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ORIGINAL PAPER

Cardanol-Based Bis(azo) Dyes as a Gasoline 91 Colorant

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Abstract Novel bis(azo) dyes were successfully prepared from the coupling of either natural cardanol or its hydrogenated derivative with a series of diazotized aromatic amines and diamines. These new dyes were fully characterized by NMR, infrared and UV–visible spectroscopy and mass spectrometry. The dyes are highly soluble in a variety of common organic solvents and gasoline as a consequence of the cardanol unit. The physical properties of gasoline according to American Society for Testing and Materials standard were unaffected by the presence of the bis(azo) dye derived from 1-(4aminophenylazo)-2-naphthol at a concentration of 6 ppm and the dye showed excellent stability over a 3 month period.

Keywords Cardanol · Bis(azo) dye · Gasoline colorant · Cashew nut shell liquid · CNSL · Red dye

Introduction

In most countries, motor gasoline tends to be classified into grades according to an octane number (e.g., premium and regular). Dye additives are used to differentiate the different grades of the gasoline so the consumers can visually recognize the gasoline grade they are using. However, gasoline is really colorless to pale yellow and therefore has to be intentionally blended with a colorant to enable identification of grades and manufacturing sources. Solvent Red 164 and 26 (Chart 1) are amongst the most common colorants in use today [1]. However, it is clear that these could be superseded by cheap new dyes having higher molar absorptivities and hydrocarbon-solubilities. In general, an inadequate solubility becomes problematic when a high concentration of dye is required to get the desired color intensity in the gasoline, while dyes that may be soluble enough but have a low absorptivity may have to be used at concentrations so high that they interfere with the fuel properties. Thus any new gasoline colorant should have a high absorptivity and organic solubility, while maintaining a low production cost and high stability with respect to both light and humidity during storage.

Described here is the preparation of soluble azo dyes **1** and **2** from cardanol, a natural alkyl phenol obtained from distillation of cashew nut shell liquid (CNSL). As shown in Chart 2, the cardanol molecule contains a long hydrocarbon chain *meta*- to the hydroxyl group, which is key in making it useful as a solubilizing aromatic component in many syntheses. In the past, several dyes have been prepared from hydrogenated cardanol and various aromatic amines for various purposes, such as oil-solubilizing agent, functionalized industrial precursors and coating materials [2–4]. For petrochemical use, synthesis

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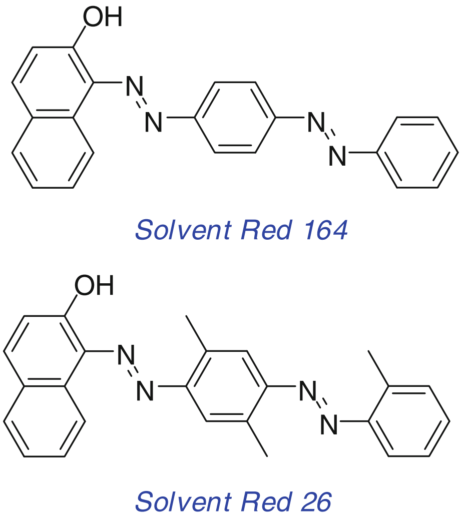


Chart 1 Structures of Solvent Red 164 and 26

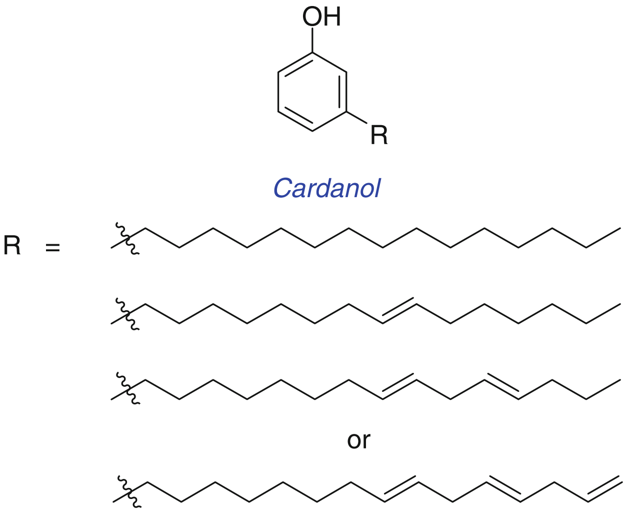


Chart 2 Structure of natural cardanol

of monoazo dyes from cardanol and aniline derivatives as fuel markers in gasoline and diesel have been reported [5]. In this study, we aimed to synthesize cardanol-based red bis(azo) dyes for coloration of the regular-type gasoline. This work follows our previous study on a cardanol-based porphyrin that exhibited improved solubility and other excellent properties for a diesel fluorescent marker [6]. Herein, we also report the investigation of the properties of motor gasoline 91 blended with the synthesized dyes according to ASTM standard and the stability of a selected dye in base gasoline 91 to evaluate their potential as colorants for commercial motor gasoline 91.

Experimental Section

Materials and Methods

All chemicals were obtained from commercial suppliers and used as purchased without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were collected in deuterated chloroform ($CDCl_3$) at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual $CHCl_3$ peak (7.26 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR spectra) and coupling constants (J) are reported in Hertz (Hz). Mass analysis was performed by using electrospray ionization time-of-flight mass spectrometry (ESI-TOF–MS) technique. Absorption spectra of dyes were collected in CH_2Cl_2 and absorption coefficients (ε) are expressed in M^{-1} cm^{-1}.

Non-commercially Available Compound

Fully hydrogenated cardanol (i.e., no alkene groups and one-compound composition by ^{1}H-NMR spectroscopic and mass spectrometric analyses) was kindly supplied by Dr. Nantanit Wanichacheva.

Bis(azo) Dye **1**

Following a published method [7], a mixture of *p*-phenylenediamine (0.108 g, 1.00 mmol) in a 6% (v/v) aqueous solution of concentrated hydrochloric acid (2.7 mL) was reacted with a solution of sodium nitrite (0.080 g, 1.0 mmol) in distilled water (3.0 mL) at −2 °C. The resulting diazonium salt was coupled by adding into an alkaline solution at −2 °C. The alkaline solution was prepared by dissolving potassium hydroxide (0.056 g, 1.0 mmol) in ethanol (2.0 mL), then cooling the solution to 0 °C and adding β-naphthol (0.144 g, 1.00 mmol) with continuous stirring. The reaction mixture was left stirring at −2 °C for an additional 1 h and then extracted with CH_2Cl_2. The organic layer was separated and dried over anhydrous Na_2SO_4. After removal of the solvent, the mixture was purified by column chromatography on silica gel [1% TEA in hexanes/ethyl acetate (1:1)] to give compound **5** as an orange solid (0.250 g, 95%). The spectral data of **5** are consistent with those previously described in a literature [8]. Then, compound **5** (0.250 g, 0.912 mmol) was diazotized and then coupled to hydrogenated cardanol (0.304 g, 0.998 mmol) in the same manner as mentioned above. The resulting crude products were extracted with CH_2Cl_2. The organic phase was separated, washed repeatedly with distilled water (4 × 20 mL), dried over anhydrous Na_2SO_4, and then concentrated to dryness. The resulting crude product was purified by column chromatography on silica gel [1% TEA in CH_2Cl_2 and then 1%

TEA in ethyl acetate/CH_2Cl_2 (1:4)] to give **1** as a red solid (0.050 g, 9% overall). m.p. 126–128 °C. ^{1}H-NMR: δ (ppm) 0.82–0.87 (m, 3H), 1.21–1.71 (m, 26H), 3.11 (t, $J = 7.8$ Hz, 2H), 6.74 (dd, $J = 8.8$ Hz, 2.8 Hz, 1H), 6.80 (d, $J = 2.8$ Hz, 1H), 6.83 (d, $J = 9.2$ Hz, 1H), 7.39–7.42 (m, 1H), 7.54–7.58 (m, 2H), 7.70–7.73 (m, 2H), 7.81 (d, $J = 8.8$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 2H), 8.54 (d, $J = 8.4$ Hz, 1H); ^{13}C-NMR: δ (ppm) 14.1, 22.7, 29.1, 29.2, 29.4, 29.5, 29.66, 29.72, 29.99, 30.03, 30.2, 31.4, 31.5, 31.9, 32.1, 113.9, 116.5, 117.1, 118.5, 122.0, 124.3, 125.3, 126.2, 128.1, 128.7, 128.8, 128.9, 129.1, 130.7, 133.4, 141.2, 144.6, 145.0, 146.2, 151.5, 158.9, 174.7; ESI-TOF–MS observed 579.578, calculated 578.362 [$(M + H)^+$; $M = C_{37}H_{46}N_4O_2$]; λ_{abs} nm (ε) 513 (31,948).

Bis(azo) Dye **2**

Following the procedure described for the synthesis of compound **1**, natural cardanol (0.304 g, 1.00 mmol) was used instead of the hydrogenated one. Compound **2** was obtained as a red solid (0.150 g, 26% overall). m.p. 100–102 °C. ^{1}H-NMR: δ (ppm) 0.77–0.85 (m, 3H), 1.18–2.74 (m, 20H), 3.05 (t, $J = 7.6$ Hz, 2H), 4.87–5.76 (m, 4H), 6.67 (dd, $J = 8.8$ Hz, 2.8 Hz, 1H), 6.73 (d, $J = 2.8$ Hz, 1H), 6.77 (d, $J = 9.6$ Hz, 1H), 7.32–7.36 (m, 1H), 7.48–7.53 (m, 2H), 7.64–7.67 (m, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H), 8.48 (d, $J = 8.4$ Hz, 1H); ^{13}C-NMR: δ (ppm) 14.1, 22.6, 22.8, 25.6, 27.2, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.5, 31.8, 32.0, 113.9, 116.4, 117.2, 118.5, 121.9, 124.3, 125.3, 126.3, 128.1, 128.8, 129.2, 130.0, 130.4, 130.7, 133.4, 141.4, 144.7, 144.9, 146.2, 151.5, 158.7, 175.0; ESI-TOF–MS observed 579.383, calculated 572.315–578.362 [$(M + H)^+$; $M = C_{37}H_{46\text{-}n}N_4O_2$; n = 0, 2, 4 or 6]; λ_{abs} nm (ε) 516 (31,345).

Bis(azo) Dye **3**

Following a previously published procedure [5], benzidine (0.184 g, 1.00 mmol) was added to a 50% (v/v) aqueous solution of concentrated hydrochloric acid (1.2 mL) and the resulting reaction mixture was vigorously stirred in an ice bath. After the mixture was cooled to −2–0 °C, a solution of sodium nitrite (0.138 g, 2.00 mmol) in distilled water (1.0 mL) was added dropwise into the reaction mixture while the reaction temperature was kept below 0 °C. Meanwhile, a 3-alkylphenoxide solution was prepared by dissolving potassium hydroxide (0.112 g, 2.00 mmol) in methanol (1.0 mL), cooling the solution to 0 °C, and then adding cardanol (0.608 g, 2.00 mmol) with continuous stirring to give a reddish-brown oil. Then the diazonium salt solution was added dropwise to the cooled 3-alkylphenoxide solution. The reaction mixture was left stirring at a temperature below 0 °C for 1 h and the azo dye product was extracted with toluene. The toluene layer was separated, washed repeatedly with distilled water (4 × 20 mL), dried over anhydrous Na_2SO_4, and then concentrated to dryness. The resulting crude product was purified by column chromatography on a silica gel [1% TEA in hexanes/ethyl acetate (4:1)] to give a yellow gummy solid (0.010 g, 1%). Due to a close R_f value of compound **3** to those of unknown byproducts, compound **3** could not be completely recovered. ^{1}H-NMR: δ (ppm) 0.84–0.90 (m, 6H), 1.23–2.80 (m, 44H), 3.13 (t, $J = 7.6$ Hz, 4H), 4.94–5.82 (m, 6H), 6.74 (dd, $J = 8.8$ Hz, 2.8 Hz, 2H), 6.81 (d, $J = 2.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 4H), 7.97 (d, $J = 8.4$ Hz, 4H); ^{13}C-NMR: δ (ppm) 13.8, 14.1, 22.6, 22.8, 25.55, 25.62, 27.2, 29.0, 29.25, 29.31, 29.39, 29.44, 29.6, 29.67, 29.72, 29.8, 31.4, 31.5, 31.8, 32.0, 113.8, 114.7, 116.4, 117.2, 123.3, 126.8, 127.5, 127.7, 128.0, 128.1, 129.3, 129.8, 129.9, 130.1, 130.4, 136.8, 141.9, 144.8, 146.1, 152.4, 158.4; MALDI-MS observed 808.674; calculated average mass 808.612–814.612 [$M = C_{54}H_{78\text{-}n}N_4O_2$; n = 0, 2, 4, 6]; λ_{abs} nm (ε) 387 (10,950).

Bis(azo) Dye **4**

Following the procedure described for bis(azo) dye **3** with slight modification, 1,5-diamino-naphthalene (0.158 g, 1.00 mmol) was diazotized and coupled with cardanol. The reaction mixture was extracted with tetrahydrofuran and saturated ammonium chloride solution. The organic layer was separated, washed repeatedly with distilled water (4 × 20 mL), dried over anhydrous Na_2SO_4, and then concentrated to dryness. The resulting crude product was purified by column chromatography (silica, 1% TEA in CH_2Cl_2) to give a yellow gummy solid (0.04 g, 5%). Due to a close R_f value of compound **4** to those of unknown byproducts, compound **4** could not be completely recovered. ^{1}H-NMR: δ (ppm) 0.77–0.83 (m, 6H), 1.18–2.74 (m, 46H), 3.13 (t, $J = 7.6$ Hz, 4H), 4.88–5.77 (m, 6H), 6.73 (dd, $J = 8.8$ Hz, 2.8 Hz, 2H), 6.77 (d, $J = 2.8$ Hz, 2H), 7.64 (t, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 7.6$ Hz, 2H), 7.83 (d, $J = 8.8$ Hz, 2H), 9.03 (d, $J = 8.4$ Hz, 2H); ^{13}C-NMR: δ (ppm) 13.8, 14.1, 22.6, 22.8, 25.5, 25.6, 27.2, 28.9, 29.0, 29.3, 29.4, 29.5, 29.6, 29.66, 29.71, 29.8, 31.5, 31.8, 32.1, 112.1, 113.8, 114.7, 116.4, 117.6, 126.1, 126.4, 126.8, 127.5, 127.9, 128.1, 129.3, 129.8, 129.9, 130.1, 130.4, 132.3, 136.8, 145.5, 146.3, 147.9, 158.3; MALDI-MS observed 782.547; calculated average mass 782.597–788.597 [$M = C_{52}H_{76\text{-}n}N_4O_2$; $n = 0, 2, 4, 6$]; λ_{abs} nm (ε) 402 (8,086).

Investigation of the Appropriate Dye Concentration for Coloration of Gasoline 91

In the case of pure **2**, a 200-ppm stock dye solution was prepared by dissolving bis(azo) dye **2** (2 mg) in base gasoline 91 to a final volume of 10 mL. A series of the solutions of **2** in base gasoline 91 at a final concentration of 4, 5, 6, 7 and 8 ppm was prepared. After that, the color of the resulting solutions was compared to that of the commercial gasoline 91, obtained from PTT Public Company Limited, Thailand by a colorimeter to find the similar color match.

In a similar manner, a 1,000-ppm stock solution of crude bis(azo) dye **2** was prepared by dissolving crude **2** (10 mg) in base gasoline 91 to a final volume of 10 mL and subsequent final concentrations of 15, 16, 17, 18, 19 and 20 ppm were compared for a color match to the commercial gasoline 91.

Effect of Bis(azo) Dye **2** on the Physical Properties of Base Gasoline 91

A 6 ppm solution of pure bis(azo) dye **2** in base gasoline 91 was prepared by dissolving pure **2** (6 mg) in base gasoline 91 in a final volume of 1 L, while a 18-ppm solution of crude **2** was prepared in the same manner by using crude **2** (18 mg) instead of the pure one. The physical properties of both dyed gasoline samples, and base gasoline 91, were investigated according to the ASTM test methods. The physical properties of dyed and undyed gasoline samples were determined twice in the second and the third month during the 3 month period of the stability test after the photophysical properties of the dye was proven to remain intact.

Quantitative Determination and Stability Test of Bis(azo) Dye **2** in Base Gasoline 91

A series of the calibration solutions of pure bis(azo) dye **2** in base gasoline 91 was prepared at final concentrations of 2, 4, 6, 8 and 10 ppm and the absorption spectra of each calibration solution were recorded by a UV/Vis spectrophotometer. The calibration curve was plotted between absorbance at 509 nm (*y*-axis) and the concentration of **2** in base gasoline 91 (*x*-axis) and the best fitting linear regression line was selected. This equation was used to quantify **2** in the stability test described below.

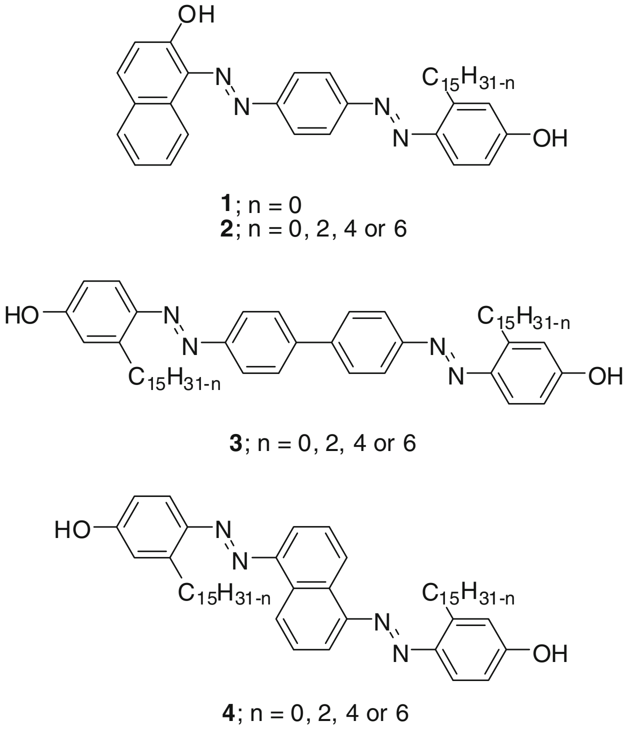
The stability test was performed with base gasoline 91 dyed with bis(azo) dye **2** at a final concentration of 6 ppm on a UV–Vis spectrophotometer. Three 6 ppm solutions of **2** in base gasoline 91 were prepared and a 5-mL aliquot was placed into each of nine sealed vials and stored up to 3 months in an ambient environment with the temperature up to 50 °C. After 1, 2 and 3 months three solutions from each flask were directly taken from the vials to the UV–Vis measurement. The quantity of **2** in the blended gasoline 91 was determined by the calibration equation.

Results and Discussion

Molecular Design

Two series of dyes were prepared. One containing cardanol and *β*-naphthol moieties joined by a 1,4-phenylene central unit (compounds **1** and **2**, Chart 3). The introduction of the *β*-naphthol group was intended to extend the conjugation in the dye structure, resulting in the red-shift of the absorption as observed in several red azo dyes, e.g., Solvent Red 164. Compound **1** differs from compound **2** at the saturation of its long alkyl chain on the cardanol moiety. Initially, the hydrogenated cardanol was employed in the synthesis of compound **1** to avoid the possible complication due to the side reaction caused by double bonds on the long alkyl chain of cardanol. The synthesis of compound **2** was included to study the possibility of using natural cardanol in the dye preparation.

The other series of bis(azo) dyes have two cardanol peripheral groups linked to each other via a 4,4′-biphenylene (compound **3**) or a 1,5-naphthylene central unit (compound **4**), considering that these linkers could possibly



1; n = 0
2; n = 0, 2, 4 or 6

3; n = 0, 2, 4 or 6

4; n = 0, 2, 4 or 6

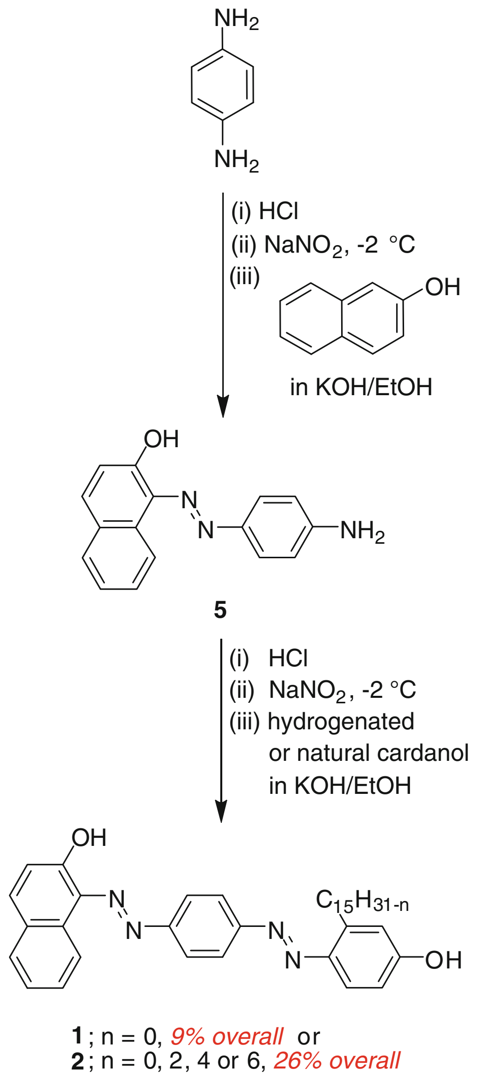
Chart 3 Target cardanol-based bis(azo) dyes **1**–**4**

provide an extended conjugation system and, subsequently, absorption in the long wavelength region. The 4,4′-biphenylene central unit in compound **3** is known to be more flexible than the 1,5-naphthylene one in compound **4** and, hence, should be beneficial to the solubility of the dye. However, the conjugation system may be disturbed by the possibility of the bond rotation in the 4,4′-biphenylene unit. This will not occur in the case of the 1,5-naphthylene linker in **4**.

Synthesis

The synthesis of bis(azo) dyes **1** and **2** relies on stepwise double diazotization (Scheme 1). Firstly, commercially available *p*-phenylenediamine was singly diazotized in a stoichiometric manner and then the resulting diazonium salt was coupled with an alkaline solution of *β*-naphthol to give the monoazo compound **5**. Subsequently, the diazonium salt of **5** was formed and coupled with a hydrogenated or natural cardanol to obtain the desired compound **1** or **2** as a red solid in 9 or 26% overall yield, respectively. The lower yield of compound **1** is attributed to the lower solubility of the hydrogenated cardanol in the reaction medium, compared to that of the natural one. Due to the steric effect from the cardanol alkyl long chain, the coupling of the diazonium salt and cardanol was found to be relatively slow in general. The reactions gave several unknown byproducts from competitive side reactions, which may be hydrolysis of the diazonium salt, salt decomposition, etc. These byproducts also caused complications in the purification step.

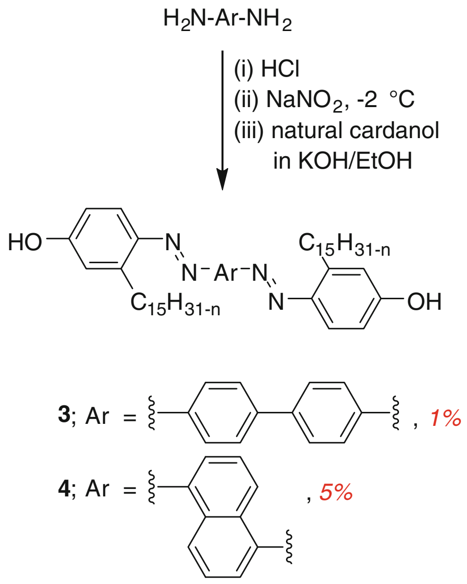
Compound **2** exhibited a satisfactory solubility (>10 mg/mL) in common organic solvents, such as CH_2Cl_2, toluene and THF, and base gasoline 91. In CH_2Cl_2, the solubility of compounds **1** and **2** (10 and >18 mg mL^{-1}, respectively) were greater than that of Solvent Red 164 (8 mg mL^{-1}). This indicated the efficient solubilizing effect of the unsaturated alkyl chain in natural cardanol. With respect to the UV–Vis absorption, compounds **1** and **2** showed absorption maxima in CH_2Cl_2 at 513 and 516 nm with absorption coefficients of 31,345 and 31,948 M^{-1} cm^{-1}, respectively. These absorption data are comparable to those of Solvent Red 164 that exhibited an absorption maximum in CH_2Cl_2 at 508 nm with an absorption coefficient of 33,627 M^{-1} cm^{-1}. Thus, the substitution of the peripheral phenyl group of the commercial Solvent Red 164 by the natural cardanol group improves the solubility of the dye and keeps the dye absorptivity equally high. Due to the higher solubility and the higher preparative yield from an easier preparation procedure (i.e., no hydrogenation of the starting cardanol was needed), compound **2** was chosen for further study.



Scheme 1 Synthesis of dyes **1** and **2**

Compounds **3** and **4** were prepared from the double diazotization of benzidine or 1,5-diaminonaphthalene, respectively, and a stoichiometric amount of cardanol, as shown in Scheme 2. Similarly to what was observed in the preparation of dyes **1** and **2**, these syntheses encountered a slow reaction rate and the formation of several byproducts that were difficult to completely isolate from compounds **3** and **4**. Therefore, compounds **3** and **4** were obtained in yields of only 1 and 5%, respectively.

As regards their absorption characteristics, both compounds **3** and **4** appeared yellow in color with absorption maxima in CH_2Cl_2 of 387 and 402 nm, and absorption coefficients of 10,950 and 8,086 M^{-1} cm^{-1}, respectively. It is clear that the absorption maxima of compounds **1** and **2** were significantly red-shifted from those of compounds **3** and **4**. It is possible that the conjugation in molecules **3** and **4** was disturbed by the bulkiness of the



Scheme 2 Synthesis of dyes **3** and **4**

long alkyl chains of the peripheral cardanol units. The disturbance of the conjugation system was even more pronounced in the case of compound **3** whose biphenyl unit encounters the phenyl-ring rotation around the phenyl–phenyl bond, compared to compound **4** which has a more rigid naphthyl central unit. However, since the expected red color was not obtained, compounds **3** and **4** were not taken into consideration in the next study.

Investigation of the Appropriate Dye Concentration for Coloration of Gasoline 91

To estimate the appropriate concentration of **2** in base gasoline 91 to give the most similar color to that of the commercial gasoline 91, the color of a solution of **2** in base gasoline 91 at a concentration of 4–8 ppm was determined in comparison with that of the commercial gasoline 91 by mean of colorimetric analysis based on a CIE L*a*b* system. The color difference was determined by the ΔE* value. The measurement was performed with all samples at once, therefore the typical measurement uncertainty resulted from the instrument components and measurement condition should not significantly affect this comparative study. The results (Table 1) revealed that a 6 ppm solution of **2** in base gasoline 91 provided the most similar color to that of the commercial gasoline 91.

To simplify and reduce the cost of the scalable production of dye **2** as a gasoline colorant, we also attempted to directly blend a crude mixture containing dye **2** in gasoline 91. The crude mixture was obtained from the same synthetic procedure as that of the pure one, except that the lengthy chromatographic purification in the second diazo-coupling was omitted. In a similar manner to pure dye **2**, a series of the solutions of crude **2** at a concentration of 10–20 ppm was prepared and their color was compared with that of the commercial gasoline 91. It was found that an 18-ppm solution of crude **2** in base gasoline 91 provided the most similar color to that of commercial gasoline 91 (Table 1). Therefore, the suggested concentration levels of

Table 1 Colorimetric data of solutions of pure and crude **2** in base gasoline 91 compared with those of commercial gasoline 91

Type of gasoline 91	L^{a}	a^{b}	b^{c}	ΔE^{*d}
Commercial	86.45	23.42	14.90	
Blended with pure **2** (concentration, ppm)				
4	90.61	17.00	12.84	7.92
5	88.86	20.29	15.53	4.00
6	86.70	24.04	18.21	3.38
7	84.70	27.79	21.90	8.44
8	82.75	31.39	24.47	12.99
Blended with crude **2** (concentration, ppm)				
15	86.15	17.23	11.83	6.92
16	86.11	17.88	11.68	6.42
17	85.57	19.06	12.17	5.22
18	83.47	22.37	13.20	3.59
19	82.45	23.64	13.59	4.21
20	81.21	25.36	13.94	5.41

[a] *L* is lightness representing from 0 (black) to 100 (white)

[b] *a* is chroma coordinate representing from +a (redness) to −a (greenness)

[c] *b* is chroma coordinate representing from +b (yellowness) to −b (blueness)

[d] ΔE^* is color difference value calculated from $\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$

pure dye **2** and its crude mixture to be used for coloration of gasoline 91 and for further study in this research are 6 and 18 ppm, respectively. Although the crude preparation was required to be used at a 3-fold higher concentration than the pure compound **2**, the yield of the crude **2** preparation compared to that of the pure **2** was significantly greater and thus its use instead potentially offers a significant cost and time saving opportunity.

Effect of Bis(azo) Dye 2 on the Physical Properties of Base Gasoline 91

This part is focused on the effect of bis(azo) dye **2** on the physical properties of base gasoline 91 to ensure that gasoline 91 blended with either the pure or crude bis(azo) dye **2** preparations still has the qualified physical properties for commercial use. A sample of base gasoline 91 containing 6 ppm of pure bis(azo) dye **2** and another containing 18 ppm of the crude bis(azo) dye **2** were tested for the physical properties using the ASTM test methods. The physical properties of both dyed gasoline samples were then compared with those of the undyed (base) gasoline 91. Each sample was tested twice in the second and the third month during the 3 month period of the stability test. The results from both measurements were almost identical and the average value is reported in Table 2. The results revealed that the physical properties of both dyed gasoline samples were not significantly different from those of undyed gasoline and followed the standard specification of the commercial gasoline 91.

Quantitative Determination and Stability Test of Bis(azo) Dye 2 in Base Gasoline 91

Generally, the azo dyes are known to be highly stable. However, under storage condition the dyes exposed to various light intensities, temperatures and humidity levels that bring about a trivial possibility for the dye degradation via, for example, anaerobic microbial process and photocatalytic destruction. Therefore, a stability test was taken into consideration in this study. A standard calibration curve of pure bis(azo) dye **2** in base gasoline 91 was prepared by plotting the absorbance at 509 nm, which is an absorption maximum of **2** in base gasoline 91, of a series of the solutions of **2** in base gasoline 91 versus the concentration of the solutions ranging from 0 to 10 ppm. A standard calibration equation was found to be $Y = 0.0607X$, with a linear correlation coefficient R^2 equal to 0.9999. This equation was then used to evaluate the stability of **2** in base gasoline fuel. Generally, commercial gasoline 91 is consumed within 3 months after it is released on to the market. Therefore, in this study, the stability test of **2** in base gasoline 91 was performed over a period of up to 3 months under ambient conditions with the temperature up to 50 °C. The test was carried out by

Table 2 Physical properties of dyed gasoline samples and undyed gasoline 91

Test item	ASTM	Limit	Type of gasoline 91		
			Undyed	Dyed with	
				Pure **2**	Crude **2**
Vapor pressure at 37.8 °C, kPa	D5191	54.5 max	53.4	53.6	53.1
Distillation at					
Initial boiling point (IBP), °C	D86–01	Report	34.4	35.8	35.9
10%, °C		Max. 70	53.0	54.0	54.6
50%, °C		90–110	95.6	96.6	96.8
90%, °C		Max. 170	123.9	123.9	124.0
Final boiling point (FBP), °C		Max. 200	156.6	156.7	156.6
Residue, % vol.		Max. 20	1.4	1.3	1.3
Solvent Washed Gum,					
mg/100 mL	D381	Max. 4	0.8	1.2	1.2
Silver strip corrosion	D130	Max. no. 1	No. 1	No. 1	No. 1
Sulfur, % w	D5453	Max. 0.05	0.0016	0.0016	0.0015
Water, % w	D604	Max. 0.7	0.117	0.112	0.092
Benzene, % v	D5580	Max. 3.8	0.49	0.50	0.49
Aromatics, % v	D5580	Max. 38	31.1	32.2	31.3
Research Octane Number (RON)	D2699	Min. 87.0	91.0	91.0	91.0

Table 3 Concentration of diazo dye **2** in base gasoline 91 after 1–3 months (initial level was 6 ppm)

Month	Concentration of 2[a] (ppm)			
	Sample 1	Sample 2	Sample 3	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

[a] Average ± standard deviation, $n = 3$

measuring the absorbance at 509 nm of a 6 ppm solution of pure **2** in base gasoline 91 after 1, 2 and 3 months by a UV–Vis spectrophotometer. The absorbance observed was then converted into the dye concentration by the above calibration equation. The results (Table 3) indicated that there was no significant change in the concentrations of **2** in each gasoline sample throughout the 3 month period and, hence, together with the above-mentioned results, it can be concluded that bis(azo) dye **2** showed stability for at least 3 months and can be practically used as a colorant in gasoline 91 production.

Conclusion

This research was on the synthesis of a series of bis(azo) dyes from cardanol, a naturally occurring compound obtained from extraction of CNSL, for use as a coloring agent in gasoline 91. Besides the desirable red color with a comparable maximum absorption and absorption coefficient to those of Solvent Red 164, the bis(azo) dye **2** showed a satisfactory solubility level in common organic solvents and base gasoline 91. Based on the colorimetric analysis, the practical concentration of **2** that gives the most similar gasoline color compared to that of the commercial one is 6 or 18 ppm when being used in pure or crude form, respectively. According to ASTM test methods, the physical properties of base gasoline 91 are unaffected by the presence of bis(azo) dye **2** in both pure and crude forms. Moreover, bis(azo) dye **2** was found to be stable in base gasoline 91 for at least 3 months. The fact that bis(azo) dye **2** offers practical synthesis from an inexpensive natural resource, a high solubility in base gasoline 91, a satisfactory stability within the fuel storage time, and the possibility to be used in its crude form in low concentration supports the conclusion that bis(azo) dye **2** can possibly serve as a fuel dye for commercial use. However, a further detailed investigation for using this dye in the actual combustion cycle is required.

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