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New azoic dyes containing (1H)-tetrazole and azido group

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Abstract

The synthesis of new azoic-dyes containing aryloxytetrazole functional group is reported. The 5-(4′-aminophenoxy)tetrazole was diazotized and coupled with the electron rich aromatic rings. All dyes were characterized by ^{1}H-NMR, ^{13}C-NMR, IR, and UV–vis spectroscopies. They all decomposed above 174 °C except dye derived from 4-nitrophenol, which released nitrogen at 86 °C to produce tar. These dyes are yellow, brown, or red in color. All dyes are soluble in basic media. The imidoyl azide derivative of dye derived from β-naphthol produced unexpected hydroxylamine derivative in refluxing 1,4-dioxane. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Azoic dyes; (1H)-Tetrazole; Diazo coupling; Imidoyl azide; Nitrene insertion

1. Introduction

Azoic dyes are the most important group of all synthetic dyes. These dyes possess a wide range of deep colors (yellow, red, orange, violet, dark blue or green) [1,2]. One of the most important points that must be considered in dye design is the solubility of dye in common solvents. This is important in terms of processibility in dyestuff industries. The most important solvent used in this industry is water due to its abundance, low cost, and environment-friendliness. To improve the solubility of dyes in water, –COONa, –SO$_3$Na and quaternary ammonium salt groups are incorporated into the structure of the dye.

The nature of (1H)-tetrazole (–CN$_4$H) group is very similar to carboxylic acid (–COOH) group with respect to acidity (pK_a ≈5) and solubility. Furthermore, it is more stable than carboxylic acid group. It has been widely used as a carboxylic acid pharmacophore in drug design [3]. Therefore, it can be used in place of carboxylic acid group in dye design for increasing solubility in water by convertion of them to their metal salt forms.

Tetrazole derivatives have been also used as anticancer, antimicrobial, antihypertensive and antiallergenic agents [4,5]. Recently, they have received increasing attention due to their particular activities and industrial applications. They form a very important family of precursors for other heterocyclic compounds containing nitrogen or sulfur moiety. For example, they can be readily converted to azides, which are very important precursors to many classes of compounds such as amines, aziridines, diaziridines, isourea, oxadiazoles, and others [6]. Therefore, introducing an azide group into the azoic dyes must lead to a wide range of new reactive azoic dyes. Imidoyl azides,

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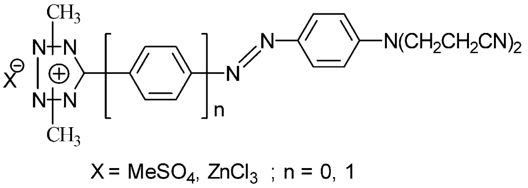


Scheme 1.

very reactive intermediates in organic chemistry and capable of a wide range of chemical reactions, release nitrogen to produce singlet imidoyl nitrenes by thermal or photochemical treatment [7].

Dabbagh and co-workers have used tetrazoles in a wide range of chemical reactions. They reported the equilibrium of 5-substituted 1- and 2-acyltetrazoles, thier thermal decomposition, and the conversion to imidoyl azides, isoureas and oxadiozoles [8–11].

There are very limited reports regarding the incorporation of tetrazole ring into azoic dyes in the literature. Vilarrasa [12,13], Shegal and coworkers [14] have reported on the incorporation of the tetrazole ring in azoic compounds by diazotization of 5-amino tetrazole followed by coupling with β-naphthol. The resulting compound was then dehydrated by heating in a polar solvent to produce naphthotetrazolo-1,2,4-triazine.

Guido et al. [15] prepared the cationic azoic dyes containing dimethyltetrazolium moiety by the diazotization of the amino group in the tetrazole ring followed by coupling with Ph–N(CH_2CH_2CN)$_2$ and then quaternizing the resulting azo-dye base (Scheme 1).

Due to increasing demand, attempts to improve the dyes for new applications is the major task for the dye industry. We believe we have found just the right system to generate new dyes to meet this demand. In this work, preparation of new family of aryloxytetrazoles-azoic and imidoyl azide-azoic dyes are reported. The advantages of these new dyes over previously reported dyes are that they can be easily converted into a wide range of stable derivatives including the imidoyl azides, imidoyl hydroxyamines and amines [8–10]. The oxygen atom has three important roles. The first and most important is its ability to separate the tetrazole functional group from the rest of the dye (no direct resonance between the tetarzole and the azo group). This allows reactions at the tetrazole center without a major change in the color of the dye. Secondly, these dyes can be converted to their water-soluble salt forms without affecting their color for the same reason. Finally, the oxygen has a stabilizing effect on the tetrazole and its derivatives. The inhibiting effect of tetrazole derivatives on copper corrosion in chloride solutions is another important property of these dyes [16].

2. Experimental

2.1. Materials

5-(4′-Aminophenoxy)tetrazole was prepared according to Ref. [17]. Nitrophenols were synthesized according to the method described in the literature [18]. Solvents were dried according to the method cited in the literature. All other chemicals

Table 1
The results of diazotization, coupling reactions and UV-vis data of the tetrazole-azoic dyes

Dye no.	Color	Decomp. point (°C)	% Yield	$^{a}\lambda_{max}$ (A, ε M^{-1}cm^{-1})
3	Yellow	227–28	78	241 (0.432, 8701), 353 (1.100, 22155)
4	Brown	86–7	28	230 (0.541, 11794), 311 (1.35, 29430)
5	Yellow	200	42	235 (0.533, 12450), 270 (0.373, 8713) 340 (1.059, 24737)
6	Red	219–220	91	235 (1.300, 25388), 273 (0.773, 15096) 408 (0.852, 16639)
7	Red	230	91	230 (1.05, 29054), 261 (0.775, 21444) 419 (0.396, 10957), 468.8 (0.414, 11455)
8	Green	174	58	234 (0.438, 30760), 242 (0.947, 66505) 406 (0.439, 32937)

[a] Measured in absolute ethanol.

Table 2
^{1}H-NMR data for the tetrazole-azoic dyes, imidoyl azide and hydroxylamine derivatives

Comp no.	^{1}H-NMR (δ ppm)	IR (cm^{-1}) (KBr)
3	(CCl_4, DMSO-d_6):[a] 8.30–10.00 (br, 2H); 7.85–8.20 (*m*, 4H); 7.60 (*d*, 2H, *J*=8 Hz); 7.10 (*d*, 2H, *J*=8Hz)	3250(s), 3030(s), 2900(s), 2750(s), 2440(s), 1610(s), 1570(s),1480(s), 1460(m),1430(s), 1270(m), 1220(s), 1140(s), 860(s),550(m)
4	(CCl_4, DMSO-d_6):[a] 10.70–12.10 (br, H); 8.25 (*d*, 2H, *J*=9 Hz); 7.25–8.10 (*m*, 3H); 7.00 (*d*, 2H, *J*=9Hz)	3100(m), 2800(m), 2750(m), 2680(m), 2600(m), 1610(s), 1590(s),1495(s), 1450(s), 1340(s), 1250(m), 1140(m), 840(m), 750(m)
5	(CCl_4, DMSO-d_6):[a] 12.30–13.60 (br, 2H); 6.90–8.90 (*m*, 7H)	3300(m), 3120(w), 2920(w), 2750(w), 2610(w), 2500(w), 1610(s),1570(s), 1530(m), 1480(m), 1450(w), 1330(m), 1250(m), 850(m)
6	(CCl_4, DMSO-d_6) [a]:11.30–15.50 (br, 2H); 7.00–9.15 (*m*, 10H)	3250(m), 3050(m), 2900(m), 2710(m), 2600(m), 1615(s), 1590(s),1530(s), 1470(s), 1410(s), 1190(s), 1140(m), 830(m), 760(m)
7	(CCl_4, DMSO-d_6):[a] 6.40 (*d*, 1H, *J*=8 Hz), 6.90 (*d*, 1H, *J*=8 Hz), 7.50–8.2 (*m*, 8H), 8.8 (*d*, 1H, 7 Hz),7.6–9.1 (br, 1H)	3030(m), 2880(m), 2700(m), 2600(m), 2440(m), 1615(s), 1490(s),1190(s), 1050(m), 830(m), 750(m)
8	($CDCl_3$, CCl_4):[a] 8.30–9.30 (br, 1H); 7.80–8.15 (*m*, 4H); 7.60 (*d*, 2H, *J*=8 Hz); 6.90 (*d*, 2H, *J*=8 Hz); 3.05 (*s*, 6H)	3050(m), 2950(m), 2750(m), 2650(m), 2500(m), 1610(s), 1600(s),1530(s), 1370(s), 1140(s), 1050(m), 850(m), 820(m)
10	Not recorded	[c]3100(w),2950(w), 2200(m), 2180(s), 1610(s), 1600(m), 1560(s), 1500(m),1330(s), 1290(s), 1220(m), 1150(s), 1080(m), 840(m), 750(m),700(m)
11	(DMSO-d_6):[b] 15.500 (*s*, 1H); 8.912 (br, 1H); 8.595 (*d*, 1H, *J*=8Hz); 7.981 (*d*, 1H, *J*=9 Hz); 7.923 (*d*, 2H, *J*=9 Hz); 7.817 (*d*, 1H, *J*=8 Hz); 7.774 (br, 1H); 7.687 (*d*, 1H, *J*=8 Hz); 7.626 (*t*, 1H, *J*=7 Hz); 7.478 (*t*, 1H, *J*=7 Hz); 7.361 (*d*, 2H, *J*=8 Hz); 7.225 (*d*, 2H, *J*=9 Hz); 6.985 (*d*, 1H, *J*=9 Hz); 3.335 (*s*,H_2O); 2.501 (quentet, solvent residue); 2.378 (*s*, 3H)	[c]3438(m),3332(m), 3060(w)1617(s), 663(s),1502(s), 1398(s), 1277(s), 1205(s),1152(s), 1095(m), 836(s), 684(m), 615(m)

[a] 90 MHz.
[b] 400 MHz.
[c] FT-IR.

were commercially graded and used without further purification.

2.2. Instruments

Proton nuclear magnetic resonance (^{1}H-NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument. Tetramethylsilane (TMS) was used as an internal reference. ^{13}C-NMR (100 MHz), ^{1}H-NMR, (400 MHz) and FT-IR (KBr) spectra were carried out in Justus Liebig University of Giessen (Germany). IR (KBr) spectra were recorded on Shimadzu 435 IR spectrophotometer. The UV-vis Spectra were measured at a Shimadzu UV-240 spectrophotometer. The elemental analysis was performed by Tarbiat Modarres University of Iran and Justus Liebig University of Germany. Melting points were taken by the Gallenkamp melting point apparatus and are uncorrected.

Table 3
The elemental analysis (CHN) for the tetrazole-azoic dyes imidoyl azide and hydroxylamine derivatives

Dye No.	Found			Calculated		
	%C	%H	%N	%C	%H	%N
3	55.18	3.83	29.46	55.32	3.57	29.77
4	NA[a]	NA	NA	47.71	2.77	29.96
5	47.80	3.13	29.96	47.71	2.77	29.96
6	61.35	3.90	24.72	61.44	3.64	25.29
7	57.95	4.89	31.89	58.24	4.89	31.70
8	57.08	3.70	25.92	61.44	3.64	25.29
11	61.88	4.02	11.65	60.50	4.20	11.76

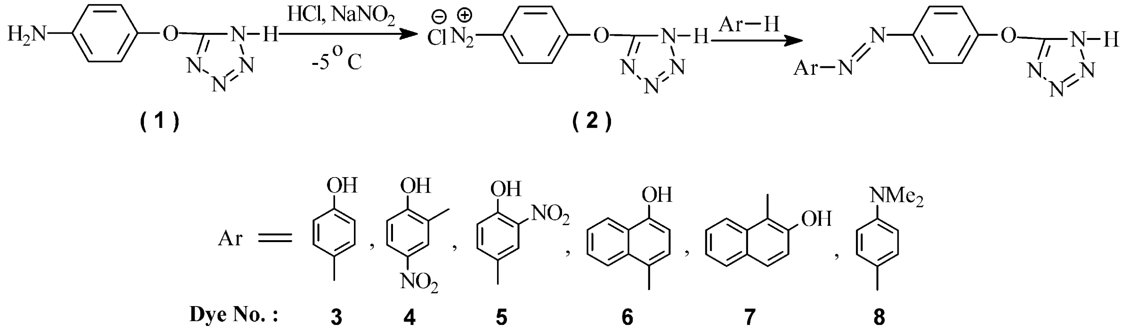
[a] Not available (unstable during crystallization).

2.3. Diazotization

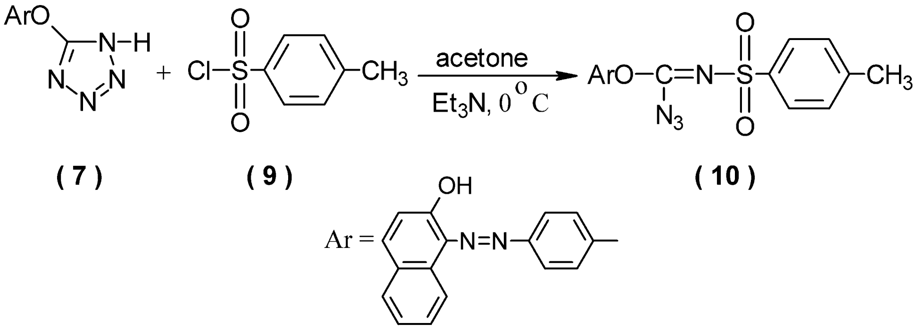
In a 50 ml beaker, 1.95 g (11.0 mmol) of 5-(4′-aminophenoxy)tetrazole (**1**) is dissolved in 8 ml of warm solution of 20% hydrochloric acid. The beaker is placed in an ice-salt bath and cooled to 0–5 °C whilst stirring vigorously, 5-(4′-ammonium-hydrochloride phenoxy) tetrazole (**2**) separated as a finely divided crystalline form. A cold solution of 0.83 g (12.0 mmol) sodium nitrite in 1.5 ml of water is added slowly while being stirring to an end-point with freshly prepared potassium iodide-starch reagent. The temperature of the solution is not allowed to rise above 5 °C. The clear and pale yellow solution of diazonium salt is stirred for an additional 5 min and immediately used in the following diazo coupling steps.

2.4. Typical experiment: Diazo coupling with phenols (dyes 3–7)

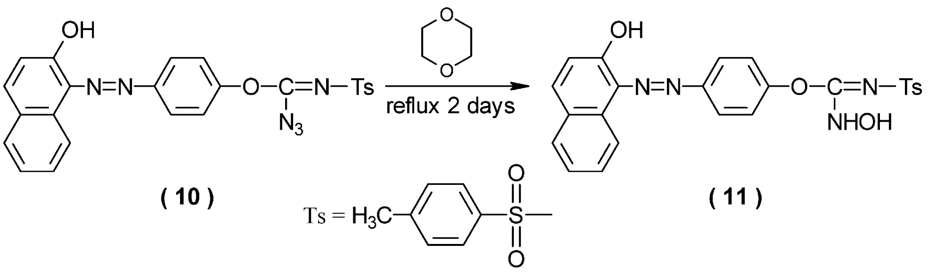
In a typical reaction 10 mmol of phenolic compound is dissolved in a solution of 2.2 g sodium



Scheme 2.



Scheme 3.



Scheme 4.

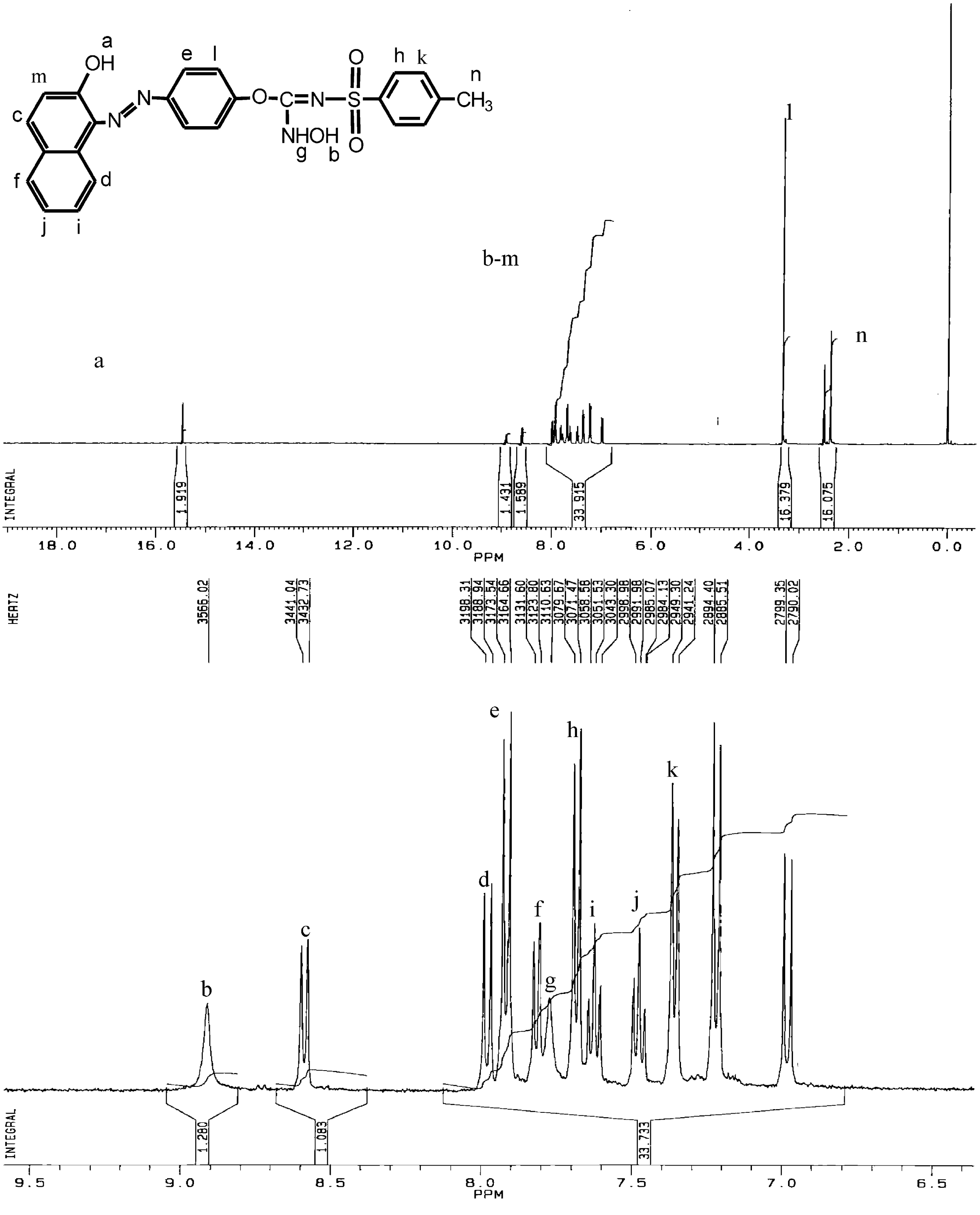


Fig. 1. ^{1}H-NMR spectra (400 MHz, DMSO-d_6) of compound (**11**).

hydroxide in 8 ml of water and cooled in an ice bath. The diazotized solution, which has been prepared in the previous section, is added slowly while being stirring. The dye is immediately formed. The mixture is additionally stirred for about 1 h and the concentrated hydrochloric acid is slowly added to the acidified cold reaction mixture. The product is filtered off with suction, washed with water until free from acid and dried in the air. Reactions yield, physical properties,

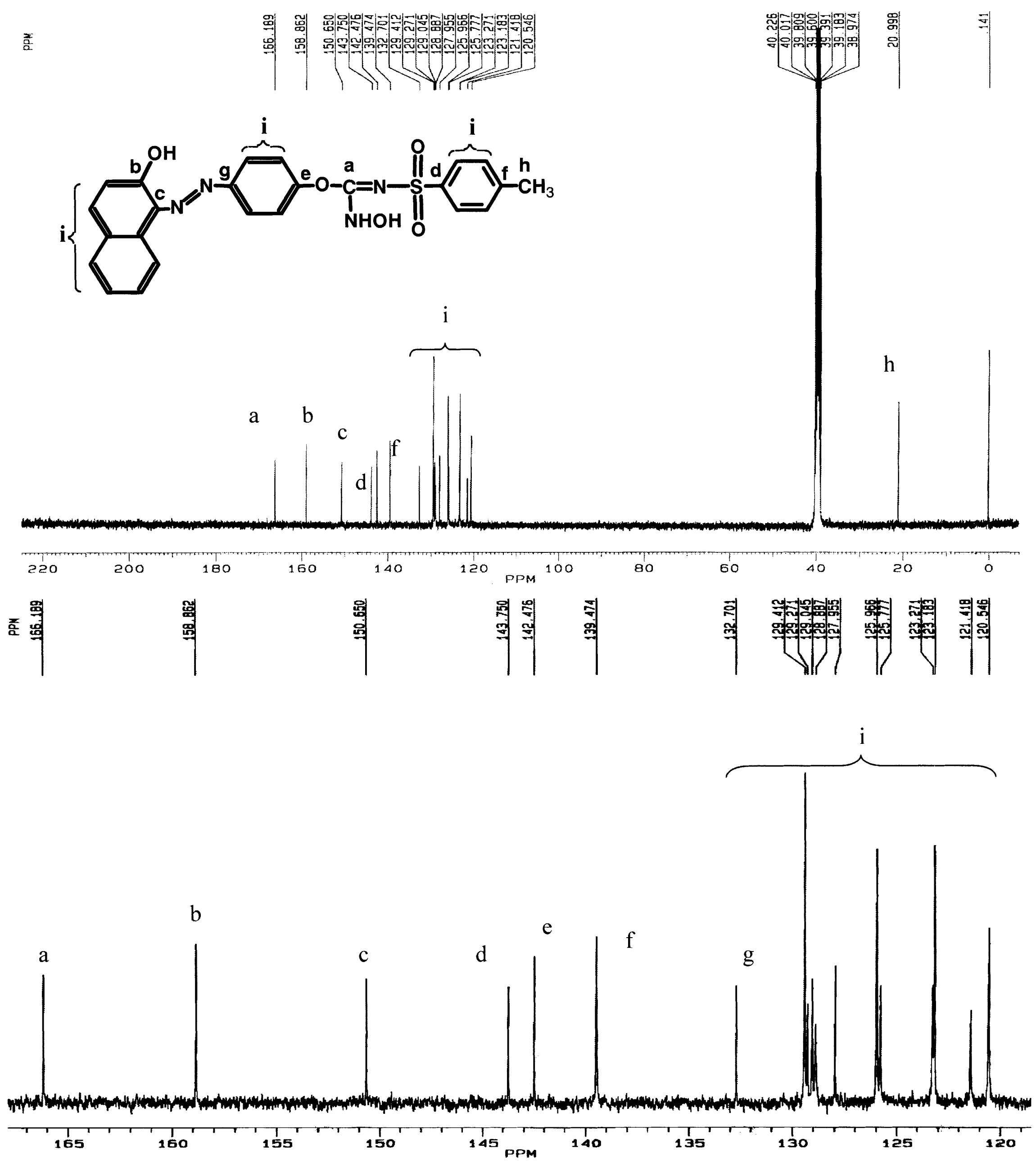


Fig. 2. ^{13}C-NMR spectra (100 MHz, DMSO-d_6) of compound (**11**).

spectroscopy data, and the results of elemental analysis are summarized in Tables 1–3.

2.5. Diazo coupling with N,N*-dimethylaniline (dye 8)*

To the diazonium salt solution, previously described, fleshly distilled *N*,*N*-dimethylaniline 1.94 g (2 ml, 16.0 mmol) is added fairly rapidly at a temperature about of 0–5 °C. A solution of 1.1 g sodium acetate in 1.6 ml water is prepared and about one-half of this solution is added to the reaction mixture in an ice bath, allowed to stand in ice for 1 h with occasional stirring. The remainder of the sodium acetate solution is added to the mixture cooled in an ice bath, left for another 30 min (with occasional stirring) and the temperature is allowed to rise to that of the laboratory. Sodium hydroxide solution (20%) is added dropwise and stirred until a distinct odor of *N*,*N*-dimethylaniline evolves from the reaction mixture. The mixture is kept at room temperature for about 1 h. The green solid is filtered off at the pump, washed first with a small amount of water, then in 3 ml of 10% acetic acid, and finally with water (58% crude yield) [18]. Reaction yield, physical properties, spectroscopy data, and the results of elemental analysis are summarized in Tables 1–3.

2.6. Imidoyl azide derivative (10)

In a 100 ml two-necked round bottom flask equipped with magnetic stirrer and dropping funnel, 0.50 g (1.51 mmol) of compound (**7**) and 0.29 g (1.51 mmol) of tosyl chloride (**9**) was dissolved in 10 ml of acetone. A solution of 0.23 ml (1.66

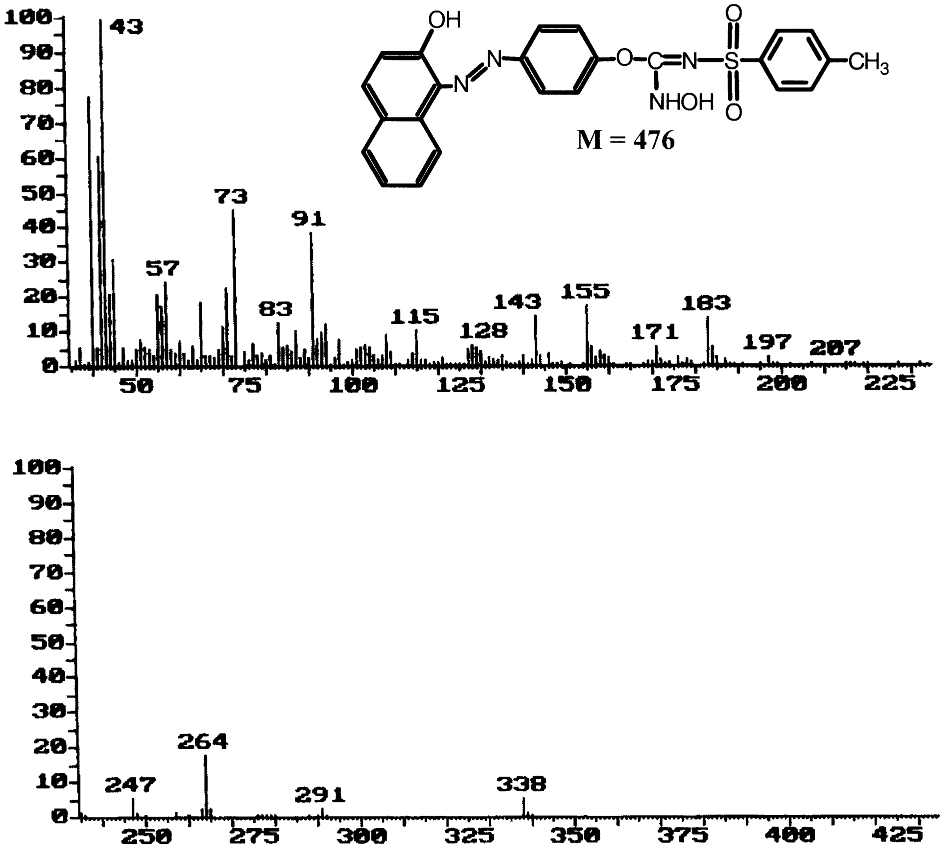


Fig. 3. Mass spectrum of compound (**11**), see Scheme 5.

mmol) triethylamine in 5 ml acetone was added dropwise to this solution at 0 °C. Triethylammonium hydrochloride salt gradually formed. The reaction mixture was stirred overnight at room temperature, poured into 100 ml of cold water, stirred for 1 h at room temperature, filtered, and then dried under vacuum at 40 °C to give 0.66 g (89.6% yield) of imidoyl azide derivative (**7**) as a dark red powder [9]. This compound decomposed at 140 °C.

2.7. *Hydoxylamine derivative (11)*

The compound (**7**) (1.00 g) and 15 ml of 1,4-dioxane were placed in a 10 ml round bottom flask equipped with magnetic stirrer and reflux condenser, and refluxed for 2 days. Progress of the reaction was traced using TLC. The solvent was removed by distillation under reduced pressure; the dark red oily residue was passed through a chromatography column using silica gel and a mixture of 40:60 *n*-hexane:ethylacetate as eluent to give a dark red powder, mp. = 208–210 °C.

^{13}C-NMR 100 MHz (DMSO-d_6), δ (ppm): 166.05, 158.72, 150.51, 143.61, 142.34, 139.33, 132.56, 129.27, 129.13, 128.91, 128.75, 127.82, 125.83, 125.64, 123.13, 123.04, 121.28, 120.41, 20.86.

3. Result and discussion

The general synthetic method is depicted in Scheme 2. The 5-(4′-aminophenoxy)-tetrazole [17] is diazotized and coupled with the electron rich aromatic rings. The experimental results are given

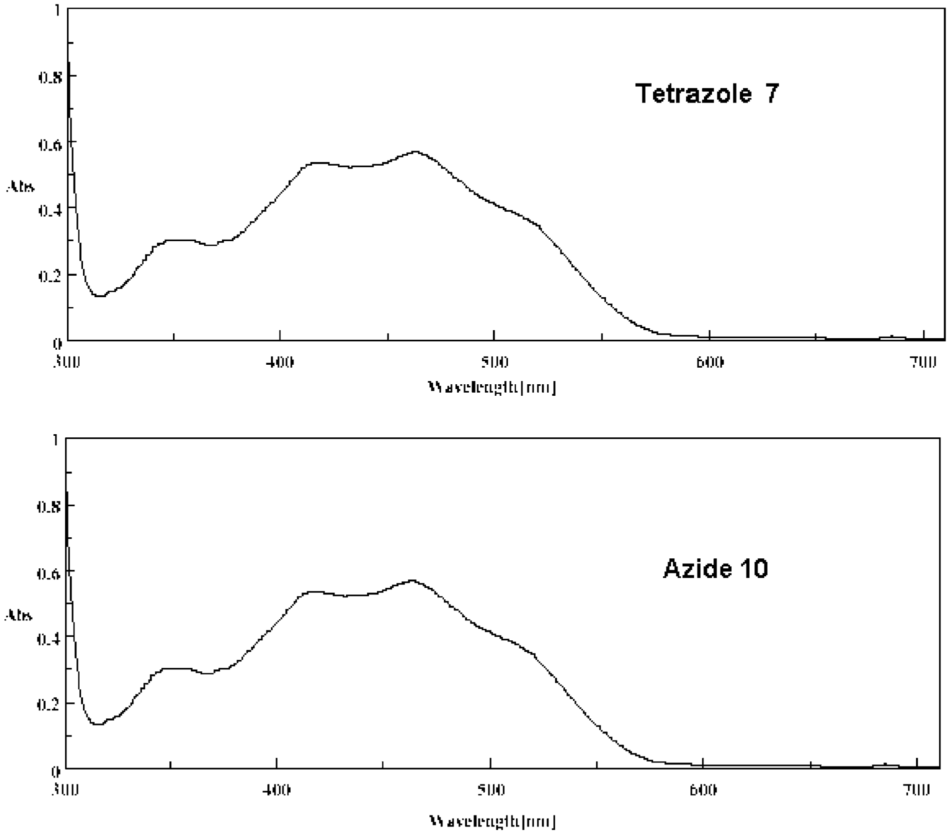
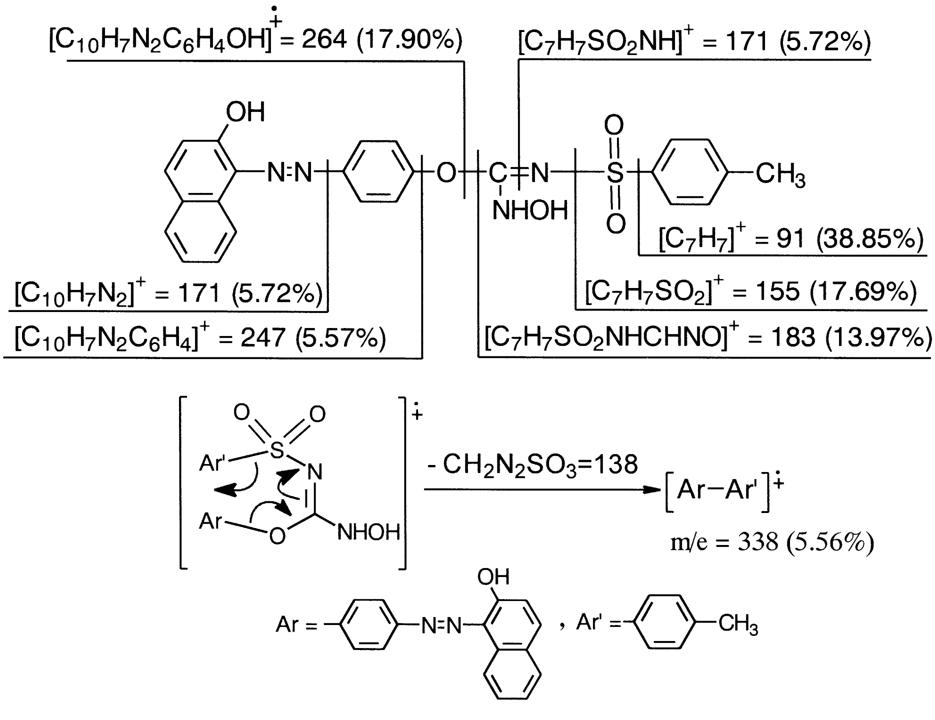


Fig. 4. Ultra violet spectra of tetrazole 7 and azide 10 (10^{-4} M, in ethanol).



Scheme 5.

in Table 1. The dyes synthesized by this method have a very deep yellow, red, or brown color. Normal melting points were not observed. They all decomposed above 174 °C except dye (**4**), which released nitrogen at 86 °C to produce tar. The ^{1}H-NMR spectra and elemental analysis (CHN) of these dyes are shown in Tables 2 and 3, respectively.

In order to observe any color change, during chemical transformations in (1H)-tetrazole ring, and seek for new dyes, the imidoyl azide derivative (**10**) of dye (**7**) was synthesized (Scheme 3). Appearance of two strong and sharp absorption bands, at 2180 and 2200 cm^{-1} (N_3 stretching bands) in FT-IR spectrum, confirmed the formation of azide dye. This azide is relatively stable and decomposes at 140 °C.

To test a new application of the new dyes, the imidoyl azide (**10**) was refluxed in 1,4-dioxane for 2 days. After removal of the solvent and purification, the product was characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, mass spectroscopy and elemental analysis. Surprisingly, no insertion product to 1,4-dioxane was observed [17]. Experimental observations indicate that the insertion of the nitrene into the O–H bond of water has taken place to form the hydroxlylamine derivative (**11**), (Scheme 4). ^{1}H-NMR and ^{13}C-NMR spectra of the product are shown in Figs. 1 and 2.

Mass spectra (Fig. 3) did not show the molecular ion peak. The fragmentation pattern is shown in (Scheme 5). Adsorption of water by the solvent during the long reaction time (2 days) must be responsible for this unexpected reaction. It should be mentioned that, because of the relatively high decomposition point of the azide (**10**) (140 °C), in relation to the boiling point of 1,4-dioxane (100–102 °C), this reaction time was necessary. This unusual reaction is under more detailed investigation.

4. Conclusion

The preparation of (1H)-tetrazole functionalized azoic dyes is reported. The structures of these dyes were characterized by UV-vis, ^{1}H NMR, IR spectroscpies and elemental analysis. All dyes synthesized in this work are soluble in basic media. The presence of oxygen atom between the tetrazole ring, imidoyl azide or imidoyl hydroxylamine groups and the rest of the dye separates the two parts of the molecule (no direct resonance between the tetrazole, imidoyl azide or imidoyl hydroxylamine and the azo functional group). This allows reactions at the tetrazole center without a major change in the color of the dye, ultraviolet spectra of tetrazole **7** is similar to that of azide **10** (Fig. 4). In addition, these dyes can be converted to their water-soluble salt forms without any important change in color for the same reason. Imidoyl azide derivative of the dye (**7**) produced hydroxylamine derivative (**11**) in refluxing 1,4-dioxane.

Acknowledgements

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