Accepted Manuscript

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PII: S0022-2860(19)30456-9

DOI: https://doi.org/10.1016/j.molstruc.2019.04.055

Reference: MOLSTR 26427

To appear in: Journal of Molecular Structure

Received Date: 15 January 2019

Revised Date: 10 April 2019

Accepted Date: 11 April 2019

Please cite this article as: H. Tezcan, Hü. Şenöz, N. Tokay, Experimental and quantum chemical studies of the structural and spectral properties of novel diazenyl formazans, *Journal of Molecular Structure* (2019), doi: https://doi.org/10.1016/j.molstruc.2019.04.055.

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Experimental and quantum chemical studies of the structural and spectral properties of novel diazenyl formazans

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ABSTRACT

A new series of 3-(*p*-substitutedphenyl)-5-phenyl-1-(4-phenyldiazenyl)phenylformazans were synthesized by coupling *p*-substituted phenyl or pyridinylhydrazones with *p*-aminoazobenzene diazonium chloride. All compounds were characterized by FT-IR, UV-Vis, ¹H NMR, and ¹³C NMR spectroscopic techniques, and HR-MS. DFT was used to calculate the molecular structures and ¹H and ¹³C chemical shift values of the synthesized compounds with PBE1PBE functional and 6-311G(2d,2p) basis set combination. The IR spectra of the novel formazans were calculated using DFT at PBE1PBE/6-311G(d,p) level of theory. The electronic absorption spectra of the optimized structures were evaluated by TD-DFT method at PBE1PBE/6-311G(2d,2p) level of theory. The absorption spectra of the synthesized diazenyl formazans were investigated in three different solvents. A good correlation was established between the experimental data and calculated results.

Keywords: Formazan, NMR, UV-Vis, substituent effect, DFT, TD-DFT

1. Introduction

Formazans are compounds containing the characteristic azohydrazone group:

$$-N=N-C=N-N-H$$

It is the main skeleton of formazans. Although aromatic formazans were first described as early as 1892 by von Pechmann and Bamberger [1,2], the chemistry of formazans was not developed until the 1940s when Kuhn and Jerchel found applications for tetrazolium salts in biochemistry as indicators for oxidation-reduction processes [3,4]. Formazans exhibit a variety of biological activities, such as antimicrobial [5-7], anti-inflammatory [5,8,9], antitubercular [5,10-12], anticancer [13-15], anti-HIV [15,16], antifertility [17], and antiproliferative [18,19] activities.

In addition, formazans are multidentate ligands; they exhibit a strong coordination and form stable complexes with heavy metals [20-22]. In the field of coordination chemistry, the interest in formazans is mainly focused on a description of their different coordination modes to metals and the novel applications of such compounds.

Formazans and their complexes are widely used as dyes and applied for different purposes as charge-generating compounds, biochemical markers for redox processes, photo- and thermo-chromic materials [20,23,24], analytical reagents [20,22], and synthons for heterocyclic compounds [20,25,26].

Theoretical quantum chemistry methods based on the density functional theory (DFT) are widely used to determine the optimized geometries, IR spectra, ¹H NMR, and ¹³C NMR chemical shifts of compounds [27-29]. Furthermore, the time-dependent density functional theory (TD-DFT) is used to predict the absorption spectra of dyes [30-32]. We have previously reported the results of TD-DFT calculations of formazans [33-35].



Scheme 1. Structures of the studied diazenyl formazans.

The aim of this work was dealt with the synthesis and characterization of 3-(*p*-substitutedphenyl)-5-phenyl-1-(4-phenyldiazenyl)phenyl formazans (**5a-5g**), and 3-(*p*-substitutedphenyl)-1-(4-phenyldiazenyl)phenyl-5-(pyridin-2-yl)formazans (**5h,5i**) (**Scheme 1**) and to provide a complete description of the spectral and physicochemical features both experimentally and theoretically. The structures of the novel hydrazone (**3i**) and diazenyl formazans (**5a-5i**) were characterized using HR-MS, FT-IR, ¹H NMR, ¹³C NMR, and UV-Vis spectroscopy methods. Additionally, we modeled their geometrical parameters, IR spectra, and ¹H and ¹³C NMR chemical shifts using DFT and UV-Vis spectra by TD-DFT methods. The frontier molecular orbitals, details of quantum molecular descriptors, and the molecular electrostatic potential analysis of the new compounds have also been described.

2. Experimental

2.1. Materials and instruments

Commercially available substituted aldehydes, hydrazines, *p*-aminoazobenzene, and other reagents were used. Organic solvents were purchased from Sigma-Aldrich and used without further purification. The melting points of the synthesized compounds were recorded using an Optimelt Automated melting point apparatus. The FT-IR absorption spectra were determined

by an ATR (Nicolet iS10) spectrometer. The NMR spectra of the synthesized compounds were recorded on a Bruker DPX 400 spectrometer (400 MHz for ¹H and 100 MHz for ¹³C) with TMS as an internal reference. Their coupling constants (*J*) were given in Hz. The electronic spectra of the synthesized diazenyl formazans were determined in DMSO, MeOH, and toluene by using a SHIMADZU UV-1800 UV-VIS spectrophotometer. Their mass spectra were recorded on an Agilent 1200/6210 high resolution mass time-of-flight (TOF) LC/MS spectrometer.

2.2. Synthesis

2.2.1. Synthesis of hydrazones (3a–3i)

The *p*-substituted phenyl or pyridinylhydrazones (**3a–3i**) were prepared according to previously reported methods [36-38]. *p*-Substituted aldehydes (**1a–1g**) were dissolved in EtOH and subsequently mixed with the hydrazines (**2**). The reaction mixtures were refluxed for 10 min, and the formed precipitates were filtered and recrystallized from EtOH. Compounds **3a–3h** have been synthesized previously while **3i** has not been reported before. The general route is outlined in **Scheme 2**.



R: -H, -F, -Cl, -CN, -NO₂, -CH(CH₃)₂, -CO₂CH₃ X: CH, N

Scheme 2. Synthesis of hydrazones and diazenyl formazans.

2.2.1.1 Methyl 4-((2-(pyridin-2-yl)hydrazono)methyl)benzoate (3i)

White crystals; yield: 88%; mp: 255 °C. FT-IR (cm⁻¹): 3289 (N–H), 2949 (Ar–H), 2866 (C–H), 1705 (C=O), 1646 (C=C), 1598 (C=N), 1454 1423, 1267, 1107, 1081, 917, 862, 766, 697.¹H NMR(CDCl₃) δ /ppm: 3.91 (s, 3H, OCH₃), 6.74–6.77 (m, 1H, ArH), 7.32–7.34 (d, J = 8.00 Hz, 1H, ArH), 7.55–7.61 (m, 1H, ArH), 7.65–7.67 (d, J = 8.00 Hz, 2H, ArH), 7.75 (s, 1H, CH), 7.97–7.99 (d, J = 8.00 Hz, 2H, ArH), 8.09–8.10 (d, J = 4.00 Hz, 1H, ArH), 8.63 (s, 1H, NH).¹³C NMR(CDCl₃) δ /ppm: 52.21 (OCH₃), 107.67 (ArC), 116.36 (ArC), 126.13 (ArC), 129.98 (ArC), 137.50 (ArC), 138.26 (ArC), 139.22 (ArC), 147.67 (ArC), 156.23 (C=N), 166.80 (C=O). UV-Vis: λ_{max_1} (DMSO): 364 nm, λ_{max_1} (MeOH): 353 nm, λ_{max_1} (toluene):354 nm. HR-MS (ESI) m/z found: [M+H]⁺ 256.1086; molecular formula C₁₄H₁₃N₃O₂ requires [M+H]⁺ 256.1207.

2.2.2. General procedure for the synthesis of formazans (5a–5i)

The diazenyl formazans (**5a–5i**) were prepared according to the literature procedure (**Scheme 2**) [39,40]. The synthesized hydrazone (5 mmol) was dissolved in pyridine (30 mL) at 0°C, followed by the addition of 20% NaOH solution (10 mL). In order to prepare *p*-aminoazobenzene diazonium chloride (**4**), sodium nitrite (5 mmol) was dissolved in water (5 mL) at 0°C and added slowly dropwise into a solution of *p*-aminoazobenzene (5 mmol) in HCl(aq) (50% v/v) (30 mL) over the duration of 1 h. The mixture was stirred for an additional 1 h. The diazonium salt of the *p*-aminoazobenzene solution then was added dropwise to the hydrazone solutions by continuous stirring for 1 h, and the reaction mixture was stirred for 3 h. Subsequently, it was poured into 250 mL of ice-cold water with continuous stirring. The resulting solid was filtered, washed with water, and recrystallized from EtOH.

2.2.2 1.3,5-diphenyl-1-(4-(phenyldiazenyl)phenyl)formazan (5a)

Dark solid; yield: 75%; mp:191 °C. FT-IR (cm⁻¹): 3052 (N–H), 3027 (Ar–H), 1597 (C=C), 1506 (C=N), 1492, 1455, 1436 (N=N), 1409, 1348, 1314, 1223, 1179, 1127, 1097, 1072,

1041, 1016, 919, 832, 753, 683, 664, 631. ¹H NMR(CDCl₃) δ /ppm: 7.39–7.56 (m, 9H, ArH), 7.67–7.69 (d, *J* = 8.00 Hz, 2H, ArH), 7.86–7.88 (d, *J* = 8.00 Hz, 2H, ArH), 7.92–7.94 (d, *J* = 8.00 Hz, 2H, ArH), 8.01–8.03 (d, *J* = 8.00 Hz, 2H, ArH), 8.16–8.18 (d, *J* = 8.00 Hz, 2H, ArH), 15.39 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 117.13 (ArC), 120.95 (ArC), 122.79 (ArC), 124.68 (ArC), 126.12(ArC), 128.07 (ArC), 128.51 (ArC), 129.13 (ArC), 129.52(ArC), 130.11 (ArC), 130.79 (ArC), 137.02 (ArC), 141.86 (ArC), 147.51 (ArC), 149.96 (ArC), 150.37 (ArC), 152.84 (C=N). HR-MS (ESI) *m*/*z* found: [M+H]⁺ 405.1845; molecular formula C₂₅H₂₀N₆ requires [M+H]⁺ 405.4665.

2.2.2.2 3-(4-fluorophenyl)-5-phenyl-1-(4-(phenyldiazenyl)phenyl)formazan (5b)

Claret red solid; yield: 78%; mp: 190 °C. FT-IR (cm⁻¹): 3050 (N–H), 3028 (Ar–H), 1596 (C=C), 1500 (C=N), 1455 (N=N), 1438, 1404, 1348, 1222, 1183, 1147, 1130, 1018, 919, 836, 767, 684, 627, 596. ¹H NMR(CDCl₃) δ /ppm: 7.13–7.17 (t, 2H, ArH), 7.43–7.56 (m, 6H, ArH), 7.64–7.66 (d, *J* = 8.00 Hz, 2H, ArH), 7.84–7.86 (d, *J* = 8.00 Hz, 2H, ArH), 7.91–7.93 (d, *J* = 8.00 Hz, 2H, ArH), 8.01–8.03 (d, *J* = 8.00 Hz, 2H, ArH), 8.12–8.16 (dd, *J* = 5.60 Hz, *J* = 3.20 Hz, 2H, ArH), 15.34 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 115.46 (ArC), 116.98 (ArC), 117.08 (ArC), 119.50 (ArC), 120.91 (ArC), 122.76 (ArC), 124.66 (ArC), 127.91 (ArC), 129.12 (ArC), 129.52 (ArC), 130.80 (ArC), 131.18 (ArC), 133.15 (ArC), 141.18 (ArC), 147.37 (ArC), 149.96 (ArC), 152.79 (C=N). HR-MS (ESI) *m*/z found: [M+H]⁺423.1712; molecular formula C₂₅H₁₉FN₆ requires [M+H]⁺423.1655.

2.2.2.3 3-(4-chlorophenyl)-5-phenyl-1-(4-(phenyldiazenyl)phenyl)formazan (5c)

Dark purple solid; yield: 68%; mp: 212 °C. FT-IR (cm⁻¹): 3058 (N–H), 3025 (Ar–H), 1596 (C=C), 1506 (C=N), 1487 (N=N), 1454, 1397, 1350, 1227, 1183, 1130, 1091, 1031, 1007, 919, 833, 766, 683. ¹H NMR(CDCl₃) δ /ppm: 7.34–7.40 (m, 4H), 7.44–7.48 (m, 4H, ArH), 7.58–7.60 (d, *J* = 8.00 Hz, 2H, ArH), 7.76–7.78 (d, *J* = 8.00 Hz, 2H, ArH), 7.85–7.87 (d, *J* = 8.00 Hz, 2H, ArH), 7.94–7.96 (d, *J* = 8.00 Hz, 2H, ArH), 8.02–8.04 (d, *J* = 8.00 Hz, 2H,

ArH), 15.36 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 117.27 (ArC), 120.88 (ArC), 122.82 (ArC), 124.67 (ArC), 127.31 (ArC), 128.63 (ArC), 129.14 (ArC), 129.55 (ArC), 130.17 (ArC), 130.85 (ArC), 133.89 (ArC), 135.59 (ArC), 140.92 (ArC), 147.35 (ArC), 150.10 (ArC), 150.14 (ArC), 152.82 (C=N). HR-MS (ESI) *m*/*z* found: [M+H]⁺439.1327; molecular formula C₂₅H₁₉ClN₆ requires [M+H]⁺439.1360.

2.2.2.4 3-(4-cyanophenyl)-5-phenyl-1-(4-(phenyldiazenyl)phenyl)formazan (5d)

Titian crystal; yield:76%; mp: 210 °C. FT-IR (cm⁻¹): 3054 (N–H), 3031(Ar–H), 2221 (C=N), 1596 (C=C), 1500 (C=N), 1454 (N=N), 1404, 1353, 1239, 1134, 1071, 1032, 919, 841, 765, 684, 628, 549. ¹H NMR(CDCl₃) δ /ppm: 7.43–7.56 (m, 6H, ArH), 7.69–7.74 (dd, *J* = 8.00 Hz, *J* = 8.00 Hz, 4H, ArH), 7.82–7.84 (d, *J* = 8.00 Hz, 2H, ArH), 7.92–7.94 (d, *J* = 8.00 Hz, 2H, ArH), 8.03–8.05 (d, *J* = 8.00 Hz, 2H, ArH), 8.26–8.28 (d, *J* = 8.00 Hz, 2H, ArH), 15.70 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 110.88 (ArC), 117.85 (ArC), 120.73 (ArC), 122.88 (ArC), 123.02 (ArC), 124.67 (ArC), 126.12 (ArC), 129.65 (ArC), 130.29 (ArC), 131.07 (ArC), 132.35 (ArC), 139.90 (ArC), 141.53 (ArC), 147.20 (ArC), 149.53 (ArC), 150.66 (ArC), 152.75 (C=N). HR-MS (ESI) *m*/*z* found: [M+H]⁺ 430.1788; molecular formula C₂₆H₁₉N₇ requires [M+H]⁺ 430.1702.

2.2.2.5 3-(4-nitrophenyl)-5-phenyl-1-(4-(phenyldiazenyl)phenyl)formazan (5e)

Claret solid; yield: 70%; mp: 240 °C. FT-IR (cm⁻¹): 3065 (N–H), 3034 (Ar–H), 1593 (C=C), 1505 (C=N), 1456 (N=N), 1405, 1335 (NO₂), 1244, 1180, 1149, 1033, 1109, 1073, 1035, 984, 922, 854, 840, 768, 752, 684, 667, 625. ¹H NMR(CDCl₃) δ /ppm: 7.44–7.57 (m, 7H, ArH), 7.71–7.74 (d, *J* = 8.00 Hz, 2H, ArH), 7.84–7.86 (d, *J* = 8.00 Hz, 2H, ArH), 7.93–7.95 (d, *J* = 8.00 Hz, 2H, ArH), 8.04–8.06 (d, *J* = 8.00 Hz, 2H, ArH), 8.29–8.34 (m, 3H, ArH), 15.79 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 118.04 (ArC), 120.71 (ArC), 122.90 (ArC), 123.95 (ArC), 124.68 (ArC), 126.19 (ArC), 129.17 (ArC), 129.68 (ArC), 131.10 (ArC), 139.90 (ArC), 141.53 (ArC), 147.18 (ArC), 148.98 (ArC), 149.81 (ArC), 150.52

(ArC), 152.87 (C=N). HR-MS (ESI) m/z found: $[M+H]^+$ 450.1648; molecular formula $C_{25}H_{19}N_7O_2$ requires $[M+H]^+$ 450.1600.

2.2.2.6 3-(4-isopropylphenyl)-5-phenyl-1-(4-(phenyldiazenyl)phenyl)formazan (5f)

Dark purple solid; yield: 57%; mp: 220 °C. FT-IR (cm⁻¹): 3064 (N–H), 3037 (Ar–H), 2931 (C–H), 1592 (C=C), 1504 (C=N), 1455 (N=N), 1404, 1335, 1242, 1148, 1132, 1034, 983, 853, 793, 683, 666, 626. ¹H NMR(CDCl₃) δ /ppm:1.34–1.36 (d, *J* = 8.00 Hz, 6H, (CH₃)₂C), 2.95–3.02 (m, 1H, CH), 7.32–7.34 (d, *J* = 8.00 Hz, 2H, ArH), 7.41–7.48 (m, 2H, ArH), 7.50–7.55 (m, 4H, ArH), 7.64–7.66 (d, *J* = 8.00 Hz, 2H, ArH), 7.85–7.87 (d, *J* = 8.00 Hz, 2H, ArH), 7.91–7.93 (d, *J* = 8.00 Hz, 2H, ArH), 8.00–8.02 (d, *J* = 8.00 Hz, 2H, ArH), 8.06–8.08 (d, *J* = 8.00 Hz, 2H, ArH), 15.24 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 24.01 (CH₃), 33.92 (CH), 116.84 (ArC), 116.94 (ArC), 120.98 (ArC), 124.68 (ArC), 126.26 (ArC), 126.30 (ArC), 126.59 (ArC), 129.11 (ArC), 129.49 (ArC), 130.07 (ArC), 130.71 (ArC), 134.60 (ArC), 147.55 (ArC), 148.98 (ArC), 149.81 (ArC), 150.52 (ArC), 152.87 (C=N). HR-MS (ESI) *m*/z found: [M+H]⁺ 447.2286; molecular formula C₂₈H₂₆N₆ requires [M+H]⁺447.2219.

2.2.2.7 *Methyl* 4-(((4-(phenyldiazenyl)phenyl)diazenyl)(2-phenylhydrazono)methyl)benzoate (5g)

Dark brown solid; yield: 78%; mp: 190 °C. FT-IR (cm⁻¹): 3050 (N–H), 3028 (Ar–H), 2966 (C–H), 1716 (C=O), 1595 (C=C), 1498 (C=N), 1455 (N=N), 1405, 1348, 1222, 1181, 1147 (C–O–C), 1072, 1016, 919, 834, 766, 684. ¹H NMR(CDCl₃) δ /ppm:3.96 (s, 3H, OCH₃), 7.42–7.56 (m, 6H, ArH), 7.68–7.70 (d, J = 8.00 Hz, 2H, ArH), 7.83–7.85 (d, J = 8.00 Hz, 2H, ArH), 7.92–7.94 (d, J = 8.00 Hz, 2H, ArH), 8.01–8.03 (d, J = 8.00 Hz, 2H, ArH), 8.10–8.12 (d, J = 8.00 Hz, 2H, ArH), 8.21–8.23 (d, J = 8.00 Hz. 2H, ArH), 15.61 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 52.13 (CH₃), 117.62 (ArC), 120.80 (ArC), 122.85 (ArC), 124.66 (ArC), 125.65 (ArC), 129.13 (ArC), 129.16 (ArC), 129.85 (ArC), 130.13 (ArC), 130.92 (ArC), 140.80 (ArC), 141.48 (ArC), 147.37 (ArC), 149.84 (ArC), 150.42 (ArC), 152.81 (C=N),

167.13 (C=O). HR-MS (ESI) m/z found: $[M+H]^+$ 463.1856; molecular formula $C_{27}H_{22}N_6O_2$ requires $[M+H]^+$ 463.1804.

2.2.2.8 3-(4-chlorophenyl)-1-(4-(phenyldiazenyl)phenyl)-5-(pyridin-2-yl)formazan (5h)

Brick red solid; yield: 50%; mp: 178 °C. FT-IR (cm⁻¹): 3039 (N–H), 2929 (Ar–H), 1588 (C=C), 1573, 1501 (C=N), 1480 (N=N), 1435, 1413, 1399, 1354, 1298, 1213, 1091, 1025, 1009, 852, 828, 768, 687. ¹H NMR(CDCl₃) δ /ppm: 6.99–7.02 (t, 1H, ArH), 7.42–7.44 (d, *J* = 8.00 Hz, 2H, ArH), 7.52–7.57 (m, 3H, ArH), 7.73–7.85 (m, 2H, ArH), 7.97–7.99 (d, *J* = 8.00 Hz, 2H, ArH), 8.07–8.14 (m, 4H, ArH), 8.16–8.18 (d, *J* = 8.00 Hz, 2H, ArH), 8.32–8.33 (d, *J* = 4.00 Hz, 1H, ArH), 14.36 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 109.02 (ArC), 119.07 (ArC), 123.17 (ArC), 124.05 (ArC), 127.80 (ArC), 128.63 (ArC), 129.22 (ArC), 131.65 (ArC), 134.20 (ArC), 135.02 (ArC), 138.38 (ArC), 141.36 (ArC), 148.33 (ArC), 152.73 (ArC), 153.65 (ArC), 154.12 (ArC), 156.32 (C=N). HR-MS (ESI) *m/z* found: [M+H]⁺ 440.1376; molecular formula C₂₄H₁₈ClN₇ requires [M+H]⁺ 440.1312.

2.2.2.9 *Methyl* 4-(((4-(phenyldiazenyl)phenyl)diazenyl)-(2-(piridin-2-yl)hydrazono)methyl) benzoate (5i)

Claret solid; yield: 55%; mp: 250 °C. FT-IR (cm⁻¹): 3074(N–H), 3004 (Ar–H), 2934 (C–H), 1716, 1573 (C=C), 1503, 1406, 1279, 1214, 1143, 1099, 1043, 1027, 923, 852, 770, 685. ¹H NMR(CDCl₃) δ /ppm:3.97 (s, 3H, OCH₃), 6.76–6.80 (m, 1H, ArH), 7.04–7.07 (m, 2H, ArH), 7.48–7.56 (m, 4H, ArH), 7.78–7.86 (m, 1H, ArH), 7.91–7.93 (d, J = 8.00 Hz, 2H, ArH), 7.98–8.00 (d, J = 8.00 Hz, 2H, ArH), 8.09–8.13 (t, 2H, ArH), 8.15–8.17 (d, J = 8.00 Hz, 1H, ArH), 8.19–8.23 (t, 2H, ArH), 14.64 (s, 1H, NH). ¹³C NMR(CDCl₃) δ /ppm: 52.23 (CH₃), 117.62 (ArC), 120.80 (ArC), 122.85 (ArC), 124.66 (ArC), 125.12 (ArC), 129.13 (ArC), 129.46 (ArC), 129.62 (ArC), 129.85 (ArC), 130.13 (ArC), 131.66 (ArC), 140.91 (ArC), 141.23 (ArC), 147.37 (ArC), 149.80 (ArC), 150.42 (ArC), 152.74 (C=N), 167.12

(C=O). HR-MS (ESI) m/z found: $[M+H]^+$ 464.1669; molecular formula $C_{26}H_{21}N_7O_2$ requires $[M+H]^+$ 464.1757.

2.3. Quantum chemical calculations

In our previous study [33], Perdew, Burke, and Ernzerhof (PBE) functional [41] with 6-311G(2d,2p) basis set provided the best results for formazans. Therefore, the geometry optimizations of the synthesized diazenyl formazans in the gas phase were also performed at the DFT level using PBE1PBE/6-311G(2d,2p) without any symmetry restrictions. The vibrational frequencies were calculated at the same level of theory for the optimized structures. Vibrational frequency analysis confirmed that all optimized geometries corresponded to minima on the potential energy surface by exhibiting all real frequencies.

However, in order to compare the experimental and calculated vibrational frequencies, the geometry optimizations and vibrational frequencies were also calculated using the PBE1PBE/6-311G(d,p) functional/basis set combination because the scale factor of this combination is known (0.9593) [42].

The molecular structures of all compounds were optimized in three different solvents (DMSO, MeOH, and toluene) at the PBE1PBE/6-311G(2d,2p) level of theory. The environmental effects were accounted for by using the polarized continuum model (PCM) [43-45].

For NMR calculations, the structures of 5a-5i were optimized with the same functional/basis set combination in chloroform by using PCM. The theoretical calculations for NMR chemical shifts were performed using the gauge-independent atomic orbital (GIAO) method [46,47]. The NMR signals of the nuclei, as well as that of TMS reference for carbon and hydrogen atoms, were calculated at the PCM-PBE1PBE/6-311G(2d,2p) level of theory in chloroform. The ¹H NMR chemical shifts were transformed to TMS scale by subtracting the calculated absolute chemical shielding of TMS (31.6396 ppm) at PCM-PBE1PBE/6-

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311G(2d,2p) level. This factor was 188.817 ppm for the ¹³C NMR chemical shifts.

In order to calculate the excitation energies, maximum absorbances (λ_{max}), and oscillator strengths of the compounds, TD-DFT [30,48-51] calculations were performed by using optimized geometries at the same level theory as for the first twenty lowest singlet–singlet transitions in the gas phase or in three different solvents (DMSO, MeOH, and toluene). In the latter case, PCM was applied to quantify the impact of the environment.

All calculations were performed using Gaussian 09 software package [52].

3. Results and Discussion

3.1. Synthesis

The substituted hydrazones (**3a**–**3i**) were prepared by the condensation of the substituted benzaldehydes (**1a**–**1g**) with phenylhydrazine or pyridinylhydrazine (**2**). Hydrazones **3a**–**3h** have been previously synthesized. The melting points of the synthesized hydrazones were in agreement with the values reported in the literature [36-38]. Methyl 4-((2-(pyridin-2-yl)hydrazono)methyl)benzoate (**3i**) is a novel pyridinylhydrazone. It was characterized by FT-IR, ¹H NMR, ¹³C NMR, and UV-Vis spectra, and HR-MS. Its spectra are given **Fig. S1** (Supplementary data).

Several procedures for the synthesis of formazans have been reported in the literature [36,40,53,54]. Novel diazenyl formazans (**5a–5i**) were prepared via the coupling reaction of substituted phenylhydrazones or pyridinylhydrazones with diazonium cation of *p*-aminoazobenzene in a basic medium at 0–5°C [39,40]. The synthetic route for the preparation of **5a–5i** is given in **Scheme 2**.

The diazenyl formazans (5a-5i) were recrystallized from EtOH in 50–78% yields. It was found that the yields of the synthesized formazans were affected by the electron withdrawing or electron donating substituents on the *para* position of 3-phenyl ring; the yields were higher for the formazans containing electron withdrawing substituents such as -F, -Cl, -CN, -

 CO_2CH_3 , and $-NO_2$ and moderate for those containing the electron donating substituent (-CH(CH₃)₂). In addition, the yields of pyridinyl formazans were lesser than those of the corresponding diazenyl formazans.

3.2. Optimized geometries

The molecular geometries of the synthesized molecules (5a-5i) were examined by DFT calculations at PBE1PBE/6-311Gl(2d,2p) level of theory in the gas phase.

There were two possible conformations for **5g** and **5h**, and four for **5i**. These conformations are shown in **Scheme S1** (Supplementary data). Their calculated heats of formation and Gibbs free energies are given in **Table S1** (Supplementary data). The data in **Table S1** demonstrates that conformation **I** of each compound, which had the lowest energy in comparison with other conformers, was the most stable conformer. Henceforth, we used only the most stable conformers of **5g**, **5h**, and **5i**.

The optimized structures of the diazenyl formazans (5a–5i) and the Mulliken partial charges of the substituents and pyridinyl groups are shown in Figs. 1 and S2 (Supplementary data) and Table 1. They were visualized by using GaussView5 program [55]. In Table 2, some selected optimized geometric parameters of the diazenyl formazans (5a–5i) and X-ray data of 1-(4-bromophenyl)-3,5-diphenylformazan [56] are listed. It was assumed that the –Br substituent of the crystal does not affect the geometric parameters of the skeletal structure of formazans. The calculated geometric parameters were in good agreement with the X-ray data of the reference crystal. It is worth noting that the optimized geometrical parameters were found for the compounds in the gas phase whereas the experimental geometrical parameters were obtained for the compounds in the solid phase. This partly explains the small differences between the experimental and calculated geometric parameters.

Because of the pseudo six-membered ring with a hydrogen bond between H and N1 (the lengths between N1 and H atoms, 1.780–1.826 Å, indicated the presence of a hydrogen bond



Fig. 1. Optimized structure of **5a** computed at PBE1PBE/6-311Gl(d,p) level in the gas phase. Mulliken partial charge (in e) for its R group is surrounded by dotted line.

in **5a-5i**), the main skeletons of the diazenyl formazans were planar. This was evident from the N1–N2–C3–N4 and N5–N4–C3–N2 dihedral angles of all studied formazans, which were found to be nearly 0° (**Table 2, Figs. 1** and **S2**). All structures were essentially planar. The 5-phenyl groups were in the same plane as that of the main skeleton but the 1- and 3-phenyl groups were out-of-plane by nearly 10° from the main skeleton (**Fig. 1**).

The Mulliken partial charge of R:H in **5a** was calculated as 0.102e and it was used as a reference compound to determine charge transfers of other compounds because it was the

	e	
~ .		
Compound	q	Δq
5a	0.102	0.000
5b	-0.230	-0.332
5c	-0.068	-0.170
5d	-0.191	-0.293
5e	-0.394	-0.496
5f	0.029	-0.073
5g	0.037	-0.065
5h	-0,067	-0.169
5i	0.039	-0.063

Table 1Calculated Mulliken partial charges of the
substituents (R) and charge transfers of 5a–5i.

Commenced			Bo	nd length	(Å)	
Compound	N1-N2	N2-C3	C3-N4	N4-N5	N5-H	N1 H
5a	1.268	1.375	1.314	1.302	1.025	1.782
5b	1.268	1.376	1.314	1.303	1.025	1.780
5c	1.268	1.375	1.314	1.302	1.025	1.784
5d	1.268	1.375	1.315	1.299	1.026	1.782
5e	1.267	1.375	1.316	1.298	1.027	1.778
5f	1.269	1.375	1.316	1.301	1.026	1.783
5g	1.268	1.375	1.315	1.300	1.026	1.780
5h	1.263	1.383	1.309	1.305	1.022	1.826
5i	1.263	1.383	1.310	1.304	1.023	1.822
X-ray	1.299	1.450	1.309	1.360	0.860	1.720
Compound			Dih	edral angl	e (°)	
Compound	N1-N2-C3-N4	N5-N4-C3-N2	N2-N1-C	1'-C6' N	V2-C3-C1"-C6"	N4-N5-C1"'-C2"
5a	-1.8	0.2	-9.2		164.2	-3.2
5b	-1.8	-0.1	-9.0		166.2	-3.6
5c	2.1	-0.3	9.9		-167.1	3.1
5d	0.2	-0.5	-5.5		168.9	-3.2
5e	2.2	-0.7	8.8		-170.6	2.6
5f	0.7	0.3	4.7		-168.9	1.9
5g	-2.3	0.7	-8.5		169.5	-2.6
5h	1.3	-1.1	-4.1		167.6	-0.9
5i	-0.1	-0.2	-4.6		170.0	-0.8
X-ray	-0.7	-4.0	4.5		166.0	-0.3

Table 2 Selected optimized geometric parameters of diazenyl formazans.

simplest structure (i.e., there was no substituent on the *para* position of the 3-phenyl ring and no N on the 5-phenyl ring). The calculated Mulliken partial charges of all substituents were than that of **5a**. It was observed that the presence of a pyridinyl group in the structure did not affect the Mulliken partial charge of substituents as expected.

3.3. Infrared spectra

The FT-IR spectrum of **3i** is given in **Fig. S1** in the Supplementary data and shows N–H, aromatic and aliphatic C–H, C=N, and C=O stretching vibrations. All vibrational wavenumbers of **3i** are given in the experimental section. The band observed at 3289 cm⁻¹ corresponded to N–H stretching vibration. The aromatic and aliphatic C–H stretching bands were observed at 2949 and 2866 cm⁻¹, respectively. The band at 1705 cm⁻¹ was assigned to C=O group. C=C and C=N stretching bands were found at 1646 cm⁻¹ and 1598 cm⁻¹, respectively.

The experimental and calculated IR spectra of the synthesized formazans can be seen in **Figure S3** (Supplementary data). The FT-IR spectra showed characteristic bands of N–H, C–H, C=N, and N=N stretching vibrations. Shifting of these bands toward lower or higher frequencies indicates whether the compound has a chelate or non-chelate structure, respectively [57]. All vibrational frequencies of the studied formazans are given in the experimental section. Some selected experimental and calculated vibrational wavenumbers of **5a–5i** are listed in **Table 3**. The experimental and calculated IR spectra of **5a** are shown in **Fig. 2**. The calculated wavenumbers were scaled down to give up the rational with the observed wavenumbers. This is because the calculated vibrational wavenumbers were higher than the experimental wavenumbers as a result of discard of anharmonicity present in a real system. For the PBE1PBE/6-311G(d,p) combination, the scaling factor is 0.9593 [42].

N–H vibrations

The N–H stretching vibrations are typically observed in the region $3350-3310 \text{ cm}^{-1}$ [58]. In FT-IR spectra of **5a–5i**, weak N–H stretching bands were observed at $3074-3039 \text{ cm}^{-1}$. The absorption bands with lower wavenumbers ($3090-3011 \text{ cm}^{-1}$) implied an intramolecular hydrogen bond and chelate structure [57]. The intramolecular hydrogen bonding in **5a** can be

	Derec		oration	iui wu	venum		m) K	л си с								
Comp	N	-H	C-H(aı	romatic)	C-H(al	iphatic)	С	=N	C	C=C	N	=N	С	=0	C(=0))-O-C
Comp	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc
5a	3052	3132	3027	3058	/		1506	1533	1597	1602	1436	1367				
5b	3050	3132	3028	3059			1500	1535	1596	1614	1455	1368				
5c	3050	3132	3031	3059			1506	1534	1596	1603	1486	1368				
5d	3054	3122	3032	3060			1500	1533	1596	1611	1454	1371				
5e	3065	3117	3034	3107			1505	1533	1593	1610	1456	1370				
5f	3064	3131	3037	3051	2931	3003	1504	1533	1592	1615	1455	1368				
5g	3050	3124	3028	3060	2996	2942	1498	1533	1595	1612	1455	1370	1716	1747	1181	1172
5h	3039	3205	2929	3049			1501	1531	1588	1609	1480	1377				
5i	3074	3198	3004	3063	2934	2942	1503	1582	1573	1613	1436	1379	1716	1748	1214	1172

Table 3Selected vibrational wavenumbers (cm^{-1}) for 5a–5i

seen in **Scheme 3**. The calculated wavenumbers for N–H stretching vibrations of 5a-5i were in the range of 3205–3117 cm⁻¹.

C–H vibrations

For aromatic phenyl structures, the C–H stretching vibrations are generally observed in the range of $3100-3000 \text{ cm}^{-1}$ [58,59]. The aromatic C–H stretching wavenumbers for the synthesized compounds were observed experimentally in the range of $3034-2929 \text{ cm}^{-1}$ while the calculated wavenumbers were found in region $3115-3049 \text{ cm}^{-1}$.

The stretching vibrations of the $-CH_3$ group are expected in the range of 2900–3050 cm⁻¹ [60]. The experimental aliphatic C–H stretching vibrations of compounds **5a–5i** were found between 2934 and 2869 cm⁻¹. The calculated spectra predicted that the C–H stretching mode of the methyl group was in the region of 3003–2942 cm⁻¹.

$C \equiv N$ vibrations

Aromatic nitriles are characterized by medium absorption bands in the region between 2240–2222 cm⁻¹ [58]. The C \equiv N stretching band of **5d** was observed at 2221 cm⁻¹ and the calculated value was 2268 cm⁻¹.

C=N vibrations

C=N stretching vibrations for hydrazines can be seen in the range of 1689-1471 cm⁻¹ [58]. It was observed at 1598 cm⁻¹ for **3i**.



Fig. 2. (a) Experimental and (b) calculated IR spectra of 5a at PBE1PBE/6-311G(d,p) level.

Formazans show C=N stretching vibrations in the range of 1450–1600 cm⁻¹. The C=N stretching band at 1510–1500 cm⁻¹ typically implies a chelate structure [57]. On the other hand, non-chelated structures typically have the C=N stretching band in the region of 1551–1565 cm¹ [57]. Based on both experimental and calculated values of C=N stretching vibrations, it was concluded that all diazenyl formazans were in the chelate form. These bands were observed experimentally in the range of 1506–1498 cm⁻¹ and their calculated wavenumbers were found in the region of 1534–1528 cm⁻¹.

C=C vibrations

In aromatic hydrocarbons, skeletal vibrations involving carbon–carbon stretching within the ring absorb in the region between 1600 and 1585 cm⁻¹ [58-60]. The characteristic C=C stretching bands were observed in the region of 1597–1573 cm⁻¹ for **5a–5i** while the calculated wavenumbers were found in the range of 1615–1602 cm⁻¹.

N=N vibrations

The N=N bands of formazans are typically observed in the region between $1400-1450 \text{ cm}^{-1}$ [57]. These bands were observed at $1436-1486 \text{ cm}^{-1}$ for **5a-5i** and calculated to be in the range of $1379-1367 \text{ cm}^{-1}$.

C=O vibrations

The C=O absorption bands of benzoate esters are generally in the region of $1730-1715 \text{ cm}^{-1}$ ¹[58]. The strong bands at 1716 cm⁻¹ in the FT-IR spectra of **5g** and **5i** were assigned to the



Scheme 3. Intramolecular hydrogen bonding of 5a.

C=O stretching mode. The calculated C=O stretching modes at 1747 and 1748 cm^{-1} were in good agreement with the experimental values.

C–O–C vibrations

The C–O stretching vibrations of esters actually consist of two asymmetric coupled vibrations, namely, C(=O)–O–C and O–C–C, of which the former is more important. These bands typically appear in the region of 1300–1000 cm⁻¹ [58]. The corresponding symmetric vibrations are of little importance. The C–C(=O)–O band is often broader and stronger than the C=O stretching vibration bands [58]. These bands were observed at 1181 and 1214 cm⁻¹ for **5g** and **5i**, respectively. The calculated wavenumbers of this vibration for both compounds was 1172 cm^{-1} .

NO₂ vibrations

The NO₂ band of **5e** was found at 1335 cm⁻¹ experimentally and 1376 cm⁻¹ by calculation. Generally, the symmetrical stretching of the NO₂ is observed in the region of 1259-1389 cm⁻¹ [58].

There was good agreement between the experimental and calculated absorption wavenumbers of the compounds. The calculated wavenumbers were generally greater than the experimental values, except for N=N and C(=O)-O-C bands.

3.4. NMR spectra

The details of the measured ¹H and ¹³C NMR data and coupling constants for **3i** and **5a–5i** are given in the experimental section.

In ¹H NMR spectrum of **3i**, the N–H signal was observed as a singlet at 8.63 ppm. The aromatic protons were recorded between 6.74 and 8.10 ppm and the C–H signal was observed as a singlet at 7.75 ppm. The methoxy protons also appeared as a singlet at 3.91 ppm. The ¹³C

NMR chemical shifts of **3i** were observed between 52.21 and 166.80 ppm. The carbon atom of C=O was recorded downfield at 166.80 ppm while the methoxy carbon was observed at 52.21 ppm. These ¹H and ¹³C NMR spectra can be seen in **Fig. S1** (Supplementary data).

The NMR spectra of the diazenyl formazans were calculated at the PCM-PBE1PBE/6-311G(2d,2p) level of theory in chloroform by using the GIAO method [46,47] and referenced by TMS. The isotropic chemical shifts of the compounds with reference to TMS in the solvent phase were calculated using PCM. ¹H and ¹³C NMR chemical shifts of TMS at the PCM-PBE1PBE/6-311G(2d,2p) level are 31.6396 ppm and 188.817 ppm, respectively. Thus, ¹H or ¹³C NMR isotropic chemical shift of any X atom was computed by using the relation CS_X = IS_{TMS} – IS_x , where IS_{TMS} and IS_X are the isotropic chemical shifts of TMS and X, respectively.

The experimental and calculated ¹H and ¹³C NMR spectra of **5a** are shown in **Fig. 3**. The full set of experimental and calculated NMR spectra can be seen in **Fig. S4** (Supplementary data), and the¹H and ¹³C-NMR signals of **5a** and **5b–5i** are given in **Tables 4** and **S2** (Supplementary data), respectively.

The observed ¹H NMR chemical shift values of **5a**–**5i** ranged from 1.34 to 15.79 ppm. The calculated ¹H NMR chemical shifts of the studied diazenyl formazans were found between 1.28 and 17.52 ppm. The N–H signal in the NMR spectra of formazans was indicative in evaluating the structure. While the N–H signal appearing downfield at 16 ppm indicated intramolecular hydrogen bonding, the upfield shifts of this signal at 10 ppm indicated a weakening of the same intramolecular hydrogen bond [60]. The N–H signals of **5a**–**5i** were observed as a singlet in the downfield region between 14.36 ppm and 15.79 ppm and calculated as 16.47–17.52 ppm. Both experimental and calculated values verified the existence of an intramolecular hydrogen bond in all of the studied diazenyl formazans (as shown in **Scheme 3**).

The chemical shifts of the aromatic protons were recorded in the range 6.76–8.34 ppm. The calculated values for the aromatic protons were found between 7.40 and 9.00 ppm. Owing to the different substituents on the 3-phenyl rings of all diazenyl formazans and N atoms on the 5-pyridinyl rings of **5h** and **5i**, the aromatic protons showed a broad range of NMR peaks. This was observed both experimentally and theoretically.

F atom has a spin number of ¹/₂ and couples strongly with protons [58]. In the case of the formazan that contains a fluorine atom, **5b**, the aromatic protons of the 3-phenyl ring appeared as a doublet-doublet at 8.12–8.16 ppm, which was attributed to proton-fluorine coupling. The corresponding calculated value was 7.44 ppm.

Methoxy protons were detected as a singlet at 3.96 and 3.97 ppm for **5g** and **5i**, respectively, and the corresponding calculated values were 3.78 and 3.99 ppm. On the other hand, the methyl protons were observed as doublets between 1.34–1.36 ppm and the calculated value was 1.28 ppm. For **5f**, the methine proton was recorded as a multiplet at 3.96 ppm and the calculated chemical shift was 2.88 ppm.



Fig. 3. (a) Experimental and (b) calculated ¹H NMR (upper) and ¹³C NMR (lower) spectra of **5a**.

Table 4

Theoretical	$^{1}\mathrm{H}$	and	^{13}C	isotropic	chemical	shifts	with
respect to TI	MS	(in pr	om) f	or 5a .			

Atom	Calc shift	Expt	Atom	Calc shift	Expt
H(N5)	17.34	15.39	C1'	158.62	152.84
H(C3')	8.79	8.16-8.18	C4'	155.74	150.37
H(C2")	8.79	8.16-8.18	C1'''	146.41	149.96
H(C6')	8.79	8.01-8.03	C3	143.41	147.51
H(C2''')	8.79	8.01-8.03	C4''''	137.67	141.86
H(C6'''')	8.66	7.92-7.94	C2'	136.12	137.02
H(C6'')	8.66	7.92-7.94	C3'''	134.85	130.79
H(C2')	8.59	7.86-7.88	C5""	134.06	130.11
H(C5')	8.59	7.86-7.88	C5'''	133.82	129.52
H(C2'''')	8.50	7.67-7.69	C3''''	133.24	129.13
H(C5'''')	8.10	7.67-7.69	C5''	132.91	129.51
H(C4'''')	7.99	7.39-7.56	C4''	131.71	128.07
H(C3'''')	7.90	7.39-7.56	C4'''	129.65	126.12
H(C3''')	7.90	7.39-7.56	C2''	129.54	126.12
H(C3")	7.90	7.39-7.56	C6"	128.69	124.68
H(C5")	7.90	7.39-7.56	C6'	117.71	120.95
H(C5''')	7.82	7.39-7.56	C2'''	117.42	117.13
H(C4")	7.77	7.39-7.56	C2""	116.75	117.13
H(C4''')	7.59	7.39-7.56			
H(C6''')	7.44	7.39-7.56	$\mathbf{\nabla}$		

The ¹³C NMR chemical shifts of **5a–5i** were recorded between 24.00 and 167.13 ppm, whereas the calculated values were found between 25.64 and 171.24 ppm. The C=O chemical shifts of **5g** and **5i** were the same and recorded downfield at 167 ppm. For these compounds, the shifts were calculated as 171.24 ppm and 171.20 ppm, respectively. The carbon atoms in characteristic C=N units appeared downfield between 147.17–156.32 ppm. In the calculated NMR spectra, these chemical shifts were found between 141.24 and 143.69 ppm. The nitrile carbon was observed at 120 ppm for **5d**. The shift of the carbon in nitrile was calculated as 126.58 ppm. Methoxy carbons were experimentally recorded at 52.13 and 52.23 ppm for **5g** and **5i**, while the calculated chemical shifts were 53.11 and 53.16 ppm, respectively. The methyl and methine carbons were recorded upfield at 24.00 and 33.92 ppm, respectively, and their calculated values were found in the range of 25.64–39.47 ppm.

A comparison of the theoretical and experimentally observed ¹H and ¹³C NMR chemical shifts of the studied compounds revealed that the calculated chemical shifts were in good compliance with the experimental findings (**Fig. 3**).

3.5. Mass spectra

The mass spectral data of **3i** and **5a–5i** are given in the experimental section. Besides FT-IR, ¹H NMR, ¹³C NMR, and UV-Vis studies, mass spectra displayed the correct molecular ions, for which the measured HR-MS data were in agreement with the calculated values of the novel synthesized hydrazone (**3i**) and diazenyl formazans (**5a–5i**).

3.6. Absorption spectra

The electronic absorption spectra of **5a–5i** were recorded in DMSO, MeOH, and toluene. The electronic properties, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, absorption wavelengths, and oscillator strengths of **5a–5i** were calculated using the TD-DFT method [30-32] with PBE1PBE functional [41] and 6-311G(2d,2p) basis set by using PCM [43-45]. The measured and calculated λ_{max_1} and λ_{max_2} values are given in **Table 5**, which also presents the calculated λ_{max} values of **5a–5i** in the gas phase.

The experimental and calculated electronic absorption spectra of **5a–5i** are given in **Fig. 4**. The characteristic peak of formazan (λ_{max_1}) is broad and generally observed in the range of

410–500 nm [36]. This peak is due to the $\pi \rightarrow \pi^*$ electronic transition in the formazan skeleton (-NH–N=C–N=N–) [36,57,61].

The sharp peak in the range of 294–350 nm (λ_{max_2}) was attributed to the $\pi \rightarrow \pi^*$ transition within the hydrogen chelate ring formed by the azo and hydrazo groups and intramolecular charge transfer in the form of a hydrogen bond [61].

	Gas		Solvent										
C	Gas -	DMSO					Me	OH			Tolu	iene	
Comp	3	Calc	Expt										
	λ_{max_1}	λ_{max_1}	λ_{max_1}	λ_{max_2}	λ_{max_2}	λ_{max_1}	λ_{max_1}	λ_{max_2}	λ_{max_2}	λ_{max_1}	λ_{max_1}	λ_{max_2}	λ_{max_2}
5a	531	496	488	344	347	496	495	344	340	558	536	351	356
5b	503	497	499	339	356	497	507	339	350	563	542	-341	359
5c	533	497	498	377	358	497	505	376	349	555	539	379	358
5d	506	498	506	373	356	499	500	371	352	540	527	373	355
5e	505	499	501	357	362	499	501	356	360	533	522	381	382
5f	501	496	507	350	352	496	510	350	345	566	547	356	352
5g	503	498	491	373	364	498	504	372	360	545	526	386	382
5h	506	501	498	370	364	501	479	369	355	505	509	369	366
5i	505	502	478	368	358	502	487	366	354	505	504	367	356

Table 5								
Experimental and calculated λ_{max}	and λ_{max}	values (i	in nm)	for all s	studied of	diazenyl	formazar	ıs.

In our experimental study, the λ_{max_1} values of **5a**–**5i** were observed in the ranges of 478– 507 nm in DMSO, 479–510 nm in MeOH, and 504–547 nm in toluene (**Fig. 4**). By calculation, the λ_{max_1} values were found between 501–533 nm in the gas phase, 496–502 nm in DMSO, 496–502 nm in MeOH, and 505–566 nm in toluene. The experimental λ_{max_2} values of **5a**–**5i** were observed between 347–364 nm in DMSO, 340–355 nm in MeOH, and 352–382 nm in toluene (**Table 5**), and the calculated λ_{max_2} values were found between 339– 377 nm in DMSO, 338–377 nm in MeOH, and 341–385 nm in toluene (**Table 5** and **Fig.4**). Both experimental and calculated results were in accordance with the values reported in the literature and indicated that chelate formation as a result of intramolecular hydrogen transfer over a six-membered ring (**Scheme 3**).

The absorption spectra are influenced by both dipole moment of solvent and substituent [61]. The polarities of the solvents decrease from DMSO to toluene (**Table 5**). The λ_{max_1} absorption bands of diazenyl formazans shifted to the higher wavelengths with the decrease in the solvent polarity. Fig. 4(a) presents the electronic absorption spectra of 5a in three different solvents. The calculated electronic absorption spectrum of 5a in toluene is given in Fig. 4(b). Fig. 4(c) shows the electronic absorption bands of 5a-5i in toluene. These results

indicated that there is a hydrogen bond between the solute and DMSO and MeOH solvent molecules. This type of hydrogen bond can complicate the chelation in the diazenyl formazans. On the other hand, a hydrogen bond was not found between the solute and toluene. Consequently, the λ_{max_1} absorption bands of **5a–5i** in toluene were at higher wavelengths than that of all studied diazenyl formazans in DMSO and MeOH.

The substituent effect on the electronic absorption spectra of diazenyl formazans can be seen in **Tables 5** and 6, and Fig. 4(c). In order to discuss this effect, the λ_{max_1} values in toluene were considered. The chemical shift values were estimated between the λ_{max_1} value of **5a** and that of substituted 5b-5i in toluene (Table 6). A hypsochromic shift is expected for a compound with an electron withdrawing group [57]. The λ_{max_1} values of 5d, 5e, and 5g, which contain electron withdrawing groups -CN, -NO₂, and -CO₂CH₃, respectively, were shorter than that of 5a. Therefore, hypsochromic effects were observed in the electronic absorption spectra of 5d, 5e, and 5g. The $\Delta \lambda_{max_1}$ values of 5h and 5i, which contained the electron withdrawing pyridinyl group (in addition to -Cl and -CO₂CH₃, respectively) were 27 and 32 nm respectively. The shortest λ_{max_1} value of 5i could be correlated to the highest hypsochromic shift (32 nm). Owing to its electron donating $-CH(CH_3)_2$ group, the λ_{max_1} value of diazenyl formazan 5f was shifted to a higher wavelength than that of 5a. It showed a bathochromic shift (-11 nm). Both **5b** and **5c** (with -F and -Cl substituents, respectively) showed slight bathochromic shifts of -6 nm and -3 nm, respectively. These results were in good agreement with the electron withdrawing inductive effect and electron donating resonance effect of -F and -Cl substituents.

Based on these results, it was evident that the calculated λ_{max} values were in good agreement with the experimental findings. This can be seen clearly in **Fig. 5**, which shows the comparison of experimental and calculated λ_{max} in toluene for the studied diazenyl formazans.



Fig. 4. (a) Electronic absorption spectra of **5a** in DMSO, MeOH, and toluene. (b) Calculated electronic absorption spectrum of **5a**. (c) Electronic absorption spectra of **5a–5i** in toluene.

There was a linear correlation between the experimental and calculated λ_{max} values of the compounds **5a–5i** in toluene and the correlation coefficient r^2 was 0.960.

Experimental chemical shifts, ΔA_{max_1} (in nin), of 3a–51 in three solvents.										
C 1	V	D	DM	ISO	Me	OH	Tol	uene		
Compound	X	K	λ_{max_1}	$\Delta \lambda_{max_1}$	λ_{max_1}	$\Delta \lambda_{max_1}$	λ_{max_1}	$\Delta \lambda_{max_1}$		
5a	СН	<i>р</i> –Н	488	0	495	0	536	0		
5b	CH	p-F	499	-11	507	-12	542	-6		
5c	CH	p–Cl	498	-10	505	-10	539	-3		
5d	CH	<i>p</i> –CN	506	-18	500	-5	527	9		
5e	CH	$p-NO_2$	501	-13	501	-6	522	14		
5f	CH	$p-CH(CH_3)_2$	507	-19	510	-15	547	-11		
5g	CH	$p-CO_2CH_3$	491	-3	504	-9	526	10		
5h	Ν	p–Cl	498	-10	479	16	509	27		
5i	Ν	$p-CO_2CH_3$	478	10	487	8	504	32		

Table 6					
Experimental	chemical shift	s, $\Delta \lambda_{max_1}$	in nm), of	5a–5i in t	three solver



Fig. 5. Relationship between experimental and calculated λ_{max_1} for 5a–5i in toluene.

The calculated electronic absorption spectra showed that the λ_{max} corresponded to the electronic transition between the frontier molecular orbitals (i.e., from HOMO to LUMO). calculated frontier molecular orbitals of **5a** and of **5b–5i** in toluene are given in **Figs. 6** and **S4** (Supplementary data), respectively. The HOMO and LUMO surfaces were visualized using GaussView 05 program [56]. As observed in **Figs. 6** and **S4** (Supplementary data), the electronic cloud distribution of the HOMOs of **5a–5i** were centralized throughout the molecules



Fig. 6. Frontier orbital pairs involved in the λ_{max_1} excitation of **5a** at TD-PCM-PBE1PBE/6-311G(2d,2p) level in toluene.

DI	Frontier					Compound				
Phase	orbital	5a	5b	5c	5d	5e	5f	5g	5h	5i
	HOMO	-5.6652	-5.6826	-5.7566	-5.9806	-6.0298	-5.5879	-5.8089	-5.8744	-5.9302
Gas	LUMO	-2.9628	-3.0199	-3.0613	-3.2055	-3.2205	-2.9386	-3.0635	-3.0831	-3.0817
	ΔE	2.7024	2.6627	2.6953	2.7750	2.8093	2.6493	2.7454	2.7914	2.8485
	HOMO	-5.7751	-5.7504	-5.7996	-5.9163	-5.9550	-5.7076	-5.8679	-5.9610	-6.0336
s DMSO	LUMO	-3.0885	-3.1013	-3.0866	-3.1476	-3.1625	-3.0828	-3.1250	-3.1710	-3.1827
0	ΔE	2.6866	2.6490	2.7130	2.7688	2.7925	2.6248	2.7429	2.7900	2.8510
1	HOMO	-5.7732	-5.7487	-5.7988	-5.9172	-5.9558	-5.7055	-5.8665	-5.9588	-6.0315
v MeOH	LUMO	-3.0858	-3.0994	-3.1125	-3.1476	-3.1628	-3.0793	-3.1236	-3.1685	-3.1805
e	ΔE	2.6874	2.6493	2.6863	2.7696	2.7930	2.6262	2.7429	2.7903	2.8510
n	HOMO	-5.7087	-5.7057	-5.7716	-5.9406	-5.9887	-5.6353	-5.8306	-5.9033	-5.9713
t Toluene	LUMO	-3.0110	-3.0482	-3.0711	-3.1623	-3.1805	-2.9922	-3.0812	-3.1051	-3.1171
	ΔE	2.6978	2.6575	2.7005	2.7783	2.8082	2.6431	2.7495	2.7982	2.8542

Table 7							
Frontier orbital	energies	of the	studied	diazeny	l formaza	ns (in	eV).

and those of their LUMOs were mainly localized on 1-phenyl ring, diazenyl groups, and the main skeleton of the molecules. The energy gaps of the compounds were found to be in the range of 2.6248–2.8542 eV from **Table 7**.

3.7. Molecular electrostatic potential

The molecular electrostatic potential (MEP) surface is a very useful tool to study the correlation between the structure and physiochemical properties of a molecule [62]. The MEP may be used to predict reactive sites for electrophilic attack (electron rich region) and nucleophilic attack (electron poor region) as the negative and positive regions of MEP are related to electrophilic and nucleophilic reactivities, respectively. The red and blue regions depict the electron rich and electron poor areas, respectively, while the green region in the MEP suggests an almost neutral site.

The MEP surfaces of **5a** and **5b–5i** were generated from the optimized geometry using GaussView 05 program [56] and are shown, respectively, in **Figs. 7** and **S5** (Supplementary data). MEPs of **5a** and **5f** showed a considerable negative potential region (yellowish-red area) around the 3-phenyl group, which was the binding site for electrophilic attack. For **5b**

and **5c**, the MEP maps showed a modest negative potential region around the 3-phenyl groups and the substituents.

The regions around the O atoms of **5e**, **5g**, and **5i** and the regions around the N atoms of the CN group in **5d** and in the pyridinyl group of **5h** and **5i** were positive and preferred sites for electrophilic attack. For all compounds, the H atoms of 5-phenyl and diazenyl groups bore the maximum brunt of positive potential. Based on calculations, the other studied molecules seemed to have almost neutral electrostatic potential. By considering the positive, negative, and neutral sites, it is possible to predict the region of the compound that can participate in intermolecular interactions and form metallic bonds.



Fig. 7. Total electron density map of 5a with the molecular electrostatic potential surface.

4. Conclusions

Nine derivatives of 3-(*p*-substitutedphenyl)-5-phenyl-1-(4-phenyldiazenyl)phenyl formazans were synthesized and characterized by FT-IR, ¹H NMR, ¹³C NMR, and UV-Vis spectroscopic techniques, and mass analysis. The optimized geometric parameters, IR, ¹H NMR, and ¹³C NMR spectra were theoretically determined by the DFT method and compared with the experimental data. There was an excellent agreement between the experimental and calculated geometric parameters and spectroscopic data. The electronic absorption spectra of the synthesized diazenyl formazans were also studied by the TD-DFT method. It was concluded that the lowest singlet excited states of the molecules were mainly derived from the HOMO-LUMO ($\pi \rightarrow \pi^*$) electron transitions. The observed and calculated UV-Vis spectra indicated that the λ_{max} values of diazenyl formazans depended on solvent polarity. The λ_{max} values decreased with an increase in polarity of the solvent. Some diazenyl formazans that contained electron withdrawing group such as -CN, -NO₂, and -CO₂CH₃ showed a hypsochromic effect in their electronic absorption spectra in toluene. The diazenyl formazans that contained electron withdrawing groups such as -F and -Cl showed bathochromic shifts in toluene as a result of two opposite effects (inductive electron withdrawing and resonance electron donating effects). The diazenyl formazan that contained $-CH(CH_3)_2$ as the electron donating group showed a bathochromic shift. Two of the synthesized diazenyl formazans that contain both pyridinyl and electron withdrawing groups -Cl and -CO₂CH₃ showed the highest hypsochromic shifts. It was observed that the calculated λ_{max_1} and λ_{max_2} values were in good agreement with the experimental findings.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in XXX.

Acknowledgements

The work was supported financially by the Research Centre of Hacettepe University (Project No: 011D03601006).

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Highlights

- Diazenylformazans were synthesized and characterized by spectroscopic techniques.
- The optimized geometries, IR, and NMR spectra were theoretically determined.
- The electronic spectra of the formazans were also studied by the TD-DFT method.
- The calculated values were in good agreement with the experimental data.