

Synthesis and Spectral Characterisation of Novel Azo-Azomethine Dyes

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The synthesis of novel azo-azomethine dye derivatives of substituted Schiff bases were carried out by the reaction of substituted 1-naphtylamine with 4-nitro and 2-chloro benzenediazonium tetrafluoroborate salts as a coupling component. These compounds were identified by IR, UV-Vis and $^1\text{H-NMR}$ spectroscopic techniques, and elemental analysis.

Introduction

A part from their purely chemical interest, azo-azomethine dyes are being increasingly used in the textile, leather and plastic industries¹. The coupling reaction between diazoniumtetra fluoroborate salt and arylamine Schiff's bases first reported by Messmer & Sziman¹⁻⁴.

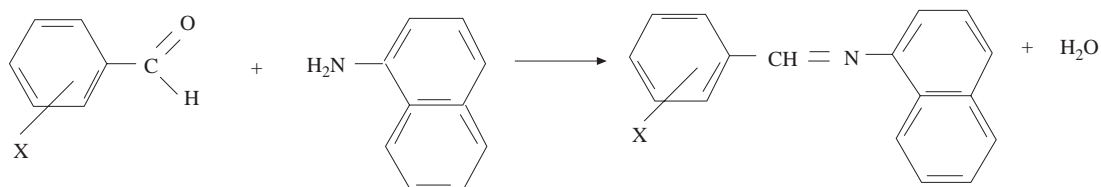
The literature contains some investigations dealing with azo-azomethine dyes, no work has been carried out describing the coupling products of 4-nitro and 2-chlorobenzenediazonium tetrafluoroborate salts and substituted benzylidine 1-naphtyl amine Schiff bases. In this study, compounds of this type were synthesised and identified by IR, UV-Vis and $^1\text{H-NMR}$ spectroscopic techniques, and elemental analysis.

Material and Method

All compounds were purified by recrystallisation and then monitored by thin-layer chromatography (TLC) and spectroscopic techniques. The melting points (mp) of the compounds were determined with a Gallenkamp electrothermal melting point apparatus. IR spectra were recorded on a Mattson 1000 FTIR spectrophotometer calibrated with polystyrene film using a KBr disc. Absorption spectra in ethanol were determined on a Unicam UV-Vis spectrophotometer. The $^1\text{H-NMR}$ spectra were taken on a Varian EM 360 L and NMR 200 MHz referencing spectrometer with tetramethylsilane (TMS) as internal standard. Elemental analysis was performed by TUBİTAK, Marmara Research Center.

Method

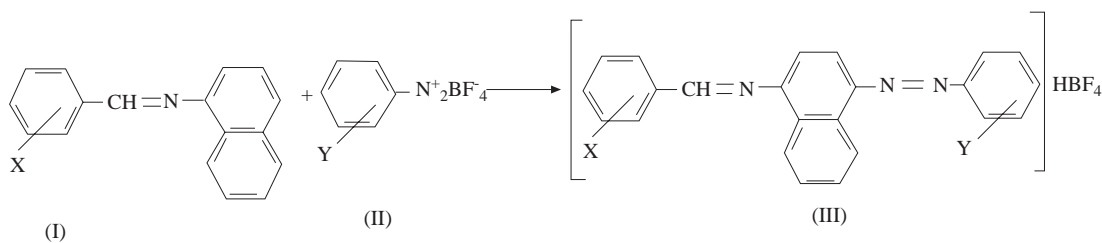
Schiff's Bases: The naphthylamine (0.2 mol) and appropriate aldehyde (0.2 mol) containing 4 drops of piperidine were heated under reflux in ethanol for 4-6 h. The Schiff's bases crystallised out on cooling and were recrystallised from ethanol several times for purification.



I

- | | |
|-----------|-------------------------|
| a; X=H | a; X= m-NO ₂ |
| b; X=p-Cl | b; X= p-NO ₂ |
| c; X=o-Cl | c; X= o-NO ₂ |

General Coupling Procedure: 4-nitro and 2-chloro benzenediazonium tetrafluoroborate salts and Schiff's bases were dried over P₂O₅ under vacuum before use. Spectroscopic-grade acetonitrile was used in all cases. The diazonium salt (0.02 mol) and the Schiff's base (0.02 mol) were dissolved in acetonitrile (100 cm³) and the solution was stirred at 20°C for 48 h. None of diazonium salt remained after this time. Diethylether was added to reaction mixture to precipitate the arylazo Schiff's base tetrafluoroborate III. The yield was determined gravimetrically, ensuring by TLC analysis that compound III had been isolated as analytically pure from solution according to the below reaction:



(I)

(II)

(III)

- | |
|------------------------|
| a; Y=p-NO ₂ |
| b; Y=o-Cl |

- | | |
|------------------------|------------------------|
| a; X=H | ; Y= p-NO ₂ |
| b; X=p-Cl | ; Y= p-NO ₂ |
| c; X=m-NO ₂ | ; Y= p-NO ₂ |
| d; X=p-OH | ; Y= p-NO ₂ |
| e; X=H | ; Y= o-Cl |
| f; X=o-Cl | ; Y= o-Cl |
| g; X=p-Cl | ; Y= o-Cl |
| h; X=p-NO ₂ | ; Y= o-Cl |

4'-nitro-4- (benzilidene-1-naphthylamino) azobenzenetetrafluoroborate salt (III a):

Yield 62 %, m.p: 230-232°C, IR (KBr) 1679cm⁻¹ (C=N), 1550 and 1332 cm⁻¹ (N=O), 1422 cm⁻¹ (N=N); UV-Vis (Et OH), 297 nm ($\pi \rightarrow \pi^*$, CH=N), 530 nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 8.35ppm (s, azomethine proton, 1H),7.08-8.70 ppm (m, arom. proton, 15H); Anal. calcd. for C₂₃H₁₇N₄O₂BF₄, C:58.97; H:3.63 found C:60.77; H:3.07.

4'-nitro-4-(4-chlorobenzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III b):

Yield 65 %, m.p: 240-242°C, IR (KBr) 1679cm⁻¹ (C=N), 1561 and 1343 cm⁻¹ (N=O), 1342 cm⁻¹ (N=N); UV-Vis (Et OH), 297 nm ($\pi \rightarrow \pi^*$, CH=N), 530 nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 8.33ppm (s, azomethine proton, 1H), 7.10-8.80 ppm (m, arom. proton, 15H); Anal. calcd. for C₂₃H₁₇N₄O₃BF₄, C:54.92; H:3.18, found C:55.87, H:3.31.

4'-nitro-4-(3-nitrobenzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III c):

Yield 59 %, m.p: 243-245°C, IR (KBr) 1676cm⁻¹ (C=N), 1566 and 1340 cm⁻¹ (N=O), 1412 cm⁻¹ (N=N); UV-Vis (Et OH), 297 nm ($\pi \rightarrow \pi^*$, CH=N), 530 nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 8.33ppm (s, azomethine proton, 1H), 7.10-8.66 ppm (m, arom. proton, 15H); Anal. calcd. for C₂₃H₁₆N₅O₄BF₄, C:53.80; H:3.12, found; C:53.67, H:3.28.

4'-nitro-2-(4-hydroxybenzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III d):

Yield 42 %, m.p: 224-226°C, IR (KBr) 1634cm⁻¹ (C=N), 1558 and 1330 cm⁻¹ (N=O), 1416 cm⁻¹ (N=N); 3273 cm⁻¹ (broad, OH) UV-Vis (Et OH), 293 nm ($\pi \rightarrow \pi^*$, CH=N), 340 nm ($\pi \rightarrow \pi^*$, CN=N); 475nm ($\pi \rightarrow \pi^*$, N=N) 522nm ($\pi \rightarrow \pi^*$, N=N); ¹H-NMR (DMSO d₆), 8.45ppm (s, azomethine proton, 1H), 6.80 ppm and 8.90 ppm (m, arom. proton, 14H); 11.95 ppm (s, hydroxyl proton, 1H) Anal. calcd. for C₂₃H₁₇N₅O₄BF₄, C:57.02; H:3.51, found C:56.46, H:4.14.

2'-Chloro-4-(benzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III e):

Yield 48 %, m.p: 195-196°C, IR (KBr) 1679cm⁻¹ (CH=N), 1422 cm⁻¹ (N=N); 1037 cm⁻¹ (Ar-Cl), UV-Vis (Et OH), 283 nm ($\pi \rightarrow \pi^*$, CH=N), 336 nm ($\pi \rightarrow \pi^*$, CN=N); 456nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 6.85ppm and 8.90 ppm (m, azomethine and arom. proton, 16 H); Anal. calcd. for C₂₃H₁₇N₃ClBF₄, C:60.32; H:3.71, found C:61.42, H:3.30.

2'-Chloro-4-(2-chlorobenzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III f):

Yield 65 %, m.p: 204-206°C, IR (KBr) 1679cm⁻¹ (CH=N), 1423 cm⁻¹ (N=N); 1036 cm⁻¹ (Ar-Cl), UV-Vis (Et OH), 283 nm ($\pi \rightarrow \pi^*$, CH=N), 458 nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 6.88 ppm and 8.90 ppm (m, azomethine and arom. proton, 16 H); Anal. calcd. for C₂₃H₁₆BF₄, C:56.09; H:3.25, found C:56.20, H:3.46.

2'-Chloro-4-(4-chlorobenzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III g):

Yield 57 %, m.p: 208-210°C, IR (KBr) 1679 cm⁻¹ (CH=N), 1422 cm⁻¹ (N=N); 1037 cm⁻¹ (Ar-Cl), UV-Vis (Et OH), 283nm ($\pi \rightarrow \pi^*$, C=N), 457 nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 6.86 ppm and 8.90 ppm (m, azomethine and arom. protons, 16 H); Anal. calcd. for C₂₃H₁₆N₃Cl₂BF₄, C:56.09; H:3.25, found C:56.03, H:3.51.

2'-Chloro-4-(4-netrobenzilidene-1-naphtylamino) azobenzenetetraflouroborate salt (III h):

Yield 38 %, m.p: 223-225°C, IR (KBr) 1679 cm⁻¹ (CH=N), 1423 cm⁻¹ (N=N); 1036 cm⁻¹ (Ar-Cl), UV-Vis (Et OH), 283 nm ($\pi \rightarrow \pi^*$, C=N), 457 nm ($\pi \rightarrow \pi^*$, N=N), ¹H-NMR (DMSO d₆), 6.88 ppm and 8.90 ppm (m, azomethine proton and arom. protons, 16 H); Anal. calcd. for C₂₃H₁₆N₄Cl O₂BF₄, C:54.94; H:3.18, found C:53.77, H:3.53.

Results and Discussion

Although the literature contain some investigations dealing with diazo and monoazo compounds^{1,5-8}, it seems that no work has been carried out describing the influence of C=N linkage having the substituents on the phenyl ring.

The UV and Visible absorption of the compounds under investigation display mainly three bands

observed in ethanol within the range 200-600 nm. The first band at 225-255 nm was assigned to the moderate energy $\pi \rightarrow \pi^*$ transition of the aromatic ring, while the second band 280-300nm is due to the low energy $\pi \rightarrow \pi^*$ transition of the azomethine group. The third band at 450-530 nm was assigned to the $\pi \rightarrow \pi^*$ transition of azo groups (Fig.1). The band was observed at 345-362 nm in analogy to the case of simple azo compound⁹.

In the spectrum of compound (III d), five bands are observed in the same region (Fig. 1). On comparing the spectra of simple monoazo compounds¹⁰ with those of the corresponding azo-azomethine derivatives, it becomes apparent that the presence of the OH group causes an apparent red shift in the maximum absorption. This shift can be explained on the basis of the existence of the intermolecular hydrogen bonding between the N=N and OH groups. This result was supported by the IR and ¹H-NMR spectra of the III d.

The IR spectra of the compounds (III d) under investigation show a weak band within the range 3350-3250 cm^{-1} corresponding to ν_{OH} . The low value reveals that the OH group is involved in an intermolecular H-bonding. The IR spectra also show a weak band, or shoulder located at 3020-2960 cm^{-1} , which is assigned to the aromatic C-H asymmetrical stretching vibration of the N=N group, leading to the band located 1440-1412 cm^{-1} region, while the other stretching vibration of the N=N in the range 1600-1580 cm^{-1} is masked by the intense bands due to the ring vibration. The band due to C=N appears as medium strong in the range 1680-1670 cm^{-1} . For compounds (III-a, b, c, d, h), the bands at 1363-1330 cm^{-1} and 1573-1531 cm^{-1} are assigned to the symmetrical and asymmetrical stretching vibration of the NO₂ group, respectively. All Ar-Cl compounds show a weak band within the 1040-1030 cm^{-1} region.

In the ¹H-NMR spectra of the compound synthesised, the resonance of the aromatic ring were observed in the range δ 8.90-6.80 ppm. The signal characteristic of the proton of the azomethine group at some compounds which were (III e,f,g,h) was obscured by the multiple signals of aromatic protons, while some compounds (III a,b,c,d) were observed in the region 8.45-8.27 ppm. The 1H-NMR spectra of compound II d show that the hydroxyl proton with intermolecular hydrogen band resonates at the lower field.

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