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# New diaminomaleonitrile-based azo-azomethine dyes; synthesis, characterization and spectral properties

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#### 1. Introduction

The use of 2,3-diaminomaleonitrile (DAMN) derivatives in synthetic dye chemistry has gained great attention in the past decade due to their impressive and useful chemical and physical properties [1-4]. DAMN has low basicity and nucleophilicity due to its impressive strong electron-withdrawing effect of two nitrile groups conjugated with the amino groups. However, DAMN has generally been found to react with substituted aromatic and/or aliphatic aldehydes, in the presence of an acid catalyst, to produce mono- and/or bis-iminated compounds [5-8]. Also, DAMN is a very attractive precursor for the formation of symmetrical Robson-type coordination compounds [9]. Furthermore, reaction of DAMN with dicarbonyl compounds to produce [1 + 2] condensed diamines is also attractive (Fig. 1) [10,11].

The presence of cyano and other electron donor and/or acceptor functions in the structure of organic compounds affects the electronic properties of such compounds [12,13] and may provide enormous potential for the synthesis of new dyes [1–4], phthalocyanines [14,15], and polydentate ligands [16,17]. This combined with the fact that azo and azomethine groups are relatively robust and chemically stable has prompted extensive study of azo-azomethine compounds as dyes and colorants [1,18]. In order to improve the spectral properties of DAMN-based azo dyes, we

# ABSTRACT

New diaminomaleonitrile-based azo-azomethine dyes were synthesized via a condensation between 2,6-bis(N-(2-amino-1,2-dicyanoetheneimino))-4-methylphenol and 5-(4-substituted-phenyl)-azo-salicyladehyde. FT-IR and <sup>1</sup>H NMR spectroscopy and mass spectrometry studies as well as elemental analysis data revealed the symmetrical bis-iminated structures of the dyes. The electrochemical behavior of the dyes has been investigated by cyclic voltammetry. The effect of various solvents with different polarities on the UV–Vis spectra of the dyes was also studied. The thermal analysis data indicated that the framework of the dyes was stable up to 285 °C.

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developed a synthetic route to obtain such dyes containing azo, azomethine, DAMN and phenol moieties. The choice of these compounds was motivated by two objectives: (i) to provide new DAMN-based azo-azomethine dyes and (ii) to study their solvatochromic behavior, electrochemical properties and thermal stability. We report here the synthesis of new family of acyclic DAMN-based azo-azomethine dyes, 3a and 3b, by condensation reaction of previously prepared diamine (1) [19] with azo-coupled salicylaldehyde derivatives, 5-(4-substituted-phenyl)azo-salicyladehyde, Fig. 2. The new dyes have been characterized by spectroscopic methods (<sup>1</sup>H NMR, UV.Vis., IR and Mass) as well as elemental analysis. Cyclic voltammograms were obtained for 3a and 3b in DMSO in order to study of electrochemical properties of the dyes. Also, the solvatochromic behavior and substituent effects of the prepared dyes in various solvents were evaluated. Furthermore, the thermal properties of the prepared dyes were examined by thermogravimetric analysis. The results indicated that the framework of the prepared dyes is stable up to 280 °C.

# 2. Experimental

# 2.1. Materials

All of the reagents and solvents involved in synthesis were of analytical grade and used as received without further purification.





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Fig. 1. Reaction of dicarbonyls with DAMN to production of diamines.

2,3-Diaminomaleonitrile, 4-nitroaniline and 4-ethylaniline were obtained from either Aldrich or Merck. 2,6-Diformyl-4-methyl phenol and related diamine, 2,6-bis(N-(2-amino-1,2-dicyanoetheneimino))-4-methylphenol, **1**, were prepared as described previously [19,20]. Azo-coupled precursors, **2a** and **2b**, were prepared as described previously [21,22].

#### 2.2. Instrumentation

The structure of all synthesized compounds was confirmed by <sup>1</sup>H NMR spectra, recorded on a Bruker AV 300 MHz spectrometer. FT-IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400–4000 cm<sup>-1</sup>. Melting points were determined on Electrothermal 9200 apparatus. C. H. N. analysis was performed on a Vario EL III elemental analyzer. Thermal analyses were performed on a Per-kin–Elmer Thermogravimetric Analyzer TG/DTA 6300 instrument. Electronic spectral measurements were carried out using Perkin–Elmer Lambda spectrophotometer in the range 200–700 nm. Mass spectra of the dyes were obtained on Ajilent Mass 5973 Network spectrometer. Cyclic voltammograms (CV) were performed using an Autolab model PGSTAT 30V potentiostat/galvanostat. All readings

were taken using three electrode potentiostatic systems in DMSO with 0.1 mol cm<sup>-3</sup> tetrabutylammonium perchlorate (electrochemical grade) as supporting electrolyte. A three electrode system was used for CV measurements in DMSO and consisted of a platinum working electrode, a platinum auxiliary electrode, and a calomel reference electrode.

#### 2.3. Synthesis

# 2.3.1. General procedure for the synthesis of azo-azomethine dyes, **3a** and **3b**

A solution of diamine, **1**, (0.17 g, 0.5 mmol) in 1:1 methanol: acetic acid (30 mL) was slowly added to a stirring solution of azocoupled precursors, **2a** and **2b**, (1 mmol) in acetic acid (30 mL) during a period of 10 min at 80–90 °C. After heating under reflux for 3 h the solution was filtered whilst hot. The appropriate product was washed with hot acetonitrile and dioxan and dried in air.

# 2.3.2. 2,6-bis((4-(4-nitro-phenylazo)-phenol)-1,2-

dicyanoetheneimino)-4-methylphenol (**3a**)

Yield: 53%, m.p. = 272–276 °C. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz):  $\delta$  2.29(s, 3H), 7.13(d, 2H, J = 8.78 Hz), 7.91(m, 2H), 8.01(d, 4H, J = 8.35 Hz), 8.06(br, 2H), 8.42(d, 4H, J = 8.35 Hz), 8.53(s, 2H), 8.62(s, 2H), 8.78(s, 2H), 11.20(s, 1H), 11.54(br, 2H). IR (KBr, cm<sup>-1</sup>); 3416, 3347, 3308, 3210(N–H), 2209, 2238(CN), 1734 (C=O), 1624 (C=N), 1609 (C=C), 1562 (phenol ring), 1523 (NO<sub>2</sub>), 1460 (N=N), 1347(NO<sub>2</sub>), 1285(C–O), 868. [M]<sup>++</sup> = 850.2 molecular ion peak is not observed. m/z = 57.1, 93.1, 120.0, 146.0, 211.1, 236.2, 265.0, 313.2, 368.3. Anal. Calcd. for C<sub>43</sub>H<sub>26</sub>N<sub>14</sub>O<sub>7</sub>: C, 60.71; N, 23.05; H, 3.08. Found: C, 60.64; N, 23.31; H, 3.16%.  $\lambda_{max}$  (nm) ( $\varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)): 260 (34,100), 374 (77,200), 426 (44,600) and 599 (7800) in DMSO.

# 2.3.3. 2,6-bis((4-(4-ethyl-phenylazo)-phenol)-1,2-

dicyanoetheneimino)-4-methylphenol (**3b**)

Yield; 44%, m.p. = 294–297 °C. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz):  $\delta$  1.21(t, 6H, *J* = 7.60 Hz), 2.29(s, 3H), 2.69(q, 4H, *J* = 7.60 Hz), 7.09(d, 2H, *J* = 8.85 Hz), 7.41(d, 4H, *J* = 7.81 Hz), 7.78(d, 4H, *J* = 7.81 Hz),



Fig. 2. Reaction of DAMN-based diamine with azo precursors.

**Table 1** Tentative assignments of some selected IR<sup>a</sup> frequencies (cm<sup>-1</sup>) of the prepared compounds.

Compound	v(C=N, cyanide)	v(N–H)	v(C=N/C=C)	v(C=0)	v(C-O)	v(N=N)	$v(NO_2)$
2a	-	_	1605, 1478	1657	1283	1460	1524,1320
2b	-	-	1604, 1479	1653	1277	1173	_
3a	2209, 2238	3347, 3308, 3210	1624, 1609	Hydrazone and/or enaminone tautomer 1734	1285	1460	1523, 1347
3b	2210, 2237	3347, 3300, 3198	1626, 1607	Hydrazone and/or enaminone tautomer 1698	1280	1460	_

<sup>a</sup> KBr discs.

7.85(d, 2H, J = 8.85 Hz), 7.93(s, 2H), 8.65(s, 2H), 8.67(s, 2H), 8.68(s, 2H), 11.22(s, 3H). IR (KBr, cm<sup>-1</sup>); 3405, 3347, 3300, 3198 (N–H), 2210, 2237 (CN), 1698 (C=O), 1626 (C=N), 1607 (C=C), 1562 (phenol ring), 1460 (N=N), 1369, 1280(C–O), 839. [M]<sup>++</sup> = 816.3 molecular ion peak is not observed. m/z = 57.1, 105.1, 129.1, 157.0, 211.1, 239.1, 344.1, 368.3. Anal. Calcd. for C<sub>47</sub>H<sub>36</sub>N<sub>12</sub>O<sub>3</sub>: C, 69.11; N, 20.85; H, 4.44. Found: C, 68.86; N, 21.02; H, 4.61%.  $\lambda_{max}$  (nm) ( $\varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)): 255 (35,700), 360 (83,200), 372 (77,400) and 415 (46,700) in DMSO.

#### 3. Result and discussion

New DAMN-drived azo-azomethines, **3a** and **3b**, have been synthesized via a condensation reaction of 2,6-bis(N-(2-amino-1,2-dicyanoetheneimino))-4-methylphenol, **1**, with 5-(4-substituted-phenyl)-azo-salicyladehyde in acetic acid. All prepared compounds, are thermally stable solids, intensely colored, soluble in DMF and DMSO and exhibited dyes characteristics. The presence of various coordination sites in bis-iminated compounds makes them very versatile species, which could potentially act as multidentate ligands.

#### 3.1. Infrared spectra

The positions of some of the prominent bands in the IR spectra of **3a** and **3b** and their assignments based on extensive data available for related compounds [1,18,23] are given in Table 1. The

total absence of v(C=0) absorption in the IR spectra of **3a** and **3b** together with the appearance of new v(C=N) absorption in the range of 1624–1626 cm<sup>-1</sup> clearly indicated that a new Schiff-base compound had formed in each case. The symmetric N=N stretching mode, in the IR spectra of **3a** and **3b**, leads to a medium intensity band at 1460 cm<sup>-1</sup>, while the v(C-O) stretching mode gives an intense band within the range 1280–1285 cm<sup>-1</sup>. Strong bands observed in the IR spectra of **3a** and **3b** in the region of 3416–3198 cm<sup>-1</sup> are due to hydrogen bonded v(OH) in the azo tautomer or v(NH) in the hydrazone and/or enaminone tautomers [1], Fig. 2. The band observed at 1698–1730 cm<sup>-1</sup> may be due to C= O groups of the hydrazone and/or enaminone tautomers, **4** and **5**, in solid state. The IR spectra of **2a** and related dye, **3a**, show strong bonds at 1347 and 1523 cm<sup>-1</sup> assigned to the NO<sub>2</sub> group [24].

# 3.2. <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of **3a** and **3b**, obtained at ambient temperature in d<sub>6</sub>-DMSO, display signals that are consistent with the proposed structures. The slightly broad signal at  $\delta_{\rm H}$  11.54 and 11.22 ppm, in the spectra of **3a** and **3b**, respectively, is assigned to the OH protons, as was confirmed by deuterium exchange when D<sub>2</sub>O was added to d<sub>6</sub>-DMSO solution and this indicates that the azo form is more stable than other forms in DMSO solution. The <sup>1</sup>H NMR spectra are dominated by intense features at 7.41–7.78 ppm, for **3a**, and 8.01–8.42 ppm, for **3b**, which belongs to the AAi'XX' spin system of the para-disubstituted benzene ring. The ratio  $\Delta \delta/J$  is



Fig. 3. The fragments observed in the mass spectra of 3a and 3b.



Fig. 4. Cyclic voltammogram for  $1\times 10^{-5}$  M of 3a and 3b in DMSO containing 0.1 M TBAP.

15.1 and 14.3 for **3a** and **3b**, respectively. Also, doublet pattern of high field signal is simplified after irradiation of low field doublet. The different CH=N protons of **3a** and **3b** exhibit two set of singlet resonance at  $\delta_{\rm H}$  8.55–8.68 ppm.

#### 3.3. Mass spectra

Some of the fragments observed in the mass spectra of the dyes are shown in Fig. 3. The peaks observed at m/z = 368.3, 313.3 and 265.1 confirm the formation of bis-iminated compounds. The peaks observed at m/z = 344.1 in the mass spectra of **3b** can be assigned to the fragment containing an ethyl group, Fig. 3.

#### 3.4. Electrochemistry

The cyclic voltammograms (CVs) of **3a** and **3b**  $(1 \times 10^{-5} \text{ mol } \text{L}^{-1})$  in the potential range -2 V to 1.50 V (versus Ag/AgCl) and for scan rates of 0.01 V s<sup>-1</sup> in DMSO containing 0.1 M TBAP supporting electrolyte are shown in Fig. 4. As can be seen from Figure 4, **3a** and

#### Table 2

Thermal analyses data for 3a and 3b.

**3b** each displays two well-defined irreversible reduction waves. The first wave is observed at ca. -1 V. This reduction process may be due to the partial reduction of the imine bonds to secondary amines (and subsequent protonation by phenol) [25]. This process may also be associated with the reduction of the azo bonds. The second wave was observed at -1.6 V and -1.1 V for **3a** and **3b**, respectively. In general, the reduction of imines is believed to occur via two well separated steps and can follow one of two mechanisms [26], with the first one electron reduction commonly occurring anywhere in the range from -1.3 to -1.8 V versus SCE for conjugated organic compounds in DMSO. On scanning from 0.0 V to positive potentials there is a multi-electron irreversible oxidation process which indicates that oxidation of the original the dyes followed by a chemical rearrangement or generation of a new chemical species.

#### 3.5. Thermal properties

In order to give more insight into the structure of the prepared dyes, the thermal studies of **3a** and **3b** have been carried out using thermogravimetry techniques. In the present investigation, the heating rates were suitably controlled at 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere and the weight loss was measured from 25 °C up to 900 °C.

The initial decomposition and inflection temperatures have been used as an indication of the thermal stability of the prepared compounds. The TG results indicate that the framework of dyes is stable up to 280 °C, Table 2. The comparison of  $T_d$  (decomposition temperature) showed that the thermal stability of **3b** is greater than **3a**, Table 2. Above decomposition temperature the TG curves of the dyes show continuous significant weight loss up to 900 °C, Fig. 5. (For **3a** see Supporting information).

The first stage of mass loss below 300  $^{\circ}$ C, which along with the endothermic peak in the DTA curve, is in agreement with the calculated values for the removal of HCN and NO<sub>2</sub> molecules from the compounds.

#### 3.6. The electronic absorption spectra and substituent effects

The electronic absorption spectra of the azo-coupled precursors and their azo-azomethine derivatives, **3a** and **3b**, recorded in DMSO at room temperature are given in Table 3.

The electronic absorption spectra of **3a** and **3b** display mainly four bands, Fig. 6. The first UV band located at 255–260 nm can be assigned to the moderate energy ( $\pi \rightarrow \pi^*$ ) transition of the aromatic rings while the second band at 360–374 nm is due to low energy ( $\pi \rightarrow \pi^*$ ) transition involving the  $\pi$ -electrons of the azo and azomethine groups [27]. It can be found that the maximum absorption band shifts bathochromically along with the increase in the electronaccepting ability of substituents in the sequence of **3b** < **3a**, consistent with an increase in molecular donor-acceptor polarization.

The  $\pi \to \pi^*$  band of *o*-hydroxy substituted azo-azomethines is also more red shifted than that of the related azo precursors because of extended  $\pi$ -resonance system. This may be inferred from (i) selective solvation, (ii) the ability of the solvent to form stronger intermolecular H-bonds with a particular tautomeric form

Compound, M.F. (M. Wt.)	Dissociation Stages	Temperature range in TG (°C)	Weight loss, found (calculated) (%)	Proposed decomposition assignment	$T_{\rm d}$ (°C)
<b>3a</b> , C <sub>43</sub> H <sub>26</sub> N <sub>14</sub> O <sub>7</sub> (850.76)	Stage I	275-300	17.22 (17.16)	The loss of $NO_2 + 2HCN$	286
	Stage II	300-390	6.12(6.08)	The loss of NO <sub>2</sub>	
	Stage III	390-900	_	The loss of remaining organic part	
<b>3b</b> , C <sub>47</sub> H <sub>36</sub> N <sub>12</sub> O <sub>3</sub> (816.87)	Stage I	265-330	13.22 (13.78)	The loss of 4 HCN	318
	Stage II	330-900	-	The loss of remaining organic part	



Fig. 5. TG-TGA curve of 3b.

Table 3Absorption spectral data of 3a, 3b and their azo precursors in DMSO.

Compounds	$\lambda_{max}/nm~(\epsilon  imes 10^4/dm mol^{-1}~cm^{-1})$	Compounds	$\lambda_{max}/nm (\epsilon \times 10^4/dm mol^{-1} cm^{-1})$
3a	260 (3.41)	3b	255 (3.57)
	374 (7.72)		360 (8.32)
	426 (4.46)		372 (7.74)
	599(0.78)		415 (4.67)
2a	246 (4.5)	2b	260 (6.36)
	382 (9.7)		347 (11.314)
	551 (1.85)		447 (3.12)

and (iii) the intramolecular and intermolecular hydrogen bonding between C—N or N—N and OH groups.

On the other hand, the absorption spectra of **3a** and **3b** display a broad band at 415–426 nm assigned to  $(\pi \rightarrow \pi^*)$  transition involving the whole electronic system of the compounds with a considerable charge-transfer (CT) character. Such a CT originates mainly from the phenolic moiety to the maleonitrile section which is characterized by high electron-accepting character.

#### 3.7. Solvent effect on the electronic spectra

The behavior of the dyes in various solvents was studied. For this purpose, the absorption spectra of **3a** and **3b** were measured in



Fig. 6. The absorption spectra of 3a and 3b in DMSO.

DMSO, DMF, THF and CH<sub>3</sub>CN at a concentration of  $5 \times 10^{-5}$  M, Fig. 7 (See Supporting information). The polarity and hydrogen bonding properties of the solvents used in the present investigation, indicated by the Kamlet–Taft parameters ( $\alpha$ ,  $\beta$ , and  $\pi^*$ ) [28], are summarized in Table 4.  $\beta$  is a scale of solvent hydrogen bond acceptor (HBA) basicities which refers to the acceptance of the proton of a hydrogen bond.  $\alpha$  is a scale of solvent hydrogen bond donor (HBD) acidities which refer to the donation of the proton.  $\pi^*$ is a scale of solvent dipolarity/polarizability which refer to the ability of solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The  $\pi^*$  value is correlated with the solvatochromic behavior values. The solvatochromic behavior of a dye is the shift of the  $\pi \to \pi^*$  band wavelength due to the presence of solvent with different polarity, which is due to the interaction between the solute and solvent molecules [29]. It was found that the absorption band at 360-374 nm generally shows bathochromic shift (positive solvatochromism) as the polarity of solvent was increased. The influence of solvents for the prepared dyes increases in the order  $DMSO > DMF > CH_3CN > THF$ . This positive solvatochromism exhibited by the dyes may be due to the effect of dipole moment changes of the excited state and/or changes in the hydrogen bonding strength in polar solvents (The  $\beta$ ,  $\mu$ /D and  $\pi^*$  values for DMSO and DMF are higher than other solvents). Furthermore, the absorption spectra of 3a in DMSO and DMF comprise a new band appearing at longer wavelength (599 and 597 nm, respectively) which exceeds by far the usual solvent shift. This behaviour may be interpreted on the basis that the solute molecules are liable to form a solvated complex with DMF and DMSO molecules, with higher



Fig. 7. The absorption spectra of 3a in solvents with different polarities.

Table 4							
Solvatochromic	parameters	(α, β	$,\pi^{*})$	of	used	solvent	s.

Solvent	α	β	$\pi^*$	٤	$\mu/D$
THF	0.00	0.55	0.55	7.58	1.74
DMSO	0.00	0.76	1.00	46.45	4.05
DMF	0.00	0.69	0.88	36.71	3.81
CH <sub>3</sub> CN	0.19	0.40	0.66	35.49	3.94

 $\beta$  values in comparison to other solvents, through an intermolecular H-bonding [27,30].

# 4. Conclusion

In the present work two new bis-iminated diaminomaleonitrilebased azo-azomethine dyes were synthesized via condensation reaction of 2,6-bis(N-(2-amino-1,2-dicyanoetheneimino))-4methylphenol with 5-(4-substituted-phenyl)-azo-salicyladehyde. The solvatochromic behaviour and substituent effects of the prepared dyes in DMSO, DMF, CH<sub>3</sub>CN and THF were evaluated. The results indicated that the  $\pi \rightarrow \pi^*$  band of these compounds, at 360–374 nm, shows bathochromic shift as the polarity of solvent was increased.

The prepared compounds are stable up to 285 °C. According to the thermal stability and absorption spectra we can conclude that these compounds may be suitable for use as recording dyes. Furthermore, the presence of various coordination sites in the prepared compounds makes them very versatile species, which could potentially act as multidentate ligands.

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#### **Electronic supplementary material**

The UV-Vis, <sup>1</sup>H NMR, IR spectra and also TG/TGA curves of **3a** and **3b** can be obtained free of charge via http://www.araku.ac.ir/ $\sim$ h\_khanmohammadi/Supporting information-5.pdf

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