CHAPTER III
EXPERIMENT

3.1 General methods

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgel 60 F_{254}). Column chromatography was performed on silica gel (Merck Kieselgel 60 G). The FT-IR spectra were recorded on a Nicolet Fourier Transformed Infrared Spectrophotometer model Impact 410. Liquid samples were dropped on a sodium chloride cell. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a Bruker model ACF200 spectrometer, which operated at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C nuclei.

The quantities of markers in diesel fuels were measured using a UV/VIS spectrophotometer model Lamda-2 from Perkin Elmer. Flash points (Pensky-Martens) of marked and unmarked diesel fuels were measured using an ISL (PMFP93) automatic flash point. The pour points of marked and unmarked diesel fuels were determined using an ISL (CPP92) automatic pour point. The kinematic viscosities of marked and unmarked diesel fuels were performed with Cannon automatic viscosity. Sulfur contents were determined using a CHNS/O analyzer model antex 9000 series from Perkin Elmer. The distillation of marked and unmarked diesel fuels were performed with an automatic distillation apparatus model MP626 from Herzog. The total acidities of marked and unmarked diesel fuels were obtained with a Mettler Toledo DL50 graphix titrator, and colors of marked and unmarked diesel fuels were observed using a petrochemical tintometer model PFX 990/P from Lovibond.

3.2 Chemicals

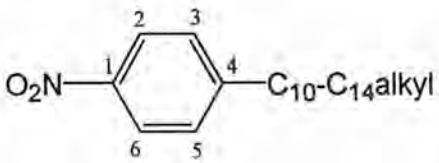
Linear alkylbenzene was obtained from the Department of Customs. Sodium nitrite, ethylenediamine, *p*-nitro aniline, *o*-nitro aniline, 4-chloro-2-nitroaniline, 4-chloro-3-nitroaniline, 2-chloro-4-nitroaniline, 2-chloro-5-nitroaniline, 2-methoxy-4-nitroaniline, phenol, resorcinol, 2,6-di-*tert*-butylphenol were purchased from Fluka. Potassium hydroxide, acetic and ethylene glycol were obtained from Carlo Erba.

Sulfuric acid and nitric acid were obtained from J.T. Baker. Formic acid was obtained from AJAX. Hydrochloric acid and catechol were obtained from BDH. Sodium acetate was obtained from M&B. Toluene, methanol, diethylamine and tin powder were obtained from Merck. Hexane and dichloromethane commercial grades were purified prior to use by distillation.

3.3 Experimental Procedures

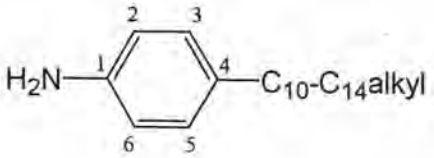
3.3.1 Syntheses

3.3.1.1 *p*-nitro-linear alkylbenzene



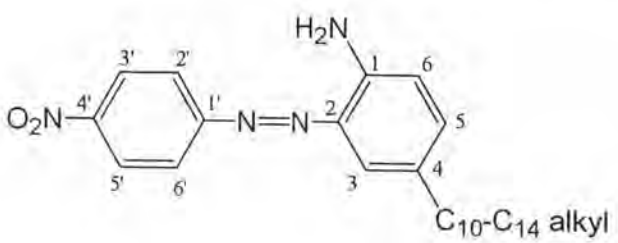
Concentrated sulfuric acid (74 g, 40 ml) was added in portions to concentrated nitric acid (50 g, 35 ml, 0.5 mole) with vigorous stirring and cooling. Linear alkylbenzene (49.3 g, 0.20 mole) was added very slowly into the above mixed acid where the reaction temperature was held at 50°C. The mixture was continually stirred for another 1 hour. This mixture was diluted with 500 ml of cold water, and the two phases were separated by a separating-funnel. The yellow liquid of product was washed 2-3 times with the cold water and collected. The unreacted linear alkylbenzene was removed by column chromatography eluted by hexane. The product (49.50 g, 85% yield) was yellow liquid with R_f 0.58 (hexane: dichloromethane (1:1)). IR (NaCl) 3084, 2927, 1604, 1522, 1466 and 1346 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.27(2H, *d*, J = 8.77 Hz) and 8.12(2H, *d*, J = 8.77 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 123.5 (2C, C-2 and C-6), 128.4 (2C, C-3 and C-5), 146.5 (1C, C-4) and 154.6 (1C, C-1).

3.3.1.2 *p*-linear alkylaniline [17]



The mixture of *p*-nitro-linear alkylbenzene (49.50 g, 0.17 mole) and tin powder (45 g, 0.38 mole), which was placed in a flask equipped with a reflux condenser, was stirred, and then 10 ml of concentrated hydrochloric acid was added through the top of the condenser. This reaction is exothermic, so the flask was dipped in a cold-water bath to control the temperature. When the initial reaction had subsided, another 10 ml of acid was poured down the condenser. The mixture was continually stirred and cooled again if the reduction became too violent. This manner was preceded until all 90 ml of acid had been added and heating was continued under reflux for an hour. The above mixture was cooled to room temperature and a solution of 75 g of sodium hydroxide was gradually added in 125 ml of water with cooling. An oily liquid product was separated, and extracted with hexane. The solution was dried and the hexane was removed by evaporation. The product (44.0 g, 99% yield) was colorless liquid with R_f 0.37 (hexane: dichloromethane (1:1)). IR (NaCl) 3467, 3384, 3026, 2925, 1622, 1606, 1516, 1495, 1458, 1375 and 1273 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.61 (2H, *s*, *br*), 6.64(2H, *d*, J = 8.32 Hz) and 6.96(2H, *d*, J = 8.32 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 115.3 (2C, C-2 and C-6), 127.7 (1C, C-4), 128.4 (2C, C-3 and C-5), and 144.0 (1C, C-1).

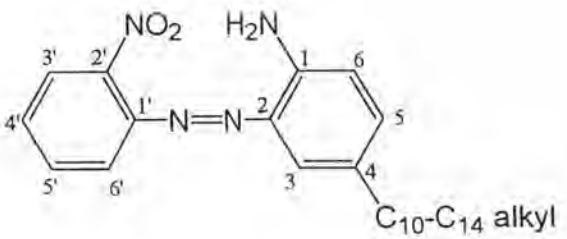
3.3.1.3 4-linear alkyl-2-(4-nitro)phenyl azo aniline (Compound **1a**) [17]



A mixture of *p*-nitro aniline (1.38 g, 0.01 mole), concentrated acid (3 ml, 0.035 mole) and 3 ml of water was heated until the solution became homogeneous. The solution was stirred vigorously while cooling down to 0°C. Then a cool solution of 10 ml 1 *N* nitrite (0.69 g of sodium nitrite) was dropped into the mixture at 0-5°C. Stirring was continued for a few minutes to complete the diazotization. Pale yellow solution of *p*-nitro aniline diazonium salt was obtained.

p-Linear alkylaniline (2.61 g, 0.01 mole) was dissolved in 20 ml methanol containing sodium acetate (0.62 g, 0.015 mole). This solution was added into *p*-nitro aniline diazonium salt solution at a rate that the temperature did not rise above 5°C. Stirring was continued for an hour and the product in the oil phase was separated from the aqueous phase. It was extracted excellently with dichloromethane and then washed 2-3 times with 20 ml distilled water. The crude product was purified by column chromatography, which was eluted by a mixture of hexane-dichloromethane (3:1). 4-Linear alkyl-2-(4-nitro)phenyl azo aniline (2.51 g, 61%yield) as a deep yellow-brown oil with R_f 0.41 (hexane: dichloromethane (1:1)) was obtained.. IR (NaCl) 3481, 3361, 3028, 2925, 1631, 1604, 1523, 1462, 1346 and 1255 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.27 (2H, *s*, *br*), 6.66 (1H, *d*, J = 8.29 Hz), 7.09 (1H, *d*, J = 8.29 Hz), 7.58 (1H, *s*), 8.06 (2H, *d*, J = 8.19 Hz), and 8.29 (2H, *d*, J = 8.19 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 118.4(1C, C-6), 124.8(1C, C-3), 125.3 (2C, C-2′ and C-6′), 125.7 (2C, C-3′ and C-5′), 130.9(1C, C-4), 132.4(1C, C-5), 138.1 (1C, C-1), 139.2 (1C, C-2), 151.8 (1C, C-4′) and 158.3 (1C, C-1′); MS (Da/e): 382, 396, 410, 424, and 438.

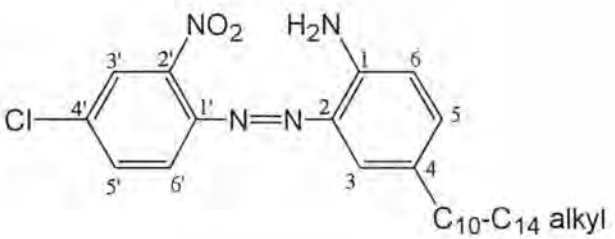
3.3.1.4 4-linear alkyl-2-(2-nitro)phenyl azo aniline (Compound **2a**)



This compound was prepared in a manner similar to the preparation of compound **1a,** except *o*-Nitroaniline (1.38 g, 0.01 mole) was used. A deep yellowish brown oil of 4-linear alkyl-2-(2-nitro)phenyl azo aniline (2.83 g, 69%yield) with R_f 0.64 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3494, 3383, 3026, 2925, 1626, 1574, 1512, 1466, 1346 and 1259 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.10 (2H, *s, br*), 6.62 (1H, *d*, J = 8.70 Hz), 6.79 (1H, *dd*, J = 1.44, 8.70 Hz), 7.38 (1H, *td*, J = 1.15, 8.45 Hz), 7.69 (1H, *d*, J = 1.44 Hz), 7.88 (1H, *td*, J = 1.15, 8.45 Hz), and 8.09 (2H, *td*, J = 1.50, 8.45 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 116.9 (1C, C-6), 122.6 (1C, C-3), 122.8 (1C, C-6′), 123.0 (1C, C-3′),.128.8 (1C, C-4), 130.5 (1C, C-5), 131.0 (1C, C-4′), 135.7 (1C, C-5′), 138.0 (1C, C-1), 138.8 (1C, C-2), 143.0 (1C, C-2′) and 147.8 (1C, C-1′).

3.3.1.5 4-linear alkyl-2-(4-chloro-2-nitro)phenyl azo aniline

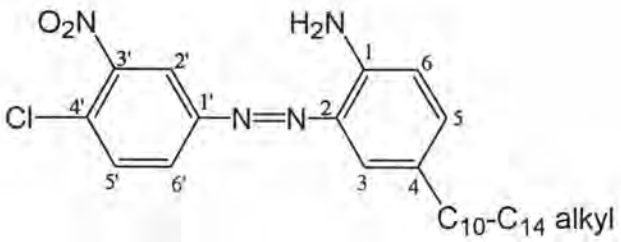
(Compound **3a**)



4-Chloro-2-nitroaniline (1.73 g, 0.01 mole) was used in a similar manner to that mentioned for the preparation of Compound **1a**. It gave a deep yellowish brown oil of 4-linear alkyl-2-(4-chloro-2-nitro)phenyl azo aniline (3.32 g, 75%yield) with R_f 0.60 (hexane: dichloromethane (1:1)). IR (NaCl) 3467, 3381, 3026, 2925, 1628, 1603, 1523, 1508, 1466, 1338, 1250 and 1130 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.25 (2H, *s, br*), 6.82 (1H, *d*, J = 8.50 Hz), 7.02 (1H, *d*, J = 8.50 Hz), 7.69 (1H, s), and 8.07 (3H, *m*); ^{13}C-NMR($CDCl_3$) δ (ppm): 115.0 (1C, C-6), 123.0 (1C, C-3), 123.3 (1C, C-6′), 123.6 (1C, C-3′), 129.0 (1C, C-4), 131.1 (1C, C-5), 131.4 (1C, C-4′), 135.8 (1C, C-5′), 138.1 (1C, C-1), 138.9 (1C, C-2), 143.8 (1C, C-2′), and 147.5 (1C, C-1′).

3.3.1.6 4-linear alkyl-2-(4-chloro-3-nitro)phenyl azo aniline

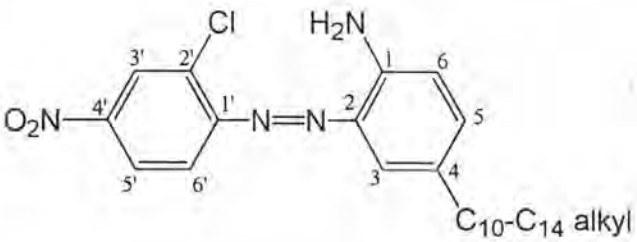
(Compound **4a**)



The same procedure as the preparation of Compound **1a** was followed, except 4-Chloro-3-nitroaniline (1.73 g, 0.01 mole) was used. A reddish brown oil of 4-linear alkyl-2-(4-chloro-3-nitro)phenyl azo aniline (3.45 g, 78%yield) with R_f 0.65 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3406, 3331, 3026, 2925, 1628, 1603, 1533, 1466, 1346, 1313 and 1130 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.46 (2H, *s*, *br*), 6.85 (1H, *d*, J = 8.40 Hz), 7.09 (1H, *d*, J = 8.40 Hz), 7.61 (1H, *s*), 7.87 (1H, *d*, J = 8.54 Hz), 8.12 (1H, *d*, J = 8.54 Hz), and 8.42 (1H, *s*); ^{13}C-NMR($CDCl_3$) δ (ppm): 115.1 (1C, C-6), 120.0 (1C, C-2′), 122.8 (1C, C-3), 129.3 (1C, C-4), 130.2 (1C, C-5′), 130.4 (1C, C-6′), 132.0 (1C, C-4′), 132.1 (1C, C-5), 137.5 (1C, C-1), 138.0 (1C, C-2), 148.3 (1C, C-3′), and 151.2 (1C, C-1′).

3.3.1.7 4-linear alkyl-2-(2-chloro-4-nitro)phenyl azo aniline

(Compound **5a**)

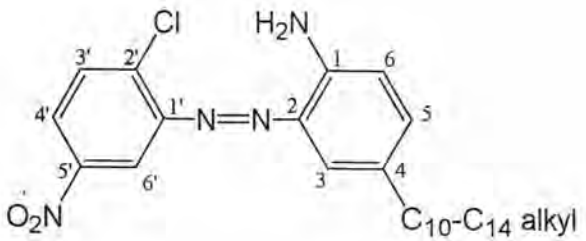


2-Chloro-4-nitroaniline (1.73 g, 0.01 mole) was used by a similar procedure to that utilized for the preparation of Compound **1a**. 4-linear alkyl-2-(2-chloro-4-nitro)phenyl azo aniline (2.57 g, 58%yield) as a deep yellowish brown oil with R_f 0.51 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3492, 3377, 3026,

2932, 1624, 1590, 1525, 1510, 1466, 1336, 1279 and 1128 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.00 (2H, *s*, *br*), 6.74 (1H, *d*, J = 8.40 Hz), 7.19 (1H, *d*, J = 8.40 Hz), 7.64 (1H, *d*, J = 1.99 Hz), 8.18 (2H, *d*, J = 8.27 Hz), 8.25 (1H, s), and 8.26 (2H, *d*, J = 8.27 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 117.5 (1C, C-6), 124.4 (1C, C-5′), 125.7 (3C, C-3, C-3′ and C-6′), 127.7 (1C, C-2′), 128.1 (1C, C-4), 129.0 (1C, C-5), 138.4 (2C, C-1 and C-2), 149.2 (1C, C-4′) and 158.0 (1C, C-1′). MS (Da/e): 417, 431, 445, 459, and 473.

3.3.1.8 4-linear alkyl-2-(2-chloro-5-nitro)phenyl azo aniline

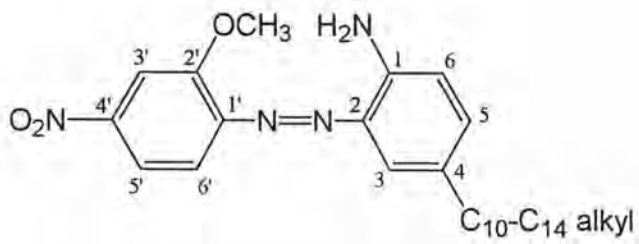
(Compound **6a**)



The same procedure was used as in the preparation of Compound **1a**, except 2-Chloro-5-nitroaniline (1.73 g, 0.01 mole) was substituted. It gave a yellowish brown oil of 4-linear alkyl-2-(2-chloro-5-nitro)phenyl azo aniline (3.23 g, 73%yield) with R_f 0.75 (hexane: dichloromethane (1:1)). IR (NaCl) 3427, 3334, 3026, 2925, 1630, 1603, 1523, 1464, 1346, 1282 and 1045 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.48 (2H, *s*, *br*), 6.84 (1H, *d*, J = 8.38 Hz), 7.16 (1H, *d*, J = 8.38 Hz), 7.54 (1H, *d*, J = 8.74 Hz), 7.68 (1H, *d*, J = 1.82 Hz), 8.38 (1H, *d*, J = 8.74 Hz), and 8.57 (1H, *s*); ^{13}C-NMR($CDCl_3$) δ (ppm): 113.0 (1C, C-6), 121.0 (1C, C-6′), 125.1 (1C, C-3), 127.8 (1C, C-4′), 129.8 (1C, C-4), 130.2 (1C, C-3′), 131.2 (1C, C-5), 135.9 (1C, C-2′), 138.3 (1C, C-1), 139.7 (1C, C-2), 147.2 (1C, C-5′), and 154.1 (1C, C-1′).

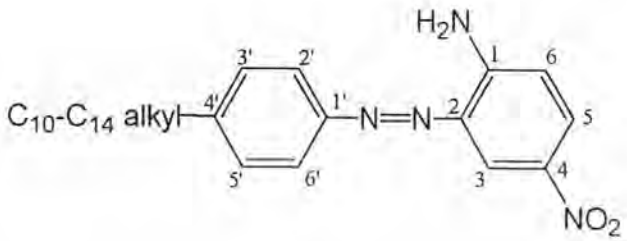
3.3.1.9 4-linear alkyl-2-(2-methoxy-4-nitro)phenyl azo aniline

(Compound **7a**)



2-Methoxy-4-nitroaniline (1.68 g, 0.01 mole) was used in a similar procedure for the preparation of Compound **1a**. It gave a deep yellowish brown oil of 4-linear alkyl-2-(2-methoxy-4-nitro)phenyl azo aniline (3.31 g, 75%yield) with R_f 0.48 (hexane: dichloromethane (1:1)). IR (NaCl) 3469, 3388, 3026, 2925, 1622, 1601, 1520, 1464, 1344, 1296, 1248 and 1038 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.89 (3H, *s*), 5.01 (2H, *s*, *br*), 6.60 (1H, *d*, J = 8.30 Hz), 6.71 (1H, *d*, J=8.30 Hz), 7.25 (1H, *m*), 7.59 (1H, *s*), 7.64 (1H, *d*, J = 2.26 Hz) and 7.75 (1H, *m*); ^{13}C-NMR($CDCl_3$) δ (ppm): 55.8 (1C, OCH_3), 111.7 (1C, C-3′), 117.0 (1C, C-6), 118.1 (1C, C-5′), 119.2 (1C, C-3), 122.0 (1C, C-6′), 128.3 (1C, C-4), 131.5 (1C, C-5), 137.1 (1C, C-1), 140.8 (1C, C-2), 143.5 (1C, C-1′), 145.4 (1C, C-4′) and 151.4 (1C, C-2′); MS (Da/e): 412, 426, 440, 454, and 468.

3.3.1.10 4-nitro-2-(4-linear alkyl)phenyl azo aniline (Compound **1b**)

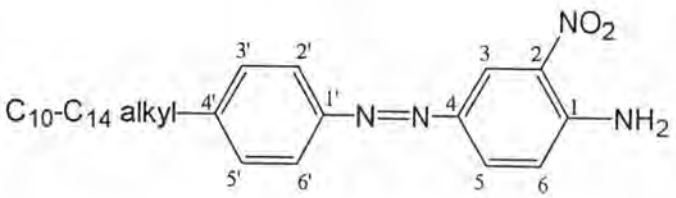


A cool mixture of *p*-linear alkylaniline (2.61g, 0.01 mole) and 3 ml of methanol was added slowly with 3 ml of concentrated hydrochloric acid. Then 2 ml of a cool 5N nitrite solution (0.69 g of sodium nitrite) was dropped into the mixture

with good stirring at 0-5 °C. The solution of *p*-linear alkylaniline diazonium salt was kept cold until the coupling reaction was preceded.

p-Nitroaniline (1.38 g, 0.01 mole) was dissolved in 20 ml of methanol containing sodium acetate (0.62 g, 0.015 mole). This solution was dropped into the well-stirred *p*-linear alkylaniline diazonium solution using a similar procedure to that used for the synthesis of Compound **1a.** The crude product was purified by column chromatography eluted by a mixture of hexane-dichloromethane (3:1). 4-Nitro-2-(4-linear alkyl)phenyl azo aniline (2.42 g, 59%yield) as a deep yellowish brown oil with R_f 0.45 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3458, 3356, 3028, 2925, 1637, 1600, 1531, 1464, 1348 and 1250 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.44 (2H, *s*, *br*), 6.60 (2H, *d*, J = 8.02 Hz), 7.14 (1H, *d*, J = 9.00 Hz), 7.55 (2H, *d*, J = 8.02 Hz), 8.29 (1H, *d*, J = 9.00 Hz) and 8.62 (1H, *s*); ^{13}C-NMR($CDCl_3$) δ (ppm): 116.6 (1C, C-6), 119.0 (1C, C-3), 123.5 (2C, C-2′ and C-6′), 126.9 (1C, C-5), 128.5 (2C, C-3′ and C-5′), 138.4 (1C, C-4), 141.0 (1C, C-2), 142.5 (1C, C-4′), 147.1 (1C, C-1) and 149.5 (1C, C-1′). MS (Da/e): 382, 396, 410, 424, and 438.

3.3.1.11 2-nitro-4-(4-linear alkyl)phenyl azo aniline (Compound **2b**)

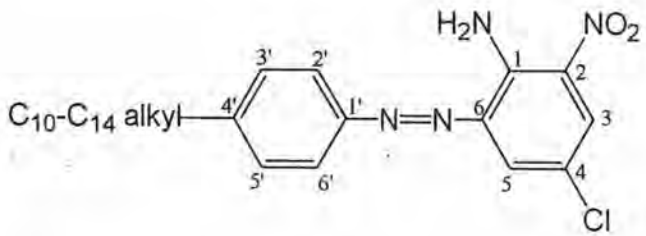


A coupling solution of *o*-nitroaniline (1.38 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar manner to that described for the synthesis of compound **1b**. A deep yellowish brown oil of 2-nitro-4-(4-linear alkyl)phenyl azo aniline (2.79 g, 67%yield) with R_f 0.60 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3499, 3386, 3029, 2920, 1627, 1603, 1574, 1514, 1466, 1344 and 1259 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.74 (1H, *d*, J = 8.44 Hz), 6.86 (2H, *dd*, J = 1.39, 7.59 Hz), 7.61 (2H, *dd*, J = 1.39, 7.59 Hz), 7.79 (1H, *dd*, J = 1.05, 8.50 Hz) and 8.37 (1H, *d*, J = 1.61 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 116.5 (1C, C-6), 119.0 (1C, C-3), 125.7 (2C, C-2′ and C-6′), 128.3 (2C, C-3′ and C-5′), 129.4 (1C, C-

5), 135.5 (1C, C-2), 142.1 (1C, C-4′), 144.8 (1C, C-4), 145.1 (1C, C-1) and 146.5 (1C, C-1′).

3.3.1.12 4-chloro-2-nitro-6-(4-linear alkyl)phenyl azo aniline

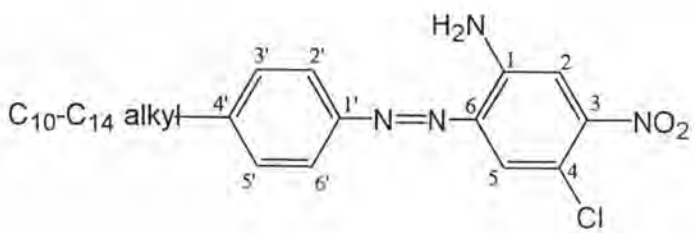
(Compound **3b**)



4-Chloro-2-nitroaniline (1.73 g, 0.01 mole) was used by a similar procedure to that mentioned for the preparation of Compound **1b**. It gave a deep yellowish brown oil of 4-chloro-2-nitro-6-(4-linear alkyl)phenyl azo aniline (3.01 g, 68%yield) with R_f 0.62 (hexane: dichloromethane (1:1)). IR (NaCl) 3492, 3383, 3026, 2922, 1628, 1603, 1520, 1510, 1466, 1338, 1250 and 1093 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.90 (2H, *d*, J = 7.56 Hz), 7.69 (2H, *d*, J = 7.56 Hz), 8.12 (1H, *s*), and 8.39 (1H, *s*); ^{13}C-NMR($CDCl_3$) δ (ppm): 121.0 (2C, C-2′ and C-6′), 125.0 (1C, C-4), 127.0 (1C, C-3), 127.7 (2C, C-3′ and C-5′), 131.3 (1C, C-5), 134.0 (1C, C-1), 135.7 (1C, C-2), 144.5 (1C, C-6), 144.8 (1C, C-4′), and 154.3 (1C, C-1′).

3.3.1.13 4-chloro-3-nitro-6-(4-linear alkyl)phenyl azo aniline

(Compound **4b**)

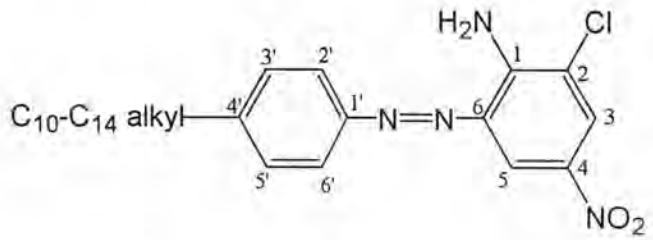


4-Chloro-3-nitroaniline (1.73 g, 0.01 mole) was used by a similar procedure to that mentioned for the preparation of Compound **1b**. A reddish brown oil of

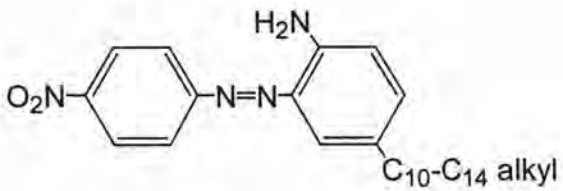
4-chloro-3-nitro-6-(4-linear alkyl)phenyl azo aniline (3.10 g, 70%yield) with R_f 0.71 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3469, 3367, 3026, 2925, 1630, 1601, 1537, 1464, 1350, 1311 and 1130 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.78 (2H, *d*, J = 7.60 Hz), 7.65 (2H, *d*, J = 7.60 Hz), 7.95 (1H, *s*), 8.11 (1H, *s*) and 8.64 (2H, *s, br*); ^{13}C-NMR($CDCl_3$) δ (ppm): 111.1 (1C, C-2), 119.7 (1C, C-4), 122.7 (2C, C-2′ and C-6′), 125.6 (1C, C-5), 128.2 (2C, C-3′ and C-5′), 137.9 (1C, C-1), 144.9 (1C, C-4′), 146.4 (1C, C-6), 148.0 (1C, C-1′) and 151.6 (1C, C-3).

3.3.1.14 2-chloro-4-nitro-6-(4-linear alkyl)phenyl azo aniline

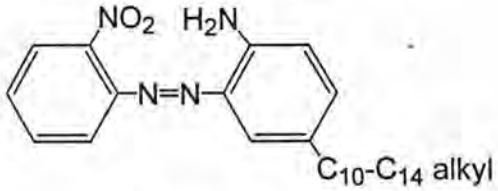
(Compound **5b**)



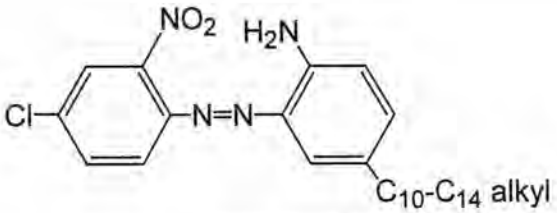
A coupling solution of 2-chloro-4-nitroaniline (1.73 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar manner to that mentioned for the synthesis of compound **1b**. The product (2.44 g, 55%yield) as deep yellowish brown oil with R_f 0.45 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3492, 3388, 3026, 2925, 1618, 1589, 1522, 1466, 1325, 1279 and 1122 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.64 (2H, *d*, 7.16 Hz), 7.13 (1H, *s, br*), 7.68 (2H, *d*, J = 7.16 Hz), 8.45 (1H, *s*), and 8.61 (1H, *s*); ^{13}C-NMR($CDCl_3$) δ (ppm): 117.6 (1C, C-3), 122.5 (1C, C-6), 124.3 (2C, C-2′ and C-6′), 127.0 (1C, C-5), 128.4 (2C, C-3′ and C-5′), 138.0 (1C, C-4), 138.6(1C, C-2), 138.8 (1C, C-4′), 146.4 (1C, C-1), and 149.0 (1C, C-1′). MS (Da/e): 417, 431, 445, 459, and 473.



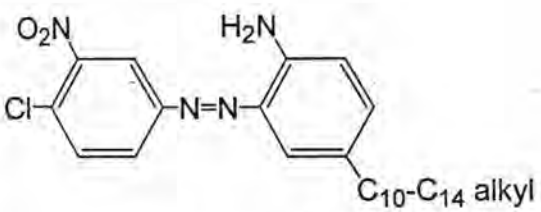
Compound 1a



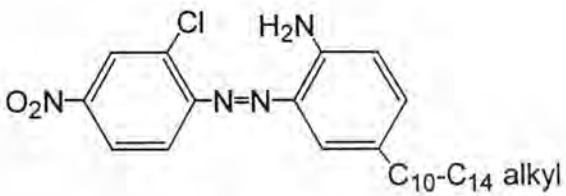
Compound 2a



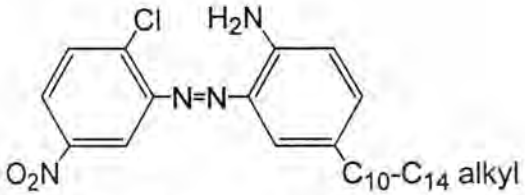
Compound 3a



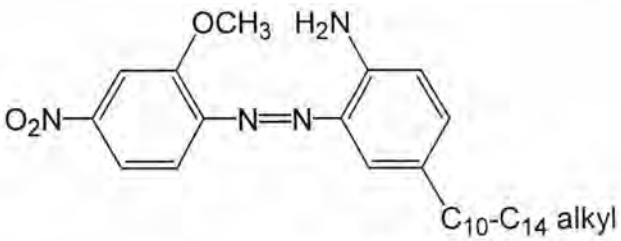
Compound 4a



Compound 5a



Compound 6a

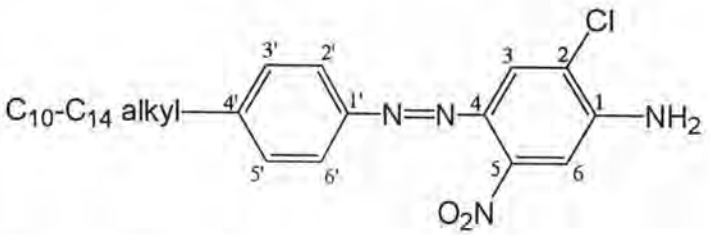


Compound 7a

Figure 4.1 The structures of phenyl azo anilines (group a)

3.3.1.15 2-chloro-5-nitro-4-(4-linear alkyl)phenyl azo aniline

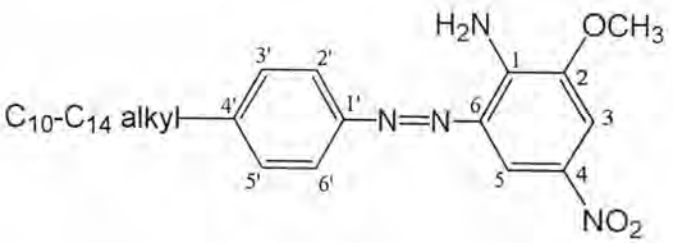
(Compound **6b**)



A coupling solution of 2-chloro-5-nitroaniline (1.73 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar procedure to that utilized for the synthesis of compound **1b**. It gave a deep yellowish brown oil of 2-chloro-5-nitro-4-(4-linear alkyl)phenyl azo aniline (3.24 g, 73%yield) with R_f 0.76 (hexane: dichloromethane (1:1)). IR (NaCl) 3473, 3354, 3026, 2925, 1628, 1603, 1527, 1464, 1346, 1250 and 1113 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.89 (2H, *d*, J = 7.46 Hz), 7.03 (1H, *s, br*), 7.51 (2H, *d*, J = 7.46 Hz), 7.89 (1H, *s*), and 8.10 (1H, *s*); ^{13}C-NMR($CDCl_3$) δ (ppm): 113.5 (1C, C-6), 120.6 (2C, C-2′ and C-6′), 124.3 (1C, C-3), 126.2 (1C, C-2), 128.2 (2C, C-3′ and C-5′), 131.0 (1C, C-4), 142.1 (1C, C-5), 143.5 (1C, C-4′), 149.1 (1C, C-1′), and 150.8 (1C, C-1).

3.3.1.16 2-methoxy-4-nitro-6-(4-linear alkyl)phenyl azo aniline

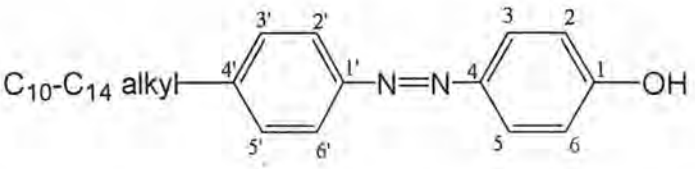
(Compound **7b**)



A coupling solution of 2-methoxy-4-nitroaniline (1.68 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar manner to that utilized for the synthesis of compound **1b**. A deep yellowish brown oil of 2-methoxy-4-nitro-6-(4-linear alkyl)phenyl azo aniline (3.09 g, 70%yield) with R_f 0.52 (hexane:

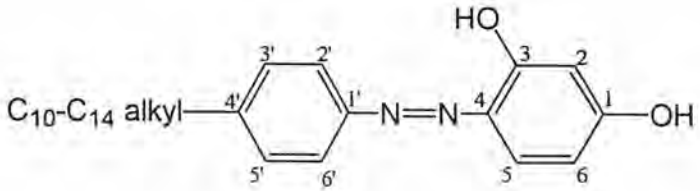
dichloromethane (1:1)) was obtained. IR (NaCl) 3475, 3355, 3020, 2925, 1628, 1585, 1522, 1460, 1342, 1296, 1246 and 1039 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.77 (3H, s), 4.35 (2H, s, *br*), 6.61 (2H, d, J=8.67 Hz), 7.65 (1H, d, J=2.36 Hz), 7.78 (2H, dd, J=8.67 Hz) and 8.31 (1H, d, J=2.36 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 55.8 (1C, OCH_3), 110.6 (1C, C-3), 111.5 (1C, C-5), 122.0 (2C, C-2′ and C-6′), 128.3 (2C, C-3′ and C-5′), 131.7 (1C, C-1), 137.2 (1C, C-4), 140.3 (1C, C-2), 140.8 (1C, C-4′) and 148.9 (2C, C-6 and C-1′); MS (Da/e): 412, 426, 440, 454, and 468.

3.3.1.17 4-(4-linear alkyl) phenyl azo phenol (Compound **1c**)



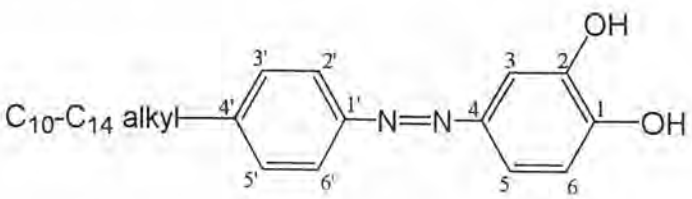
The cool solution of *p*-linear alkylaniline diazonium salt was prepared using a similar procedure in the synthesis of compound **1b**. This solution was added dropwise into phenolate ions solution, where phenol (0.94 g, 0.01 mole) was dissolved in 10 ml of methanol containing potassium hydroxide (0.84 g, 0.015 mole) at a rate that the temperature did not rise above 5°C. The reaction mixture was stirred for an hour, and then the product was extracted from the mixture by treating with dichloromethane. The dichloromethane phase was washed 2-3 times with 20 ml distilled water, and evaporated to dryness. A deep yellowish brown oil of 4-(4-linear alkyl) phenyl azo phenol (2.88 g, 79%yield) with R_f 0.66 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3600-3200, 3026, 2924, 1589, 1466, 1377 and 1248 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.27 (1H, *s*, *br*), 6.92 (1H, *d*, J = 8.06 Hz), 7.10 (2H, *dd*, J = 8.40, 2.16 Hz), 7.66 (1H, *d*, J = 8.06 Hz), and 7.84 (2H, *dd*, J = 8.43, 2.16 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 116.0 (2C, C-2 and C-6), 122.6 (2C, C-2′ and C-6′), 124.9 (2C, C-3 and C-5), 128.1 (2C, C-3′ and C-5′), 146.9 (1C, C-4′), 149.6 (1C, C-4), 151.0 (1C, C-1′), and 158.7 (1C, C-1).

3.3.1.18 3-hydroxy-4-(4-linear alkyl)phenyl azo phenol (Compound 2c)



A coupling solution of resorcinol (1.10 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar manner to that utilized for the synthesis of compound **1c**. A deep reddish brown oil of 3-hydroxy-4-(4-linear alkyl) phenyl azo phenol (2.99 g, 78%yield) with R_f 0.26 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3500-3200, 3041, 2925, 1604, 1510, 1469, 1406 and 1248 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.30 (1H, *s*, *br*), 6.47 (1H, *d*, J = 2.40 Hz), 6.56 (1H, *d*, J = 8.72 Hz), 7.23 (2H, *d*, J = 8.36 Hz), 7.65 (1H, *dd*, J = 2.40, 8.72 Hz), and 7.68 (2H, *d*, J = 8.36 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 103.9 (1C, C-2), 109.6 (1C, C-6), 121.1 (2C, C-2′ and C-6′), 126.0 (1C, C-5), 128.9 (2C, C-3′ and C-5′), 132.8 (1C, C-4), 147.3 (1C, C-4′), 149.7 (1C, C-1′), 158.4 (1C, C-3), and 162.4 (1C, C-1).

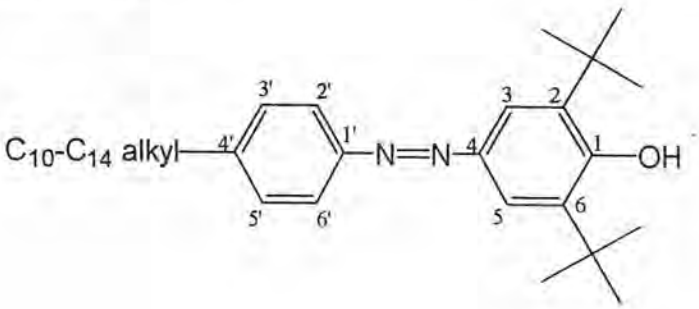
3.3.1.19 2-hydroxy-4-(4-linear alkyl)phenyl azo phenol (Compound 3c)



Catechol (1.10 g, 0.01 mole) was used by a similar procedure to that mentioned for the preparation of Compound **1c**. It gave a deep reddish brown oil of 2-hydroxy-4-(4-linear alkyl)phenyl azo phenol (3.09 g, 81%yield) with R_f 0.44 (hexane: dichloromethane (1:1)). IR (NaCl) 3600-3200, 3028, 2925, 1604, 1512, 1454, 1389 and 1250 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.12 (1H, *s*, *br*), 6.89 (2H, *dd*, J = 1.38, 7.38 Hz), 7.02 (1H, *d*, J = 8.35 Hz), 7.12 (1H, *s*), 7.71 (2H, *dd*, J = 1.38, 7.38 Hz), and 7.83 (1H, *d*, J = 8.35 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 109.8 (1C, C-3), 116.1

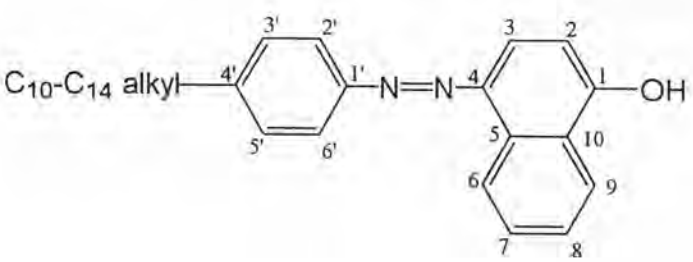
(1C, C-5), 116.9 (1C, C-6), 121.1 (2C, C-2′ and C-6′), 128.8 (2C, C-3′ and C-5′), 139.8 (1C, C-4′), 145.4 (1C, C-2), 147.0 (1C, C-4), 147.3 (1C, C-1) and 150.7 (1C, C-1′).

3.3.1.20 2,6-di-*tert*-butyl-4-(4-linear alkyl)phenyl azo phenol (Compound **4c**)



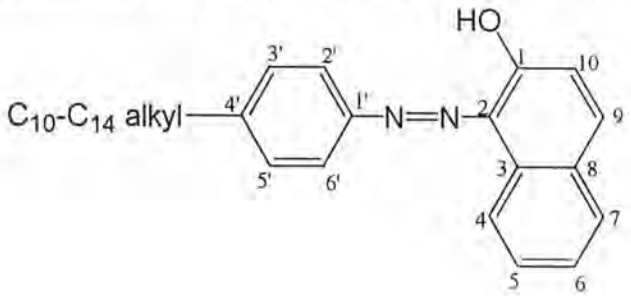
A coupling solution of 2,6-di-*tert*-butylphenol (2.06 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar manner to that described for the synthesis of compound **1c**. A deep reddish brown oil of 2,6-di-tert-butyl-4-(4-linear alkyl)phenyl azo phenol (3.11 g, 65%yield) with R_f 0.70 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3643, 3600-3200, 3026, 2925, 1603, 1483, 1466, 1363 and 1230 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.57 (18H, *s*), 5.31 (1H, *s, br*), 6.94(2H, *d*, J = 7.33 Hz), 7.70 (2H, *d*, J = 7.33 Hz), and 7.82 (2H, *s*); ^{13}C-NMR ($CDCl_3$) δ (ppm): 114.0 (1C, C-4), 119.8 (2C, C-3 and C-5), 124.7 (2C, C-2′ and C-6′), 127.3 (1C, C-3′), 128.3 (1C, C-5′), 135.7 (2C, C-2 and C-6), 139.6 (1C, C-4′), 150.6 (1C, C-1′), and 154.0 (1C, C-1).

3.3.1.21 4-(4-linear alkyl) phenyl azo naphthol (Compound **5c**)



A coupling solution of α-naphthol (1.44 g, 0.01 mole) was treated with *p*-linear alkylaniline diazonium solution using a similar procedure to that described for the synthesis of compound **1c**. A deep reddish brown thick of 4-(4-linear alkyl) phenyl azo naphthol (3.04 g, 73%yield) with R_f 0.66 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3600-3200, 3060, 2924, 1624, 1599, 1549, 1452, 1358 and 1265 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.70 (1H, *s*, *br*), 6.83 (1H, *d*, J = 7.50 Hz), 7.19 (1H, *d*, J = 7.80 Hz), 7.25 (1H, *t*, J = 7.43 Hz), 7.39 (2H, *d*, J = 7.50 Hz), 7.44 (1H, *dd*, J = 1.55, 7.30 Hz), 7.59 (1H, *t*, J = 7.31 Hz), 7.73 (1H, *d*, J = 7.58 Hz), and 8.18 (1H, *d*, J = 7.80 Hz); ^{13}C-NMR($CDCl_3$) δ (ppm): 109.7 (1C, C-2), 121.7 (1C, C-3), 123.1(1C, C-9), 124.2 (2C, C-2′ and C-6′), 125.5 (1C, C-10), 126.3 (2C, C-7 and C-8), 128.0 (1C, C-6), 128.7 (2C, C-3′ and C-5′), 129.6 (1C, C-5), 139.5 (1C, C-4′), 143.2 (1C, C-4), 147.0 (1C, C-1′) and 154.8 (1C, C-1); MS (Da/e): 388, 402, 416, 430, and 440.

3.3.1.22 2-(4-linear alkyl) phenyl azo naphthol (Compound **6c**)



β-Naphthol (1.44 g, 0.01 mole) was used by a similar procedure to that utilized for the preparation of Compound **1c**. It gave a deep reddish brown oil of 2-(4-linear alkyl) phenyl azo naphthol (2.89 g, 69%yield) with R_f 0.38 (hexane: dichloromethane (1:1)) was obtained. IR (NaCl) 3600-3200, 3028, 2925, 1626, 1601, 1510, 1454, 1379, 1271 and 1213 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.81 (1H, *s*, *br*), 6.92 (2H, *d*, J = 7.88 Hz), 7.22 (1H, *d*, J = 8.83 Hz), 7.51 (1H, *t*, J = 7.01 Hz), 7.58 (1H, *d*, J = 8.21 Hz), 7.68 (2H, *d*, J = 7.88 Hz) and 7.71 (3H, *m*); ^{13}C-NMR($CDCl_3$) δ (ppm): 118.5 (1C, C-10), 123.1 (2C, C-2′ and C-6′), 124.3 (1C, C-6), 126.3 (1C, C-5), 126.4 (1C, C-4), 127.8 (3C, C-7, C-3′ and C-5′), 128.0 (2C, C-3 and C-8), 133.6 (1C, C-9), 135.0 (1C, C-2), 143.1 (1C, C-4′), 147.0 (1C, C-1), and 150.5 (1C, C-1′).

3.3.2 Treatment of markers

3.3.2.1 Preparation of 1,000-ppm stock marker solution

Each 1,000-ppm stock marker solution was prepared by dissolving 0.05 g of each marker with toluene, and made up to 50 ml in a volumetric flask.

3.3.2.2 Preparation of marked HSD

Aliquot of 0.5 ml of each 1,000-ppm stock marker solution was pipetted into volumetric flask 50 ml, and made up with unmarked HSD. The marked 10 ppm HSD was obtained.

3.3.3 Detection of markers

Extraction with fuel immiscible reagent was used as a method for the detection of marked HSD in this study. This reagent system not only extracted the markers from HSD, but it caused the marker to react or complex, producing a clearly defined color that could identify the HSD to its source.

All markers were observed for their developed color in the extracted phase by shaking the 10 ppm marked HSD with 2% potassium hydroxide in ethylene glycol using the volume ratio of marked HSD to extractant as 6:1. HSD containing 10 ppm of compound **1a**, which gave an intense red coloration, was chosen to study for suitable extractant system.

3.3.3.1 Suitable extractant system for the detection of markers in HSD

In this study, the extractant systems were divided into 2 major systems, including acid and basic system. Acid systems were hydrochloric acid, formic acid, and acetic acid. Basic systems were potassium hydroxide, diethylamine and ethylenediamine.

3.3.3.1.1 Acid system

The marked HSD (30 ml) was shaken with 10% hydrochloric acid in cosolvent (5 ml) comprising 40% propylene glycol and 60% methanol for 30 seconds, and then allowed to stand. The lower phase, which developed color, was drawn off for measuring the maximum absorption in the visible region from 350 to

750 using UV/VIS spectrophotometer. This procedure was repeated except that 10% formic and 10% acetic acid in the same cosolvent were individually used.

3.3.3.1.2 Basic system

HSD containing 10 ppm of compound **1a** (30 ml) was shaken with 1% potassium hydroxide in cosolvent (5 ml) comprising 40% propylene glycol and 60% methanol for 30 seconds. The extracted phase was measured maximum absorption using an UV/VIS spectrophotometer. This manner was repeated except that 2%, 3%, 4% and 5% potassium hydroxide dissolving in 40% propylene glycol and 60% methanol were individually used.

Both diethylamine and ethylenediamine systems were studied using a similar manner in 3.3.3.1.1 except that 10%, 20%, 30%, 40% and 50% of amine in cosolvent comprising 40% propylene glycol and 60% methanol was invidually used instead of potassium hydroxide.

3.3.3.2 Optimum shaking time

Aliquot of 10 ppm of compound **1a** in HSD (30 ml) was shaken with suitable extractant (5 ml) from 3.3.3.1 comprising 50% ethylenediamine, 20% propylene glycol and 30% methanol for 10 seconds. It was then left until two phases were separated, the lower phase was drawn off and recorded the UV/VIS absorption at its λ_{max}. This procedure was repeated except that 20, 30, 40 and 50 seconds were individually used.

3.3.3.3 Efficiency of extractant system

Efficiency of extractant system was studied by comparing the amount of marker, which was extracted into the extracted phase to the amount of markers originally added to HSD. The calibration curve of compound **1a** dissolving in extractant was produced to determine the amount of marker in the extracted phase.

3.3.3.3.1 Calibration curve of compound 1a dissolving in extractant

Compound **1a** dissolving in the extractant that comprised 50% ethylenediamine, 20% propylene glycol and 30% methanol at 30 ppm was measured for its λ_{max} using UV-VIS spectrophotometer. The concentration of marker in extractant was prepared at 10, 20, 30 and 40 ppm, and then each developed color was measured for absorbance at its λ_{max}. The calibration curve was a plot between absorbance and the concentration of marker in extractant.

3.3.3.3.2 Extracted percentage of extractant

Aliquot of 4 ppm of compound **1a** in HSD (30 ml) was extracted by an extractant comprising 50% ethylenediamine, 20% propylene glycol and 30% methanol for 30 seconds (the volume ratio = 6:1). The UV-VIS absorption of the extracted phase was compared to the above standard calibration to determine the concentration of compound **1a** in the extracted phase. The observed concentration was calculated into the weight of the marker in the extracted phase and then compared to the weight of the marker originally added into the HSD. The extracted percentage of extractant was obtained.

3.3.3.4 Quantitative determination of markers in marked commercial HSD

3.3.3.4.1 Quantitative determination of markers at 6:1 volume ratio of marked HSD to extractant

The extracted phase of all marked HSD at 15 ppm were measured for their λ_{max} using UV-VIS spectrophotometer except for some marked HSD, which gave over absorbance, including 4 ppm of compound 1a and compound 5a, 2 ppm of compound 1b, 0.5 ppm of compound 5b, and 5 ppm of compound 1c, compound 2c, compound 4c and compound 5c. The obtained absorbance of each marker was used to estimate the range of the concentration in its calibration curve.

3.3.3.4.1.1 Calibration curve of 4-linear alkyl-2-(4-nitro)phenyl azo aniline (compound **1a**)

The standard calibration curve of compound **1a** was prepared at 4, 5, 6 and 7 ppm of the marker in HSD by pipetting 0.20, 0.25, 0.30 and 0.35 ml of the stock marker solution 1,000 ppm into 50 ml volumetric flask, respectively, and made up with unmarked HSD.

Then 30 ml of each concentration of marked HSD was shaken with 5 ml of extractant for 30 seconds. When two phases were observed, the lower phase was drawn off for the UV/VIS absorption measurement at its λ_{max}. The calibration curve was plotted between absorbance and the concentration of marker in HSD.

3.3.3.4.1.2 Calibration curve of 4-linear alkyl-2-(2-nitro)phenyl azo aniline (compound **2a)**

The procedure in section 3.3.3.4.1.1 was repeated except that 4, 6, 8 and 10 ppm of 4-linear alkyl-2-(2-nitro)phenyl azo aniline in HSD were used.

3.3.3.4.1.3 Calibration curve of 4-linear alkyl-2-(4-chloro-2-nitro)phenyl azo aniline (compound **3a)**

The procedure in section 3.3.3.4.1.1 was repeated except that 10, 15, 20 and 25 ppm of 4-linear alkyl-2-(4-chloro-2-nitro)phenyl azo aniline in HSD were used.

3.3.3.4.1.4 Calibration curve of 4-linear alkyl-2-(2-chloro-4-nitro)phenyl azo aniline (compound **5a)**

The procedure in section 3.3.3.4.1.1 was repeated except that 0.5, 1, 2, and 3 ppm of 4-linear alkyl-2-(2-chloro-4-nitro)phenyl azo aniline in HSD were used.

3.3.3.4.1.5 Calibration curve of 4-linear alkyl-2-(2-chloro-5-nitro)phenyl azo aniline (compound **6a**)

The procedure in section 3.3.3.4.1.1 was repeated except that 10, 14, 16 and 18 ppm of 4-linear alkyl-2-(2-chloro-5-nitro)phenyl azo aniline in HSD were used.

3.3.3.4.1.6 Calibration curve of 4-linear alkyl-2-(2-methoxy-4-nitro)phenyl azo aniline (compound **7a**)

The procedure in section 3.3.3.4.1.1 was repeated except that 5, 9, 13 and 15 ppm of 4-linear alkyl-2-(2-methoxy-4-nitro)phenyl azo aniline in HSD were used.

3.3.3.4.1.7 Calibration curve of 4-nitro-2-(4-linear alkyl)phenyl azo aniline (compound **1b)**

The procedure in section 3.3.3.4.1.1 was repeated except that 1, 2, 3 and 4 ppm of 4-nitro-2-(4-linear alkyl)phenyl azo aniline in HSD were used.

3.3.3.4.1.8 Calibration curve of 2-nitro-4-(4-linear alkyl)phenyl azo aniline (compound **2b)**

The procedure in section 3.3.3.4.1.1 was repeated except that 4, 6, 8 and 10 ppm of 2-nitro-4-(4-linear alkyl)phenyl azo aniline in HSD were used.

3.3.3.4.1.9 Calibration curve of 4-chloro-2-nitro-6-(4-linear alkyl)phenyl azo aniline (compound **3b)**

The procedure in section 3.3.3.4.1.1 was repeated except that 5, 10, 15 and 20 ppm of 4-chloro-2-nitro-6-(4-linear alkyl)phenyl azo aniline in HSD were used.

3.3.3.4.1.10 Calibration curve of 2-chloro-4-nitro-6-(4-linear alkyl)phenyl azo aniline (compound **5b**)

The procedure in section 3.3.3.4.1.1 was repeated except that 0.3, 0.5, 0.7 and 0.9 ppm of 2-chloro-4-nitro-6-(4-linear alkyl)phenyl azo aniline in HSD were used.

3.3.3.4.1.11 Calibration curve of 2-chloro-5-nitro-4-(4-linear alkyl)phenyl azo aniline (compound **6b**)

The procedure in section 3.3.3.4.1.1 was repeated except that 6, 8, 10 and 12 ppm of 2-chloro-5-nitro-4-(4-linear alkyl)phenyl azo aniline in HSD were used.

3.3.3.4.1.12 Calibration curve of 2-methoxy-4-nitro-6-(4-linear alkyl)phenyl azo aniline (compound **7b**)

The procedure in section 3.3.3.4.1.1 was repeated except that 10, 15, 20 and 25 ppm of 2-methoxy-4-nitro-6-(4-linear alkyl)phenyl azo aniline in HSD were used.

3.3.3.4.1.13 Calibration curve of 4-(4-linear alkyl) phenyl azo phenol (compound **1c**)

The procedure in section 3.3.3.4.1.1 was repeated except that 1, 2, 3 and 4 ppm of 4-(4-linear alkyl)phenyl azo phenol in HSD were used.

3.3.3.4.1.14 Calibration curve of 3-hydroxy-4-(4-linear alkyl) phenyl azo phenol (compound **2c**)

The procedure in section 3.3.3.4.1.1 was repeated except that 1, 2, 3 and 4 ppm of 3-hydroxy-4-(4-linear alkyl)phenyl azo phenol in HSD were used.

3.3.3.4.1.15 Calibration curve of 2,6-di-tert-butyl-4-(4-linear alkyl)phenyl azo phenol (compound **4c**)

The procedure in section 3.3.3.4.1.1 was repeated except that 10, 15, 20 and 25 ppm of 2,6-di-tert-butyl-4-(4-linear alkyl)phenyl azo phenol in HSD were used.

3.3.3.4.1.16 Calibration curve of 4-(4-linear alkyl) phenyl azo naphthol (compound **5c**)

The procedure in section 3.3.3.4.1.1 was repeated except that 2, 3, 4 and 5 ppm of 4-(4-linear alkyl)phenyl azo naphthol in HSD were used.

3.3.3.4.2 Quantitative determination of markers at the suitable ratio of marked HSD to extractant

Some marked HSD, which gave the distinguish color at the concentrations that were not 5 ppm, were prepared at 5 ppm, except for compound **5b**, which was prepared at 3 ppm in HSD. Each marked HSD was shaken with an extractant in volume ratio, which was prepared according to Table 3.1. Then the extracted phase was measured its λ_{max} by UV/VIS spectrophotometer to obtain a suitable ratio of marked HSD to extractant.

Table 3.1 Volume of marked HSD and extractant in each volume ratio

Markers	Concentration (ppm)	Ratio I			Ratio II		
		Ratio	Volume (ml)		Ratio	Volume (ml)	
			Marked HSD	Extractant		Marked HSD	Extractant
5a	5	1:1	5	5	2:1	10	5
7a	5	15:1	75	5	16:1	80	5
1b	5	3:1	15	5	4:1	20	5
5b	3	0.8:1	4	5	1:1	5	5
7b	5	16:1	80	5	18:1	90	5

3.3.3.4.2.1 Calibration curve of 4-linear alkyl-2-(2-chloro-4-nitro)phenyl azo aniline (compound **5a**) **at ratio 2:1**

Compound **5a** was prepared at concentrations of 3-6 ppm in HSD for the calibration curve, then 10 ml of each concentration of marked HSD was extracted by shaking with 5 ml of extractant. The extracted phase was drawn off and the UV/VIS absorbance was measured at its λ_{max}. The calibration curve was a plot between absorbance and the concentration of marker in HSD.

3.3.3.4.2.2 Calibration curve of 4-linear alkyl-2-(2-methoxy-4-nitro)phenyl azo aniline (compound **7a**) **at ratio 15:1**

The procedure in section 3.3.3.4.2.1 was repeated except that 75 ml of 3, 5, 7 and 9 ppm of compound **7a** in HSD were used instead of compound **5a** 3-6 ppm.

3.3.3.4.2.3 Calibration curve of 4-nitro-2-(4-linear alkyl)phenyl azo aniline (compound **1b**) **at ratio 3:1**

The procedure in section 3.3.3.4.2.1 was repeated except that 15 ml compound **1b** in HSD was used instead of compound **5a**.

3.3.3.4.2.4 Calibration curve of 2-chloro-4-nitro-6-(4-linear alkyl)phenyl azo aniline at ratio 1:1

The procedure in section 3.3.3.4.2.1 was repeated except that 5 ml of 2-5 ppm of compound **5b** in HSD was used instead of compound **5a** 3-6 ppm.

3.3.3.4.2.5 Calibration curve of 2-methoxy-4-nitro-6-(4-linear alkyl)phenyl azo aniline at ratio 1:1

The procedure in section 3.3.3.4.2.1 was repeated except that 90 ml of compound **7a** in HSD was used instead of compound **5a**.

3.3.4 Effects of marker on the physical properties of marked HSD

HSD containing 3 ppm of 2-chloro-4-nitro-6-(4-linear alkyl)phenyl azo was prepared by pipetting 3 ml of 1,000 ppm stock marker solution into a 1,000 volumetric flask, and made up with unmarked HSD. Physical properties of marked and unmarked HSD were studied according to the ASTM methods as described in Table 3.2

Table 3.2 The ASTM testing methods of marked and unmarked HSD

Test items	Test methods ASTM
API gravity@60°F	D1298
Specific gravity@15.6/15.6°C	D1298
Calculated cetane index	D976
Kinematic viscosity@40°C, cSt	D445
Pour point, °C	D97
Flash point, °C	D93
Sulfur content, %wt	D5453
Copper strip corrosion (3 hrs, 50 °C)	D130
Distillation	D86
Total acid number, mgKOH/g	D664
Color	D1500

3.3.5 Stability of markers in HSD

The marked HSD at 5 ppm concentration of compound **1a**, compound **5a**, compound **7a**, compound **1b**, compound **5b**, compound **7b** and compound **5c** were prepared and stored for three months. The quantity of each marker contained in HSD was determined monthly by extracting with a reagent comprising 50 % ethylenediamine, 20% propylene glycol and 30% methanol at a suitable ratio (from section 3.3.3.4.2). Then the extracted phase was measured by UV-VIS spectrophotometer. The measured absorbances were compared with the calibration curves in sections 3.3.3.4.1.1, 3.3.3.4.2.1, 3.3.3.4.2.2, 3.3.3.4.2.3, 3.3.3.4.2.5 and 3.3.3.4.2.4, respectively.