

A synthesis of some new 4-arylidene-5(4*H*)-oxazolone azo dyes and an evaluation of their solvatochromic behaviour

Samieh Fozooni,^a Ahmad Momeni Tikdari,^{a*} Hooshang Hamidian,^b
and Hojatollah Khabazzadeh^a

^aDepartment of Chemistry, Shahid Bahonar University of Kerman, Kerman, 76135-133, Iran

^bDepartment of Chemistry, Payame Noor University (PNU), Kerman, Iran

E-mail: amomeni_uk@yahoo.com

Abstract

Nine novel 4-arylidene-5(4*H*)-oxazolone azo dyes were synthesized in good yield by reacting sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoylamino]acetate with suitable aldehydes in the presence of Ph₃P/CCl₄ and acetonitrile at room temperature. Sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoylamino]acetate was obtained by diazotization of 4-aminohippuric acid and coupling with *N,N*-dimethylaniline. These dyes were characterized by elemental and spectral analyses and the solvatochromic behaviour in various solvents was evaluated.

Keywords: 5(4*H*)-Oxazolone azo dyes, solvents' effect, diazotization, synthesis, Ph₃P/CCl₄, acetonitrile

Introduction

Many heterocyclic compounds are used extensively in disperse dye chemistry for textile or nontextile applications. These dyes are now marketed to produce a full range of dispersed dyestuffs without the use of colorants based on heteroaromatic diazo components. Most of the heterocyclic dyes are derived from the diazo components consisting of five-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring.^{1,2}

The azo dyes containing heterocyclic rings result in brighter and often deeper shades than their benzene analogs. On the other hand, they are very important in applications such as disperse dyes for polyester fibers, reprography, functional dye and nonlinear optical systems, photodynamic therapy, and lasers.³⁻⁹

The 5(4*H*)-oxazolones are important synthons for the synthesis of several biologically active molecules. Also, they are precursors of amino acids containing an aromatic side chain. A number

of methods are available for the synthesis of azlactones including the use of acetic anhydride and sodium acetate, acetic anhydride and lead acetate, polyphosphoric acid, sulfur trioxide/dimethyl formamide complex, perchloric acid, and carbodiimides. Recently, synthesis of oxazolones has been reported by using anhydrous zinc chloride or bismuth (III) acetate as catalysts.¹⁰⁻¹⁵

It is well known that triphenylphosphane in combination with tetrachloromethane provides reagents that have manifold uses and are finding increasing application in preparative chemistry for halogenation, dehydration, and P-N linking reagents. Of more general importance is the tertiary phosphane/tetrachloromethane system, as chlorinating and dehydrating agent for sensitive substrates to the aggressive and readily hydrolyzed acid chlorides such as PCl₅, P(O)Cl₃, thionyl chloride and sulfonyl chloride. A great advantage can also be seen in its ability to the demands made by the various donor strengths of the substituents chosen for attachment to the phosphorus atom.¹⁶⁻¹⁸

Herein, we wish to report a novel method for synthesis of some new 4-arylidene-5(4*H*)-oxazolone azo dye derivatives from sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoylamino]acetate and corresponding aldehydes in the presence of PPh₃ and CCl₄ at room temperature.

Results and Discussion

Sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoyl amino] acetate was prepared by diazotization of 4-aminohippuric acid in nitrosyl hydrochloric acid followed by coupling with *N,N*-dimethylaniline to give yellow crystals in good yield. Then 4-arylidene-5(4*H*)-oxazolone azo dyes (**3a-i**) were synthesized by classical Erlenmeyer reaction, involving condensation of sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoylamino] acetate with corresponding aldehydes in presence of acetic anhydride and sodium acetate under refluxing condition (method A). In method B, We found that Ph₃P/CCl₄ reagent easily converted the compound **2** to 4-arylidene-5(4*H*)-oxazolone azo dyes (**3a-i**) under refluxing with corresponding aldehydes and NEt₃ in CCl₄. In this investigation, at first triphenylphosphane reacts with carbon tetrachloride to give triphenylphosphonium chloride. Next compound **A** is formed along with the generation of triphenylphosphane oxide. Then aromatic aldehydes are condensed with **A** to give the 4-arylidene-5(4*H*)-oxazolone azo dye products. A reasonable mechanism is shown in Scheme 1. In method C, we investigated the effect of acetonitrile as a solvent on the Ph₃P/CCl₄ reaction. It was seen that with Ph₃P/CCl₄/ MeCN an excellent yield of highly pure product was obtained at room temperature and short time whereas two previous methods were carried out at high temperature, long time and moderate yields (Table1). The choice of acetonitrile was based on a review by Appel^{19,20} where it was pointed out that acetonitrile can have marked accelerating effect on Ph₃P/CCl₄ reactions, owing to its high dielectric constant and solvating ability compared to CCl₄ itself. Other merit of this method is for sensitive substrates to hydrolyze in the acidic solution.

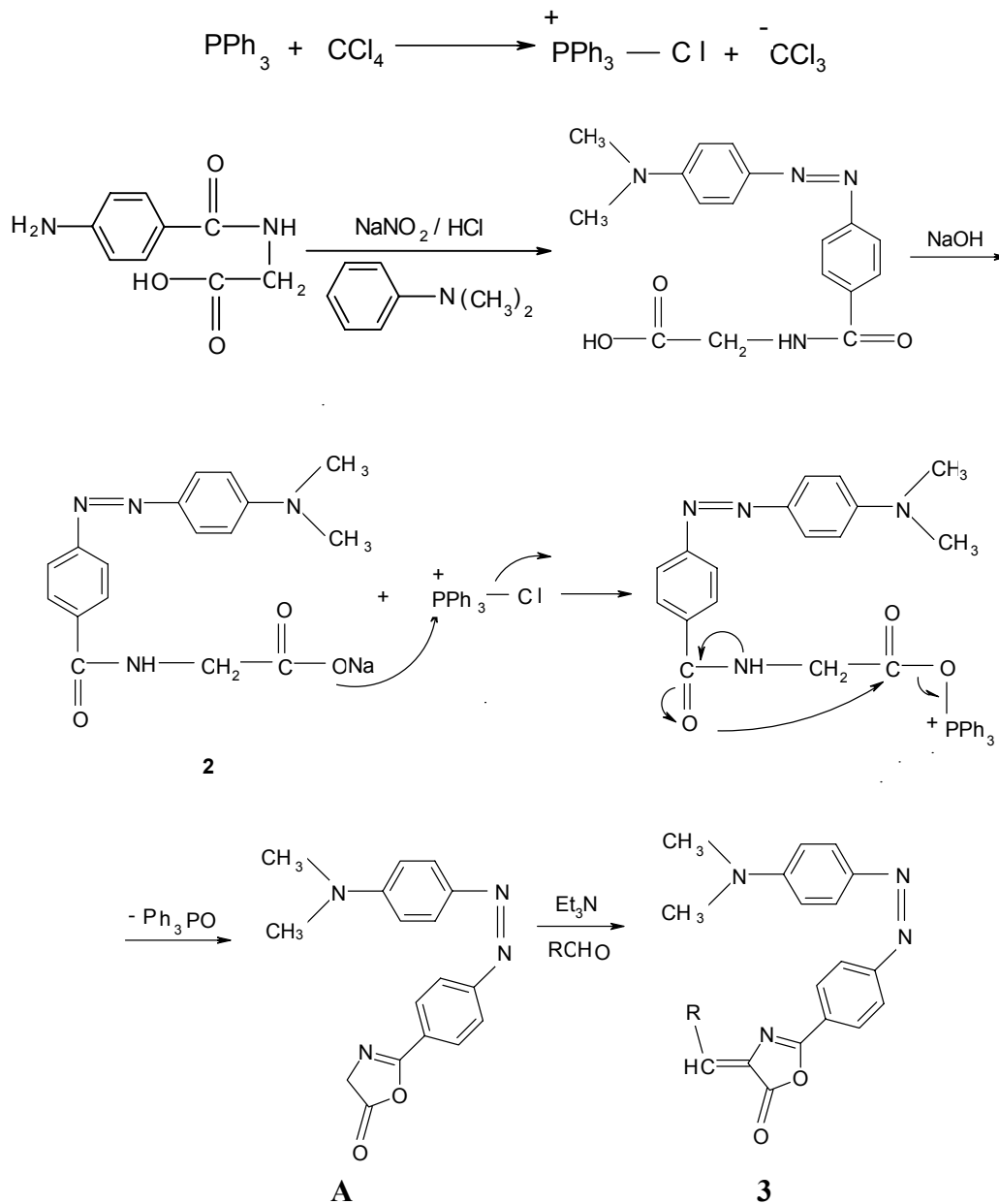
**3a:** $\text{R}_1 = \text{C}_6\text{H}_5$ **3b:** $\text{R}_2 = 4\text{-ClC}_6\text{H}_4$ **3c:** $\text{R}_3 = 2,4\text{-Cl}_2\text{C}_6\text{H}_3$ **3d:** $\text{R}_4 = 4\text{-MeOC}_6\text{H}_4$ **3e:** $\text{R}_5 = 2\text{-MeOC}_6\text{H}_4$ **3f:** $\text{R}_6 = 4\text{-MeC}_6\text{H}_4$ **3g:** $\text{R}_7 = 3\text{-O}_2\text{NC}_6\text{H}_4$ **3h:** $\text{R}_8 = \text{C}_4\text{H}_3\text{O}$ **3i:** $\text{R}_9 = \text{C}_4\text{H}_3\text{S}$ **Scheme 1**

Table1. Yield (%) of dyes **3a-i** by three methods

Products	Method A	Method B	Method C
3a	78	80	85
3b	67	72	78
3c	78	83	90
3d	66	70	75
3e	59	63	70
3f	65	69	74
3g	76	80	86
3h	85	89	92
3i	75	78	83

The absorption spectra of these oxazolone azo dyes **3a-i** were recorded in various solvents at the concentration of 10^{-6} M, and the results are given in Table 2. We found that the electronic absorption of these oxazolone azo dyes indicated a regular variation with the polarity of solvents, which did not change significantly. These dyes, apparently, did not exhibit a strong solvent dependence. The maximum absorption of these dyes shifted in the order: DMF > acetone > chloroform. The spectral shifts of dye **3a** in various solvents are shown in Fig 1. The maximum absorption of dye **3a** showed bathochromic shift in DMF and acetone, with respect to the maximum absorption in chloroform (e.g. λ_{\max} is 494 nm in DMF, 492 nm in acetone, and 490 nm in chloroform). The same trends of absorption shifts in various solvents were observed for the entire series of dyes **3a-i**, as shown in Table 2. The substituent effects of the heterocyclic azo dyes **3a-i** were evaluated. The spectral shifts of dyes **3a-i** in chloroform at a concentration of 10^{-6} are given in Table 3. We found that the dyes **3d** and **3e** contain an electron donor group methoxy on the 4th and 2nd position of phenyl group substituted on the 4th position of oxazolone ring, so that the λ_{\max} of dye **3d** and **3e** showed hypsochromic shift of -6 and -2 relative to the dye **3a**, respectively.

Dye **3g** contains an electron acceptor group (nitro) in the 3rd position of the phenyl group substituted on the 4th position of the oxazolone ring, so that the λ_{\max} of dye **3g** showed bathochromic shift of +13 nm relative to **3a**, λ_{\max} of dyes **3b** and **3c** is +4 nm and +10 nm longer than that of dye **3a**, due to weaker electron acceptor of chloro group in the para and ortho, para positions of phenyl group substituted on the 4th position of oxazolone ring, respectively, λ_{\max} of dye **3h** showed bathochromic shift of +3 nm relative to **3a** and λ_{\max} of dye **3i** is +4 nm longer than that of dye **3a**.

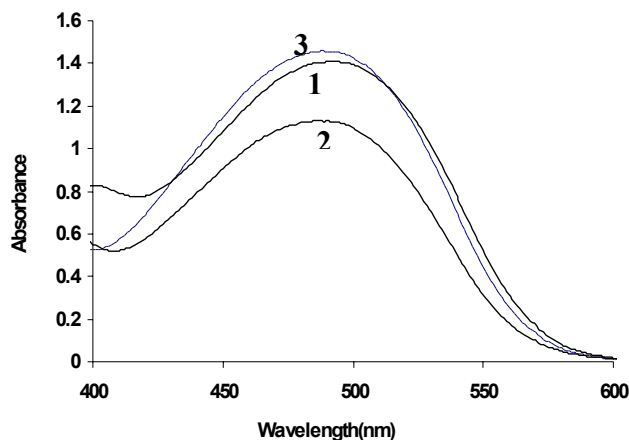


Figure 1. Absorption spectra of dye 1. DMF; 2. acetone; 3. chloroform.

Table 2. Absorption spectra of dyes **3a-i** in various solvents

Products	DMF	Acetone	Chloroform
3a	494	492	490
3b	499	498	494
3c	506	503	500
3d	490	488	484
3e	493	490	488
3f	496	494	492
3g	511	506	503
3h	506	499	493
3i	506	500	494

The ϵ_r value of solvents: DMF = 36.7; chloroform = 4.8.

Table 3. Substituent effect of dyes **3a-i** in chloroform

Products	λ_{\max}	R	$\Delta\lambda^a$	$\log\epsilon$
3a	490	C ₆ H ₅	—	6.16
3b	494	4-ClC ₆ H ₄	+4	6.11
3c	500	2,4-Cl ₂ C ₆ H ₃	+10	6.01
3d	484	4-MeOC ₆ H ₄	-6	6.05
3e	488	2-MeOC ₆ H ₄	-2	6.17
3f	492	4-MeC ₆ H ₄	+2	6.05
3g	503	3-O ₂ N C ₆ H ₄	+13	6.01
3h	493	C ₄ H ₃ O	+3	6.08
3i	494	C ₄ H ₃ S	+4	6.14

^aRelative to **3a**.

Experimental Section

General Procedures. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded with the MATTSON 1000 FT-IR spectrophotometer. Nuclear magnetic resonance spectra were recorded on the BRUKER DRX-500 AVANCE spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained by SHIMADZU QP 1100EX. Elemental analyses were performed by the Iranian Oil Company using a Heracus CHN-O-Rapid analyzer. UV spectra were recorded using a GBC Scientific Equipment (CINTRA 5) UV visible spectrometer.

General preparative procedures

Sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl} benzoyl amino] acetate. In a 125-mL Erlenmeyer flask, 4-aminohippuric acid (0.01 mol) was added to 2% sodium carbonate solution (30 mL) until it was dissolved by boiling. The solution was then cooled and sodium nitrite (0.01 mol) was added, with stirring, until it was dissolved. The solution was cooled by placing it in an ice bath, and then concentrated hydrochloric acid (2 mL) and water (3 mL) were added. By acidifying the solution, a powdery yellow precipitate of the diazonium salt was separated.

N,N-Dimethylaniline (0.01 mol) and glacial acetic acid (0.01 mol) was mixed. The solution of *N,N*-dimethylaniline acetate was added to suspension of diazotized hippuric acid, with stirring, and acid-stable form of the dye was separated. A stiff paste was formed in 5–10 min and then sodium hydroxide (5g) was added to produce the orange sodium salt. The product was collected using saturated sodium chloride solution. The crude product was crystallized from water (**2**). Orange crystals, decomposed >270 yield is 81%. IR (KBr): $\nu = 3354, 1716 \text{ cm}^{-1}$. $^1\text{H NMR}$ (500 MHz, DMSO- d_6): 3.07 (s, 6H, 2CH₃), 3.61 (d, 2H, *J* 4.4 Hz, CH₂), 6.84 (d, 2H, *J* 8.9 Hz, ArH), 7.80-7.82 (m, 4H, ArH), 7.92 (broad, 1H, NH), 7.98 (d, 2H, *J* 8.5, ArH) ppm. $^{13}\text{CNMR}$ (500 MHz, DMSO- d_6): 40.69, 112.44, 122.46, 125.93, 128.94, 136.03, 143.52, 153.67, 154.69. C₁₇H₁₇O₃N₄Na (348.33) calcd. C 58.65, H 4.88, N 16.08; found. C 58.54, H 4.92, N 16.18.

Method A. Preparation of 4-arylidene-5(4*H*)-oxazolone azo dyes with Erlenmeyer method

A mixture of finely divided, anhydrous sodium acetate (0.01 mol), appropriate aldehyde (0.01mol), sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoylamino] acetate (0.01mol), and acetic anhydride (40 mL) was heated with intermittent shaking until the mixture is transformed from an orange, semi-solid mass to a deep red liquid (2 h). The mixture was then cooled to room temperature and the crystalline product was separated by filtration. The crude product was recrystallized from toluene.

Method B. Preparation of 4-arylidene-5(4*H*)-oxazolone azo dyes with PPh₃/CCl₄. A mixture of sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoylamino] acetate (0.01mol), PPh₃ (0.01mol), corresponding aldehyde (0.01mol) and NEt₃ (1 mL) was dissolved in CCl₄ (25 mL). The solvent was evaporated after the reaction system was refluxed for 6h. The residue was

precipitated in water and ethanol and then was purified with toluene to give the corresponding 4-arylidene-5(4*H*)-oxazolone azo dye products.

Method C. Preparation of 4-arylidene-5(4*H*)-oxazolone azo dyes with PPh₃/CCl₄ in acetonitrile. A mixture of sodium 2-[4-{2-[4-(dimethylamino)phenyl]-1-diazenyl}benzoyl amino] acetate (0.01mol), PPh₃ (0.01mol), CCl₄ (0.01mol, 1 mL), the corresponding aldehyde (0.01mol) and NEt₃ (1 mL) was dissolved in acetonitrile (25 mL). The solvent was evaporated after the reaction system was stirred at room temperature for 30 minutes. The residue was precipitated in water and ethanol and then was purified with toluene to give the corresponding 4-arylidene-5(4*H*)-oxazolone azo dye products.

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-phenylmethylidene]-5(4*H*)oxazolone (3a). Dark red crystals. m.p.: 234–235°C. yield (85%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 3.17 (s, 6H, 2CH₃), 6.81 (d, 2H, *J* 8.9 Hz, ArH), 7.30 (s, 1H, *J* 8.9 Hz, Vinyl), 7.50-7.56 (m, 3H, ArH), 7.97 (d, 2H, *J* 8.8 Hz, ArH), 8.02 (d, 2H, *J* 8.4 Hz, ArH), 8.28 (d, 2H, *J* 7.3 Hz, ArH), 8.33 (d, 2H, *J* 8.4 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 40.76, 111.77, 122.46, 125.93, 126.02, 129.25, 29.57, 131.55, 131.83, 132.75, 133.66, 133.82, 153.40, 156.46, 163.44. C₂₄H₂₀N₄O₂ (396.429) calcd: C 72.75, H 5.05, N, 14.13; found: C 72.69, H 5.01, N 14.19. MS *m/z*: 396 (11%, M⁺), 368 (25%), 224 (40%), 148 (62%), 120 (100%).

4-[1-(4-Chlorophenyl)methylidene]-2-(4-{2-[4-(dimethylamino)phenyl]-diazenyl}phenyl)-5(4*H*)-oxazolone (3b). Dark brown crystals. m.p.: 260–261°C. yield (78%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 3.17 (s, 6H, 2CH₃), 6.81 (d, 2H, *J* 9.1 Hz, ArH), 7.23 (s, 1H, Vinyl), 7.51 (d, 2H, *J* 8.6 Hz, ArH), 7.97 (d, 2H, *J* 9.1 Hz, ArH), 8.01 (d, 2H, *J* 8.6 Hz, ArH), 8.21 (d, 2H, *J* 8.5 Hz, ArH), 8.32 (d, 2H, *J* 8.6 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 40.65, 111.96, 123.139, 125.66, 126.16, 129.66, 129.82, 130.11, 130.14, 130.23, 132.59, 133.91, 134.32, 137.66, 144.38, 153.57, 156.88, 164.09, 167.75. C₂₄H₁₉N₄O₂Cl (430.875) calcd. C 66.93, H 4.41, N 13.00; found. C 66.85, H 4.52, N 13.09. MS *m/z*: 432 (4%, M+2), 430 (12%, M⁺), 402 (20%), 224 (37%), 148 (65%), 120 (100%).

4-[1-(2,4-Dichlorophenyl)methylidene]-2-(4-{2-[4-(dimethylamino)phenyl]-diazenyl}phenyl)-5(4*H*)-oxazolone (3c). Dark brown crystals. m.p.: 247–248°C. yield (90%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 3.17 (s, 6H, 2CH₃), 6.82 (d, 2H, *J* 9.0 Hz, ArH), 7.40 (s, 1H, Vinyl), 7.46 (d, 1H, *J* 8.6 Hz, ArH), 7.54 (d, 1H, *J* 1.8 Hz, ArH), 7.97 (d, 2H, *J* 9.0 Hz, ArH), 8.01 (d, 2H, *J* 8.5 Hz, ArH), 8.31 (d, 2H, *J* 8.5 Hz, ArH), 8.98 (d, 1H, *J* 8.5 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 40.65, 111.96, 123.17, 125.02, 126.22, 128.13, 128.72, 129.99, 130.22, 134.39, 135.49. C₂₄H₁₈N₄O₂Cl₂ (465.32) calcd. C 61.97, H 3.87, N 12.04; found. C 61.82, H 3.85, N 12.11. MS *m/z*: 468 (1%, M+4), 466 (6%, M+2), 464 (10%, M⁺), 436 (20%), 224 (32%), 148 (60%), 120 (100%).

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-(4-methoxyphenyl)methylidene]-5(4*H*)-oxazolone (3d). Dark red crystals. m.p.: 294–295°C. yield (75%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$; ¹H NMR (500 MHz, DMSO-d₆): $\delta = 3.16$ (s, 6H, 2CH₃), 3.94 (s, 3H, OCH₃), 6.81 (d, 2H, *J* 9.3 Hz, ArH), 7.06 (d, 2H, *J* 8.9 Hz, ArH), 7.27 (s, 1H, Vinyl), 7.96 (d, 2H, *J* 10.3 Hz,

ArH), 7.99 (d, 2H, *J* 10.6 Hz, ArH), 8.25 (d, 2H, *J* 8.8 Hz, ArH), 8.30 (d, 2H, *J* 8.6 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 40.64, 55.86, 111.96, 114.99, 123.06, 126.06, 126.21, 127.18, 129.47, 131.84, 132.08, 134.99, 153.47, 156.49, 162.67, 162.69, 168.33. C₂₅H₂₂N₄O₃ (426.45) calcd. C 70.44, H 5.16, N 13.14; found: C, 70.35; H, 5.22; N, 13.21. MS *m/z*: 426 (15%, M⁺), 398 (24%), 224 (30%), 148 (50%), 120 (100%).

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-(2-methoxyphenyl)

methylidene]-5(4*H*)-oxazolone (3e). Dark red crystals. m.p.: 264–265°C. yield (70%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 3.17 (s, 6H, 2CH₃), 3.97 (s, 3H, OCH₃), 6.81 (d, 2H, *J* 9.1 Hz, ArH), 6.98 (d, 1H, *J* 8.3 Hz, ArH), 7.16 (t, 1H, *J* 7.6 Hz, ArH), 7.48 (t, 1H, *J* 7.8 Hz, ArH), 7.92 (s, 1H, Vinyl), 7.97 (d, 2H, *J* 9.1 Hz, ArH), 8.00 (d, 2H, *J* 8.6 Hz, ArH), 8.31 (d, 2H, *J* 8.6 Hz, ArH), 8.94 (d, 1H, *J* 7.9 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 40.72, 56.11, 111.19, 111.93, 121.49, 123.08, 123.19, 126.11, 126.24, 129.62, 133.09, 133.39, 144.27, 153.44, 156.51, 159.74, 163.17, 168.34, 178.03. C₂₅H₂₂N₄O₃ (426.45) calcd. C 70.44, H 5.16, N 13.14; found: C 70.53, H 5.06, N 13.25. MS *m/z*: 426 (15%, M⁺), 398 (23%), 224 (31%), 148 (55%), 120 (100%).

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-(4-methylphenyl)methylidene]-

5(4*H*)-oxazolone (3f). dark red crystals. m.p.: 243–244°C. yield (74%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 2.48 (s, 3H, CH₃), 3.17 (s, 6H, 2CH₃), 6.81 (d, 2H, *J* 9.1 Hz, ArH), 7.30 (s, 1H, Vinyl), 7.35 (d, 2H, *J* 8.0 Hz, ArH), 7.97 (d, 2H, *J* 9.1 Hz, ArH), 8.00 (d, 2H, *J* 8.6 Hz, ArH), 8.17 (d, 2H, *J* 8.1 Hz, ArH), 8.32 (d, 2H, *J* 8.5 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 22.27, 40.72, 111.92, 123.09, 125.96, 126.13, 128.77, 129.65, 130.19, 131.44, 132.32, 132.98, 133.07, 142.53, 144.24, 153.44, 156.54, 163.16, 168.29. C₂₅H₂₂N₄O₂ (410.45) calcd: C 73.19, H 5.36, N 13.65; found: C 73.09, H 5.42, N 13.54 MS *m/z*: 410 (8%, M⁺), 382 (20%), 224 (42%), 148 (70%), 120 (100%).

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-(3-nitrophenyl)methylidene]-

5(4*H*)-oxazolone (3g). red-brown crystals. m.p.: 268–269°C. yield (86%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 3.17 (s, 6H, 2CH₃), 6.81 (d, 2H, *J* 8.9 Hz, ArH), 7.24 (s, 1H, Vinyl), 7.38 (d, 1H, *J* 7.7 Hz, ArH), 7.51 (d, 2H, *J* 8.2 Hz, ArH), 7.82 (d, 1H, *J* 7.9 Hz, ArH), 7.96–8.02 (m, 2H, ArH), 8.22 (d, 2H, *J* 8.2 Hz, ArH), 8.32 (d, 2H, *J* 8.3 Hz, ArH) ppm. ¹³CNMR (500 MHz, DMSO-d₆): 40.72, 111.94, 123.15, 125.61, 126.21, 129.69, 129.85, 130.14, 130.24, 132.55, 133.95, 134.27, 137.67, 144.27, 153.53, 156.82, 167.85. C₂₄H₁₉N₅O₄ (441.42) calcd: C 65.33, H 4.31, N 15.86; found: C 65.42, H 4.29, N 15.79. MS *m/z*: 441 (10%, M⁺), 413 (25%), 224 (33%), 148 (63%), 120 (100%).

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-(2-furyl)methylidene]-5(4*H*)-

oxazolone (3h). red-brown crystals. m.p.: 242–243°C. yield (92%). IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. ¹H NMR (500 MHz, DMSO-d₆): 3.16 (s, 6H, 2CH₃), 6.71 (d, 1H, *J* 1.8 Hz, Furyl), 6.81 (d, 2H, *J* 9.0 Hz, ArH), 7.22 (s, 1H, Vinyl), 7.63 (d, 1H, *J* 3.4 Hz, Furyl), 7.73 (s, 1H, Furyl), 7.96 (d, 2H, *J* 9.0 Hz, ArH), 7.99 (d, 2H, *J* 8.5 Hz, ArH), 8.29 (d, 2H, *J* 8.5 Hz, ArH) ppm. (500 MHz, DMSO-d₆): ¹³CNMR: 40.71, 111.92, 114.27, 118.52, 120.60, 123.10, 125.79, 126.13, 129.66, 131.09, 144.27, 147.08, 151.07, 153.46, 163.17, 167.57. C₂₂H₁₈N₄O₃ (386.39) calcd: C 68.42, H

4.66, N 14.50; found: C 68.49, H 4.68, N 14.41. MS m/z : 386 (10%, M^+), 224 (40%), 148 (60%), 120 (100%).

2-(4-{2-[4-(Dimethylamino)phenyl]-1-diazenyl}phenyl)-4-[1-(2-thienyl)methylidene]-5(4H)-oxazolone (3i). Dark red crystals. m.p.: 255–256°C. yield (83%), IR (KBr): $\nu = 1815, 1716 \text{ cm}^{-1}$. $^1\text{H NMR}$ (500 MHz, DMSO- d_6): 3.17 (s, 6H, 2CH₃), 6.81 (d, 2H, J 9.01 Hz, Ar), 7.22 (t, 1H, J 4.8 Hz, Thienyl), 7.54 (s, 1H, Vinyl), 7.69 (d, 1H, J 3.4 Hz, Thienyl), 7.79 (d, 1H, J 5.0 Hz, Thienyl), 7.97 (d, 2H, J 8.9 Hz, ArH), 8.00 (d, 2H, J 8.5 Hz, ArH), 8.31 (d, 2H, J 8.5 Hz, ArH) ppm. $^{13}\text{CNMR}$ (500 MHz, DMSO- d_6): 40.73, 111.93, 123.13, 125.11, 125.87, 126.14, 128.40, 129.68, 131.57, 135.40, 135.75, 138.20, 144.26, 153.45, 156.55, 162.64, 167.44. C₂₂H₁₈N₄O₂S (402.45) calcd: C 65.68, H 4.47, N 13.92; found: C 65.56, H 4.58, N 13.84. MS m/z : 402 (13%, M^+), 224 (32%), 148 (55%), 120 (100%).

Acknowledgements

The authors appreciate the cooperation of the Department of Chemistry, Shahid Bahonar University of Kerman, for supporting this investigation.

References and Footnotes

1. Weaver, M. A.; Shuttleworth, L. *Dyes and Pigments* **1982**, *3*, 81.
2. Maradia, H. R.; Patel, V. S. *J. Serb. Soc.* **2001**, *66*(2), 87.
3. Towns, A. D. *Dyes and Pigments* **1999**, *42*, 3.
4. Gupta, S.; Sivasubramanian, A.; Rodrigues, L. M.; Esteves, A. P.; Hrdina, R.; Oliveira-Compos, A. M. F. *Dyes and Pigments* **2007**, *75*, 82.
5. Tsai, P. C.; Wang, I. J. *Dyes and Pigments* **2007**, *74*, 578.
6. Maradiya, H. R.; Patel, V. S. *J. Braz. Soc.* **2001**, *12*, 710.
7. Razus, A. C.; Birzan, L.; Surugiu, N. M. *Dyes and Pigments* **2007**, *74*, 26.
8. Singh, K.; Singh, S.; Taylor, J. A. *Dyes and Pigments* **2002**, *54*, 189.
9. Naik, S. J.; Halkar, U. P. *ARKIVOC* **2005**, (viii), 141.
10. Shamsunder, R. Y. *Synthesis* **1975**, 749.
11. Paul, S.; Nanda, P.; Gupta, R.; Loupy, A. *Tetrahedron Lett.* **2004**, *45*, 425.
12. Crawford, M.; Little, W. T. *J. Chem. Soc.* **1959**, 729.
13. Beccalli, E. M.; Clerici, F.; Gelmi, M. L. *Tetrahedron* **1999**, *55*, 781.
14. Boekelheide, V.; Schramm, M. *J. Org. Chem.* **1949**, *14*, 298.
15. Kumar, P.; Mishra, H. D.; Mukerjee, A. K. *Synthesis* **1980**, 836.
16. Yang, Y. H.; Shi, M. *Tetrahedron Lett.* **2005**, *46*, 6285.
17. Yang, Y. H.; Shi, M. *Tetrahedron* **2006**, *62*, 2420.
18. Bovin, A. N.; Chekhlov, A. N.; Svetkov, E. N. *Tetrahedron Lett.* **1990**, *31*, 5361.
19. Appel, A. *Angew. Chem. Internat. Edit.* **1975**, *14*, 801.
20. Burton, G.; Elder, J. S.; Fell, S. C. M.; Stachulaki, A. V. *Tetrahedron Lett.* **1988**, *29*, 3003.