



Synthesis of Some Substituted Formazans and *bis* Formazans

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Received: 8 October 2013;

Accepted: 10 December 2013;

Published online: 1 September 2014;

AJC-15847

Novel 1-(*p*-aminophenyl)-3-(*p*-substituted phenyl)-5-phenylformazan compounds (**2a-f**) and 1,1'-([1,1'-biphenyl]-4,4'-yl)*bis*(3-(*p*-substituted phenyl)-5-phenylformazan compounds (**3a-f**) were synthesized by diazo coupling reactions of the prepared hydrazones (**1a-f**) with diazonium salts of phenylenediamine and benzidine, respectively. Novel mono-formazans were obtained with high yields under mild reaction conditions and were crystallized from methanol. *Bis*-formazans were purified by flash column chromatograph over silica gel. The structures of formazans and *bis*-formazans were confirmed by elemental analysis, HR-MS and their spectral behaviours were investigated using ¹H NMR, ¹³C NMR, FT-IR techniques. The absorption characteristics of the compounds were examined by UV-visible spectra.

Keywords: Formazan dyes, Formazan, *Bis*-formazan, Diazo coupling, Spectroscopy.

INTRODUCTION

Formazans have attracted attention because of their medicinal applications such as antiviral¹, antifungal², anti-fertility³, antiinflammatory⁴, antitubercular⁵, antimicrobial⁶, anti-plasmodium activity⁷. Oxidation of deeply coloured formazans furnish tetrazolium salts and reduction of tetrazolium salts easily give formazans. These compounds are used as a marker of vitality⁸, because of their oxidation-reduction properties. Tetrazolium salt/formazan systems are also used in choosing anti-cancer drug⁹ and colourimetric determination of bioreducibility of cells¹⁰.

The π -electrons in formazan compounds remarkably enhance the formation of metal complexes which results a bathochromic shift. Formazans and their metal complexes are used as dyes in wool and polyamide fibers that are stable to sunlight and water¹¹ and they are also known as ecologically friendly dyes¹². They easily make complexation with metals because of their polydentate ligand properties¹³⁻¹⁵. Furthermore, formazans are also used for trace element determination¹⁶⁻¹⁷.

The mentioned importance of formazan compounds encouraged us to synthesize novel formazans. For this purpose, -H, -COOCH₃, -NO₂, -CN, -Cl, -Br substituted benzaldehyde phenylhydrazones were reacted with *p*-phenylenediamine to obtain 1-(*p*-aminophenyl)-3-(*p*-substituted phenyl)-5-phenylformazans (**2a-f**) and reacted with benzidine to obtain 1,1'-([1,1'-biphenyl]-4,4'-yl)*bis*(3-(*p*-substituted phenyl)-5-phenylformazan derivatives (**3a-f**).

EXPERIMENTAL

The UV-visible spectra of all formazans synthesized in this study were recorded with UV-1700 Pharma Spectrophotometer using 1 cm quartz cells in 10⁻⁴ mol L⁻¹ CH₂Cl₂. The IR spectra were obtained on Thermo, Nicolet IS10-FTIR spectrometer between 4000 and 400 cm⁻¹. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer using CDCl₃ and ¹³C NMR spectra were performed 100 MHz spectrometer using CDCl₃. All the elemental analysis studies were carried out using a LECO-CHNS- 932 elemental analyser. Melting points were determined with an electrothermal melting point apparatus and were uncorrected. HR-MS results of compounds were obtained via Agilent TOF LC/MS 1200/6210.

The hydrazones (**1a-f**) were prepared according to the literature procedures^{18,19}.

General procedure for the synthesis of compounds (2a-f): The formazans **2a-f** were prepared according to the literature procedures²⁰⁻²². The hydrazones **1a-f** (0.01 mol) was dissolved in methanol (35 mL) and sodium hydroxide (1.76 g) was added to this solution. Diazonium chloride of *p*-phenylenediamine was prepared from *p*-phenylenediamine (1.08 g, 0.01 mol) in concentrated HCl (2.5 mL) with sodium nitrite (0.76 g, 0.01 mol) dissolved in water (5 mL). This solution was added to hydrazone solution at -5 °C. This mixture was stirred for 2 h at -5 °C and stored 2 days. Compounds **2a-f** were crystallized from methanol.

1-(*p*-Aminophenyl)-3,5-diphenylformazan (2a): (2.68 g, 85 %) was obtained as deep red crystals of m.p. 197 °C.

(KBr, ν_{\max} , cm^{-1}): 3460, 3381, 3346, 3208, 3050-2950, 1624, 1601, 1506, 1431. λ_{\max}/nm (CH_2Cl_2): 266, 300, 490. δ_{H} 4.13 (s, 2H, NH_2), 6.76 (d, J 8.0, 2H, ArH), 7.03 (t, J 8.0, 1H, ArH), 7.31-7.44 (m, 7H, ArH), 7.80 (d, J 8.0, 2H, ArH), 8.13 (d, J 8.0, 2H, ArH), 15.00 (s, 1H, NH). δ_{C} 149.73 (N-C=N), 145.09, 143.89, 140.84, 137.77, 129.45, 128.26, 127.41, 125.97, 124.33, 122.95, 114.92 (ArC). m/z (ESI) for $\text{C}_{19}\text{H}_{17}\text{N}_5$: calcd. $[\text{M} + \text{H}]^+$: 316.1557; found: 316.1530. Anal. calcd.: C 72.36, H 5.43, N 22.21 (%). Found: C 72.56, H 5.43, N 22.96 (%).

1-(*p*-Aminophenyl)-3-(*p*-methoxycarbonylphenyl)-5-phenylformazan (2b): (2.98 g, 80 %) was obtained as deep red crystals of m.p. 212 °C. (KBr, ν_{\max} , cm^{-1}): 3464, 3364, 3208, 3050-2952, 1704, 1625, 1503, 1434. λ_{\max}/nm (CH_2Cl_2): 253, 360, 490. δ_{H} 3.93 (s, 3H, OCH_3), 4.17 (s, 2H, NH_2), 6.78 (d, J 8.4, 2H, ArH), 7.07 (t, J 7.2, 1H, ArH), 7.35-7.44 (m, 4H, ArH), 7.80 (d, J 8.4, 2H, ArH), 8.08 (d, J 8.0, 2H, ArH), 8.21 (d, J 8.0, 2H, ArH), 15.26 (s, 1H, NH). δ_{C} 167.29 (C=O), 149.94 (N-C=N), 144.81, 143.53, 142.33, 139.77, 129.66, 129.43, 128.51, 125.48, 124.39, 123.56, 115.21, 115.11, 114.94 (ArC), 52.04 (OCH_3). m/z (ESI) for $\text{C}_{21}\text{H}_{19}\text{N}_5\text{O}_2$ calcd. $[\text{M} + \text{H}]^+$: 374.1561; found: 374.1531. Anal. calcd.: C 67.55, H 5.13, N 18.76 (%). Found: C 67.86, H 5.04, N 18.74 (%).

1-(*p*-Aminophenyl)-3-(*p*-nitrophenyl)-5-phenylformazan (2c): (2.63 g, 73 %) was obtained as deep red crystals of m.p. 231 °C. (KBr, ν_{\max} , cm^{-1}): 3472, 3377, 3210, 3020, 1620, 1500, 1446. λ_{\max}/nm (CH_2Cl_2): 264, 397, 481. δ_{H} = 4.20 (s, 2H, NH_2), 6.78 (d, J 8.4, 2H, ArH), 7.10 (t, J 8.0, 1H, ArH), 7.30-7.44 (m, 6H, ArH), 7.79 (d, J 8.4, 2H, ArH), 8.28 (d, J 8.4, 2H, ArH), 15.40 (t, 1H, NH). δ_{C} 129.53, 125.97, 125.01, 124.49, 124.13, 123.76, 115.44, 114.97 (ArC). m/z (ESI) for $\text{C}_{19}\text{H}_{16}\text{N}_6\text{O}_2$ calcd. $[\text{M} + \text{H}]^+$: 361.1408; found: 361.1337. Anal. calcd.: C 63.30, H 4.40, N 23.30 (%). Found: C 63.04, H 4.46, N 22.95 (%).

1-(*p*-Aminophenyl)-3-(*p*-cyanophenyl)-5-phenylformazan (2d): (2.79 g, 82 %) was obtained as claret red crystals of m.p. 220 °C. (KBr, ν_{\max} , cm^{-1}): 3476, 3377, 3212, 3030, 2207, 1628, 1487, 1451. λ_{\max}/nm (CH_2Cl_2): 252, 362, 484. δ_{H} 4.17 (s, 2H, NH_2), 6.77 (d, J 8.5, 2H, ArH), 7.09 (t, J 7.0, 1H, ArH), 7.35-7.43 (m, 4H, ArH), 7.68 (d, J 8.5, 2H, ArH), 7.78 (d, J 8.7, 2H, ArH), 8.24 (d, J 8.7, 2H, ArH), 15.31 (s, 1H, NH). δ_{C} 144.66 (N-C=N), 138.91, 132.13, 129.49, 125.95, 124.45, 123.90, 115.30, 114.95 (ArC), 110.13 (-CN). m/z (ESI) for $\text{C}_{20}\text{H}_{16}\text{N}_6$ calcd. $[\text{M} + \text{H}]^+$: 341.1509; found: 341.1477. Anal. calcd.: C 70.50, H 4.70, N 24.70 (%). Found: C 69.92, H 4.71, N 24.56 (%).

1-(*p*-Aminophenyl)-3-(*p*-chlorophenyl)-5-phenylformazan (2e): (2.34 g, 67 %) was obtained as claret red crystals of m.p. 209 °C. (KBr, ν_{\max} , cm^{-1}): 3468, 3354, 3211, 2920, 2853, 1625, 1511, 1470. λ_{\max}/nm (CH_2Cl_2): 264, 325, 387, 510. δ_{H} 4.16 (s, 2H, NH_2), 7.03 (d, J 6.9, 2H, ArH), 7.05 (t, J 3.9, 1H, ArH), 7.26-7.52 (m, 6H, ArH), 7.78 (d, J 8.7, 2H, ArH), 8.06 (d, J 8.7, 2H, ArH), 15.04 (s, 1H, NH). δ_{C} 149.90 (N-C=N), 144.94, 143.67, 139.94, 136.35, 133.18, 129.40, 128.36, 127.19, 124.38, 123.18, 114.96, 114.93 (ArC). m/z (ESI) for $\text{C}_{19}\text{H}_{16}\text{ClN}_6$ calcd. $[\text{M} + \text{H}]^+$: 350.1167; found: 350.1123. Anal. calcd.: C 65.33, H, 4.58, N 20.06 (%). Found: C 65.62, H 5.02, N 19.68 (%).

1-(*p*-Aminophenyl)-3-(*p*-bromophenyl)-5-phenylformazan (2f): (2.99 g, 76 %) was obtained as claret red

crystals of m.p. 207 °C. (KBr, ν_{\max} , cm^{-1}): 3464, 3322, 3213, 3037, 1621, 1504, 1448. λ_{\max}/nm (CH_2Cl_2): 264, 326, 384, 508. δ_{H} 4.16 (s, 2H, NH_2), 6.77 (d, J 8.7, 2H, ArH), 7.04 (t, J 6.8, 1H, ArH), 7.26-7.69 (m, 6H, ArH), 7.78 (d, J 8.5, 2H, ArH), 8.00 (d, J 8.5, 2H, ArH), 15.05 (s, 1H, NH). δ_{C} 148.90 (N-C=N), 143.88, 142.63, 138.93, 135.80, 130.27, 128.37, 126.49, 123.36, 122.19, 120.19, 120.44, 113.95, 113.91 (ArC). m/z (ESI) for $\text{C}_{19}\text{H}_{16}\text{BrN}_6$ calcd. $[\text{M} + \text{H}]^+$: 394.0662; found: 394.0558. Anal. calcd.: C 57.72, H 4.05, N 17.72 (%). Found: C 57.01, H 4.19, N 17.93 (%).

General procedure for the synthesis of compounds (3a-f): The hydrazones **1a-f** (0.02 mol) was dissolved in methanol (70 mL) and sodium hydroxide (3.52 g) was added to this solution. Diazonium chloride of benzidine was prepared from benzidine (1.84 g, 0.01 mol) in concentrated HCl (5 mL) with sodium nitrite (1.52 g, 0.02 mol) in water (10 mL). This solution was added to the hydrazone solution at -5 °C. This mixture was stirred for 2 h at -5 °C. and stored 2 days. Each *bis* formazan compounds **3a-f** were purified by flash column chromatography over silica gel. (EtOAc-hexane, 1:4)

1,1'-([1,1'-Biphenyl]-4,4'-yl)bis(3,5-diphenylformazan) (3a): (3.05 g, 51 %) was obtained as deep red crystals of m.p. 175 °C. (KBr, ν_{\max} , cm^{-1}): 3062, 2960, 2924, 1593, 1510, 1443. λ_{\max}/nm (CH_2Cl_2): 260, 303, 501. δ_{H} 6.99 (t, J 2.4, 2H, ArH), 7.13-7.38 (m, 8H, ArH), 7.46 (m, 6H, ArH), 7.70 (m, 4H, ArH), 7.79 (d, J 8.4, 4H, ArH), 8.16 (d, J 8.4, 4H, ArH), 15.23 (s, 2H, NH). δ_{C} 128.43, 127.88, 127.39, 127.06, 126.66, 125.92, 124.83, 118.52, 117.47 (ArC). m/z (ESI) for $\text{C}_{38}\text{H}_{30}\text{N}_8$ calcd. $[\text{M} + \text{H}]^+$: 599.2653; found: 599.2681. Anal. calcd.: C 76.23, H 5.05, N 18.72 (%). Found: C 76.02, H 5.71, N 18.66 (%).

1,1'-([1,1'-Biphenyl]-4,4'-yl)bis(3-(*p*-methoxycarbonylphenyl)-5-phenylformazan (3b): (4.00 g, 56 %) was obtained as deep red crystals of m.p. 200 °C. (KBr, ν_{\max} , cm^{-1}): 3287, 3046, 2948, 1715, 1601, 1494, 1431. λ_{\max}/nm (CH_2Cl_2): 251, 335, 495. δ_{H} 3.87 (s, 6H, OCH_3), 7.18 (t, J 7.4, 2H, ArH), 7.31 (d, J 8.5, 4H, ArH), 7.40 (d, J 7.6, 4H, ArH), 7.56-7.64 (m, 4H, ArH), 7.70 (d, J 8.5, 4H, ArH), 8.02 (d, J 8.5, 4H, ArH), 8.14 (d, J 8.5, 4H, ArH), 15.64 (t, 2H, NH). δ_{C} 166.17 (-C=O), 146.28 (N-C=N), 140.84, 140.02, 139.08, 128.78, 128.50, 128.25, 127.91, 127.77, 127.11, 126.68, 126.56, 125.93, 124.36, 118.71, 117.59, 112.10 (ArC), 51.06 (OCH_3). m/z (ESI) for $\text{C}_{42}\text{H}_{34}\text{N}_8\text{O}_4$ calcd. $[\text{M} + \text{H}]^+$: 715.2762; found: 715.2742. Anal. calcd.: C 70.58, H 4.79, N 15.68 (%). Found: C 70.72, H 4.80, N 15.56 (%).

1,1'-([1,1'-Biphenyl]-4,4'-yl)bis(3-(*p*-nitrophenyl)-5-phenylformazan (3c): (4.27 g, 62 %) was obtained as deep red crystals of m.p. 168 °C. (KBr, ν_{\max} , cm^{-1}): 3066, 3027, 2924, 1664, 1506, 1451. λ_{\max}/nm (CH_2Cl_2): 265, 380, 491. δ_{H} 7.35 (t, J 7.8, 2H, ArH), 7.43 (d, J 7.4, 4H, ArH), 7.52 (d, J 7.4, 4H, ArH), 7.68-7.77 (m, 8H, ArH), 7.83 (d, J 8.4, 4H, ArH), 8.33 (d, J 8.4, 4H, ArH), 15.88 (s, 2H, NH). δ_{C} 146.09 (N-C=N), 128.59, 127.93, 127.19, 126.93, 126.81, 125.95, 124.89, 122.86, 118.87, 117.68 (ArC). m/z (ESI) for $\text{C}_{38}\text{H}_{28}\text{N}_{10}\text{O}_4$ calcd. $[\text{M} + \text{H}]^+$: 689.2376; found: 689.2356. Anal. calcd.: C 66.27, H 4.10, N 20.34 (%). Found: C 66.92, H 4.12, N 20.60 (%).

1,1'-([1,1'-Biphenyl]-4,4'-yl)bis(3-(*p*-cyanophenyl)-5-phenylformazan (3d): (4.22 g, 65 %) was obtained as deep red crystals of m.p. 154 °C. (KBr, ν_{\max} , cm^{-1}): 3050, 2964,

2908, 2215, 1601, 1506, 1459. λ_{\max}/nm (CH_2Cl_2): 248, 266, 340, 494. δ_{H} 6.99 (t, J 6.0, 2H, ArH), 7.26- 7.53 (m, 8H, ArH), 7.60- 7.76 (m, 8H, ArH), 7.83 (d, J 8.0, 4H, ArH), 8.27 (d, J 8.0, 4H, ArH), 15.88 (s, 2H, NH). δ_{C} 146.12 (N-C=N), 140.85, 140.35, 138.97, 138.37, 131.26, 128.56, 127.94, 127.16, 126.80, 125.94, 124.83, 118.80, 118.43, 117.61 (ArC), 109.46 (-CN). m/z (ESI) for $\text{C}_{40}\text{H}_{28}\text{N}_{10}$ calcd. $[\text{M} + \text{H}]^+$: 649.2534; found: 649.2551. Anal. calcd.: C 74.06, H 4.35, N 21.59 (%). Found: C 74.18, H 4.36, N 21.62 (%).

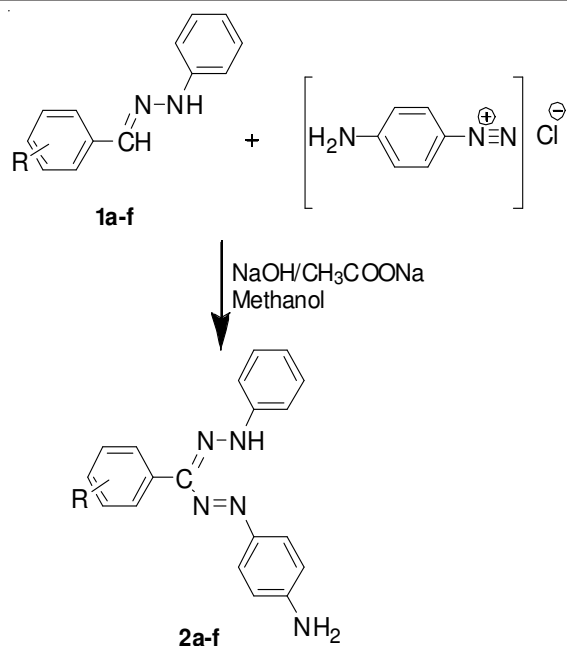
1,1'-([1,1'-Biphenyl]-4,4'-yl)bis(3-(*p*-chlorophenyl)-5-phenylformazan (3e): (3.94 g, 59 %) was obtained as deep red crystals of m.p. 145 °C. (KBr, ν_{\max} , cm^{-1}): 3068, 3033, 2927, 2850, 1660, 1504, 1445. λ_{\max}/nm (CH_2Cl_2): 268, 314, 501. δ_{H} 7.27 (t, J 7.3, 2H, ArH), 7.36-7.49 (m, 8H, ArH), 7.54-7.71 (m, 8H, ArH), 7.77 (d, J 6.8, 4H, ArH), 8.09 (d, J 6.8, 4H, ArH), 15.55 (s, 2H, NH). δ_{C} 147.40 (N-C=N), 140.84, 140.39, 140.16, 135.97, 133.49, 129.82, 129.49, 129.25, 128.93, 128.54, 128.11, 127.67, 127.37, 127.06, 126.94, 119.60, 118.50, 112.92 (ArC). m/z (ESI) for $\text{C}_{38}\text{H}_{28}\text{Cl}_2\text{N}_8$ calcd. $[\text{M} + \text{H}]^+$: 668.1814; found: 668.1821. Anal. calcd.: C 68.37, H 4.23, N 16.78 (%). Found: C 68.90, H 4.26, N, 16.62 (%).

1,1'-([1,1'-Biphenyl]-4,4'-yl)bis(3-(*p*-bromophenyl)-5-phenylformazan (3f): (4.99 g, 66 %) was obtained as deep red crystals of m.p. 161 °C. (KBr, ν_{\max} , cm^{-1}): 3060, 3031, 2918, 2845, 1598, 1503, 1454. λ_{\max}/nm (CH_2Cl_2): 242, 268, 318, 501. δ_{H} 7.29 (t, J 7.7, 2H, ArH), 7.43-7.49 (m, 8H, ArH), 7.56-7.72 (m, 8H, ArH), 7.78 (d, J 8.5, 4H, ArH), 8.03 (d, J 8.5, 4H, ArH), 15.56 (s, 2H, NH). δ_{C} 147.27 (N-C=N), 140.71, 136.25, 131.26, 129.65, 129.26, 129.02, 128.69, 127.87, 127.64, 127.43, 127.14, 126.69, 121.50, 119.32, 118.20 (ArC). m/z (ESI) for $\text{C}_{38}\text{H}_{28}\text{Br}_2\text{N}_8$ calcd. $[\text{M} + \text{H}]^+$: 757.0831; found: 757.0842. Anal. calcd.: C 60.33, H 3.73, N 14.81 (%). Found: C 60.76, H 3.65, N 14.69 (%).

RESULTS AND DISCUSSION

We described here the synthesis of *bis*-formazans. First, we planned to obtain *bis* formazans from the coupling reaction of hydrazones with diazonium salts of *p*-phenylenediamine and benzidine. However, the reaction of **1a** and *p*-phenylenediamine produced the mono-formazan **2a** instead of *bis*-formazan. (Fig. 1). Formation of **2a** showed that only one of the amino group of *p*-phenylenediamine has been converted to diazonium salt. **2a** was obtained from the reaction of **1a** with *p*-phenylenediamine even the excess amount of NaNO_2 was used. Formation of mono-diazonium salt of *p*-phenylenediamine can be explained by the most probably unstable resonance form III given in Fig. 2. This result led us to synthesize the novel formazans **2b-f**.

As mentioned before, reaction of phenylenediamine with excess NaNO_2 did not give *bis*-diazonium salt. For this reason, we used benzidine instead of phenylenediamine to prepare *bis*-diazonium salt. When we performed the reaction of **1a** with diazonium salt of benzidine, *bis* formazan **3a** was obtained successfully. This result indicated that benzidine has been easily converted to *bis* diazonium salt in the case of using the same molar ratio of benzidine and NaNO_2 (1:1). This method allowed the synthesis of novel *bis* formazans **3b-f** by the reaction of **1b-f** with *bis* diazonium salt of benzidine (Fig. 3).



R(a-f)= -H, *p*-COOCH₃, *p*-NO₂, *p*-CN, *p*-Cl, *p*-Br

Fig. 1. Synthesis of formazans

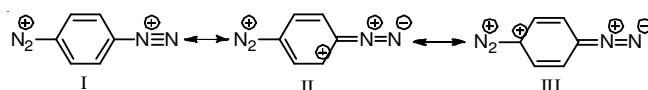
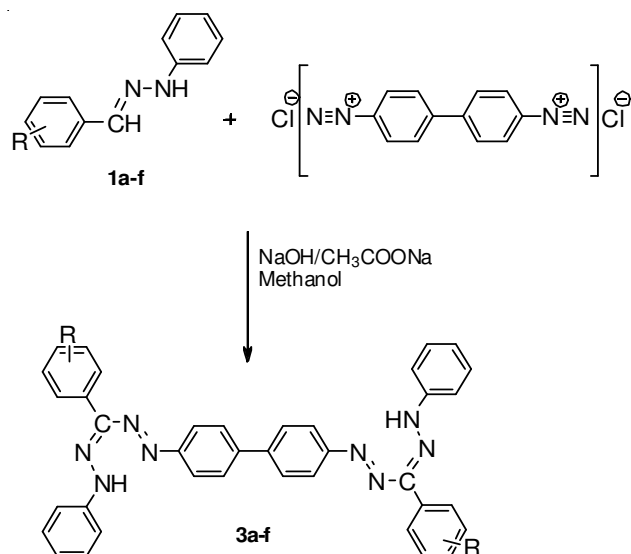


Fig. 2. Resonance structure of diazonium cation of phenylenediamine



R(a-f)= -H, *p*-COOCH₃, *p*-NO₂, *p*-CN, *p*-Cl, *p*-Br

Fig. 3. Synthesis of *bis*-formazans

Formazan compounds form intramolecular hydrogen bonds between the lone pair of N(1) and the hydrogen atom on the N(5). So, formazans have a chelated hydrogen-bridge structure²³ (Fig. 4). FT-IR spectra of the synthesized compounds showed a weak N-H stretching band at about 3000 cm^{-1} and the N-H signal of the formazan in the ¹H NMR spectrum was observed at about 15-16 ppm. These showed that the structure has intramolecular hydrogen bonds.

Signals at 4.13-4.18 ppm in the ^1H NMR spectra of mono-formazans **2a-f** indicate the presence of *p*-amino protons of phenyl ring and intense stretching band of NH_2 was also observed at about 3400 cm^{-1} in its FT-IR spectra.

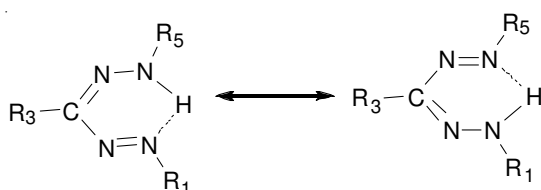


Fig. 4. Molecular chelation and tautomerization

Depending on the substituents, formazans have different colours and make absorptions at different wavelengths. For this reason, the study of UV-visible spectra of formazans is important. Their spectra exhibit mainly four absorption bands²⁴. The first band observed in the wavelength range of 216-239 nm is assigned to that of $\pi\text{-}\pi^*$ transition of -C=C- bond on phenyl moiety. The second band 240-285 nm is attributed to the low energy $\pi\text{-}\pi^*$ transition of -C=N- bond. The third sharp band within 300-350 nm is due to $\pi\text{-}\pi^*$ transition of -N=N- band. The characteristic fourth broad band is generally observed at 410-500 nm due to $n\text{-}\pi^*$ transitions of -N=N- band of formazan structure. This band can be shifted to 600 nm depending upon the structure.

For mono-formazans **2a-f**, λ_{max} values were observed at 490, 481, 484, 510 and 508 nm but for *bis*-formazans **3a-f**, λ_{max} values were observed at 495, 491, 494 and 501 nm. In all cases, strong electron withdrawing groups such as -NO_2 and -CN shifted the characteristic fourth band of formazans (hypsochromic effect). Any changes on the characteristic fourth band of -Cl and -Br substituted *bis*-formazans were not observed while this band shifted to higher wavelength in mono-formazans.

Conclusion

Novel mono and *bis* formazans have been synthesized from easily available starting materials and under mild reaction conditions. Mono formazans were obtained with high yields. This method allowed for the synthesis of *bis* formazans from

benzidine diazonium salt. The structures of the novel compounds identified by using elemental analysis, ^1H NMR, ^{13}C NMR, FT-IR, UV-visible techniques and LC-MS.

ACKNOWLEDGEMENTS

The authors thank Hacettepe University for financial support (BAP project 011D03601006). Thanks are also due to Assist. Prof. Dr. Habibe Tezcan and Prof. Dr. Canan Unaleroglu for valuable advice.

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