethylenetetrimine-*p*-nitrophenyl azo was synthesized from the reaction of *p*-nitroaniline and monophenolate diimine ion, to yield a

brown solid: with 66.2% (3.33 g) yield, m.p. 134-135 °C. The structure of Dye 9 is as follows:



Dye 9

The infrared spectrum (Fig. 62a) revealed the absorption peaks at $3,410\text{ cm}^{-1}$ (N-H stretching of amine), $1,686\text{ cm}^{-1}$ (C=N stretching of imine), $1,601\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,508\text{ cm}^{-1}$ and $1,342\text{ cm}^{-1}$ (N-O stretching of nitro group), and $1,176\text{ cm}^{-1}$ (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 63a) revealed the presence of a substituted benzene ring at δ_{H} 8.38 (2H, *d*, 9.0 Hz, position 5, 5'), and 7.97 (2H, *d*, 9.0 Hz, position 3, 3'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 2, 2', 8 and 8' were attributed at 7.50 (2H, *d*, 2.0 Hz), and 7.45 (2H, *d*, 2.0 Hz), respectively. Position 10 and 10' were assigned at 3.99 (4H, *t*, 8.0 Hz), position 11 and 11' at 3.63 (4H, *t*, 8.0 Hz), and position 12 and 12' at 2.27 (4H, *t*, 8.0 Hz), respectively. The assignments are concluded in Table 4-12.

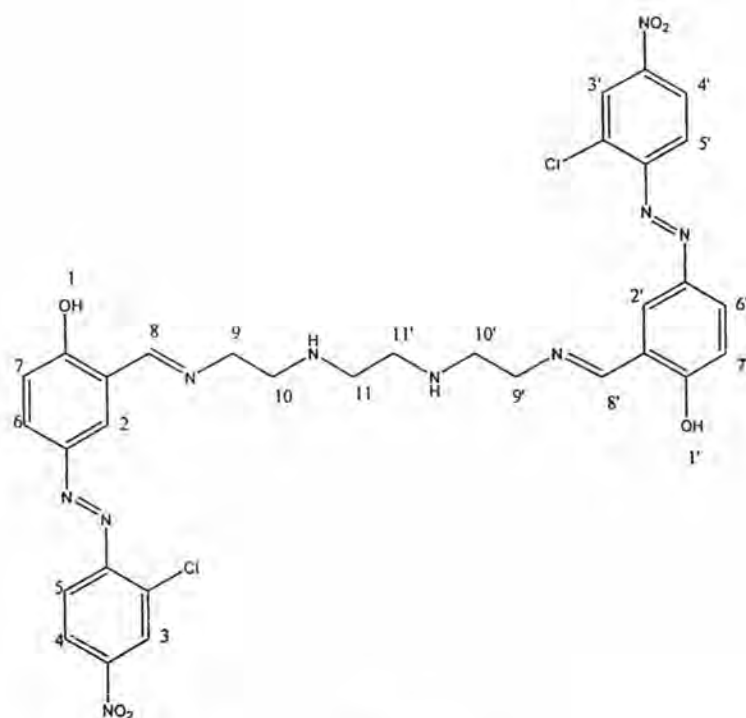
Table 4-12: The $^1\text{H-NMR}$ spectral data of Dye 9

Position	δ_{H} , multiplicity, J (Hz)
2, 2'	7.50, d, 2.0
3, 3'	7.97, d, 9.0
5, 5'	8.38, d, 9.0
8, 8'	7.45, d, 2.0
10, 10'	3.99, t, 8.0
11, 11'	3.63, t, 8.0
12, 12'	2.27, t, 8.0

The $^{13}\text{C-NMR}$ spectrum (CDCl_3) (Fig. 64a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_{C} 161.6 ppm and 164.8 ppm, respectively. From the spectrum, it indicated that the signals at δ_{C} 58.4, 56.8, and 53.6 were attributed to $-\text{CH}_2$ carbons at position 10, 10', 11, 11', 12 and 12', respectively. Both $-\text{CH}$ atoms adjacent to the azo of a coupled aromatic were apparent at 146.0 ppm. The spectrum also revealed the signal of position m at 150.7 ppm.

4.2.10 Bis (salicylaldehyde) N, N'-triethylenetetramine-2-chloro-4-nitrophenyl azo [Dye 10]

Bis (salicylaldehyde) N, N'-triethylenetetramine-2-chloro-4-nitrophenyl azo was synthesized from the reaction of 2-chloro-4-nitroaniline and diphenolate diimine ion, to yield a brownish-orange solid: with 61.2% (3.29 g) yield, m.p. 166-167 °C. The structure of Dye 10 is as follows:



Dye 10

The infrared spectrum (Fig. 68a) revealed the absorption peaks at $3,386\text{ cm}^{-1}$ (N-H stretching of amine), $1,660\text{ cm}^{-1}$ (C=N stretching of imine), $1,518\text{ cm}^{-1}$ and $1,344\text{ cm}^{-1}$ (N=O stretching of nitro group), $1,119\text{ cm}^{-1}$ and $1,045\text{ cm}^{-1}$ (C-Cl stretching of chloro group).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 69a) revealed the presence of a substituted benzene ring at $\delta_{\text{H}} 8.42$ (2H, *d*, 2.5 Hz, position 5, 5'), and 8.21 (2H, *d*, 2.5 Hz, position 3, 3'). Protons at the positions 9 and 9' appeared at $\delta_{\text{H}} 4.25$ (4H, *t*, 6.0 Hz), position 10 and 10' at 3.88 (4H, *t*, 6.0 Hz), and position 11 and 11' at 2.18 (4H, *s*). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 2, 2', 7, and 7' appeared at 7.50 (2H, *m*), and 7.04 (2H, *d*, 1.0 Hz), respectively. The assignments are concluded in Table 4-13.

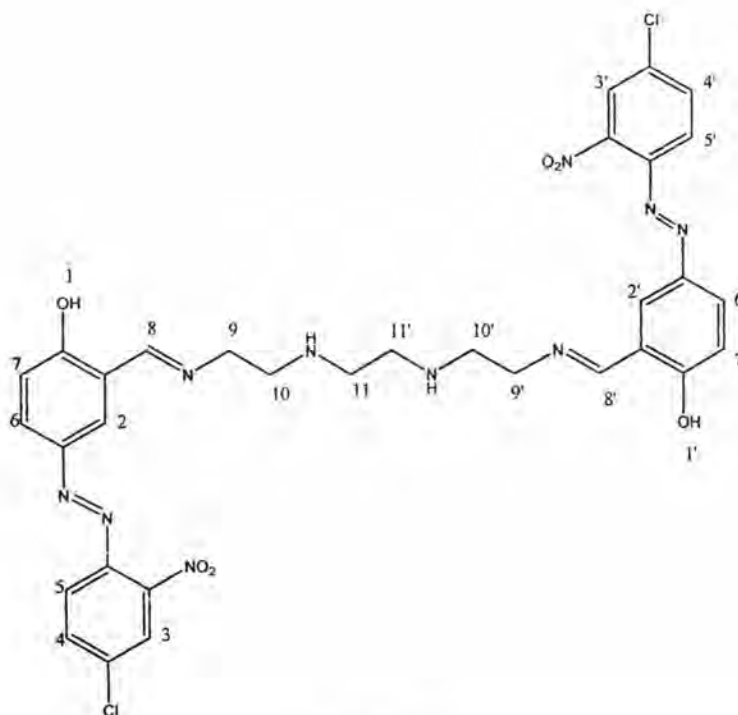
Table 4-13: The ¹H-NMR spectral data of Dye 10

Position	δ_H , multiplicity, <i>J</i> (Hz)
2, 2'	7.50, m
3, 3'	8.21, d, 2.5
5, 5'	8.42, d, 2.5
7, 7'	7.04, d, 1.0
9, 9'	4.25, t, 6.0
10, 10'	3.88, t, 6.0
11, 11'	2.18, s

The ¹³C-NMR spectrum (CDCl₃) (Fig. 70a) revealed the presence of phenoxy carbon and imino carbon from the signals at δ_C 161.6 ppm and 164.0 ppm, respectively. The ¹³C shifts of the benzene ring carbons occurred at 117.6-137.0 ppm. From the spectrum, it indicated that the signals at δ_C 58.3, 53.5, and 57.5 were attributed to -CH₂ carbons at position 9, 9', 10, 10', 11, and 11', respectively. Both -CH atoms adjacent to the azo of a coupled aromatic were apparent at 146.0 ppm.

4.2.11 Bis (salicylaldehyde) N, N'-triethylenetetramine-4-chloro-2-nitrophenyl azo [Dye 11]

Bis (salicylaldehyde) N, N'-triethylenetetramine-4-chloro-2-nitrophenyl azo was synthesized from the reaction of 4-chloro-2-nitroaniline and diphenolate diimine ion, to yield a brown liquid: with 61.0% (3.28 g) yield. The structure of Dye 11 is as follows:



Dye 11

The infrared spectrum (Fig. 74a) revealed the absorption peaks at $3,278\text{ cm}^{-1}$ (O-H stretching of phenol), $1,662\text{ cm}^{-1}$ (C=N stretching of imine), $1,523\text{ cm}^{-1}$ and $1,350\text{ cm}^{-1}$ (N=O stretching of nitro group), $1,464\text{ cm}^{-1}$ (C=C stretching of aromatic), $1,071\text{ cm}^{-1}$ (C-Cl stretching of chloro group).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 75a) revealed the presence of a substituted benzene ring at δ_{H} 8.08 (2H, *t*, 1.0 Hz, position 4, 4'). Protons at the positions 9 and 9' were assigned at δ_{H} 3.92 (4H, *s*), position 10 and 10' at 3.60 (4H, *d*, 5.5 Hz), and position 11 and 11' at 2.92 (4H, *d*, 4.0 Hz). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 2, 2', 7, and 7' appeared at 7.55 (2H, *m*), and 7.03 (2H, *s*), respectively. The assignments are concluded in Table 4-14.

Table 4-14: The $^1\text{H-NMR}$ spectral data of Dye 11

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
2, 2'	7.55, <i>m</i>

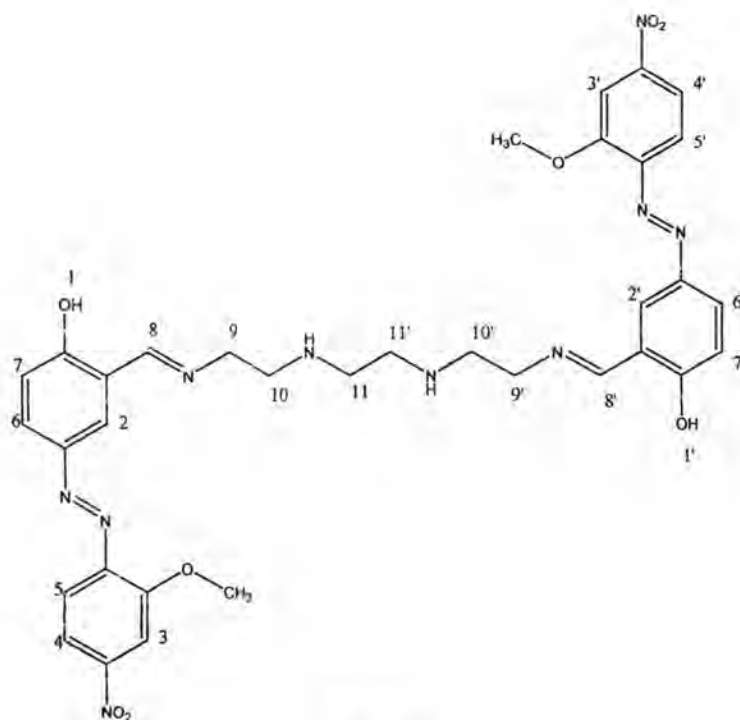
Table 4-14: The ¹H-NMR spectral data of Dye 11 (continue)

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
4, 4'	8.08, t, 1.0
7, 7'	7.03, s
9, 9'	3.92, s
10, 10'	3.60, d, 5.0
11, 11'	2.92, d, 4.0

The ¹³C-NMR spectrum (CDCl₃) (Fig. 76a) revealed the presence of phenoxy carbon and imino carbon signals at δ_{C} 161.5 ppm and 166.2 ppm, respectively. The ¹³C shifts of the benzene ring carbons were assigned at 117.5-137.0 ppm. From the spectrum, it indicated that the signals at δ_{C} 58.6, 53.314, and 57.0 were attributed to -CH₂ carbons at position 9, 9' 10, 10' 11, and 11'. Both -CH atoms adjacent to the azo of a coupled aromatic were apparent at 146.3 ppm.

4.2.12 Bis(salicylaldehyde) N, N'-triethylenetetramine-2-methoxy-4-nitrophenyl azo [Dye 12]

Bis(salicylaldehyde) N, N'-triethylenetetramine-2-methoxy-4-nitrophenyl azo was synthesized from the reaction of 2-methoxy-4-nitroaniline and diphenolate diimine ion, to yield a brown liquid: with 63.2% (3.37 g) yield. The structure of Dye 12 is as follows:



Dye 12

The infrared spectrum (Fig. 80a) revealed the absorption peaks at $3,101\text{ cm}^{-1}$ (N-H stretching of amine), $2,841\text{ cm}^{-1}$ (O-H stretching of phenol), $1,664\text{ cm}^{-1}$ (C=N stretching of imine), $1,529\text{ cm}^{-1}$ and $1,350\text{ cm}^{-1}$ (N-O stretching of nitro group), $1,279\text{ cm}^{-1}$ (C-N stretching of amine), and $1,151\text{ cm}^{-1}$ (C-O stretching of phenol).

The $^1\text{H-NMR}$ spectrum (CDCl_3) (Fig. 81a) revealed the presence of a substituted benzene ring at δ_{H} 7.78 (2H, *s*, position 6 and 6'), and 7.66 (2H, *t*, 2.5 Hz, position 5 and 5'). This spectrum also revealed the existence of a coupled diimine in the marker dye, whose δ_{H} at the positions 2 and 2' were assigned at 7.41 (2H, *t*, 8.5 Hz). The assignments are concluded in Table 4-15.

Table 4-15: The $^1\text{H-NMR}$ spectral data of Dye 12

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
2, 2'	7.41, <i>t</i> , 8.5
3, 3'	3.75, <i>s</i>

Table 4-15: The ¹H-NMR spectral data of Dye 12 (continue)

Position	δ_{H} , multiplicity, <i>J</i> (Hz)
5, 5'	7.66, t, 2.5
6, 6'	7.78, s

The ¹³C-NMR spectrum (CDCl₃) (Fig. 82a) revealed the presence of phenoxy carbon and imino carbon signals at δ_{C} 160.0 ppm and 161.4 ppm, respectively. The ¹³C shifts of the benzene ring carbons occurred at 108.1-136.9 ppm. From the spectrum, it indicated that the signals at δ_{C} 57.8, 55.7, and 58.8 were attributed to -CH₂ carbons at position 10, 10', 11, 11', 12 and 12', respectively. Both -CH atoms adjacent to the azo of a coupled aromatic were apparent at 145.5 ppm.

4.3 The use of marker dyes in diesel oil

4.3.1 Suitable extracted system

In system A, solution of 2% KOH, ethylenediamine, and diethylenetriamine in various systems were tried to extract marker dyes from marked diesel oil into the extracted phase. The colors of the extracted phase were observed including unmarked diesel oil extraction. The results were given in Table 4-16.

Table 4-16: The color of the extracted phase in system A at usable level of marker 5 ppm.

Dye	2% KOH in EG	10% ED/EG	20% ED/EG	10% ED/PG	20% ED/PG	10% DET/PG	20% DET/PG
Unmarked	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
No. I	Orange	Reddish orange	Pale orange	Reddish orange	Pale orange	Reddish orange	Pale orange

Table 4-16: The color of extracted phase in system A at usable level of marker 5 ppm. (continue)

Dye	2% KOH in EG	10% ED/EG	20% ED/EG	10% ED/PG	20% ED/PG	10% DET/PG	20% DET/PG
No.2	Pale purple	Purple	Purple	Pale purple	Dark purple	Pale purple	Dark purple
No.3	---	---	Yellow	---	Dark yellow	---	Dark yellow
No.4	Red	Reddish purple	Pale purple	Reddish purple	Purple	Reddish purple	Purple
No.5	Red	Pale red	Pale red	Reddish orange	Pale purple	Reddish orange	Pale purple
No.6	Purple	Pale purple	Purple	Purple	Dark purple	Purple	Dark purple
No.7	---	---	Pale yellow	---	Pale yellow	---	Pale yellow
No.8	Purple	Pale red	Reddish orange	Purple	Dark purple	Purple	Dark purple
No.9	Red	Red	Red	Red	Pale purple	Red	Pale purple
No.10	Purple	Pale purple	Purple	Pale purple	Dark purple	Pale purple	Dark purple
No.11	---	---	Yellow	---	Dark yellow	---	Dark yellow
No.12	Pale violet	Purple	Pale violet	Dark purple	Pale violet	Dark purple	Pale violet

From the results of the extraction in Table 4-16, 20% of ethylenediamine in ethylene glycol solution, 20% ethylenediamine in propylene glycol solution, and 20% diethylenetriamine in propylene glycol solution were the effective extracted systems that can be extracted all of marker dyes from marked diesel oil. Furthermore, when comparing in toxic aspect, propylene glycol was preferred to use since ethylene glycol

was carcinogenic compound that may be harmful to the user and may generate pollution problems. In case of cost, ethylenediamine was cheaper than diethylenetriamine; thus the suitable extracted solution in system A which was 20% ethylenediamine in propylene glycol solution.

For system B, 10% of hydrochloric acid in various solvents were used to determine the suitable extracted solution for all marker dyes. The results of the extraction were given in Table 4-17.

Table 4-17: The color of extracted phase in system B at usable level of marker 5 ppm.

Dye	10% HCl (aq)	10% HCl in MeOH	10% HCl in EG	10% HCl in PG	10% HCl in 3:2 PG-MeOH
Unmarked	-	-	-	-	Colorless
No.1	-	-	-	-	Pale yellow
No.2	-	-	-	-	Pale yellow
No.3	-	-	-	-	Pale yellow
No.4	-	-	-	-	Pale yellow
No.5	-	-	-	-	Pale yellow
No.6	-	-	-	-	Pale yellow
No.7	-	-	-	-	Pale yellow
No.8	-	-	-	-	Pale yellow
No.9	-	-	-	-	Pale yellow
No.10	-	-	-	-	Pale yellow
No. 11	-	-	-	-	Dark yellow
No.12	-	-	-	-	Dark yellow

From Table 4-17, it is shown that 10% HCl in the solution of propylene glycol and methanol at the ratio 3:2 was the only solution that could be extracted all of the marker dyes from marked diesel oil.

Comparing system A to system B, it was indicated that the extraction with 20% of ethylenediamine in propylene glycol solution gave a more clearly distinguishable colors

to the yellow shade of diesel oil than that extracted with 10% HCl in the solution of propylene glycol and methanol at a volume ratio of 3:2. Therefore 20% of ethylenediamine in propylene glycol solution was the suitable extracted solution for all marker dyes in this research.

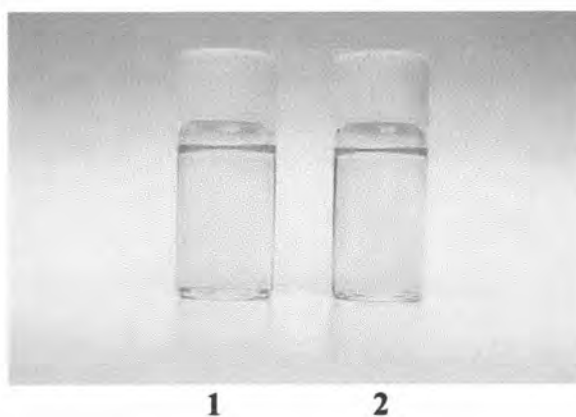


Fig. 4-1: Comparison of marked (1) and unmarked diesel oil (2)

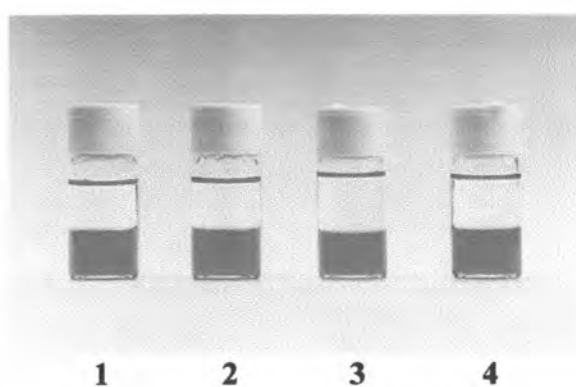


Fig. 4-2: The detection of Dye 1, Dye 2, Dye 3 and Dye 4

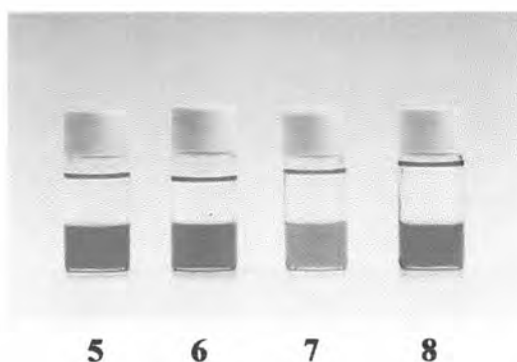


Fig. 4-3: The detection of Dye 5, Dye 6, Dye 7 and Dye 8

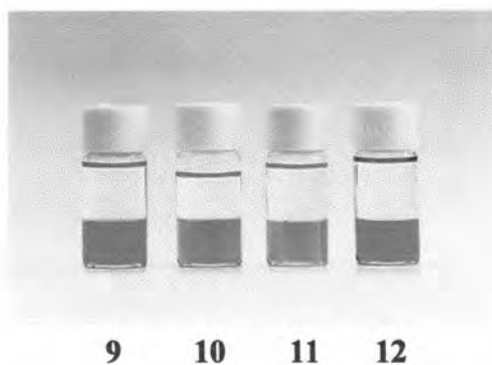
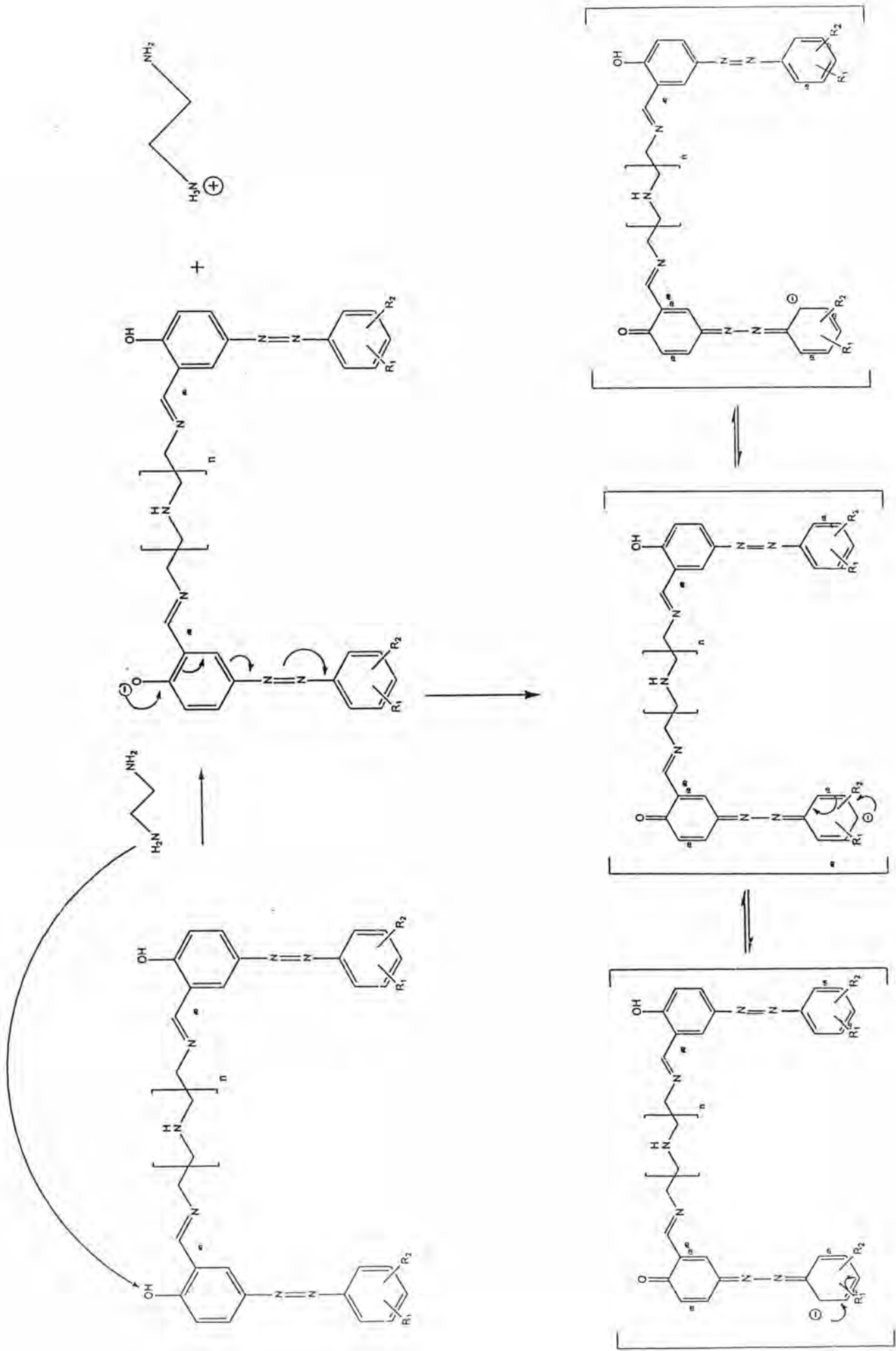


Fig. 4-4: The detection of Dye 9, Dye 10, Dye 11 and Dye 12

The colors of the marker dyes were visible by complexation reaction of ethylenediamine and marker dyes. The complexation mechanism was proposed under schemed below.



From this mechanism, it is shown that the negative charge would appear in the *para* and *ortho*-position on the azo group. If an electron-withdrawing group occupies the *para* or *ortho*-position on the azo group, the structure is stabilized by an inductive effect. Moreover, if the substituent at the *para* or *ortho*-position on the azo group is nitro group, the structure is stabilized not only on the inductive effect but also on the resonance effect, because nitro group could distribute the negative charge throughout its structure.

4.3.2 The optimum shaking time of the extraction

Dye 12 was used to determine the optimum shaking time of the extraction with 20% ethylenediamine in propylene glycol solution. The absorbance was measured by using UV/VIS spectrophotometer. The optimum shaking time that gave the highest absorbance was selected. The results of UV/VIS measurement were given in Table 4-18.

Table 4-18: The variation of shaking time of the extraction

Shaking time (seconds)	Maximum wavelength	Absorbance
10	534.01	0.23
20	534.99	0.23
30	537.00	0.26
40	539.94	0.27
50	541.97	0.29

From Table 4-18, it was shown that the 50 seconds of shaking with 20% ethylenediamine in propylene glycol solution gave the highest absorbance. Therefore in every experiment in this research, the extraction of all marker dyes was shaken for at least 50 seconds.

4.3.3 Suitable concentration of each marker dye in diesel oil

The suitable extracted solution, 20% ethylenediamine in propylene glycol solution, was used to monitor suitable concentration of each marker dyes in diesel oil. The extraction was done at volume ratio of 6 parts marked diesel oil to 1 part extracted solution, and the results were listed in Table 4-19.

Table 4-19: The suitable concentration of each marker dyes in diesel oil

Dye No.	1	2	3	4	5	6	7	8	9	10	11	12
Concentration (ppm)	1	1	10	3	4	1	3	4	1	3	5	4

From Table 4-19, it was shown that suitable concentration of these synthetic marker dyes extracted in the ratio of marked diesel oil were 10 ppm. The concentration of dye 1, 2, 6, and 10 were 1 ppm while dye 4, 7, and 9 were 3 ppm. As for dye 5, 8, and 12, the suitable concentration in diesel oil were 4 ppm, dye 11 was 5 ppm, and dye 3 was 10 ppm.

4.3.4 The maximum wavelength and absorbance of marker dyes

Each of marker dye was extracted with 20% ethylenediamine in propylene glycol solution, in a volume ratio of marked diesel to the extracted solution 6:1, to determine the maximum wavelength and its absorbance. The results were given in Table 4-20.

Table 4-20: The maximum wavelength and absorbance of each marker dye.

Dye No.	Maximum wavelength (nm)	Absorbance	Ratio of marked diesel to extractant	Visual color
1	533.90	0.37	1:1	Pale purple

Table 4-20: The maximum wavelength and absorbance of each marker dye. (continue)

Dye No.	Maximum wavelength (nm)	Absorbance	Ratio of marked diesel to extractant	Visual color
2	552.26	0.42	1:1	Dark purple
3	486.94	0.74	8:1	Dark yellow
4	538.11	0.45	3:1	Purple
5	529.86	0.60	4:1	Pale purple
6	553.83	0.43	1:1	Dark purple
7	426.97	0.34	4:1	Pale yellow
8	552.15	0.43	3:1	Dark purple
9	527.16	0.67	4:1	Pale purple
10	552.51	0.33	1:1	Dark purple
11	482.07	0.44	6:1	Dark yellow
12	561.74	0.45	5:1	Pale violet

4.3.5 Percentage recovery of marker dye in the extracted phase

Dye 6 was used to determine the percentage recovery of marker dye in the extracted phase. The standard calibration curve of the extracted dye was shown in Figure 4-5.

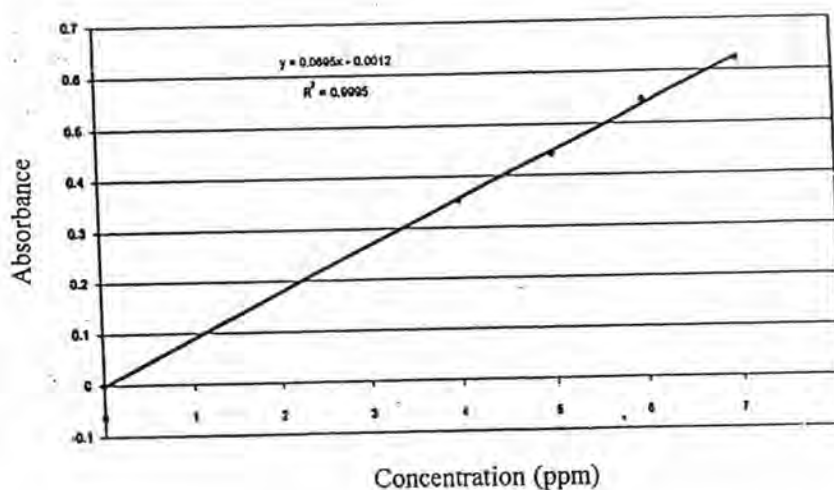


Fig. 4-5: The standard calibration curve of the extracted dye

Table 4-21: The measured absorbance of Dye 6 at the maximum wavelength (553.80 nm).

Time	Absorbance
1	0.43
2	0.43
3	0.43
average	0.43

From the standard calibration curve, linear equation of Dye 6 is $y = 0.0895x - 0.0012$. And from the results in Table 4-21, the average absorbance at 553.80 nm of Dye 6 was 0.43 therefore the average quantity of it in the extracted phase will be 4.92 ppm. This meant the recovery percentage of the extracted dye in the extracted phase was 97.4 ± 0.2 . It was concluded that the standard calibration curves of all marker dyes were done at 97.4 ± 0.2 % of the extraction.

4.3.6 Effects of marker dyes on the physical properties of marked diesel oil

Marked diesel oil of dye 1 was used to study the effects of marker dye on physical properties of marked diesel oil using ASTM methods and compared the results with unmarked diesel oil. The results of the tests were list in Table 4-22.

Table 4-22: The results of physical properties test of marked diesel oil

Test items	ASTM	Standard	Marked	Unmarked
API gravity @ 60 °F	D 1298	Report	38.6	38.7
Specific gravity @ 15.6/15.6 °C	D 1298	Report	0.8325	0.8332
Calculated cetane index	D 976	47 min	57	57
Kinematics viscosity @ 40 °C, cSt	D 445	1.8-4.1	3.159	3.183
Pour point, °C	D 97	10	-8	-8
Flash point (P.M.), °C	D 93	52	65	67
Sulfur content, %wt	D 5453	0.05	0.0430	0.0429
Copper strip corrosion, Number (3 hrs., @ 50 °C)	D 130	No.1	No.1	No.1
Distillation: (Correct. Temp.)	D 86			
IBP, °C		Report	175	177
10% rec., °C		Report	210.2	211.2
50% rec., °C		Report	278	279
90% rec., °C		357 max	351.4	351.9
Color	D 1500	2.0 max	L < 0.5	L < 0.5
	Visual	-	Yellow	Yellow
Total acid number, mg KOH/g	664		0.01	0.02

From the results, it revealed that the physical properties of marked diesel oil were not significantly different from unmarked diesel oil. Hence, it was concluded

that this marker dye did not have any effects on the physical properties of marked diesel oil.

4.3.7 Quantitative determination of marker dyes in diesel oil

The standard calibration curve of each marker dye in diesel oil was done by adding each marker dye into diesel oil at 5 different concentrations, extracting them with 20% ethylenediamine in propylene glycol solution, and measuring absorbance to create the standard calibration curves between the absorbance and their concentrations.

The standard calibration equations and their correlation coefficients are given in Table 4-23, while the standard calibration curves of all marker dyes are shown in the Appendix section.

Table 4-23: The standard calibration equations for the quantitative determination and their correlation coefficients of marked diesel oil.

Dye	Equation	Correlation Coefficient (R ²)
No.1	$Y = 0.0729 X + 0.0004$	0.9999
No.2	$Y = 0.0828 X + 0.0009$	0.9994
No.3	$Y = 0.1463 X + 0.0021$	0.9998
No.4	$Y = 0.0934 X - 0.0038$	0.9993
No.5	$Y = 0.1192 X + 0.0008$	0.9998
No.6	$Y = 0.0889 X - 0.0012$	0.9995
No.7	$Y = 0.0885 X + 0.0009$	0.9995
No.8	$Y = 0.0842 X + 0.0047$	0.9998
No.9	$Y = 0.1330 X - 0.003$	0.9991
No.10	$Y = 0.0669 X - 0.0029$	0.9998
No.11	$Y = 0.0705 X - 0.0068$	0.9994
No.12	$Y = 0.0885 X + 0.0009$	0.9995

From Table 4-23, it was shown that the correlation coefficients of the marker dyes were close to 1, meaning that they could be used in quantitative determinations. In such manner, it may be used to approximately indicate the concentration of marked diesel oil in the field test with a color strip paper like the universal indicator paper. Fig. 4-5 is the example of this application.



Fig. 4-6: The extracted solution of bis (salicylaldehyde) N, N'-ethylenediimine-2-chloro-4-nitrophenyl azo in different concentration (ppm)

4.4 Stability of marker dyes in diesel oil

All marker dyes were studied their stability in diesel oil by monthly monitoring the quantities of marker dyes in diesel oil in the period of three months of storage. The results of the stability of all marker dye in diesel oil were listed in Table 4-24.

Table 4-24: The stability of marker dyes in diesel oil within three months of storage.

Dye	Absorbance at its maximum wavelength			Concentration of marked diesel oil (ppm)		
	1 st month	2 nd month	3 rd month	1 st month	2 nd month	3 rd month
No.1	0.37	0.37	0.37	5.05	5.04	5.04
No.2	0.42	0.42	0.42	5.05	5.04	5.02
No.3	0.74	0.74	0.74	5.05	5.04	5.04
No.4	0.45	0.46	0.46	4.91	4.93	4.94
No.5	0.60	0.60	0.60	4.99	4.99	5.01
No.6	0.43	0.44	0.44	4.90	4.91	4.91

Table 4-23: The stability of marker dyes in diesel oil within three months of storage. (continued)

Dye	Absorbance at its maximum wavelength			Concentration of marked diesel oil (ppm)		
	1 st month	2 nd month	3 rd month	1 st month	2 nd month	3 rd month
No.7	0.34	0.35	0.36	3.78	3.97	4.01
No.8	0.43	0.43	0.43	5.07	5.06	5.07
No.9	0.67	0.67	0.67	5.04	5.02	5.00
No.10	0.33	0.33	0.33	4.96	4.97	4.96
No.11	0.44	0.43	0.43	6.29	6.52	6.52
No.12	0.45	0.45	0.45	5.07	5.07	5.07

From Table 4-24, it revealed that the concentrations of all marker dyes measured in each months were slightly different from the original concentrations meaning that all marker dyes were stable at least three months of storage in diesel oil.