Synthesis, Characterization, and Tautomeric Properties of Some Azo-azomethine Compounds

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Z. Naturforsch. **2012**, *67b,* 159 – 164; received December 27, 2011

The primary azo compound 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene reacts with some aliphatic and aromatic diamines and yields the corresponding azo-azomethine compounds. These compounds were characterized by elemental analysis, IR, UV/Vis, and NMR spectroscopy. The primary azo compound exists entirely in the azo form in solution as well as in the solid phase. The tautomeric structure of azo-azomethine compounds heavily depends on the solvent and the substituents. Aliphatic diamine-based compounds favor the enol-imine tautomer while aromatic diamine-based compounds have structures that lie between the two enol-imine and keto-amine tautomers due to a relatively strong intramolecular hydrogen bond. The compounds exhibit positive solvatochromism (bathochromic shift) so that their absorption bands move toward longer wavelengths as the polarity of the solvents increases. In addition, UV/Vis spectrophotometry has shown that the studied compounds have molar extinction coefficients larger than 40000.

Key words: Dye, Azo-azomethine, Schiff Base, Hydrogen Bonding, Tautomerism

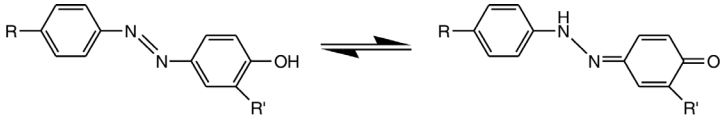
Introduction

Azo compounds are very important molecules and have received much attention in fundamental and applied chemistry [1 – 5]. The well-known applications of azo dyes in acid-base indicators and chemical sensors and as electron transfer catalysts have attracted the interest of many investigators [6, 7]. Several azo dyes have been employed in liquid crystal displays due to their non-ionic character and their solubility in the liquid crystal hosts [8]. The introduction of a salicylaldimine leads to azo-Schiff bases or azo-azomethine dyes and may result in new and better microoptoelectronic devices [9].

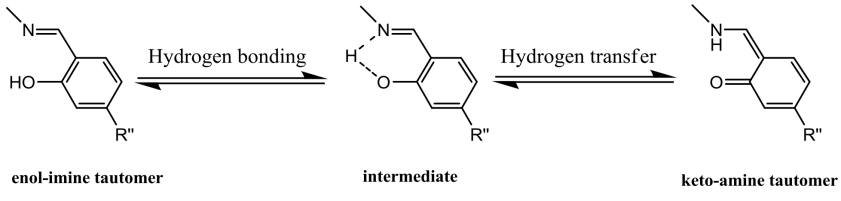
Hydroxyazo compounds can undergo azo/hydrazone tautomerization, in which the azo tautomer is the more stable one (Scheme 1) [10].

On the other hand, α-hydroxy salicylaldimine compounds can undergo enol-imine/keto-amine tautomerization by H-atom transfer from the hydroxyl oxygen to the imine nitrogen probably *via* intramolecular hydrogen bonding (Scheme 2) [9, 11 – 13].

Solvents and substituents have a remarkable influence on the relative stability of the two tautomers [14]. Such tautomerizations are very important not only in fundamental research but also for some applications. The two tautomers have substantially different color and chemical properties and hence different applica-



Scheme 1. Azo/hydrazone tautomerization.



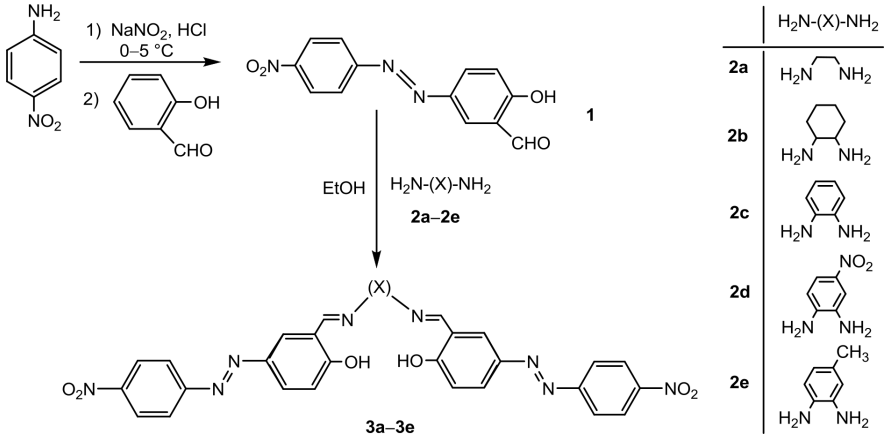
Scheme 2. Enol-imine/keto-amine tautomerization in azomethine compounds.

Table 1. Analytical data and physical properties of **1** and the azo-azomethine derivatives **3a** – **3e**.

Compound	Empirical formula	Formula weight	Color	M. p. (°C)	Yield (%)	— Calculated (found) (%) —		
1	$C_{13}H_9N_3O_4$	271.23	orange-yellow	194 – 196	92	57.57 (57.49)	3.34 (3.60)	15.49 (15.45)
3a	$C_{28}H_{22}N_8O_6$	566.52	brown-red	293 – 295	87	59.36 (58.87)	3.91 (4.11)	19.78 (20.04)
3b	$C_{32}H_{28}N_8O_6$	620.61	red	285 – 287	89	61.93 (61.36)	4.55 (4.85)	18.06 (18.43)
3c	$C_{32}H_{22}N_8O_6$	614.57	brown	275 – 277	94	62.54 (62.00)	3.61 (3.95)	18.23 (18.62)
3d	$C_{32}H_{21}N_9O_8$	659.56	brown-orange	211 – 214	57	58.27 (57.86)	3.21 (3.42)	19.11 (19.52)
3e	$C_{33}H_{24}N_8O_6$	628.59	red-brown	288 – 290	90	63.05 (62.50)	3.85 (4.05)	17.83 (18.33)

IR	OH (cm^{-1})	$CH_{aliphatic}$ (cm^{-1})	CHO (cm^{-1})	C=N (cm^{-1})	N=N (cm^{-1})	Phenol ring (cm^{-1})	NO_2 (cm^{-1})	C–O (cm^{-1})
1	–	–	1657	–	1523	1477	1342	1284
			2753	–	1523	1477	1342	1284
			2854	–	1523	1477	1342	1284
3a	3429	2858 – 2927	–	1635	1522	1489	1342	1290
3b	3469	2854 – 2912	–	1631	1518	1491	1342	1288
3c	–	–	–	1614	1518	1489	1342	1290
3d	–	–	–	1618	1518	1491	1344	1290
3e	–	–	–	1616	1518	1485	1340	1290

Table 2. Characteristic IR absorption bands of **1** and the azo-azomethine derivatives **3a** – **3e**.



Scheme 3. Azo-azomethine compounds.

tions [15]. They display thermochromism and photochromism [13]. Hydrogen bonding and/or transfer is also very important in some living metabolism in which tautomerization is an essential step [16].

Keeping these features in mind, we decided to synthesize a series of azo-azomethine compounds and investigate their electronic and solvatochromic behavior.

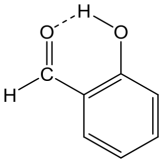
Results and Discussion

Synthesis of the compounds

The azo-azomethine compounds **3a** – **3e** were synthesized in a two-step process (Scheme 3). In the first step, salicylaldehyde was coupled with 4-nitroaniline to produce 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene (**1**). The reaction of **1** with a series of diamines afforded the corresponding azo-azomethine compounds **3**, the analytical data of which are summarized in Table 1. They are soluble in common organic solvents such as DMSO, DMF, and THF.

Infrared spectroscopy

The characteristic IR absorption bands of **1** and their azo-azomethine derivatives **3a** – **3e** are shown in Table 2. The IR spectrum of **1** exhibits a band at 1523 cm^{-1} due to the stretching vibration of the azo (N=N) group. In addition, a strong band at 1657 cm^{-1} due to the stretching vibration of the aldehydic C=O bond and two weak bands at 2753 and 2854 cm^{-1} due to the aldehydic C–H bond vibration confirm the proposed azo tautomer. A medium to strong band at 1284 cm^{-1} may be assigned to the $\nu_{(C\text{-}O)}$ vibration which also confirms the existence of the azo tau-



Scheme 4. Intramolecular hydrogen bonding in salicylaldehyde.

tomer [18]. In addition, the absence of the corresponding bands for the ketone carbonyl (C=O) and hydrazine (N–H) groups at about 1700 cm^{-1} and 3300 cm^{-1} exclude the presence of the hydrazone tautomer.

The IR spectrum of **1** does not show the band due an OH stretching frequency. This feature has already been reported for salicylaldehyde itself as well as for other salicylaldehyde derivatives and supports the presence of an intramolecular hydrogen bond (Scheme 4) [19, 20].

The IR spectra of the azo-azomethines **3a** – **3e** show the presence of the C=N band while the characteristic bands due to an aldehyde group are absent. The C–O stretching mode in the range 1288 – 1290 cm^{-1} and the stretching frequency of N=N at about 1520 cm^{-1} indicate that the compounds exist exclusively in the azo form. The absence of bands at about 1700 and 3300 cm^{-1} due to ketone carbonyl (C=O) and hydrazine (N–H) groups also exclude the keto-amine tautomer.

The IR studies strongly suggest that these compounds behave differently regarding the enol-imine/keto-amine tautomerization. While **3a** and **3b** exist exclusively in the enol-imine tautomer, all phenylenediamine-based compounds **3c** – **3e**, have structures that lie between the two enol-imine and keto-amine tautomers due to a relatively strong intramolecular hydrogen bond. The stretching frequencies of the imine (C=N) group are observed at 1614, 1618 and 1616 cm^{-1} for **3c**, **3d** and **3e**, respectively. Compound **3c** has the least C=N stretching frequency which means it has the strongest hydrogen bonding. The corresponding bands for **3a** and **3b** were observed at higher frequencies at 1635 and 1631 cm^{-1}, respectively, suggesting the double bond character of the C=N bond.

The OH stretching frequency is observed at 3429 (**3a**) and 3469 cm^{-1} (**3b**). In contrast, the corresponding band does not appear in the spectra of phenylenediamine and **1**. This result confirms our postulate regarding the presence of a relatively strong intramolecular hydrogen bond in compounds **3c** – **3e**. A similar situation has already been reported in salicylaldehyde [19, 20].

Table 3. ^{1}H NMR signals of **1** and the azo-azomethine derivatives **3a** – **3e**.

NMR	CHO	OH	C=N	Ar–H
1	10.06 (s)	11.46 (s)	–	7.14 – 8.41
3a	–	–	–	–
3b	–	14.10 (s)	8.50 (s)	6.99 – 8.40
3c	–	10.25 (s)	8.85 (d)	7.00 – 8.50
3d	–	10.38 (s)	9.07 (s)	6.74 – 8.77
3e	–	–	–	–

NMR spectroscopy

The ^{1}H NMR spectra of the compounds were recorded using [D_6]DMSO (**3c**, **3d**) and $CDCl_3$ (**3b** and **1**) as a solvent. Compounds **3a** and **3e** were not sufficiently soluble for ^{1}H NMR investigations.

The ^{1}H NMR spectrum of **1** shows a singlet at δ = 11.46 ppm which disappears after adding deuterated water, hence it was assigned to the hydroxyl proton [5, 11, 18]. Another singlet at δ = 10.06 ppm was assigned to the aldehyde proton (Table 3) [18]. In comparison, the corresponding protons of salicylaldehyde were observed at about 11 and 9.8 ppm. The spectrum does not show a broad band at 4 – 6 ppm which is typical for an NH proton. This result in addition with the presence of the hydroxyl proton confirms the existence of the enol-imine tautomer and excludes the keto-amine form.

The singlet at δ = 10.06 ppm due to the aldehyde proton of **1** disappeared through the reaction with diamines. Instead, the ^{1}H NMR spectra of **3b** – **3d** exhibit signals at about δ = 8.50 – 9.07 ppm due to the imine proton.

In the ^{1}H NMR spectra of **3c** and **3d** the salicylic hydroxyl proton was observed at 10.25 and 10.38 ppm, respectively. The OH signal disappeared after the addition of deuterated water [5, 11, 18]. The chemical shift of the hydroxyl group is a measure of the hydrogen bonding/transfer ability of azo-azomethine dyes [9, 21, 22]. The presence of the OH signal at 10 – 11 ppm for **3c** and **3d** indicates intramolecular hydrogen bonding [9] while a remarkable shift toward 14 ppm in **3b** indicates the presence of the enol-imine tautomer. This signal disappeared very slowly and instead, a signal in the range 5 – 6 ppm appeared due to an NH proton which suggests the enol-imine to keto-amine tautomerization.

In the ^{1}H NMR spectrum of **3c**, the imine proton signal splits into a doublet due to a coupling with the hydroxyl proton. Indeed, as a result of a relatively strong hydrogen bond, this proton is sensed by the hydroxyl proton which is now located mainly on the imine ni-

trogen. In other words, **3c** prefers the keto-amine tautomer over the enol-imine tautomer.

UV/Vis spectrophotometry

Band assignment

The UV/Vis spectrum of **1** displays mainly two bands at r. t. The first band located at 258 – 270 nm can be assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring [11]. The second band located at 360 – 370 nm corresponds to a $\pi \rightarrow \pi^*$ transition involving the π electrons of the azo group [12, 23]. The latter band confirms the existence of the azo tautomer since in case of the keto-amine tautomer, there should be an absorption band at about 450 nm or higher [18]. These two absorption bands shift to higher wave lengths in the azo-azomethines **3a** – **3e** due to the extension of the conjugated system as a result of coupling.

The electronic absorption spectra of the azo-azomethine compounds were investigated in organic solvents of different polarity. The results show that there are three characteristics absorption bands in all studied solvents except DMSO. The first band at about 230 – 290 nm is due to a $\pi \rightarrow \pi^*$ electron transition of the aromatic ring [11, 12]. The second band at 370 – 395 nm corresponds to a $\pi \rightarrow \pi^*$ transition involving the π-electrons of the azo and azomethine groups [12, 23]. The broad band observed in the range 470 – 580 nm can be assigned to an intramolecular charge transfer interaction involving the whole molecule [12]. The strong broadness of the intermolecular CT band supports the existence of an enol-imine/keto-amine tautomeric equilibrium originating from the OH group in *ortho*-position to the nitrogen of the imine group. Thus the CT band may be

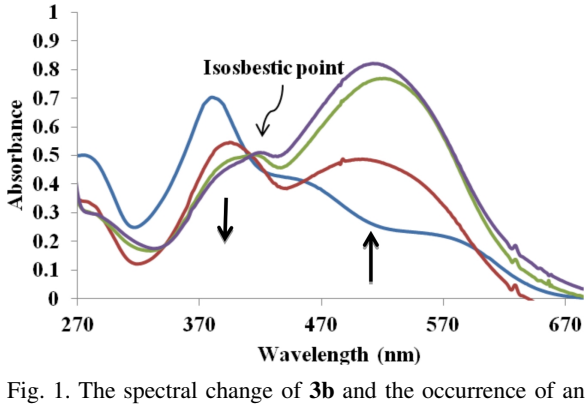


Fig. 1. The spectral change of **3b** and the occurrence of an isosbestic point due to slow tautomerization in DMF solution.

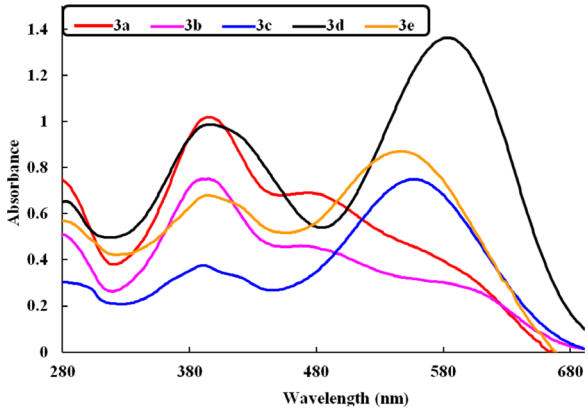


Fig. 2. Absorption spectra of the prepared dyes **3a** – **3e** in DMF.

considered as a composite band resulting from the absorption of the two equilibrium species. The absorption in the lower energy region is due to the enol-imine form while the one in the higher energy region can be attributed to the keto-amine species [12]. This behavior seems to be quite common for azo or azomethine compounds having a hydroxy group in *ortho*-position to the N=N or C=N bond on the aromatic ring [11, 12].

For azo-azomethines **3a** and **3b**, the second absorption band is more intense than the third one indicating the existence of the enol-imine tautomer. The relative intensity of this band decreases slowly after a long period of time indicating a relatively slow tautomerization into the corresponding keto-amine tautomer. The presence of an isosbestic point in the UV/Vis spectrum of **3b** strongly supports such a slow tautomerization (Fig. 1).

For azo-azomethines **3c** – **3e**, the third band at about 470 – 580 is more intense with respect to the second one indicating an intramolecular hydrogen bond for these compounds (Fig. 2).

Solvatochromic behavior

The electronic absorption spectra of the compounds were recorded in four organic solvents, DMSO, DMF, CH_2Cl_2, and THF, at a concentration of approximately 2×10^{-5} M in the range from 200 to 700 nm. The results indicate that the absorption bands at 370 – 395 nm are solvent-dependent and shift toward higher wavelengths with increasing solvent polarity (positive solvatochromism) in all solvents, except DMSO (Table 4). The different behavior in DMSO may be due to its higher basicity and/or the change of solvation of the solute

Table 4. Absorption spectral data of **3a – 3e** in various organic solvents; λ_{max} (nm) (ε dm^{-1} in mol^{-1} cm^{-1}).

Compound	DMSO	DMF	CH_2Cl_2	THF
3a	273 (37900)	271 (37900)	233 (55000)	238 (41900)
	393 (33300)	392 (51100)	281 (39500)	277 (30100)
	469 (19800)	485 (33900)	382 (69700)	382 (55800)
			477 (8300)	473 (14400)
3b	258 (44300)	275 (26100)	233 (58500)	487 (5200)
	382 (44500)	389 (38000)	282 (47700)	280 (25400)
	477 (14700)	484 (22100)	384 (75900)	382 (52700)
			484 (25100)	487 (5200)
3c	275 (27600)	298 (14300)	234 (44700)	436 (27800)
	382 (40000)	387 (18800)	277 (32600)	305 (65000)
		554 (37500)	384 (48400)	436 (27800)
			547 (6600)	
3d	277 (44000)	279 (32700)	236 (69500)	238 (40200)
	385 (76000)	393 (49400)	276 (35700)	272 (41800)
		581 (68300)	382 (77900)	370 (83600)
			511 (5800)	509 (7100)
3e	275 (41200)	266 (29200)	230 (30300)	238 (36500)
	377 (55400)	393 (34000)	278 (21400)	278 (39100)
		543 (43600)	384 (35200)	382 (57900)
			512 (5600)	509 (8200)

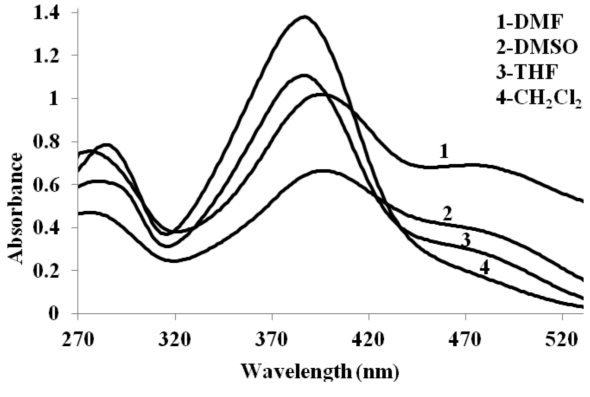


Fig. 3. Effect of solvent on the relative stability of the intramolecular hydrogen bonding in **3a**.

molecules on going from the ground to the excited state [24]. A similar red shift has also been observed for the intramolecular CT band appearing in the range 470 – 580 nm (Fig. 3). This positive solvatochromism may be explained on the principle that the excited state is more polar than the ground state and hence will be more stabilized in more polar solvents [12].

In this work, five novel azo-azomethine compounds shown in Scheme 3 were synthesized from the reaction of 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene with a series of diamines. According to the spectroscopic data, the primary azo compound exists in the azo form in solution and in the solid. Aliphatic diamine-based azo-azomethine compounds favor the enol-imine tautomer while aromatic diamine-based compounds have structures that lie between the two enol-imine/keto-amine tautomers due to a relatively strong hydrogen bond between the nitrogen atom of the azomethine group, and the hydroxyl proton. In addition, spectrophotometric studies in different solvents indicate a positive solvatochromism.

Experimental Section

Materials and measurements

All reagents and solvents were used as supplied by Merck and were used without further purification. 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene (**1**) was prepared according to a literature procedure [17]. NMR spectra were recorded on a Bruker 200 MHz spectrometer. Elemental analyses were performed on an EURO 3000 instrument. Absorbance spectra were recorded using a spectrophotometer Agilen 8453 equipped with a thermostated bath (Huber polystat cc1); the temperature of the cell holder was maintained at 25 ± 0.1 °C. FT-IR spectra were recorded on a WQF-510 spectrophotometer in the region of 3000 – 400 cm^{-1} on KBr pellets. Melting points of all compounds were determined on an Electrothermal apparatus.

*General procedure for the synthesis of **3a – 3e***

A solution of diamine **2** (**2a – 2e**) (2 mmol) in absolute EtOH (10 mL) was added to a stirring solution of 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene (**1**) (4 mmol) in absolute EtOH during a period of 30 min at 50 °C. The mixture was heated in a water bath for 2 h at 80 °C with stirring, then cooled and let to stand at ambient temperature. The product was collected by filtration, washed successively with diethyl ether and dried in air. Physical and spectroscopic data: Tables 1 – 4.

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