Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 2989-2993

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13465

Synthesis and Spectral Properties of 1-Substituted Phenyl-3-(*p*-methoxycarbonyl)phenyl-5-phenylformazans

HÜLYA SENÖZ[1,*], EBRU YILDIRIM[1] and HABIBE TEZCAN[2]

[1]Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe 06800, Ankara, Turkey
[2]Department of Chemistry, Faculty of Gazi Education, Gazi University, Teknikokullar 06500, Ankara, Turkey

*Corresponding author: Tel: +90 31 22977960; E-mail: senoz@hacettepe.edu.tr

(*Received*: 18 January 2012; *Accepted*: 5 December 2012) AJC-12503

Formazans **1-14** were prepared by the coupling reaction of phenylhydrazones and diazonium salts of aniline or -NO_2, -CH_3, -OCH_3, -I, substituted anilines. The phenylhydrazones were synthesized by condensation of benzaldehyde or methyl-4-formylbenzoate with phenylhydrazine. The structures of the compounds were confirmed by IR, ^{1}H NMR and ^{13}C NMR. The dependence of λ_{max} upon the type of substituents and their positions on the phenyl ring was investigated using UV-visible spectra.

Key Words: Formazan, Diazo coupling, Dyes, Spectroscopy.

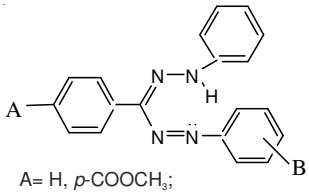
INTRODUCTION

Since the first synthesis of formazan by Von Penchman[1,2], the investigation of formazans by chemists, biologists, technologists and other specialists has been ongoing[3]. Because of the presence of conjugate *p*-system in formazans, the redox reactions of these compounds are typical. The main areas of practical application are isomerization and tautomeric transformations, and enhanced acidity and basicity[4-7]. Formazans form tetrazolium salts when they are oxidized[8]. Tetrazolium salts are reduced back to formazans by enzymes in the cell and stain tissue. The tetrazolium-formazan system is classified as a marker of vitality[9] and this feature enables the determination of activity on tumor cells. This feature is the cause of an increasing interest in the chemistry of formazans.

In this study, novel formazans with various substituents attached to the 1-substituted phenyl-3-(*p*-metoxycarbonyl) phenyl were synthesized (Fig. 1), their structures and spectral behaviours were investigated by using elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, and UV-visible spectra. The aim of this study is to clarify the spectral behaviour of novel formazans in some application areas, such as medical, analytical, drug applications, the dye industry and new organic synthesis. It is also speculated that these compounds may be more suitable for use in the fields than known substituted formazans.

EXPERIMENTAL

The UV-visible spectra of all the formazans synthesized in this study were obtained with UNI CAM UV2-100 UV/visible spectrophotometer using 1 cm quartz cells in 10^{-4} mol L^{-1} CH_3OH using 325 nm UV lamp in the range of 200-600 nm. The IR spectra were obtained on Thermo, Nicolet IS10-FTIR spectrometer between 4000 and 400 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectral studies were performed on a Bruker 400 MHz spectrometer using $CDCl_3$. All the elemental analysis studies were carried out using a LECO-CHNS- 932 elemental analyzer. Melting points were determined with an electrothermal melting point apparatus and are uncorrected.



A= H, *p*-$COOCH_3$;
B= (*o*,*m*,*p*)- NO_2,-CH_3,-OCH_3, -I

Fig. 1. Structure of the studied formazan derivatives

General procedure: The synthesis of substituted formazans were carried out using benzaldehyde (or substituted benzaldehydes), phenylhydrazine and aniline. Benzaldehyde (or substituted benzaldehydes) were reacted with phenylhydrazine at pH 5-6 to obtain benzaldehyde phenylhydrazone (or substituted benzaldehydephenylhydrazones). These hydrazones were then coupled with the corresponding benzenediazonium chloride at *ca.* -5 ºC[10-12].

Synthesis of 1,3,5-triphenylformazan (TPF) (1): Benzaldehyde (1.06 g, 0.01 mol) was dissolved in methanol (25 mL)

and phenylhydrazine (1.08 g, 0.01 mol) was gradually added with constant stirring at pH 5-6. The procedure was completed in 0.5 h. The resulting yellow hydrazone was left on the bench overnight and then was filtered and recrystallized from methanol. The benzaldehyde phenylhydrazone (1.96 g, 0.01 mol) was dissolved in methanol (35 mL) and (35 mL) buffer solution [sodium hydroxide (2.50 g), sodium acetate (3.50 g) and methanol (200 mL)] by constant stirring. In another flask benzenediazonium chloride solution was prepared using aniline (0.93 g, 0.01 mol) concentrated HCl (5 mL) and sodium nitrite (0.75 g) at -5 ºC. This solution was added to the benzaldehyde phenylhydrazone solution dropwise with constant stirring to form formazan. The solution was stirred for 2 h at the same temperature and stored for 2 days. Each compound was recrystallized from methanol giving cherry red crystals. Yield 80 %, m.p. 174 ºC (Lit[11] 172-174 ºC).

Other compounds were prepared in similar manner and characterization data of **2-14** were given.

3-(*p*-Methoxycarbonylphenyl)-1,5-diphenylformazan (2): Claret red crystals, yield 84 %, m.p. 172 ºC. IR (λ_{max} in cm^{-1}): 3050-3000 (aromatic CH), 2943 (aliphatic CH), 3070 (NH), 1606 (aromatic C=C), 1715 (C=O), 1513 (C=N), 1350 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.88 (s, 3H, OCH_3), 7.32-8.26 (m, 14H, Ar-H), 15.68 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.09 (OCH_3), 118.96-141.89 (Ar-C), 147.62 (C=N), 167.21 (C=O). Anal. calcd. for $C_{21}H_{18}N_4O_2$: C, 70.36; H, 5.06; N, 15.64. Found: C, 70.95; H, 5.09; N, 15.64.

1-(*o*-Nitrophenyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (3): Red brown crystals, yield 81 %, m.p. 194 ºC. IR (λ_{max} in cm^{-1}): 3050-3000 (aromatic CH), 2944 (aliphatic CH), 3062 (NH), 1609 (aromatic C=C), 1719 (C=O), 1518 (C=N), 1324 (NO_2), 1371 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.04 (s, 3H, OCH_3), 7.12- 8.48 (m, 13H, Ar-H), 15.65 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.24 (OCH_3), 116.92-142.87 (Ar-C), 152.83 (C=N), 166.98 (C=O). Anal. calcd. for $C_{21}H_{17}N_5O_4$: C, 62.50; H, 4.24; N, 17.36. Found: C, 62.95; H, 4.92; N, 17.55.

1-(*m*-Nitrophenyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (4): Rusty brown crystals, yield 85 %, m.p. 191 ºC. IR (λ_{max} in cm^{-1}): 3040 (aromatic CH), 2951 (aliphatic CH), 3090 (NH), 1616 (aromatic C=C), 1715 (C=O), 1513 (C=N), 1340 (NO_2), 1350 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 4.48 (s, 3H, OCH_3), 7.40- 8.46 (m, 13H, Ar-H), 15.29 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.18 (OCH_3), 111.63-149.29 (Ar-C), 149.77 (C=N), 167.01 (C=O). Anal. calcd for $C_{21}H_{17}N_5O_4$: C, 62.50; H, 4.24; N, 17.36. Found: C, 62.91; H, 4.78; N, 17.65.

1-(*p*-Nitrophenyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (5): Dark brown crystals, yield 77 %, m.p. 198 ºC. IR (λ_{max} in cm^{-1}): 3000 (aromatic CH), 2944 (aliphatic CH), 3087 (NH), 1602 (aromatic C=C), 1719 (C=O), 1537 (C=N), 1320 (NO_2), 1400 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.47 (s, 3H, OCH_3), 7.24- 8.40 (m, 13H, Ar-H), 15.36 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.20 (OCH_3), 113.47- 146.82 (Ar-C), 150.43 (C=N), 166.76 (C=O). Anal. calcd. for $C_{21}H_{17}N_5O_4$: C, 62.50; H, 4.24; N, 17.36. Found: C, 62.80; H, 4.64; N, 17.73.

1-(*o*-Tolyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (6): Rusty brown crystals, yield 82 %, m.p. 207 ºC. IR(λ_{max} in cm^{-1}): 3040-3000 (aromatic CH), 2952 (aliphatic CH), 3025 (NH), 1609 (aromatic C=C), 1707 (C=O), 1515 (C=N), 1370 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 2.50 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 7.26- 8.20 (m, 13H, Ar-H), 15.58 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 29.21 (CH_3), 52.14 (OCH_3), 112.98- 145.36 (Ar-C), 151.65 (C=N), 168.62 (C=O). Anal. calcd. for $C_{22}H_{20}N_4O_2$: C, 70.94; H, 5.42; N, 15.04. Found: C, 71.25; H, 6.01; N, 15.21.

1-(*m*-Tolyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (7): Bright brown crystals, yield 77 %, m.p. 158 ºC. IR (λ_{max} in cm^{-1}): 3040 (aromatic CH), 2842-2940 (aliphatic CH), 3019 (NH), 1609 (aromatic C=C), 1707 (C=O), 1506 (C=N), 1355 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 2.49 (s, 3H, CH_3), 3.44 (s, 3H, OCH_3), 7.32-8.26 (m, 13H, Ar-H), 15.69 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 29.47 (CH_3), 52.37 (OCH_3), 112.15-146.24 (Ar-C), 150.54 (C=N), 167.65 (C=O). Anal. calcd. for $C_{22}H_{20}N_4O_2$: C, 70.94; H, 5.42; N, 15.04. Found: C, 71.34; H, 5.69; N, 15.67.

1-(*p*-Tolyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (8): Rush brown crystals, yield 83 %, m.p. 175 ºC. IR (λ_{max} in cm^{-1}): 3050 (aromatic CH), 2995-2944 (aliphatic CH), 3062 (NH), 1603 (aromatic C=C), 1717 (C=O), 1506 (C=N), 1378 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 2.46 (s, 3H, CH_3), 3.55 (s, 3H, OCH_3), 7.32- 8.25 (m, 13H, Ar-H), 15.68 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 28.15 (CH_3), 52.88 (OCH_3), 115.34- 147.44 (Ar-C), 152.18 (C=N), 168.23 (C=O). Anal. calcd. for $C_{22}H_{20}N_4O_2$: C, 70.94; H, 5.42; N, 15.04. Found: C, 71.46; H, 5.55; N, 15.35.

1-(*o*-Anisidyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (9): Purplish red crystals, yield 80 %, m.p. 163 ºC. IR (λ_{max} in cm^{-1}): 3000 (aromatic CH), 2952 (aliphatic CH), 3020 (NH), 1589 (aromatic C=C), 1707 (C=O), 1509 (C=N), 1349 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.85 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.96-8.15 (m, 13H, Ar-H), 15.38 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 51.67 (OCH_3), 52.84 (OCH_3), 112.21- 148.45 (Ar-C), 151.85 (C=N), 167.58 (C=O). Anal. calcd. for $C_{22}H_{20}N_4O_3$: C, 68.02; H, 5.19; N, 14.43. Found: C, 68.35; H, 5.40; N, 14.00.

1-(*m*-Anisidyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (10): Purplish red crystals, yield 80 %, mp 161 ºC. IR (λ_{max} in cm^{-1}): 3000-3050 (aromatic CH), 2964 (aliphatic CH), 3011 (NH), 1609 (aromatic C=C), 1709 (C=O), 1509 (C=N), 1349 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.94 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.86- 8.24 (m, 13H, Ar-H), 15.62 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 51.82 (OCH_3), 52.56 (OCH_3), 115.48-148.69 (Ar-C), 150.93 (C=N), 168.32 (C=O). Anal. calcd. for $C_{22}H_{20}N_4O_3$: C, 68.02; H, 5.19; N, 14.43. Found: C, 68.43; H, 5.56; N, 14.10.

1-(*p*-Anisidyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (11): Rusty brown crystals, yield 77 %, m.p. 184 ºC. IR(λ_{max} in cm^{-1}): 3000 (aromatic CH), 2956 (aliphatic CH), 3025 (NH), 1604 (aromatic C=C), 1707 (C=O), 1504 (C=N), 1344 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.88 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.90- 8.19 (m, 13H, Ar-H), 15.88 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 51.26 (OCH_3), 52.35 (OCH_3), 113.62-147.71 (Ar-C), 150.24 (C=N), 166.92 (C=O). Anal. calcd. for $C_{22}H_{20}N_4O_3$: C, 68.02; H, 5.19; N, 14.43. Found: C, 68.18; H, 5.28; N, 14.26.

1-(*o*-Iodophenyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (12): Brown crystals, yield 99 %, m.p.

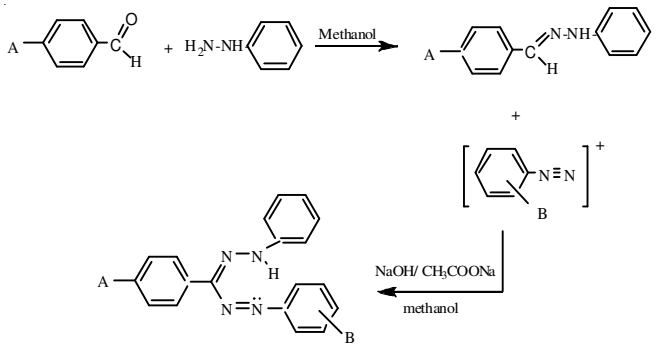
205 ºC. IR(λ_{max} in cm^{-1}): 3040 (aromatic CH), 2940 (aliphatic CH), 3030 (NH), 1605 (aromatic C=C), 1703 (C=O), 1522 (C=N), 1359 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.88 (s, 3H, OCH_3), 6.92- 8.18 (m, 13H, Ar-H), 15.07 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.77 (OCH_3), 112.67- 148.91 (Ar-C), 152.45 (C=N), 167.45 (C=O). Anal. calcd. for $C_{21}H_{17}N_4O_2I$: C, 57.12; H, 3.54; N, 11.59. Found: C, 57.85; H, 4.07; N, 11.87.

1-(*m*-Iodophenyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (13): Dark purplish crystals, yield 97 %, mp 200 ºC. IR(λ_{max} in cm^{-1}): 3056 (aromatic CH), 2945 (aliphatic CH), 3087 (NH), 1602 (aromatic C=C), 1712 (C=O), 1539 (C=N), 1377 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.88 (s, 3H, OCH_3), 6.82- 8.13 (m, 13H, Ar-H), 15.39 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.38 (OCH_3), 113.81- 148.61 (Ar-C), 155.63 (C=N), 168.04 (C=O). Anal. calcd. for $C_{21}H_{17}N_4O_2I$: C, 57.12; H, 3.54; N, 11.59. Found: C, 57.76; H, 3.39; N, 11.72.

1-(*p*-Iodophenyl-3-(*p*-methoxycarbonylphenyl)-5-phenyl formazan (14): Purplish red crystals, yield 69 %, m.p. 202 ºC. IR (λ_{max} in cm^{-1}): 3039 (aromatic CH), 2945 (aliphatic CH), 3093 (NH), 1608 (aromatic C=C), 1714 (C=O), 1528 (C=N), 1397 (N=N). ^{1}H NMR ($CDCl_3$) δ ppm: 3.88 (s, 3H, OCH_3), 6.82-8.13 (m, 13H, Ar-H), 15.49 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ ppm: 52.81 (OCH_3), 115.61-149.58 (Ar-C), 154.38 (C=N), 168.93 (C=O). Anal. calcd. for $C_{21}H_{17}N_4O_2I$: C, 57.12; H, 3.54; N, 11.59. Found: C, 57.39; H, 3.96; N, 11.89.

RESULTS AND DISCUSSION

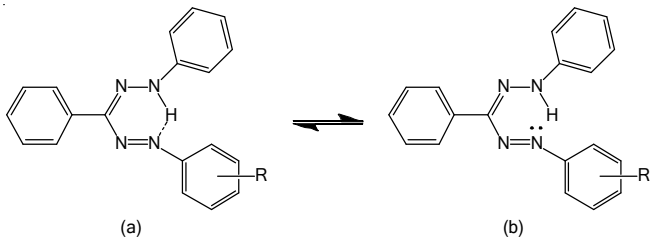
Synthesis and determination of structures of formazans: In this study, 1,3,5-triphenylformazan (**1**) and new 1-substituted phenyl-3-(*p*-methoxycarbonyl)phenyl-5-phenyl formazans were synthesized (**2-14**). The formazans were prepared by the coupling reactions of hydrazones with benzendiazonium chlorides, in a basic medium under 0 ºC. The hydrazones were obtained by the condensation reaction of phenyl hydrazine with aldehyde (or substituted aldehydes). This route proved to be time consuming and laborious. However, the advantage of this route was that it is possible to synthesize both symmetric and asymmetric formazans and could be conducted with common chemicals present in all laboratories. Although purifying the resultant product was difficult[10], formazans were synthesized in high yields. The reaction route is given in **Scheme-I**.



Scheme-I: The route followed in the synthesis of formazans

The IR data of formazans (**1-14**) reveal the C=N stretching bands between 1539-1504 cm^{-1}. C=N absorption values determine either a chelate or non-chelate structure of the formazans (**Scheme-II**). The C=N stretching band at 1510-1500 cm^{-1} shows chelate structures. However, the C=N stretching band at 1561-1551 cm^{-1} shows non-chelate structures[11,12]. For the studied formazans, **1-14**, chelate structures (**Scheme-IIa**) were found to be dominant while non-chelate structures (**Scheme-IIb**) were few in equilibrium.

The lower values of the N=N stretching bands 1410-1350 cm^{-1} are probably due to the intramolecular hydrogen bond and some chelate ring resonance. The N=N stretching band of the chelate form of 1,3,5-triphenylformazan was located at 1357 cm^{-1} and the non-chelate form was located[13] at 1461 cm^{-1}. In addition, the lower values of absorption bands N-H 3090-3011 cm^{-1} show chelate structure[4]. Chelate structures have a six-membered conjugated system in which *p*-electrons are delocalized. Hence, the double bond characteristic decreases. The stretching bands of C=N, N=N and N-H were observed at lower frequencies. Other IR data can be evaluated in a similar manner: aromatic CH, aliphatic CH, C=O, C=C stretching peaks and NO_2 vibration band were observed in the expected regions.



Scheme-II: Chelate and non-chelate structures

The ^{1}H NMR data showed that the aromatic hydrogen peaks of 1,3,5-triphenylformazan were observed between 7.22-8.09 ppm. Each of the three phenyl rings of the formazan has a different electron density, so the peaks of each aromatic H showed a broad range[14]. The electron withdrawal effect of substituent bonded phenyl rings and the double bond resonance in the structure of **2-5** caused the aromatic hydrogen peaks to shift towards lower fields, while the electron donating effect of substituent bonded phenyl rings in the structure of **9-14** caused a shift in the aromatic hydrogen peaks towards higher fields. Because of the weak electron donating effect of CH_3, in formazans **6-8**, we observed that the values of chemical shifts of aromatic-H were similar to that of 1,3,5-triphenylformazan.

1,3,5-Triphenylformazan and other formazans **2-14**, exhibited sharp NH signals in the downfield region between 15.29-15.88 ppm (^{1}H, s), indicative of an intramolecular hydrogen bond, which decreases electron density around the proton and thus moves the proton absorption to the lower field[15,16]. Fig. 2 gives the ^{1}H NMR spectra of formazan **3** as an example.

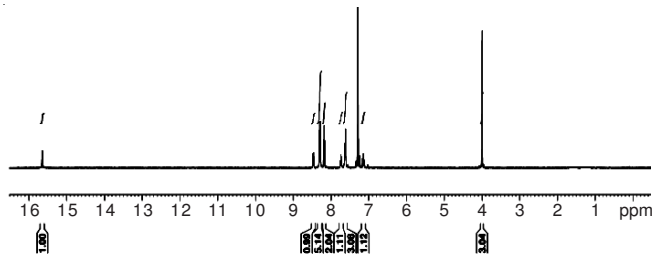
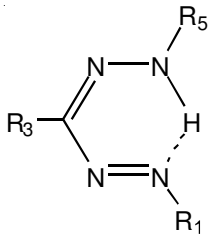


Fig. 2. ^{1}H NMR spectra of formazan **2**

^{13}C NMR data revealed that **8** aromatic C signals were observed in contrast to the expected 12 for **1** and **2**. This proved the presence of toutomerization and chelate formation for these formazans[12]. For **3-14**, *p*-substituted compounds gave **12** aromatic C signals and *o*- and *m*- substituted compounds gave **14** aromatic C signals. The C atoms of the imino-C (C=N), -CH_3, -OCH_3, -C=O appeared in their expected chemical fields.

Structural analysis of the chelate form proved that this was the EZ (*trans-syn*) isomer (**Scheme-III**). The majority of formazans with this structure were characterized by the presence of a low-field signal of NH in the ^{1}H NMR spectra and the lack of absorption bands in their IR spectra at 3500-3100 cm^{-1} [13]. The chemical shift of the imino carbon atom of these compounds in ^{13}C NMR spectra was observed at δ 148-151 ppm. The results of *ab initio* quantum-chemical calculations of all possible conformations of these compounds suggest that the EZ configuration was the most stable. To a large extent, this structure was stabilized by a bridging N-H….N hydrogen bond in the six-membered chelate ring where proton transfer is possible.[4,17] All the spectroscopic results support that the studied formazans (**1-14**) have EZ configuration.



Scheme-III: EZ configuration of formazan

Table-1 lists all the peaks observed in the UV-visible region for the studied compounds, **1-14**. The spectra exhibited three main absorption peaks[3,18]. The first broad peak λ_{max1} is characteristics of the formazan skeleton due to π-π^* and n-π^* electronic transitions in the skeleton. This peak is generally observed at 410-500 nm and shifted to 600 nm depending on the structure[19,20]. The λ_{max2} and λ_{max3} peaks are sharp and appeared at around the 300-350 nm and 270-300 nm corresponding hydrazone skeleton and originated from the π-π^* and n-π^* electronic transitions in the -N=N- and -C=N- groups.

The λ_{max1} value of 1,3,5-triphenylformazan (**1**) at 480 nm shifted to lower wavelength (hypsochromic effect) 477 nm when the 3-phenyl ring was substituted with the -$COOCH_3$ group at *p*-position (**2**). This is in good accordance with the -$COOCH_3$ withdrawing effect of the ester group. The λ_{max1} values were observed at 480, 470 and 480 nm compounds **3-5**. The fact that the λ_{max1} of **3** and **5** showed a slight shift towards a higher wavelength compared to **2** is not in accordance with the electron withdrawing effect of the -NO_2 group. This can only be explained by the formation of an intramolecular H-bond between the hydrogen atom of N-H and the oxygen atom of the -NO_2 group attached to the *o*-position of the 1-phenyl ring for **3** (**Scheme-IV**) and that of the intermolecular H-bond for **5**. This diminishes the resonance effect of the *o*-NO_2 group and decreases its electron withdrawing effect. The significant shift in the case of the *m*-NO_2 ($\Delta\lambda_{max}$ = 7 nm, hypsochromic effect) is due to the dominance of the withdrawing inductively.

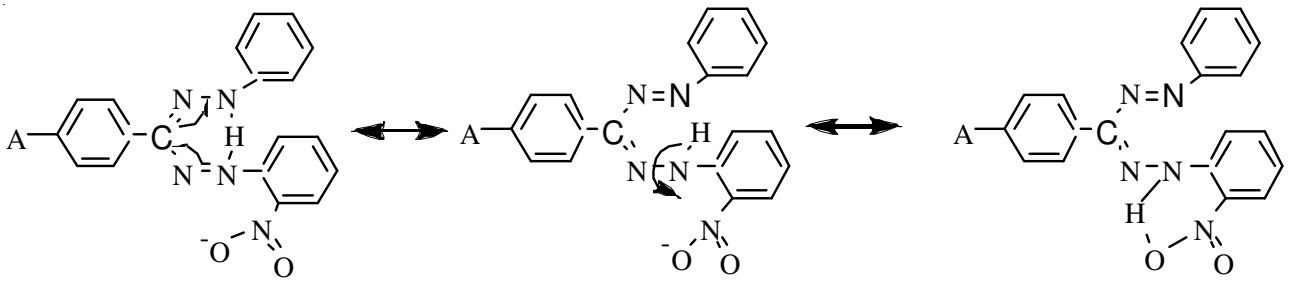
TABLE-1
UV-VISIBLE ABSORPTION MAXIMA* OF FORMAZANS (**1-14**)

Compound	Substituents, B	λ_{max1} (nm)	λ_{max2} (nm)	λ_{max3} (nm)
1	H	480	320	240
2	H	477	319	241
3	*o*-NO_2	480	310	230
4	*m*-NO_2	470	310	235
5	*p*-NO_2	480	315	235
6	*o*-CH_3	485	325	230
7	*m*-CH_3	477	325	240
8	*p*-CH_3	480	320	240
9	*o*-OCH_3	475	340	245
10	*m*-OCH_3	480	320	240
11	*p*-OCH_3	495	320	245
12	*o*-I	485	320	220
13	*m*-I	475	365	245
14	*p*-I	490	360	245

*UV spectra were recorded in CH_3OH 10^{-4} mol/L

For compounds **6-8**, the λ_{max1} values were shifted to 485, 477, 480 nm respectively. These values are in accordance with the electron donating effects of the -CH_3 group while shifting to 475, 480, 495 were explained by the resonance electron donating effect and inductive electron withdrawing effect of the -OCH_3 group for compounds **9-11**.

In -I substituted compounds **12-14**, the λ_{max1} values were shifted to 485, 475, 490 nm, while in compound **2**, the λ_{max1} value was 477 nm. As it is known, iodine is affected by inductive electron withdrawing and resonance electron donating effects which have an opposing effect on each other. Since iodine has lower electronegativity, the inductively electron withdrawing effect is less than the electron donating effect by resonance. Hence, iodine showed the $\Delta\lambda_a$ = + 8 nm bathocromic effect at the *o*-position. However, at the *m*-position, the resonance effect was very weak and there was only a decreased inductive effect. For this reason the hypsochromic effect was observed to be as little as $\Delta\lambda_a$= -2 nm. For the case of *p*-position the resonance



Scheme-IV: Hydrogen bond formation between the -NO_2 and N-H groups

effect of iodine is dominating. That is why λ_{max1} shifted towards as high a wavelength as $\Delta\lambda_a = +13$ nm (bathocromic effect).

These results are shown in Fig. 3-a to compare unsubstituted **1** and monosubstituted formazan **2** and in Fig. 3-b to compare monosubstituted **2** with disubstituted formazans **9-11**.

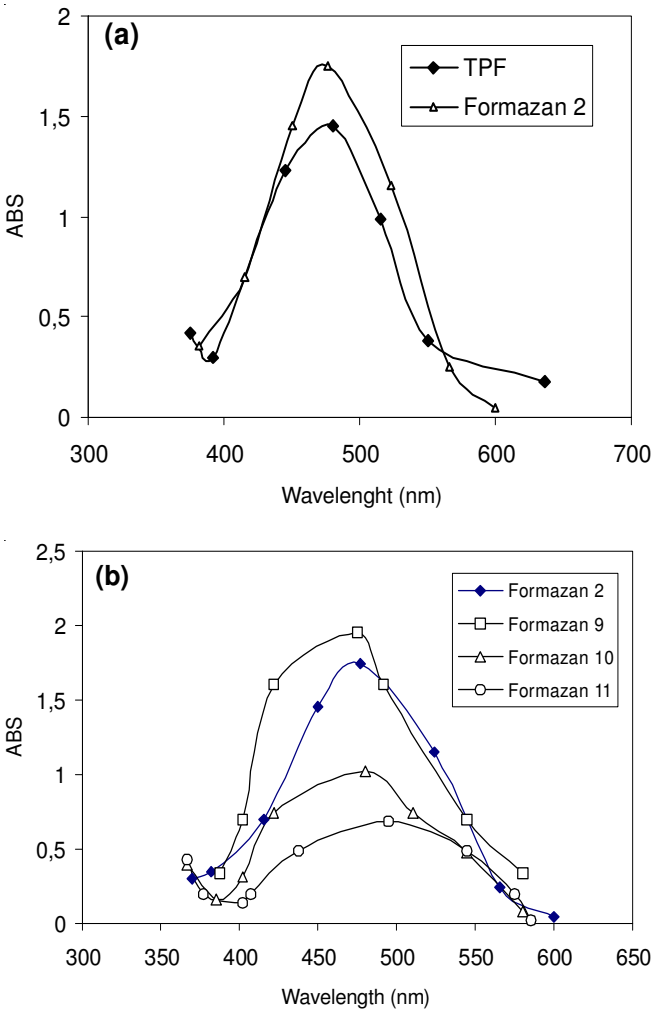


Fig. 3. UV-visible spectra of: (a) compound **2** compared with 1,3,5-triphenylformazan; (b) compounds **9-11** compared to **2** (in CH_3OH 10^{-4} mol/L)

Conclusion

We have synthesized **13** new formazans and elucidated their structures by elemental and spectral analysis. The spectral behaviours of all the formazans *via* ^{1}H NMR, ^{13}C NMR, IR, and UV-visible spectra. IR and NMR spectra showed that the studied formazans **1-14** may be extensively in the chelate and a little in the non-chelate structures in equilibrium. The formation of an intramolecular hydrogen bond between the lone pair of nitrogen with the hydrogen of NH into chelate structure decreases electron density around the proton and thus moves the proton absorption to a lower field. In the evaluation of UV spectra, it was seen that they were in accordance with the characteristic peaks of formazans and the effects of substituents on absorption lmax were observed in the expected regions.

ACKNOWLEDGEMENTS

This work was supported financially by Hacettepe University (Research Center Office/Projects No: 09D12601001).

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