CHAPTER IV

RESULTS AND DISCUSSION

In this research, red azo dyes were synthesized for using as dye in gasoline 91. A series of azo dyes was prepared by a coupling reaction of cardanol with a diazonium salt of aromatic amines. Varying the aromatic central unit of the azo dyes enabled the investigation of effects of central units on dye formation, solubility and photophysical behavior of the azo compounds. Moreover, a β-naphthol group was introduced into the dye molecular structure as a terminal unit as it has been previously reported that this chromophore resulted in the increase in absorption wavelength of the molecule, leading to red azo dyes.

4.1 Synthesis of azo dyes

Most of resulting dyes in this synthesis exhibited moderate solubility in common organic solvents. In all cases, the presence of cardanol in molecular structure of azo dyes enables the enhanced solubility in organic solvent and petroleum product due to the presence of a long hydrocarbon chain. Effects of central units on dye formation and solubility were discussed herein.

4.1.1 Azo dye 6 from cardanol and benzidine diamine

The synthesis of compound **6** was successfully performed by coupling reaction of the diazonium salt of benzidine with an alkaline solution of cardanol. Compound **6** was obtained yellow gummy solid in a low yield (1%). Due to the presence of the hydroxyl groups in the molecule of **6** that might interact with Si-OH group of silica gel in column chromatography, 1% TEA was mixed into the eluent system. However, this strategy was failed to improve the yield of **6**. In regard to the solubility, compound **6** can be moderately dissolved in common organic solvents, such as toluene and CH_2Cl_2 (~11.9 mg/mL).

4.1.2   Azo dye 7 from cardanol and 1,5-diamino-naphthalene

Compound 7 was synthesized by coupling reaction of the diazonium salt of 1,5-diamino-naphthalene and cardanol. The resulting dye was purified by column chromatography using 1% TEA in CH_2Cl_2 as the solvent system, leading to yellow gummy solid of compound 7 in 5% yield. Azo dye 7 cannot be completely removed from silica gel because of the high polarity of the two groups of –OH in the structure of compound 7 although the 1% TEA was used. Regards the solubility, compound 7 exhibited moderate solubility in toluene and CH_2Cl_2 (~2.63 mg/mL) but less soluble than other synthetic azo dyes in this research, which is attributed to the introduction of a more rigid fused aromatic ring in the center of the molecule.

4.1.3   Azo dye 8 from cardanol and *o*-phenylenediamine

According to TLC analysis, ^{1}H-NMR and mass spectrum, an attempt to prepare disazo dye compound 8 by coupling reaction of the diazonium salt of *o*-phenylenediamine and cardanol was failed. It is attributed to steric restriction between two -NH$_2$ groups that are in ortho positions to each other on the benzene moiety.

4.1.4   Azo dye 9 from cardanol and *m*-phenylenediamine

Azo dye 9 was successfully obtained by coupling reaction of the diazonium salt of *m*-phenylenediamine and cardanol. Reaction crude was found difficult to purify. The purification problem was the remaining cardanol starting material and that other by-products cannot be completely removed from the desirable dye by column chromatography. ^{1}H-NMR Spectrum showed the peaks of spectrum at 6.81, 7.61, 7.74, 7.94, 8.34 ppm that indicated that compound 9 was successfully synthesized but cannot be elucidated from the peaks of cardanol starting material (**Figure A-9**). Mass spectrum of the resulting product (**Figure A-10**) showed the molecular peak of compound 9 at m/z 733.160, indicating the occurrance of this disazo dye. The crude of compound 9 was moderately dissolved in toluene and CH_2Cl_2 (~2.91 mg/mL).

4.1.5 Azo dye 10 from cardanol and *p*-phenylenediamine

Synthesis of compound **10** was successfully performed by coupling reaction of the diazonium salt of *p*-phenylenediamine and cardanol, following a published method [40]. An attempt to completely isolate the resulting dye by column chromatography from cardanol and other side products was failed. ^{1}H-NMR Spectral analysis indicated the characterist peaks of compound **10** at 6.67, 6.74, 7.59, 7.73 ppm which cannot be elucidated from the peaks of cardanol and other side products (**Figure A-11**). The molecular peak at m/z 733.064 in mass spectrum of the crude disazo dye **10** as shown in **Figure A-12** confirmed the formation of compound **10** and the presence of the unremovable products. This resulting crude dye can be moderately dissolved in organic solvents, such as toluene and CH_2Cl_2 (~49.0 mg/mL).

4.1.6 Azo dye 11 from cardanol and 2-nitro-1,4-phenylenediamine

Synthesis of compound **11** was conducted by coupling reaction of the diazonium salt of 2-nitro-1,4-phenylenediamine and cardanol, following a published method [40]. Compound **11** cannot be completely separated from the starting material and other side products by column chromatography. The difficulties encounter in purification was the same as found in the purification of compound **9** and **10**. ^{1}H-NMR signals at 6.71, 6.78, 6.88, 7.66, 7.96, 8.70 ppm indicated that compound **11** was obtained (**Figure A-13**). Accordingly, the mass spectra of compound **11** was found at m/z 781.572 together with that of other by-products as shown in **Figure A-14**. The crude of compound **11** was more soluble in common organic solvents, such as toluene and CH_2Cl_2 (~56.7 mg/mL), than compound **10** due to the steric hindrance generated by a NO_2 group at the central benzene unit.

4.1.7 Azo dye 12 from cardanol and 4-amino-*N,N*-dimethyl-aniline

Compound **12** was successfully synthesized by coupling reaction of the diazonium salt of 4-amino-*N,N*-dimethyl-aniline and cardanol. The desirable dye was completely purified by column chromatography using 1% TEA in CH_2Cl_2, affording compound **12** as yellow oil in 8% yield. Compound **12** can be moderately dissolved in organic solvents, such as toluene and CH_2Cl_2 (~42.0 mg/mL).

4.1.8 Azo dye 13 from cardanol and 1-naphthylamine

This monoazo dye was synthesized to use as a model for the synthesis of disazo dye in compound **7**. Synthesis of azo dye **13** was carried out by coupling reaction of the diazonium salt of 1-naphthylamine and cardanol. Due to the similar polarity of compound **13** and cardanol starting material, the target compound could not be completely separated. From the integration in ^{1}H-NMR spectrum, the ratio of compound **13** and cardanol starting material was found to be 1:2.2. The calculated yield of this compound in the mixture form is 62%. With respect to the solubility, compound **13** was moderately dissolved in toluene and CH_2Cl_2 (~48.3 mg/mL).

4.1.9 Azo dye 14 from cardanol and 4-nitro-1-naphthylamine

Compound **14** was synthesized by coupling reaction of the diazonium salt of 4-nitro-1-naphthylamine and cardanol. Purification by column chromatography using 1% TEA in CH_2Cl_2 gave a mixture of compound **14** and cardanol starting material in the ratio of 1:0.9 as yellow gummy solid due to the similar polarity of them. The calculated yield of this compound in the mixture form is 64%. The solubility of dye **14** in common organic solvents, such as toluene and CH_2Cl_2, was found to be moderate (~28.0 mg/mL).

4.1.10 Azo dye 17 from hydrogenated cardanol, *p*-phenylenediamine and β-naphthol

Compound **17** was successfully synthesized by coupling reaction of the diazonium salt of *p*-phenylenediamine and the alkaline solution of β-naphthol, followed by coupling reaction of monoazo intermediate **16** and hydrogenated cardanol, leading to compound **17** as a red solid. Hydrogenated cardanol was used to eliminate the possible side reactions of olefinic double bonds in coupling reaction. The resulting dye was purified by column chromatography using 1% TEA in CH_2Cl_2 to move starting material that remained in the crude product and then used 1% TEA in ethyl acetate/CH_2Cl_2 (1:4) to elute compound **17**. It was found that the ultimate yield was 9%. This azo dye exhibited moderate solubility in common organic solvents, such as toluene and CH_2Cl_2 (~2.80 mg/mL).
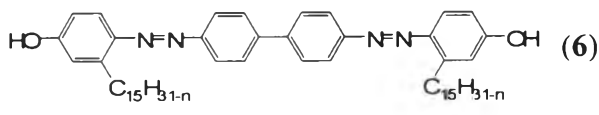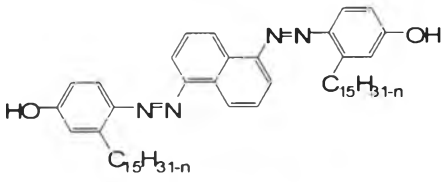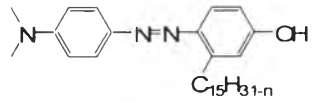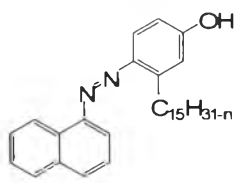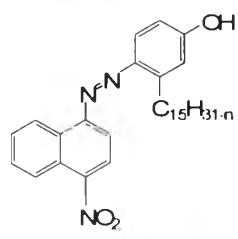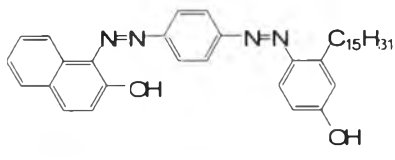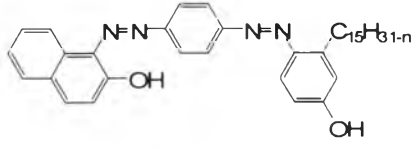
4.1.11 Azo dye 18 from cardanol, *p*-phenylenediamine and β-naphthol

Synthesis of compound **18** was achieved in the same manner as described in the synthesis of compound **17**, except that non-hydrogenated cardanol was used instead. Purification by column chromatography afforded compound **18** as a red solid in 26% overall yield. The higher yield in this synthesis compared to that observed in the preparation of **17** is attributed to the higher solubility of the starting non-hydrogenated cardanol in the reaction medium compared to that of hydrogenated cardanol. Azo dye **18** exhibited satisfactory solubility in a variety of common organic solvents, such as toluene, CH_2Cl_2 and $CHCl_3$, and in the gasoline fuel (~15.2 mg/mL).

4.2 Photophysical properties of azo dyes

Due to the synthesis of compound **8** was failed and purification of compound **9**, **10** and **11** could not be separated into pure form, thus, the photophysical properties of compound **6**, **7**, **12**, **13**, **14**, **17** and **18** were investigated and summarized in Table 4-1.

Table 4-1 Observed absorption maxima and molar absorptivities of selected azo compounds.

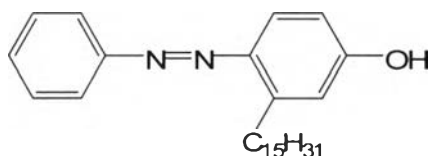| Compound	λ_{max} (nm)[a]	ε_{max} ($M^{-1}cm^{-1}$)	
		CH_2Cl_2	Toluene
(6)	387	10950	10193
(7)	402	8086	9275
(12)	407	18894	19227
(13)	379	N/A[b]	N/A[b]
(14)	407	N/A[b]	N/A[b]
(17)	513	31948	31780
(18)	516	31345	31406

[a] Obtained from CH_2Cl_2 solution.

[b] Due to the purification of compound **13** and **14**, affording a mixture form of desirable compound and cardanol, molar absorptivity was not determined.

According the results in Table 4-1, an absorption maximum of compound **6** (CH_2Cl_2) was observed at 387 nm (**Figure B-1**), exhibiting yellow color. Compared to a central benzene in **7**, a more flexible benzidine unit in **6** led to less conjugation in central aromatic ring system. Thus, a small shift in λ_{max} to shorter wavelength in compound **6** compared to compound **7** was observed. However, molar absorptivities of **6** in CH_2Cl_2 and toluene were higher than those of **7**.

When compared with compound **13** that also bears the naphthalene ring, absorption of **7** is slightly red shifted due to the effect of two azo groups that extend to longer wavelength of absorption and increase intensity of the resulting dye. The color of compound **7** is yellow and the molar absorptivities in CH_2Cl_2 and toluene were 8086 and 9275 respectively, while those of compound **13** was not obtained due to the purification of compound **13**, leading to a mixture form of **13** and cardanol that cannot be completely separated.

Compound **12** exhibited the maximum absorption at 407 nm and strong yellow color, compared with **6** and **7**, with the molar absorptivities of 18894 and 19227 in CH_2Cl_2 and toluene, respectively, attributed to the presence of N,N-dimethylamino group, which acted as an auxochrome to intensify the color of azo dye. However, when compared with previously reported data of compound **19** (**Figure 4-1**) whose structure has no N,N-dimethylamino group, the effect of this group seem to be insignificant in this monoazo structure as compound **19** showed the comparable molar absorptivity (19740) [42]. Regards the maximum absorption, compound **12** exhibited the higher absorption at longer wavelength than compound **19**, whose maximum absorption was observed at 356 nm [42]. This observation is resulted from the electron-releasing effect of N,N-dimethylamino group, leading to bathochromic shift in compound **12**.

Figure 4-1 Structure of compound **19**.

It has been known that as the number of aromatic rings increases, the absorption moves to longer wavelengths [8]. This conclusion is consistent with the comparison between compound **13** bearing a naphthyl ring and compound **19** bearing a phenyl group as its constituent structure. The substitution of a phenyl group with a naphthyl group in monoazo structure shifted the maximum absorption from 356 nm (compound **19**) to 379 nm (compound **13**).

The effect of a NO_2 group was demonstrated by the comparison between the spectral data of compound **13** and those of compound **14**. The maximum absorption of dye **14** (407 nm) was found to be 28 nm red shifted compared with that of compound **13** (379 nm), indicating that the introduction of the strong electron withdrawing NO_2 group causes slight bathochromic shift in the absorption due to enhanced delocalization of electrons [16].

It can be seen in **Figure 2-2** in chapter 2 that molecular structures of commercial red azo dyes **1** and **2** have β-naphthol ring as an important part of the molecules. Thus, we sought to synthesize compound **17** from p-phenylenediamine, β-naphthol and hydrogenated cardanol to have the similar structural construction as these commercial dyes. It was expected that introduction of cardanol in the synthesis will enhance the solubility of the dye, while maintain absorption of the compound in red region with high absorptivity. The maximum absorption of the pure dye **17** was observed at 513 nm in CH_2Cl_2 as shown in **Figure B-6**, which is almost equal to that of compound **1** (512 nm) [41]. Similarly, the molar absorptivities of compound **17** (31948 and 31780 in CH_2Cl_2 and toluene, respectively) comparable to that of compound **1** (30000) [41]. Therefore, it can conclude that the introduction of cardanol in azo dye **17** structure maintain the absorption and high absorptivity of the dye.

Due to the use of natural cardanol, easier than using hydrogenated cardanol, compound **18** was synthesized. UV-Vis Spectrum of compound **18** (**Figure B-7**) exhibited the similar maximum absorption (516 nm), and molar absorptivities (31345 and 31406 in CH_2Cl_2 and toluene, respectively) to those of compound **17**. Due to the better preparative yield and comparably satisfactory physical and spectral properties compared to compound **17**, compound **18** was chosen to test the physical properties in gasoline 91 in further parts.

4.2 Physical properties of azo dyes in gasoline 91

4.3.1 Quantitative determination of azo dye 18 in gasoline 91

A standard calibration curve of azo dye **18** in gasoline 91 was prepared by plotting absorbance at 509 nm of a series of the solutions of **18** in base gasoline 91 with the concentration ranging from 0 to 10 ppm **(Figure B-10)**.

The standard calibration equation of azo dye **18** in gasoline 91 was found to be $Y = 0.0607X$ with the correlation coefficient equal to 0.9999. This equation is used to evaluate the stability of the azo dye **18** in gasoline fuel.

4.3.2 Colorimetric analysis of azo dye 18 in gasoline 91

In this study, colorimetric analysis was performed to find the appropriate concentration of azo dye **18** in base gasoline 91 that gives the most similar color as the commercial gasoline 91. In Table 4-2, L, a and b values of solutions of azo dye **18** in base gasoline 91 at $4-8$ ppm were compared with those of commercial gasoline 91. It revealed that the 6 ppm of azo dye **18** in base gasoline provided the most similar values of L, a and b to commercial gasoline 91 as shown in **Figure 4-2**. Therefore, a solution of azo dye **18** in base gasoline 91 at this concentration was chosen for commercial use and was taken to further study.

Table 4-2 Colorimetric data of azo dye **18** in base gasoline 91 compared with commercial gasoline 91.

Concentration (ppm)	L	a	b
4	90.61	17.00	12.84
5	88.86	20.29	15.53
6	86.70	24.04	18.21
7	84.70	27.79	21.90
8	82.75	31.39	24.47
Commercial gasoline 91	86.45	23.42	14.90

where L = lightness represents 0 (black) to 100 (white)

a = chroma coordinate represents +a (redness) to −a (greenness)

b = chroma coordinate represents +b (yellowness) to −b (blueness)

Figure 4-2 Comparison between a shade of color of a 6-ppm azo dye **18** solution in base gasoline 91 (left) and that of commercial gasoline 91 (right).

4.3.3 Colorimetric analysis of crude of azo dye 18 in gasoline 91

Due to the similarity of the absorption and ^{1}H-NMR spectra of crude azo dye and pure azo dye **18**, direct use of the crude dye in gasoline 91 was proposed to overcome the complication of the synthesis of **18** and to facilitate the scalable preparation. The crude mixture of dye **18** was obtained from the same synthetic procedure as that of pure **18**, except that the chromatographic purification was omitted. The resulting crude was taken to the colorimetric analysis to find the appropriate concentration of crude of azo dye **18** in base gasoline 91 that gives the most similar color as the commercial gasoline 91. The results are summarized in Table 4-3.

Table 4-3 Colorimetric data of crude of azo dye **18** in base gasoline 91 compared with commercial gasoline 91.
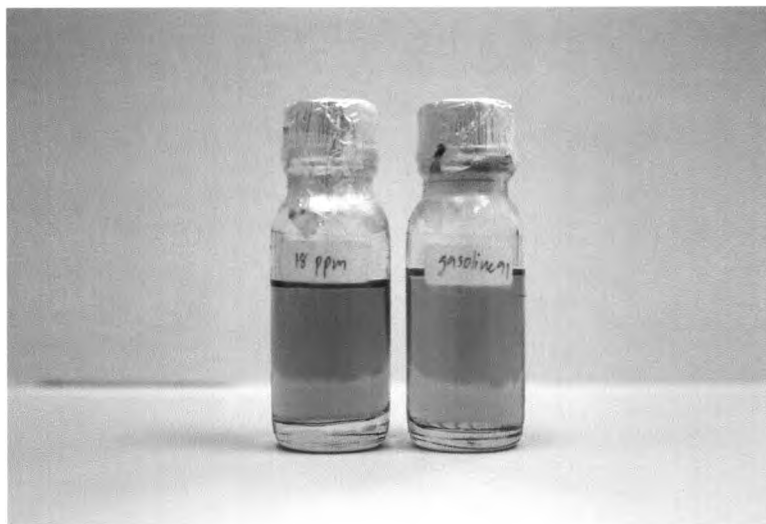
Concentration (ppm)	L	a	b
10	91.65	8.94	8.44
11	91.61	8.92	9.06
12	90.71	10.64	9.18
13	88.44	13.84	10.33
14	88.24	14.62	10.40
15	86.15	17.23	11.83
16	86.11	17.88	11.68
17	85.57	19.06	12.17
18	83.47	22.37	13.20
19	82.45	23.64	13.59
20	81.21	25.36	13.94
Commercial gasoline 91	86.42	23.44	14.93

where L = lightness represents 0 (black) to 100 (white)

a = chroma coordinate represents +a (redness) to −a (greenness)

b = chroma coordinate represents +b (yellowness) to −b (blueness)

In Table 4-3, L, a and b values of solutions of crude of azo dye **18** in base gasoline 91 at the concentration of 10–20 ppm were compared with commercial gasoline 91. It indicated that at the concentration of 18 ppm, a solution of azo dye crude **18** in base gasoline provided the most similar values of L, a and b to commercial gasoline 91 as shown in **Figure 4-3**. Therefore, this concentration is suggested for large scale production of gasoline.

Figure 4-3 Comparison between a shade of color of a 18-ppm crude azo dye
18 solution in base gasoline 91 (left) and that of commercial
gasoline 91 (right).

4.3.4 Effect of azo dye 18 on physical properties of gasoline 91

This part focuses on the investigation of the physical properties of dyed
gasoline to ensure that the addition of azo dye **18** or crude of azo dye **18** will not
significantly affect the physical properties of the base gasoline 91. Samples of base
gasoline 91 containing 6 ppm of azo dye **18** and that containing 18 ppm of crude of
azo dye **18** were tested for physical properties using the ASTM methods. The
physical properties of both dyed gasoline samples were compared with those of
undyed gasoline 91. The results are summarized in Table 4-4.

Table 4-4 Physical properties of dyed gasoline samples and undyed gasoline 91.

Test items	ASTM	Limit	Result		
			Undyed	Dyed	
				with **18**	with crude **18**
Vapor pressure @ 37.8 °C, kPa	D 5191	54.5 max	53.4	53.6	53.1
Distillation					
-IBP, °C		Report	34.4	35.8	35.9
-10%, °C		70 max	53.0	54.0	54.6
-50%, °C	D 86-01	90 - 110	95.6	96.6	96.8
-90%, °C		170 max	123.9	123.9	124.0
-FBP, °C		200 max	156.6	156.7	156.6
-Residue, % vol.		2.0 max	1.4	1.3	1.3
Solvent Washed Gum, mg/100 ml	D 381	4 max	0.8	1.2	1.2
Silver strip corrosion	D 130	No.1 max	No.1	No.1	No.1
Sulfur, %wt.	D 5453	0.05 max	0.0016	0.0016	0.0015
Water, %wt.	D 6304	0.7 max	0.117	0.112	0.092
Benzene, %vol.	D 5580	3.8 max	0.49	0.50	0.49
Aromatics, %vol.	D 5580	38 max	31.1	32.2	31.3
Research Octane Number; RON	D 2699	87.0 min	91.0	91.0	91.0

The results from Table 4-4 indicated that the physical properties of both dyed gasoline samples were not significantly different from those of undyed gasoline. Thus, the presence of azo dye **18** or crude azo dye **18** does not have any significant effect on the physical properties of gasoline 91. Therefore, it is likely that this azo dye can be used as dye in gasoline in both pure and crude forms.

4.4 Stability test of azo dye in gasoline 91

Generally, gasoline 91 is consumed within 3 months after released to the market. Therefore, in this study, the stability test of the azo dye **18** in gasoline 91 was designed to be performed in a period of 3 months. The test was carried out by measuring absorbance of λ_{abs} at 509 nm of a solution of **18** in base gasoline 91 at the concentration of 6 ppm after 1–3 months by using a spectrophotometer. The absorbance at 509 nm was converted into the azo dye concentration by the above-mentioned calibration equation.

Table 4-5 Stability of compound **18** (6 ppm) in gasoline 91 in term of concentration.

Month	Concentration in gasoline 91 (ppm)			
	1st	2nd	3rd	Average
1	5.96±0.07	6.10±0.07	6.03±0.07	6.03±0.07
2	5.97±0.07	6.11±0.07	6.06±0.07	6.05±0.07
3	5.97±0.08	6.12±0.08	6.06±0.08	6.05±0.08

The results shown in Table 4-5 indicated that there were no significant differences in the concentrations of azo dye in each gasoline samples throughout the period of 3 months and hence the azo dye **18** exhibited the stability for at least 3 months and could be practically used as a dye in gasoline 91.