



## Synthesis and Characterization of Some Novel Linear Azo-Azomethine Compounds Based on 1-Bromo, 4-[4-(4-Nitrophenylazo) Phenoxy] Butane

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### ABSTRACT

The reaction of some carbocyclic and heterocyclic Schiff bases with the synthesized 1-bromo, 4-[4-(4-nitrophenylazo) phenoxy] butane and formation of novel linear azo-azomethine compounds in good to excellent yields were investigated. The compounds were fully characterized by UV-Vis, FT-IR, <sup>1</sup>H NMR spectroscopic techniques and elemental analysis. Effects of various solvents on their visible absorption spectra at a concentration of 10<sup>-5</sup>-10<sup>-6</sup> M were estimated. The color of the dyes is discussed with respect to the substituent therein. Introduction of an electron-withdrawing group into the para-position of azomethines produces bathochromic shift of the absorption peak in all solvents. The key features of these reactions are, in turn, their operational simplicity, mild reaction conditions and easily-accessed starting materials. Prog. Color Colorants Coat. 5(2012), 23-33. © Institute for Color Science and Technology.

### 1. Introduction

Having versatile applications in miscellaneous areas such as electrophotography, laser printing, reversible optical storage, nonlinear optical (NLO) devices and liquid crystalline displays (LCDs), azo compounds have been of utmost importance as colorants [1-6].

On growing demands for preparation of new materials better suited for these technological applications, we were prompted to design and synthesize new colorants having special characteristics. Regarding that compounds with azo benzene groups show substantial photochromic effects, it can be deduced that

such linear systems having azo benzene and azomethine moieties (Schiff-bases) would be exceptionally promising for these new applications. The significant optical features of these groups can be mainly attributed to the (E)- to (Z)- photoisomerisation of the azobenzene group upon irradiation with different wavelength beams which change the absorption of these dyes in a reversible way [7-17].

Another reason behind the ever-expanding interest in preparation of azo compounds containing Schiff-base ligands lies in their wide use as dyestuff in textile industry which is prominently due to their excellent

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coloring features. As well as all aforementioned applications, they also can be utilized in photonic devices, electro-optic modulators and components of optical communication systems owing to their second order nonlinear optical properties. Hence, it is no wonder why these kinds of dyes have been the matter of discussion in recent research [18-21].

Regarding their outstanding features and in continuation of our efforts into the synthesis and investigation of new azo compounds [22-26], herein we report synthesis of some novel linear etherized azo-azomethine compounds prepared from 1-bromo, 4-[4-(4-nitrophenylazo) phenoxy] butane and a number of Schiff-base ligands.

## 2. Experimental

### 2.1. Material and instrumentation

All reagents were of the highest purity available, purchased from Merck Chemical Companies and were used without further purification. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer. All melting points were determined on an electrothermal melting point apparatus. Infrared spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer. The  $^1\text{H}$  NMR spectra were obtained on a FT-NMR (500MHz) Bruker apparatus spectrometer, and the chemical shifts are expressed in  $\delta$  ppm using TMS as an internal standard. UV-Vis absorption spectra were obtained using a Pharmacia Biotech Spectrophotometer.

### 2.2. A general procedure for the synthesis of azomethines (1a-i)

These compounds were prepared through condensation of 4-aminophenol (0.003 mol) with some carbocyclic and heterocyclic aldehydes (0.003 mol) by refluxing the reagents in absolute ethanol (EtOH) ( $50 \times 10^{-6} \text{ m}^3$ ) in the presence of a few drops of acetic acid, as catalyst, at  $T = 353.15 \text{ K}$ . The procedure was carried on until no starting material could be detected on TLC test plate. The reaction was completed in about 1-2 hours. Having cooled down to room temperature, the solution was added into ice-water mixture. The reaction mixture was then vacuum filtered and the obtained crude imines were purified using recrystallization from DMF. The physical and spectral properties of the purified dyes are summarized in Table 1.

### 2.3. 4-(4-Nitrophenylazo) phenol (2)

Dissolving 4-Nitroaniline (0.003 mol) in EtOH ( $10 \times 10^{-6} \text{ m}^3$ ) and  $\text{H}_2\text{O}$  ( $30 \times 10^{-6} \text{ m}^3$ ) utilizing concentrated sulfuric acid, the mixture was cooled to  $276.15 \text{ K}$ . Then, a solution of  $\text{NaNO}_2$  (0.003 mol) in  $\text{H}_2\text{O}$  ( $5 \times 10^{-6} \text{ m}^3$ ), was poured dropwise into the mixture and stirred for 45-60 min. When added a solution of phenol (0.003 mol) in water ( $10 \times 10^{-6} \text{ m}^3$ ), the mixture was stirred for an additional 1 hour while being maintained at pH 8-9, using NaOH solution (0.5 M). Next, dilute hydrochloric acid (10 %) in conjunction with water was added and the resulting precipitate collected by filtration was crystallized from EtOH/ $\text{H}_2\text{O}$  solution.

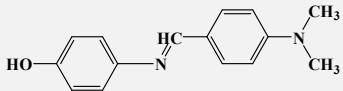
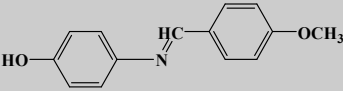
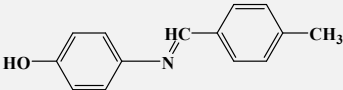
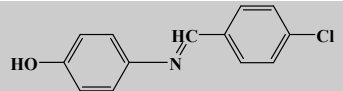
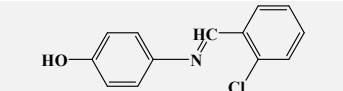
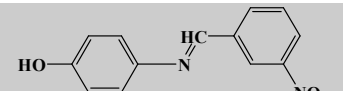
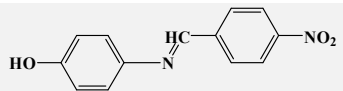
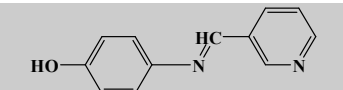
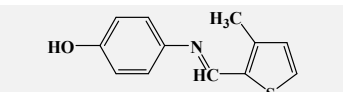
Red solid (92%).Mp:  $208-210 \text{ }^\circ\text{C}$ . UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 368. IR (KBr):  $\nu$  3410, 3070, 1580, 1505, 1458, 1400, 1360, 1278, 1130, 860  $\text{cm}^{-1}$ . Yield:  $^1\text{H}$  NMR (DMSO- $d_6$ ): 8.29 (2H, d,  $J = 8.5 \text{ Hz}$ , Ar-H), 7.90 (4H, dd,  $J = 8.5 \text{ Hz}$ ,  $J = 5.7 \text{ Hz}$ , Ar-H), 7.10 (2H, d,  $J = 5.6 \text{ Hz}$ , Ar-H), 5.85 (1H, s, Ar-OH). Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_3$ : C, 59.26; H, 3.73; N, 17.28%. Found: C, 59.12; H, 3.57; N, 17.21%.

### 2.4. 1-Bromo -4 -(4-nitrophenylazo) phenoxy-butane as target product (3)

To prepare compound 3, 4-(4-Nitrophenylazo) phenol 2 (0.004 mol) was dissolved in DMF ( $40 \times 10^{-6} \text{ m}^3$ ) with potassium carbonate (0.02 mol), and a 6-fold excess of 1,4-dibromobutane (0.024 mol) being added simultaneously. Afterwards, the mixture was refluxed for 6 hours followed by filtering in order to remove excess 1, 4-dibromobutane, acetone was added in which the product was insoluble. The filtrate was then dissolved in  $\text{CH}_2\text{Cl}_2$  and  $\text{H}_2\text{O}$  (1:1). Having successively washed the organic phase with dilute hydrochloric acid (10 %) and water, the organic fraction was dried over sodium sulfate and the solvent was removed under reduced pressure. In the end, the highly pure product was obtained after recrystallization from DMF.

Orange solid with metallic luster (88 %). Mp:  $98-100 \text{ }^\circ\text{C}$ . UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 360. IR (KBr):  $\nu$  3070, 2850, 1600, 1520, 1340, 1246, 1130, 860  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.05 (quintet, 2H,  $\text{CH}_2$ ,  $J = 3.3 \text{ Hz}$ ), 2.15 (quintet, 2H,  $\text{CH}_2$ ,  $J = 3.4 \text{ Hz}$ ), 3.55 (t, 2H,  $\text{CH}_2$ ,  $J = 6.4 \text{ Hz}$ ), 4.16 (t, 2H,  $\text{CH}_2$ ,  $J = 6.4 \text{ Hz}$ ), 7.06 (d, 2H, Aro.-H,  $J = 6.9 \text{ Hz}$ ), 8.00 (d, 2H, Aro.-H,  $J = 6.9 \text{ Hz}$ ), 8.04 (d, 2H, Aro.-H,  $J = 6.9 \text{ Hz}$ ), 8.40 (d, 2H, Aro.-H,  $J = 6.9 \text{ Hz}$ ).

**Table 1:** The structure, physical and spectral data of synthesized azomethine (1a-i).

Yield(%)	$\lambda_{\max}$ (nm) in DMF	FT-IR ( $\text{cm}^{-1}$ )	Color	Mp $^{\circ}\text{C}$	Chemical structure	Compound
85	348	3400, 2900, 1610, 1540, 1500	Yellow	294-296		1a
82	321	3200, 2880, 1608, 1503, 1440	Yellow	198-200		1b
84	325	3000, 2700, 1610, 1504, 1440	Dark yellow	208-210		1c
88	330	3200, 2880, 1618, 1500, 1440	Yellow	182-184		1d
85	333	3250, 2900, 1608, 1500, 1440	Yellow	156-158		1e
92	330	3080, 2800, 1618, 1512, 1440	Yellow	164-166		1f
98	336	3420, 2890, 1580, 1504, 1440	Orange	194-196		1g
94	330	3000, 2750, 1585, 1500, 1424	Yellow	218-220		1h
90	336	3100, 2800, 1608, 1502, 1446	Yellow	160-162		1i

#### 2.4.1. 1,4-bis-(4-nitrophenylazo) phenoxybutane as by-product (3a)

The compound 3a was not soluble in used solvents; so it was easily separated and crystallized from the solution.

Orange solid (12 %).Mp: 254 – 256  $^{\circ}\text{C}$ . UV-Vis (DMF),  $\lambda_{\max}$  (nm) 360. IR (KBr):  $\nu$  3070, 2850, 1600, 1520, 1340, 1246, 1130, 860  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.10 (quintet, 4H,  $\text{CH}_2$ ), 4.23 (triplet, 4H,  $\text{CH}_2$ ), 7.10 (d, 4H, Aro.-H,  $J = 8.9$  Hz), 8.02 (overlapped, 8H, Aro.-H), 8.40 (d, 4H, Aro.-H,  $J = 8.9$  Hz). Anal.Calcd for

$\text{C}_{28}\text{H}_{24}\text{N}_6\text{O}_6$ : C, 62.22; H, 4.48; N, 15.55%. Found: C, 62.13; H, 4.36; N, 15.37%.

#### 2.5. A general procedure for synthesis of azo-azomethine compounds (4a-i)

In the next stage,  $\text{K}_2\text{CO}_3$  (0.002 mol) was added to the compound 3 dissolved in DMF and submitted to 3 hours refluxes in DMF. Pouring the mixture into the ice-cooled water and acidified with dilute hydrochloric acid (10%), the resulting precipitate was filtered off and partitioned

between  $\text{CH}_2\text{Cl}_2$  and  $\text{H}_2\text{O}$ . The organic phase was then washed with  $\text{Na}_2\text{CO}_3$  solution and  $\text{H}_2\text{O}$ , dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated under reduced pressure. Likewise the previously described procedure, recrystallization was carried out using DMF.

#### 2.5.1. 1-[4-(4-nitrophenylazo)] phenoxy, 4-(4-(dimethylamino)benzylideneamino) phenoxy butane (4a):

Orange solid (72 %). Mp: 270 – 272 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 333. IR (KBr):  $\nu$  3100, 2900, 1600, 1506, 1360, 1240, 1020  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  1.92 (m, 4H,  $\text{CH}_2$ ), 3.20 (s, 6H, N- $\text{CH}_3$ ), 4.10 (t, 2H,  $\text{OCH}_2$ , J = 5.7 Hz), 4.22 (t, 2H,  $\text{OCH}_2$ , J = 5.7 Hz), 6.98 (d, 2H, Aro.-H, J = 9.1 Hz), 7.12 (d, 2H, Aro.-H, J = 8.8 Hz), 7.20 (d, 2H, Aro.-H, J = 8.8 Hz), 7.64 (d, 2H, Aro.-H, J = 8.9 Hz), 7.96 (d, 2H, Aro.-H, J = 8.8 Hz), 8.03 (d, 2H, Aro.-H, J = 8.7 Hz), 8.07 (d, 2H, Aro.-H, J = 6.5 Hz), 8.40 (d, 2H, Aro.-H, J = 8.79 Hz), 8.96 (s, 1H, =CH). Anal. Calcd for  $\text{C}_{31}\text{H}_{31}\text{N}_5\text{O}_4$ : C, 69.26; H, 5.81; N, 13.03%. Found: C, 69.04; H, 5.70; N, 13.21%.

#### 2.5.2. 1-[4-(4-nitrophenylazo)]phenoxy, 4-(4-(methoxy)benzylideneamino) phenoxy butane (4b):

Orange solid (75 %). Mp: 202 – 204 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 336. IR (KBr):  $\nu$  3090, 2900, 1600, 1505, 1340, 1230, 1010  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{DMSO-d}_6$ )  $\delta$  1.98 (m, 4H,  $\text{CH}_2$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ), 4.03 (t, 2H,  $\text{OCH}_2$ , J = 5.7 Hz), 4.12 (t, 2H,  $\text{OCH}_2$ , J = 5.7 Hz), 6.86 (d, 2H, Aro.-H, J = 7.7 Hz), 6.92 (d, 2H, Aro.-H, J = 7.8 Hz), 6.99 (d, 2H, Aro.-H, J = 7.9 Hz), 7.16 (br, 2H, Aro.-H), 7.79 (br, 2H, Aro.-H), 7.92 (m, 4H, Aro.-H), 8.30 (d, 2H, Aro.-H, J = 7.9 Hz), 8.36 (s, 1H, =CH). Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_5$ : C, 68.69; H, 5.38; N, 10.68%. Found: C, 68.55; H, 5.20; N, 10.88%.

#### 2.5.3. 1-[4-(4-nitrophenylazo)]phenoxy, 4-(4-(methyl)benzylideneamino)phenoxy butane (4c):

Orange solid (80 %). Mp: 210 – 212 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 343. IR (KBr):  $\nu$  3080, 2910, 1600, 1520, 1340, 1230, 1020  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{DMSO-d}_6$ )  $\delta$  2.00 (m, 4H,  $\text{CH}_2$ ), 2.44 (s, 3H,  $\text{CH}_3$ ), 4.10 (t, 2H,  $\text{OCH}_2$ , J = 5.8 Hz), 4.19 (t, 2H,  $\text{OCH}_2$ , J = 5.6 Hz), 6.96 (d, 2H, Aro.-H, J = 8.7 Hz), 7.05 (d, 2H, Aro.-H, J = 8.6 Hz), 7.28 (d, 2H, Aro.-H, J = 8.7 Hz), 7.80 (br, 2H, Aro.-H),

7.99 (m, 4H, Aro.-H), 8.38 (d, 2H, Aro.-H, J = 8.9 Hz), 8.47 (s, 1H, =CH). Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_4$ : C, 70.85; H, 5.55; N, 11.02%. Found: C, 70.76; H, 5.46; N, 10.88%.

#### 2.5.4. 1-[4-(4-nitrophenylazo)] phenoxy, 4-(4-(chloro)benzylideneamino)phenoxy butane (4d):

Orange solid (82 %). Mp: 220 – 222 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 350. IR (KBr):  $\nu$  3060, 2880, 1596, 1500, 1336, 1134, 1010, 814  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.10 (m, 4H,  $\text{CH}_2$ ), 4.13 (t, 2H,  $\text{OCH}_2$ , J = 5.6 Hz), 4.21 (t, 2H,  $\text{OCH}_2$ , J = 5.8 Hz), 6.98 (m, 2H, Aro.-H), 7.08 (m, 2H, Aro.-H), 7.26 (d, 2H, Aro.-H, J = 7.1 Hz), 7.46 (d, 2H, Aro.-H, J = 8.4 Hz), 7.88 (d, 2H, Aro.-H, J = 8.3 Hz), 8.02 (m, 4H, Aro.-H), 8.40 (d, 2H, Aro.-H, J = 8.5 Hz), 8.49 (s, 1H, =CH). Anal. Calcd for  $\text{C}_{29}\text{H}_{25}\text{ClN}_4\text{O}_4$ : C, 65.84; H, 4.76; Cl, 6.70; N, 10.59%. Found: C, 65.69; H, 4.69; N, 10.66%.

#### 2.5.5. 1-[4-(4-nitrophenylazo)] phenoxy, 4-(2-(chloro) benzylideneamino)phenoxy butane (4e):

Orange solid (84 %). Mp: 210 – 212 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 354. IR (KBr):  $\nu$  3060, 2920, 1596, 1500, 1340, 1248, 1138, 1008, 826  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{DMSO-d}_6$ )  $\delta$  2.08 (m, 4H,  $\text{CH}_2$ ), 4.14 (t, 2H,  $\text{OCH}_2$ , J = 5.8 Hz), 4.19 (t, 2H,  $\text{OCH}_2$ , J = 5.6 Hz), 7.00 (d, 2H, Aro.-H, J = 6.8 Hz), 7.08 (d, 2H, Aro.-H, J = 7.0 Hz), 7.34 (d, 2H, Aro.-H, J = 8.6 Hz), 7.44 (m, 3H, Aro.-H), 8.02 (m, 4H, Aro.-H), 8.30 (d, 1H, Aro.-H, J = 6.9 Hz), 8.40 (d, 2H, Aro.-H, J = 7.2 Hz), 8.99 (s, 1H, =CH). Anal. Calcd for  $\text{C}_{29}\text{H}_{25}\text{ClN}_4\text{O}_4$ : C, 65.84; H, 4.76; Cl, 6.70; N, 10.59%. Found: C, 65.62; H, 4.85; N, 10.52%.

#### 2.5.6. 1-[4-(4-nitrophenylazo)]phenoxy, 4-(3-(nitro)benzylideneamino)phenoxy butane (4f):

Orange solid with metallic luster (85 %). Mp: 161 – 163 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 355. IR (KBr):  $\nu$  3080, 2960, 1600, 1518, 1340, 1250, 1118, 1006, 830  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.10 (m, 4H,  $\text{CH}_2$ ), 4.15 (t, 2H,  $\text{OCH}_2$ , J = 5.6 Hz), 4.22 (t, 2H,  $\text{OCH}_2$ , J = 5.8 Hz), 7.00 (d, 2H, Aro.-H, J = 6.7 Hz), 7.09 (d, 2H, Aro.-H, J = 7.1 Hz), 7.34 (d, 2H, Aro.-H, J = 6.7 Hz), 7.69 (t, 1H, Aro.-H, J = 7.9 Hz), 8.02 (m, 4H, Aro.-H), 8.28 (d, 1H, Aro.-H, J = 7.6 Hz), 8.35 (m, 1H, Aro.-H), 8.40 (m, 2H, Aro.-H), 8.61 (s, 1H, =CH), 8.77 (s, 1H, Aro.-H). Anal. Calcd for  $\text{C}_{29}\text{H}_{25}\text{N}_5\text{O}_6$ : C, 64.56; H, 4.67; N, 12.98%. Found: C, 64.43; H, 4.58; N, 12.88%.

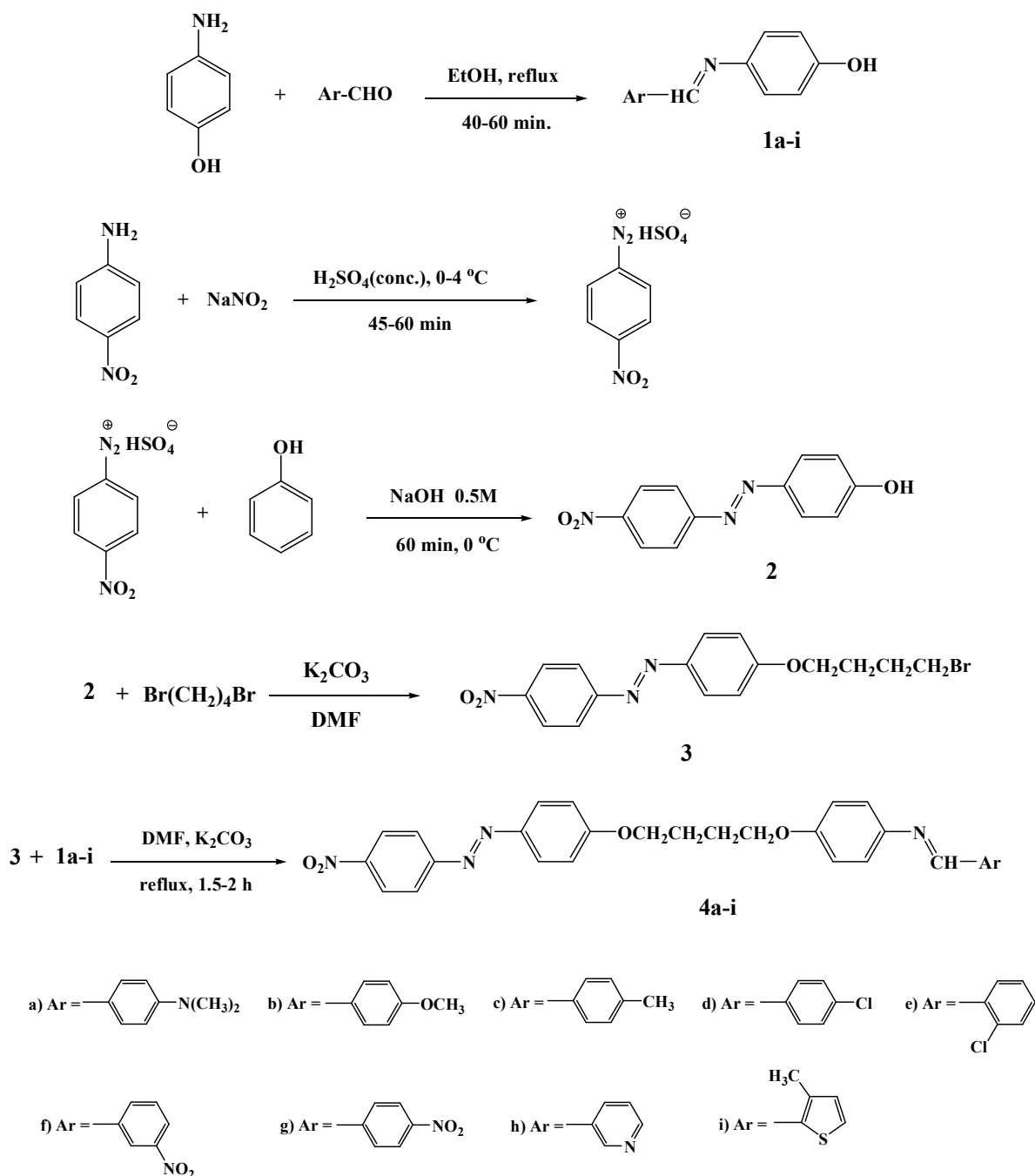


Figure 1: The structure of synthesized azo-azomethine compounds.

### 2.5.7. 1-[4-(4-nitrophenylazo)]phenoxy, 4-(4-(nitro)benzylideneamino)phenoxy butane (4g):

Orange solid (92 %). Mp: 212 – 214 °C. UV-Vis (DMF),  $\lambda_{\text{max}}$  (nm) 363. IR (KBr):  $\nu$  3080, 2910, 1578, 1518, 1318, 1250, 1138, 1042, 834  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$

2.12 (m, 4H,  $\text{CH}_2$ ), 4.15 (t, 2H,  $\text{OCH}_2$ ,  $J = 5.6$  Hz), 4.22 (t, 2H,  $\text{OCH}_2$ ,  $J = 5.6$  Hz), 7.01 (m, 2H, Aro.-H), 7.08 (m, 2H, Aro.-H), 7.34 (d, 2H, Aro.-H,  $J = 8.0$  Hz), 8.02 (m, 4H, Aro.-H), 8.12 (d, 2H, Aro.-H,  $J = 8.1$  Hz), 8.36 (d, 2H, Aro.-H,  $J = 8.7$  Hz), 8.40 (m, 2H, Aro.-H), 8.63

(s, 1H, =CH). Anal.Calcd for  $C_{29}H_{25}N_5O_6$ : C, 64.56; H, 4.67; N, 12.98%. Found: C, 64.47; H, 4.61; N, 12.91%.

### 2.5.8. 1-[4-(4-nitrophenylazo)]phenoxy, 4-((pyridine-3-yl)methyleneamino)phenoxy butane (4h):

Orange solid with metallic luster (88 %). Mp: 186 - 188 °C. UV-Vis (DMF),  $\lambda_{max}$  (nm) 353. IR (KBr):  $\nu$  3060, 2920, 1590, 1510, 1340, 1250, 1138, 1010, 828  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.10 (m, 4H,  $CH_2$ ), 4.14 (t, 2H,  $OCH_2$ ,  $J = 5.7$  Hz), 4.22(t, 2H,  $OCH_2$ ,  $J = 5.7$  Hz), 7.00 (m, 2H, Aro.-H), 7.09 (m, 2H, Aro.-H), 7.30 (m, 2H, Aro.-H), 7.47 (t, 1H, Aro.-H,  $J = 6.2$  Hz), 8.00 (m, 4H, Aro.-H), 8.35 (d, 1H, Aro.-H,  $J = 7.9$  Hz), 8.40 (m, 2H, Aro.-H), 8.57 (s, 1H, =CH), 8.74 (br, 1H, Aro.-H), 9.06 (s, 1H, Aro.-H). Anal.Calcd for  $C_{28}H_{25}N_5O_4$ : C, 67.87; H, 5.09; N, 14.13%. Found: C, 67.73; H, 5.00; N, 14.02%.

### 2.5.9. 1-[4-(4-nitrophenylazo)]phenoxy, 4-((3-methylthiophen-2-yl)methyleneamino)phenoxy butane (4i):

Orange solid with metallic luster (80 %). Mp: 178 - 180 °C. UV-Vis (DMF),  $\lambda_{max}$  (nm) 352. IR (KBr):  $\nu$  3050, 2930, 1600, 1500, 1340, 1240, 1118, 1012, 830  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.08 (m, 4H,  $CH_2$ ), 2.50 (s, 1H,  $CH_3$ ), 4.12 (t, 2H,  $OCH_2$ ,  $J = 5.7$  Hz), 4.21(t, 2H,  $OCH_2$ ,  $J = 5.8$  Hz), 6.96 (m, 3H, Aro.-H), 7.07 (m, 2H, Aro.-H), 7.26 (d, 2H, Aro.-H,  $J = 8.3$  Hz), 7.44 (d, 1H, Aro.-H,  $J = 4.7$  Hz), 8.02 (m, 4H, Aro.-H), 8.41 (m, 2H, Aro.-H), 8.66 (s, 1H, =CH). Anal.Calcd for  $C_{28}H_{26}N_4O_4S$ : C, 65.35; H, 5.09; N, 10.89%. Found: C, 65.46; H, 5.04; N, 10.96%.

## 3. Result and discussion

### 3.1. Synthesis and characterization

Our aim to synthesize target compounds 4a-i, was achieved via a three-step process in which, initially a series of Schiff-bases were prepared through condensation of carbocyclic and heterocyclic aldehydes with 4-aminophenol by refluxing in absolute EtOH in the presence of a few drops of acetic acid as catalyst. The synthesized azomethines were in excellent yields and their structures were featured by M.P., UV-Vis and IR spectroscopic techniques (see Figure 1 and Table 1).

In the next step, azo dye 2 was prepared by the reaction of 4-nitroaniline and phenol via classical diazotization and coupling reactions to serve as foundation in the desirable products. In pursuit of our goal for synthesis of 1-Bromo-4-(4-nitrophenylazo) phenoxybutane as basic intermediate to attain compound 3, the pre-made compound 2 was permitted to treat with excess 1,4-dibromobutane in the presence of a base under refluxing condition. Finally, target linear azo-azomethine products 4a-i were synthesized by the reaction of compound 3 with a series of pre-made carbocyclic and heterocyclic synthetic Schiff-bases 1a-i in the presence of potassium carbonate as base (see Figure 1 and Table 2). Structures of the compounds were fully characterized by elemental analysis (M.P.) and spectroscopic techniques (UV-Vis, IR and  $^1H$  NMR).

As anticipated, these reactions proceeded reasonably clean under refluxing condition and no unwanted side reactions or by-products were observed with the exception of alkylation reaction in the synthesis of compound 3, for which a slight formation of bisazo by-product 3a was discerned (Figure 2).

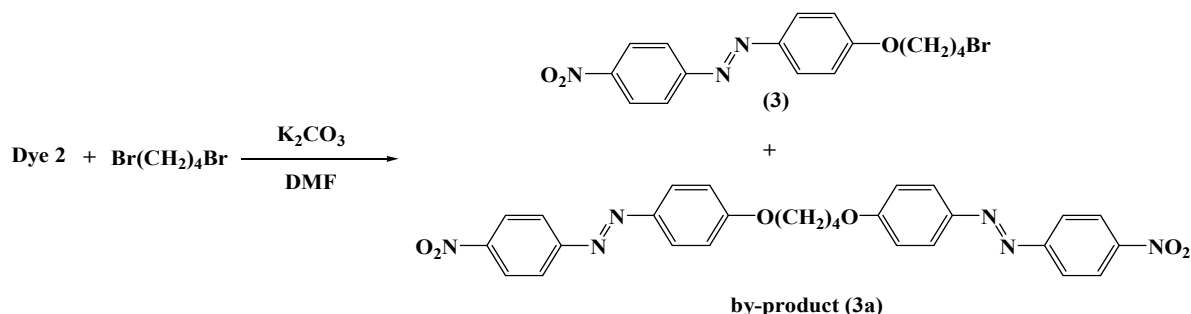
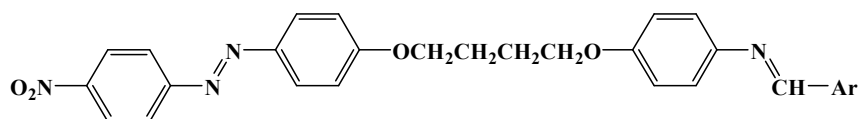


Figure 2: The structure of the synthesized compounds 3 and by-product 3a.

**Table 2:** The structure, physical and spectral data of synthesized azo-azomethines(4a-i).


Yield %	$\lambda_{\max}$ (nm) inDMF	Color	Mp <sup>o</sup> C	Empirical formula	Ar.	Compound
72	333	Orange	270-272	C <sub>31</sub> H <sub>31</sub> N <sub>5</sub> O <sub>4</sub>		4a
75	336	Orange	202-204	C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>5</sub>		4b
80	343	Orange	210-212	C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub>		4c
82	350	Orange	220-222	C <sub>29</sub> H <sub>25</sub> N <sub>4</sub> O <sub>4</sub> Cl		4d
84	354	Orange	210-212	C <sub>29</sub> H <sub>25</sub> N <sub>4</sub> O <sub>4</sub> Cl		4e
85	355	Orange	178-180	C <sub>29</sub> H <sub>25</sub> N <sub>5</sub> O <sub>6</sub>		4f
92	363	Orange	212-214	C <sub>29</sub> H <sub>25</sub> N <sub>5</sub> O <sub>6</sub>		4g
88	353	Metallic Orange	168-188	C <sub>28</sub> H <sub>25</sub> N <sub>5</sub> O <sub>4</sub>		4h
80	352	Metallic Orange	178-180	C <sub>28</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> S		4i

The structures of compounds were confirmed by their spectral data in deuterio-chloroform (CDCl<sub>3</sub>), deuterio-dimethylsulfoxide (DMSO-d<sub>6</sub>), and the signals were reported at TMS as the internal reference.

The IR spectral frequencies of synthesized compounds were carried out using KBr pellets as described in experimental Section. In all synthesized compounds, the azo (-N=N-) groups were observed at the range of 1500-1520 cm<sup>-1</sup>. The presence of imine (-CH=N-) group was also confirmed by FTIR spectroscopy.

The positions of these bands are almost the same for imines, namely 1578 cm<sup>-1</sup> to 1600 cm<sup>-1</sup> for synthesized compounds 4a-i. Physical and characterization data for all synthesized compounds are given in experimental Section and some selected IR data for compounds 1a-i are given in Table 1.

In <sup>1</sup>H NMR spectra of azo-azomethines 4a-i, the triplet of -OCH<sub>2</sub> and quintet of -CH<sub>2</sub> methylene protons appeared at 4.03-4.22 and 1.92-2.12 ppm, respectively. Also a significant singlet signal of imines =CH protons

was emerged at 8.36-8.99 ppm. The aromatic protons for all compounds were observed from 6.86 to 8.77 ppm in the  $^1\text{H}$  NMR spectra. Therefore, all assigned chemical shifts clearly confirm the formation of compounds 4a-i.

### 3.2. Solvent and substituent effects on the UV-Vis absorption spectra

It has long been known that UV-Vis/near-IR absorption spectra of chemical compounds especially those including azobenzene moiety influenced by the surrounding media and solvents can bring about a change in the position, intensity, and the shape of absorption bands [27]. In order to study solvent and substituent effects on spectral features of the dyes, we recorded their absorption spectra of azo-azomethines 4a-i in various solvents at a concentration of  $10^{-5}$ - $10^{-6}$  M in the range of 300-700 nm (Table 3), in which the solvents are arranged in the order of increasing solvent polarity scale ( $\pi^*$ ). The UV-Vis spectra of all synthesized compounds in studied solvents exhibited  $\lambda_{\text{max}}$  in the range of 325 to 372 nm which can be attributed to  $n \rightarrow \pi^*$  and/or  $\pi \rightarrow \pi^*$  electronic transitions of  $-\text{N}=\text{N}-$  and  $-\text{CH}=\text{N}-$  moieties. The dyes displayed a single main absorption peak without a shoulder in all solvents in the dark. The  $\lambda_{\text{max}}$  of all compounds were found to show a strong solvent dependency, denoting bathochromic effect (positive solvatochromism) in more polar solvents (Figure 3). On

the other hand, all studied dyes, exhibit a red shift as a result of an increase in the solvent polarity scale ( $\pi^*$ ). The spectral shift is mainly due to solute-solvent interactions that give rise to a better stabilization of the  $\pi^*$  orbital as compared to the  $\pi$  orbital in polar solvents. This fact accentuated on the contribution of both azomethine branches to the shifts of absorption spectra. Therefore, while azo group was constant in all dyes being considered, those containing electron withdrawing groups on azomethine parts represent higher values of  $\lambda_{\text{max}}$  in basic solvents such as DMSO and DMF.

The study of substituent effects bears a good deal of relation with the changes of  $\lambda_{\text{max}}$  in these dyes. As described earlier [23, 24], it can be implied that the more electron-withdrawing is a substituent, the greater is its  $\lambda_{\text{max}}$ . In this regard, our expectation that the compound possessing nitro group (4g) should show the highest value of  $\lambda_{\text{max}}$  was met. In contrast, the blue shift was observed for compounds 4a and 4b which is a direct result of having electron-donating groups. Given that the strong electron-withdrawing groups enhance the delocalization of conjugated system in such dyes, this behavior can be explained (Figure 4). As the full study of solvatochromic features and optical properties of all synthesized azo-azomethine compounds is beyond the scope of this paper, we will postpone it to our forthcoming work.

**Table 3:** Solvatochromic data [ $\lambda_{\text{max}}$ (nm)] for compounds 4a-i in 13 solvents with  $\pi^*$  values by Kamlet et al [28-30].

Compounds Solvents	$\pi^*$	4a $\lambda_{\text{max}}$ (log $\epsilon$ )	4b $\lambda_{\text{max}}$ (log $\epsilon$ )	4c $\lambda_{\text{max}}$ (log $\epsilon$ )	4d $\lambda_{\text{max}}$ (log $\epsilon$ )	4e $\lambda_{\text{max}}$ (log $\epsilon$ )	4f $\lambda_{\text{max}}$ (log $\epsilon$ )	4g $\lambda_{\text{max}}$ (log $\epsilon$ )	4h $\lambda_{\text{max}}$ (log $\epsilon$ )	4i $\lambda_{\text{max}}$ (log $\epsilon$ )
Diethyl ether	0.24	326(4.05)	325(4.09)	332(3.31)	339(5.07)	342(4.90)	345(5.42)	351(5.20)	339(3.01)	340(4.61)
Ethyl acetate	0.45	327(4.49)	325(4.17)	334(3.99)	343(4.55)	340(3.33)	348(4.59)	354(4.17)	342(3.88)	339(3.24)
Dioxane	0.49	327(4.03)	326(4.41)	337(5.03)	342(5.24)	344(3.89)	351(3.44)	357(6.25)	341(4.32)	342(3.78)
Ethanol	0.54	330(4.59)	332(4.40)	340(4.02)	346(5.72)	348(4.80)	352(6.03)	361(5.64)	349(5.04)	340(5.80)
Acetone	0.62	332(4.23)	334(4.28)	338(4.69)	345(5.23)	348(5.26)	353(4.11)	360(6.07)	345(6.34)	342(6.89)
Acetonitrile	0.66	330(4.49)	330(4.41)	338(3.72)	348(5.17)	349(4.09)	352(5.29)	358(4.23)	348(4.53)	346(5.09)
Chloroform	0.69	327(4.51)	328(4.48)	335(3.57)	345(4.95)	344(4.32)	347(3.89)	357(3.42)	344(3.76)	342(3.54)
Dichloro-methane	0.73	330(4.41)	331(4.33)	340(4.45)	348(6.01)	350(5.60)	352(4.74)	359(4.67)	347(5.34)	345(6.74)
DMF	0.88	333(4.59)	336(4.51)	343(5.42)	350(5.87)	354(4.70)	355(7.45)	363(5.92)	353(4.36)	352(5.69)
DMSO	1.00	337(4.51)	338(5.11)	349(4.98)	355(5.91)	357(4.22)	362(6.40)	372(6.18)	358(7.03)	355(3.94)



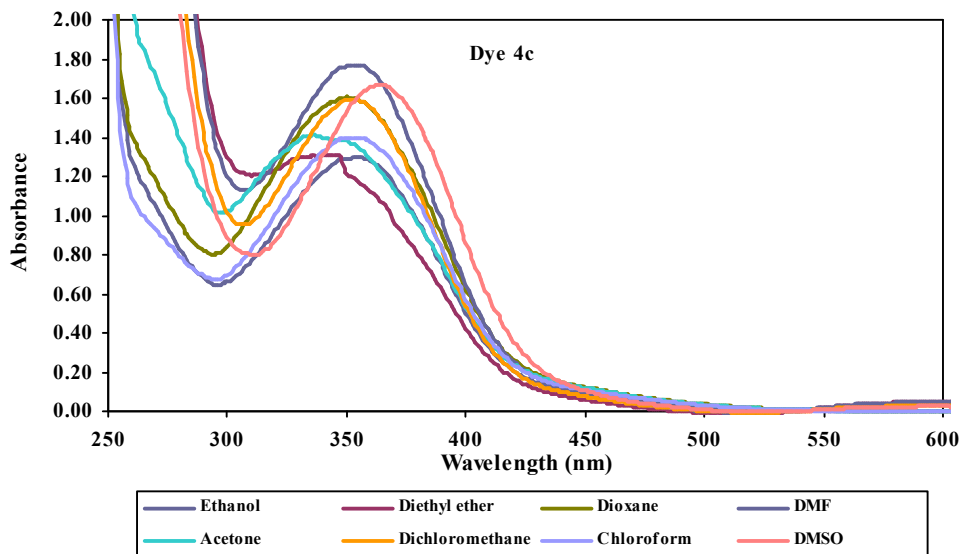


Figure 3: Electronic absorption spectra of compound 4c in different solvents.

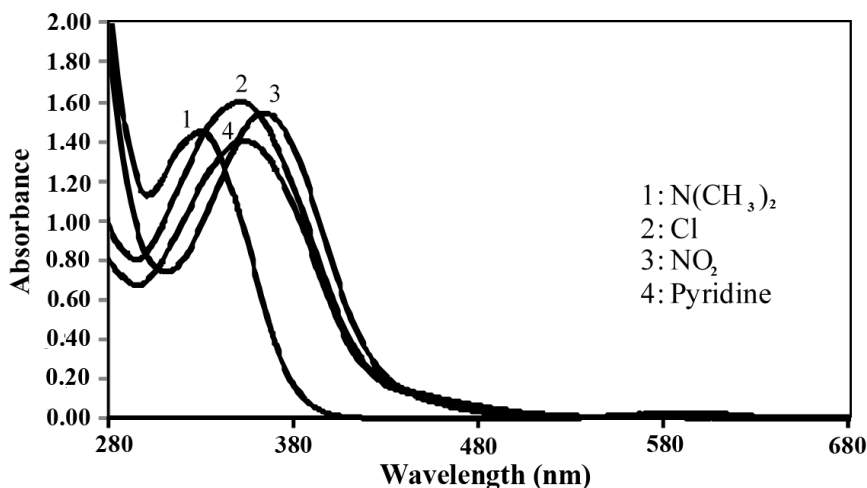


Figure 4: Electronic absorption spectra of compounds 4a, 4d, 4g and 4h in DMF.

#### 4. Conclusions

In summary, we have reported the synthesis of some novel linear azo-azomethine containing ether link compounds (4a-i) based on 1-bromo, 4-[4-(4-nitrophenylazo) phenoxy] butane (3) and pre-made carbocyclic and heterocyclic Schiff-bases (1a-i) was reported. The molecular structures of prepared compounds were confirmed by <sup>1</sup>H NMR, FTIR and UV-Vis spectra. These compounds were prepared in good yield via recrystallization procedures. The electronic

absorption spectra of dyes were recorded in solvents with different physical-chemical properties. A large bathochromic shift (positive solvatochromism) of these compounds was observed upon increasing the solvent polarity ( $\pi^*$ ). Also, introduction of electron-drawing group in the imine component resulted in the bathochromic effect in studied solvents. Probably, the obtained azo-azomethines could be used in mixtures with other LCs for LC displays.

## 5. References

1. T. Xie, D. Wang, L. Zhu, C. Wang, T. Li, X. Zhou, M. Wang, Application of surface photovoltage technique to the determination of conduction types of azo pigment films, *J. Phys. Chem. B.*, 104(2000), 8177-8181.
2. L. Lucarelli, V. Nadochenko, J. Kiwi, Environmental photochemistry: quantitative adsorption and FTIR studies during the TiO<sub>2</sub>-photocatalyzed degradation of orange II, *Langmuir.*, 16(2000), 1102-1108.
3. Y. Qian, G. Wang, G. Xiao, B. Lin, Y. Cui, The first-order molecular hyperpolarizability and thermal stability of charge-transfer azo diol and azo aldimine., *Dyes Pigm.*, 75(2007), 460-465.
4. F. Qiu, Y. Cao, H. Xu, Y. Jiang, Y. Zhou, J. Liu, Synthesis and properties of polymer containing azo-dye chromophores for nonlinear optical applications, *Dyes Pigm.*, 75(2007), 454-459.
5. B. K. So, H. J. Kim, S. M. Lee, H. H. Song, J. H. Park, Novel bent-shaped liquid crystalline compounds: IV. Dimesogenic compounds containing 2-hydroxy-1,3-dioxypolyene and azobenzene-emesogens, *Dyes Pigm.*, 70(2006), 38-42.
6. R. Gimenez, M. Millaruelo, M. Pinol, J. L. Serrano, A. Vinales, R. Rosenhauer, T. Fischer, J. Stumpe, Synthesis, thermal and optical properties of liquid crystalline terpolymers containing azobenzene and dye moieties, *Polym.*, 46(2005), 9230-9242.
7. J. A. Delaire, K. Nakatani, Linear and nonlinear optical properties of photochromic molecules and materials, *Chem. Rev.*, 100(2000), 1817-1845.
8. K. Ichimura, Photoalignment of liquid-crystal systems., *Chem. Rev.*, 100(2000), 1847-1873.
9. J. C. Paulo, L. M. Carvalho, A. M. C. Fonseca, M. M. Raposo, Photochromic properties of thienylpyrrole azo dyes in solution, *Tetrahedron Lett.*, 47(2006), 3711-3714.
10. A. H. Uladzimir, V. S. Svetlana, V. T. Nelson, H. Landa, M. S. Diane, R. K. Brian, Azobenzene liquid crystalline materials for efficient optical switching with pulsed and/or continuous wave laser beams, *Opt Express*, 18(2010), 8697-8704.
11. A. Iwan, D. Pocięcha, A. Sikora, H. Janeczek, M. Węgrzyn, Characterisation and mesomorphic behaviour of new aliphatic-aromatic azomethines containing ester groups, *Liq. Cryst.*, 37(2010), 1479-1492.
12. A. Iwan, H. Janeczek, B. Jarzabek, P. Rannou, Mesomorphic behavior of symmetrical and unsymmetrical azomethines with two imine groups, *Mater.*, 2(2009), 38-61.
13. A. Iwan, H. Janeczek, B. Jarzabek, M. Domanski, P. Rannou, Characterization, optical and thermal properties of new azomethines based on heptadecafluoroundecyloxybenzaldehyde, *Liq. Cryst.*, 36(2009), 873-883.
14. A. Iwan, H. Janeczek, M. Domanski, P. Rannou, Synthesis, characterization and mesomorphic properties of new unsymmetrical azomethine-type liquid crystals derived from 4-biphenyl carboxaldehyde, *J. Mol. Liq.*, 151(2010), 30-38.
15. P. A. Henderson, C. T. Imrie, Semiflexible liquid crystalline tetramers as models of structurally analogous copolymers, *Macromol.*, 38(2005), 3307-3311.
16. A. R. Abbasi, Z. Rezvani, K. Nejati, Synthesis and properties of new liquid crystalline compounds containing an alkoxyphenylazo group, *Dyes Pigm.*, 70(2006), 71-75.
17. L. Hamryszak, H. Janeczek, E. Schab-Balcerzak, New thermotropic symmetrical and unsymmetrical azomethine with azobenzene unit and fluorinated alkyl chain: Synthesis and characterization, *J. Mol. Liq.*, 165(2012), 12-20.
18. A. Yavrian, T. V. Galstian, M. Piche, Photo induced absorption and refraction in azo dye doped PMMA films: the aging effect, *Opt. Mater.*, 26(2004), 261-265.
19. K. Ogawa, J. Harada, Aggregation controlled proton tautomerization in salicylideneanilines, *J. Mol. Struct.*, 647(2003), 211-216.
20. M. Matsui, M. Tsuge, K. Funabiki, K. Shibata, H. Muramatsu, K. Hirota, M. Hosoda, K. Tai, H. Shiozaki, M. Kim, K. Nakatsu, Synthesis of azo chromophores containing a perfluorocyclo-alkenyl moiety and their second-order optical nonlinearity, *J. Fluorine Chem.*, 97(1999), 207-212.
21. I. Zadrozna, E. Kaczorowska, Synthesis and characteristics of azo chromophors for nonlinear-optical application, *Dyes Pigm.*, 71(2006), 207-211.
22. M. R. Yazdanbakhsh, N. O. Mahmoodi, S. Dabiry, Preparation and characterization of diazenyl quinolin-8-ol with trifluoromethyl substituents, *Mendeleev Commun.*, 3(2006), 192-194.
23. M. R. Yazdanbakhsh, A. Mohammadi, Synthesis, substituent effects and solvatochromic properties of

- some disperse azo dyes derived from N-phenyl-2, 2'-iminodiethanol, *J. Mol. Liq.*, 148(2009), 35-39.
24. M. R. Yazdanbakhsh, A. Mohammadi, E. Mohajerani, H. Nemati, N. Hosain-Nataj, A. Moheghi, E. Naemikhah, Novel azo disperse dyes derived from N-benzyl-N-ethyl-aniline: Synthesis, solvatochromic and optical properties, *J. Mol. Liq.*, 151(2010), 107-112.
25. M. R. Yazdanbakhsh, M. Abasnia, M. Sheykhani, M. Leila, Synthesis, characterization and application of new azo dyes derived from uracil for polyester fibre dyeing, *J. Mol. Struct.*, 977(2010), 266-273.
26. M. R. Yazdanbakhsh, A. Mohammadi, M. Abbasnia, Some heterocyclic azo dyes derived from thiazolyl derivatives; synthesis, substituent effects and solvatochromic studies, *Spectrochim. Acta, Part A*, 77(2010), 1084-1087.
27. R. Christian, Solvatochromic dyes as solvent polarity indicators, *Chem. Rev.*, 94(1994), 2319-2358.
28. C. Reichardt, Solvents and solvent effects in organic chemistry, Weinheim Wiley-VCH, 2003.
29. M. J. Kamlet, J. L. Abboud, M. H. Abraham, R. W. Taft, linear solvation energy relationship: 23: a comprehensive collection of the solvatochromatic parameters  $\rho$ ,  $\alpha$  and  $\beta$  and some methods for simplifying the generalized solvatochromatic equation, *J. Org. Chem.*, 48(1983), 2877-2887.
30. D. R. Lide (Ed.), Handbook of Chemistry and Physics, 76th Edition, CRC Press, Boca Raton, 1995.