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General and Simple Method for the Synthesis of 3-nitroformazan Using Arenediazonium Tosylates

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Abstract: A general and simple procedure for the synthesis of 3-nitroformazan using arenediazonium tosylates was developed. This convenient procedure can be applied for the preparation of 3-nitroformazans containing electron-donating or electron-withdrawing groups. First the anomaly 1,5-bis(4-methoxyphenyl)-3-nitroformazan was synthesized as the mixture of TSSC (*trans-syn, s-cis*) and previously unknown for 3-nitroformazans TASC (*trans-anti, s-cis*) isomers. The structure and spectral characteristics of TASC isomer were explained using quantum-chemical calculation with TDDFT/B3LYP/6–31++G(d,p) level of theory.

Keywords: Arenediazonium tosylates, azo-coupling, diazonium salts, formazans, quantum-chemical calculations, TDDFT.

1. INTRODUCTION

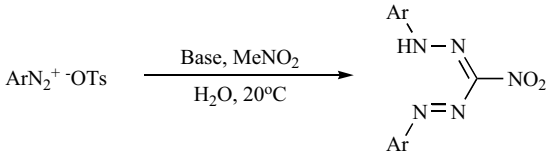
Formazans and their derivatives have been well-known since 19th century [1]. Formazan derivatives are widely used as reagents for trace metal analysis [2] and labels for the detection of metabolism paths [3]. Also, formazans are applied in organic chemistry as substrates in the synthesis of dithizones [4], azo-containing heterocycles [5, 6] and stable radicals [7]. The most important representatives are 3-nitroformazans, which have found application as nitrogen-rich analogues of β-diketimine ligands [8, 9]. The most common method of 3-nitroformazan synthesis is the interaction of diazonium salts with nitromethane in alkaline solutions [8, 10, 11]. It should be noted that working with arenediazonium chlorides and tetrafluoroborates is potentially dangerous and inconvenient due to their explosive properties and low stability. It has been demonstrated recently that the presence of p-toluenesulfonate anion as a counter-ion in diazonium salts leads to decrease of traditional hazards, and significantly increase their reactivity in common reactions [12–15].

In this paper we describe a new convenient synthetic procedure for the synthesis of various substituted 3-nitroformazans from arenediazonium tosylates. Also, the detailed investigations of 4,4'-methoxy substituted 3-nitroformazan isomerism have been carried out using experimental methods and quantum chemical calculations.

2. RESULTS AND DISCUSSION

Firstly, we report that arenediazonium tosylates react smoothly with nitromethane in aqueous solutions in the presence of base forming the corresponding 3-nitroformazans (Scheme **1**, Table **1**).

The resulting 3-nitroformazans were formed as colored microcrystalline solids and were isolated by simple filtration without further purification.



Scheme 1. Reaction of pure arenediazonium tosylates **1a-h** with nitromethane.

The yields of 3-nitroformazans strongly depend on the amount of nitromethane and the nature of base. The use of NaOH as a base (Method A) allowed carrying out a reaction with the equimolar amount of nitromethane, but the yields of obtained formazans decreased significantly due to the diazotate formation and for this reason the 3-nitroformazans from the arenediazonium tosylates with electron-withdrawing groups were formed only in trace amounts. Thus, we were not able to obtain 3-nitroformazans **2f-g** from appropriate arenediazonium tosylates in the presence of NaOH. However, the 3-nitroformazans could be prepared in high yields using NaOAc as a mild base (Method B), but the full conversion of arenediazonium tosylates was required nonstoichiometric amount of nitromethane. The quantity of nitromethane correlated with the electron-donating effects of the substituent in the benzene ring. For example, the salt **1d** fully reacted only with 8-molar excess of nitromethane. This fact can be explained by the low electrophilicity of the diazonium cation bearing electron-donating groups. Low electrophilicity of diazonium cations require a higher concentration of nucleophilic species. Similar results in 3-nitroformazans synthesis were obtained by K.G. von Eschwege [4, 16]. The 3-nitroformazans bearing electron-donating groups were prepared with lower yields. The arenediazonium tosylates with electron-withdrawing groups (**1e**, **1f**, **1g**, **1h**) required only 4-molar excess of nitromethane.

Also, we have found that 3-nitroformazans can be synthesized from anilines with diazonium salts formed *in situ* (Scheme **2**, Table **2**) (Method C).

In this case water solution of NaOAc and nitromethane was added to a solution of arenediazonium tosylates in acetic acid prepared by a known method [12]. According to the described proce-

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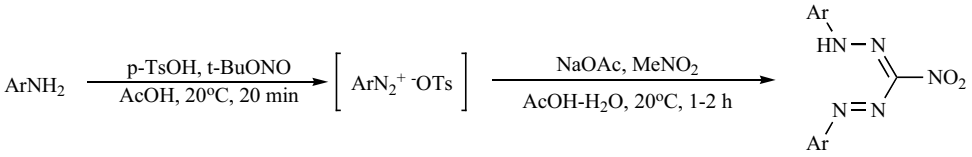
Table 1. The preparation of 3-nitroformazan 2a-h from ADTs.

Entry	Ar	Base	$MeNO_2$ Equivalent	Yield (%)	Yield[lit] (%)
1	Ph (**2a**)	NaOH NaOAc	1 6	60 64	50.1[8]
2	4-MeC_6H_4 (**2b**)	NaOH NaOAc	1 6	84 67	88[4]
3	4-BuC_6H_4 (**2c**)	NaOH	1	50	76[16]
4	4-$MeOC_6H_4$ (**2d**)	NaOH NaOAc	1 8	49* 60*	59[4]
5	4-BrC_6H_4 (**2e**)	NaOH NaOAc	1 4	52 80	-
6	4-CNC_6H_4 (**2f**)	NaOAc	4	75	-
7	4-$NO_2C_6H_4$ (**2g**)	NaOAc	4	65	-
8	4-$MeO_2CC_6H_4$ (**2h**)	NaOAc	4	78	-

* Combined yield of both isomers



Scheme 2. One-pot preparation of 3-nitroformazans **2a-l** from aromatic amines (Method C).

dure we obtained a range of 3-nitroformazan derivatives containing both electron-donating and electron-withdrawing groups in modest to excellent yields. The formazan **2l** containing the diazenyl group and formazans **2f,h** were previously unknown and they have a potential application as ligands for heavy metals.

A typical synthesis of 3-nitroformazans was performed using 4 mmol of amine. However, the method C can be used on a greater scale; for example, 3-nitroformazans **2a,b,g,h,k** were synthesized using 50 mmol of aromatic amine with 90, 89, 88, 70 and 70% yields respectively.

We found that 3-nitroformazans (**2a-2c, 2e-2l**) were obtained as TSSC (*trans-syn, s-cis*) according to NMR and UV-Vis spectra (see experimental). These data are in good agreement with previously published results [8]. However, the formazan **2d** was obtained as the mixture of two isomers according to elemental analysis and HPLC. These two isomers were isolated as individual substances by flash-chromatography on a dry column (n-hexane /AcOH = 150:1 as eluent) with 84% and 16% composition respectively. The NMR and UV-Vis spectra of both isomers were undergone the detail study.

It was found that isolated compounds are geometrical isomers according to NMR, UV spectra and elemental analysis. More than 20 types of isomers were described previously for formazans, and only the TSSC conformation was isolated before for 3-nitroformazans [8].

Unfortunately, we could not grow crystals for X-ray characterization of isolated products. Therefore quantum chemical calculations were implemented for structure investigations. The geometry optimizations of formazans in a gas phase were carried out at DFT/B3LYP/6–31++G(d,p) level of theory. The eight possible conformations for formazans were reported before [17] and there are two the most stable isomers for our 3-nitroformazan **2d** according to present quantum calculation. The frequency analysis has confirmed that the obtained geometries of the isomers are really equilibrium. The Cartesian coordinates, relatives energies (respected to the isomer with the lowest energies) for all isomers are given in supplementary material. Fig. (**1**) demonstrates the equilibrium geometries of ground electronic state and the relative energies (*respected to TSSC isomer*) for TSSC (*trans-syn, s-cis*) and TASC *(trans-anti, s-cis)* isomers. The content of TASC isomer is 3.3% and TSSC one is 96.7% in the mixture and the portion of other isomers is very negligible according to the average using Boltzmann distribution at room temperature. So the further calculations (NMR and UV-vis spectra) for mixture are referred to only TSSC and TASC isomers. It should be noted that the total energy calculations including the COSMO show that the solvent effects weakly on the relative energy of all isomers (the discrepancy is less than 5 %). Therefore further calculations were carried out in the gas phase.

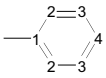
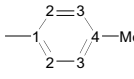
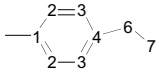
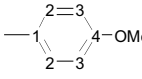
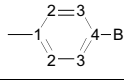
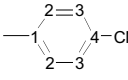
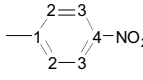
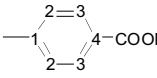
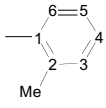
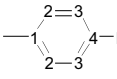
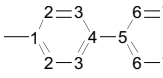
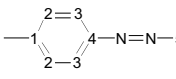
The electronic structure and NMR and UV-vis spectra of TASC and TSSC isomers of **2d** were investigated using DFT and TDDFT methods. Note that the recent theoretical investigations show that the application of the DFT and TDDFT methods for the simulation of the NMR and UV-vis spectra leads to a good agreement with experimental ones [18-23]. Thus, the choice of TDDFT for the simulation of the considered spectra is adequate.

Calculated nuclear magnetic shieldings for two isomers are given in the supplementary material. The chemical shifts based on the reference of hydrogens of tetramethylsilane (TMS) (31.91 ppm) are calculated at the same level of theory. The calculated and measured chemical shifts are represented in supplementary material.

There is a good agreement between the calculated and the experimental NMR shifts (see supporting information, table **S9**) for each isolated isomers. Just a little discrepancy was found and can be explained by the limitations of a single molecule approach in quantum chemical investigations.

We carried out the study of UV-Vis spectra of the isolated isomers of **2d** (Fig. **2**). The electronic absorption spectra of the formazan solution in DCM are shown in Fig. (**2**). It was observed that the

Table 2. Results of one-pot formazans preparation from aromatic amines.

Entry	Ar	$MeNO_2$ Equivalent	Yield/Yield[lit] (%)
1	 (**2a**)	5	89/50.1[8]
2	 (**2b**)	8	89/ 88[4]
3	 (**2c**)	14	81/76[16]
4	 (**2d**)	9	82*/59[4]
5	 (**2e**)	8	80/-
6	 (**2f**)	6	87/-
7	 (**2g**)	4	85/-
8	 (**2h**)	8	67/-
9	 (**2i**)	15	72/75[4]
10	 (**2j**)	15	71/-
11	 (**2k**)	12	96/-
12	 (**2l**)	11	58/-

* Combined yield of both isomers.

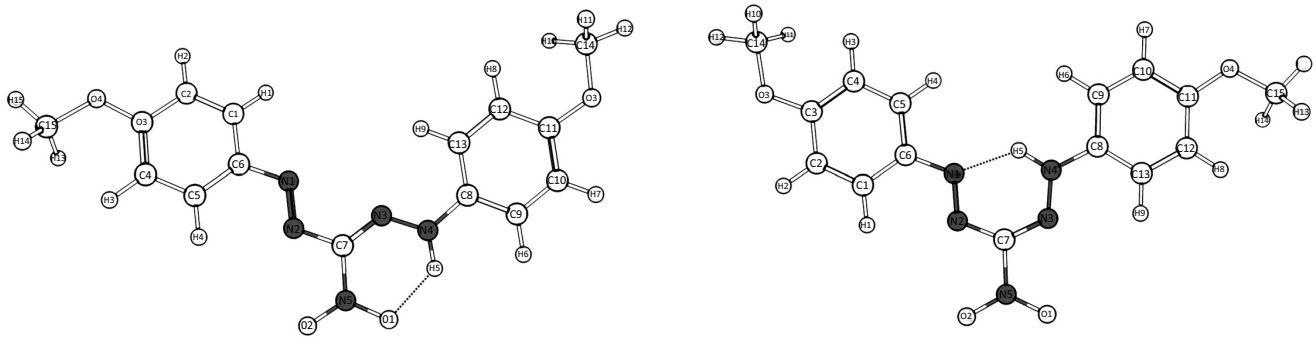


Fig. (1). Left: The molecular structures of the TASC *(trans-anti, s-cis)* isomer of **2d** (relative energy 2.08 kcal/mol). Right: The molecular structures of the TSSC (*trans-syn, s-cis*) isomer of **2d** (relative energy 0 kcal/mol).

intensity of the first spectrum band for the TSSC form is larger than one for the TASC form.

For the interpretation of this difference the vertical excitation energies (VEE) and its oscillator strengths were calculated using TDDFT/B3LYP/6–31++G(d,p). The calculated VEE and oscillator strengths for TSSC (*trans-syn, s-cis*) and TASC (*trans-anti, s-cis*) isomers are given in supporting information.

As seen from the Table **S10** the oscillator strength of the $S_0 \rightarrow S_1$ electronic transition for TASC is significantly larger than the one for TSSC. These results explained the different color of isomers and

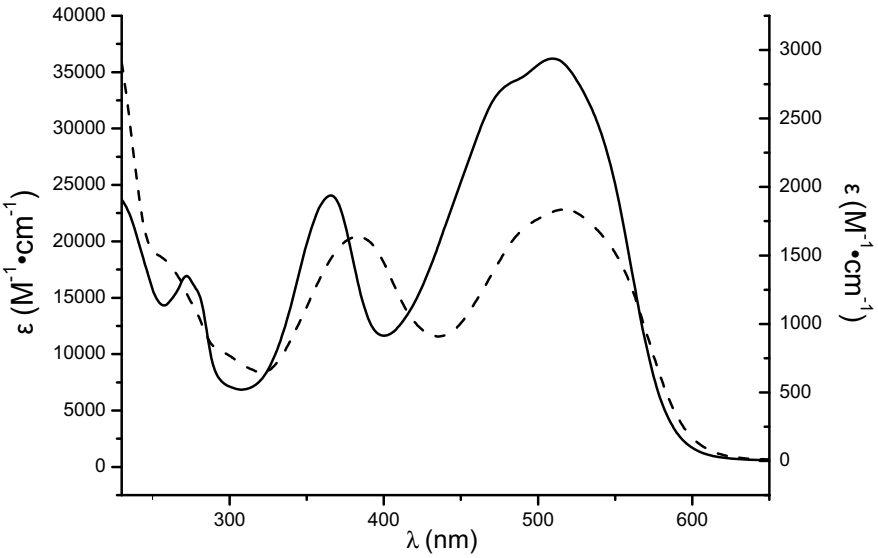


Fig. (2). Experimental UV-vis spectra of TSSC (straight, left dial) and TASC (dotted, right dial) isomers of **2d**.

the intensity of electronic absorption spectra of ones. It should be noted that the excited states (from 1 to 5) were formed by the electron transitions from HOMO, HOMO-1, HOMO-2 to LUMO and LUMO+1.

3. EXPERIMENTAL

All organic reagents and solvents were purchased from commercial suppliers (Sigma-Aldrich and Fluka) and were used as received. Arenediazonium tosylates were prepared according to the described procedure [12].

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-300 and Bruker Avance III 400 MHz instruments. Chemical shifts were reported in ppm downfield from TMS (0 ppm). Elemental analysis was performed using the Elementar Vario Macro cube CHNS. Absorption spectra were registered on the Specord 250 PLUS UV-Vis spectrophotometer, FT-IR spectra were recorded on PerkinElmer Spectrum BX II spectrometer in the range of 4000–400 cm^{-1} in KBr pellets. Melting points were determined on the Mettler Toledo Melting point system MP50.

The geometry optimizations of formazans in a gas phase were carried out at the density functional (DFT) level of theory using a B3LYP functional [24, 25] and 6–31++G(d,p) basis set. Nuclear magnetic shields were calculated at the same level of theory for all isomers of **2d**. Vertical electronic energies were calculated using TDDFT/B3LYP/6–31++G(d,p) level of theory for all isomers in the gas phase and using the conductor-like screening model (COSMO) [26] for the simulation of the solvent effects. The dielectric constant was 4.7113 for $CDCl_3$. All calculations were performed with GAUSSIAN 09 [27] on the ''SKIF" supercomputer at the Tomsk State University (Tomsk, Russia).

Reaction of ADT **1a-e** with $MeNO_2$ in the presence of NaOH (**Method A**); General procedure.

The solution of $MeNO_2$ (109 μl, 2 mmol) and NaOH (0.16 g, 4 mmol) in H_2O (2 ml) in small portions was added to the aqueous solution (20ml) of ADT (4 mmol, **2a**-1.105 g; **2b**-1.160 g; **2c**-1.330 g; **2d**-1.225 g; **2e**-1.421 g) at 20°C under stirring for 10 min. After 10 min of stirring the resulting solution was filtered and the precipitate was washed with H_2O (100 ml) (Table **1**).

Reaction of ADT **1a, b, d-h** with $MeNO_2$ in the presence of NaOAc (**Method B**); General procedure.

The solution of $NaOAc{\cdot}3H_2O$ (4.42 g, 32 mmol) in H_2O (20 ml) was added to a solution of ADT (4 mmol, **2a**-1.105 g; **2b**-1.160 g; **2d**-1.225 g; **2e**-1.421 g; **2f**-1.205 g; **2g**-1.285 g; **2h**-1.337 g) in H_2O (20 ml) at 20°C. Then $MeNO_2$ (55 μl, 1 mmol) was added with stirring by portions every 5 min (the final amount of $MeNO_2$: **2a**-12 mmol, 660 μl; **2b**-12 mmol, 660 μl; **2d**-16 mmol, 880 μl; **2e**-8 mmol, 440 μl; **2f**-8 mmol, 440 μl; **2g**-8 mmol, 440 μl; **2h**-8 mmol, 440 μl). After full conversion of diazonium salt the resulting solution was filtered and the precipitate was washed with H_2O (150 ml) (Table **1**).

Synthesis of 3-nitroformazans **2a-l** from aromatic amines (**Method C**); General procedure.

t-BuONO (715 μl, 6 mmol) and aromatic amine (4 mmol, **2a**-aniline 365 μl, **2b**-4-methylaniline 0.4286 g, **2c**-4-butylaniline 0.5969 g, **2d**-4-methoxyaniline 0.4926 g, **2e**-4-bromoaniline 0.6881 g, **2f**-4-cyanoaniline 0.4726 g, **2g**-4-nitroaniline 0.5525 g, **2h**-4-(methoxycarbonyl)aniline 0.6046 g, **2i**-2-methylaniline 0.4286 g, **2j** - 4-iodoaniline 0.8761 g, **2k**-4-aminobiphenyl 0.6769 g, **2l**-4-(phenyldiazenyl)aniline 0.7889 g) were added to the solution of p-TsOH (0.95g, 5 mmol) in AcOH (6 ml). Then, the resulting solution was stirred for 5-30 min until full conversion of starting amine. Then the aqueous solution (35 ml) of $NaOAc{\cdot}3H_2O$ (17.68 g, 130 mmol) and $MeNO_2$ (55 μl, 1 mmol) was added to the reaction mixture at 20°C. $MeNO_2$ was added by portions every 5 min with stirring until the diazonium salt was fully converted (the final amount on $MeNO_2$: **2a**-10 mmol, 550 μl; **2b**-16 mmol, 880 μl; **2c** –28 mmol, 1540 μl; **2d**-18 mmol, 990 μl; **2e**-16 mmol, 880 μl; **2f**-12 mmol, 660 μl; **2g**-8 mmol, 440 μl; **2h**-16 mmol, 880 μl; **2i**-30 mmol, 1650 μl; **2j**-30 mmol, 1650 μl; **2k** - 24 mmol, 1320 μl; **2l**-22 mmol, 1210 μl). After that the resulting solution was filtered, and the precipitate was washed with H_2O (150 ml). The resulting product was reprecipitated from 1,4-dioxane and water (Table **2**).

3-nitro-1,5-phenyl formazan (2a). Orange-red microcrystalline solid. Yield 89%. Mp= 163 °C; Mp^{lit}= 161 °C [11]; FT-IR (KBr): 3118, 1553, 1355, 1339, 1284, 1074, 862, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (t, 2H, J=7.2 Hz, C_4-H), 7.54-7.49 (m, 4H, C_3-H), 7.74 (d, 4H, J=7.8 Hz, C_2-H), 15.3 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 120.1 (C_3), 125.3 (C_1), 129.9 (C_2), 130.1 (C_4), 146.3 (C_5) ppm. UV–vis (CH_2Cl_2): λ_{max}=450 nm (ε = 46650); 325 nm (ε = 24910); 263 nm (ε = 13720); 266 nm (ε = 16855).

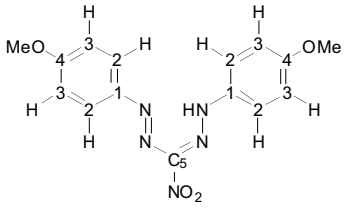
3-nitro-1,5-(4-methylphenyl) formazan (2b). Scarlet microcrystalline solid. Yield: 89%. Mp= 163 °C; Mp^{lit}= 160-162 °C [10]; FT-IR (KBr): 3502, 2950, 1628, 1548, 1354, 1283, 1070, 867,

816 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.42 (s. 6H, Me), 7.29 (d, 4H, J=8.1 Hz, C_3-H), 7.62 (d, 4H, J=8.4 Hz, C_2-H), 15.41 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5 (Me), 119.9 (C_3), 124.9 (C_4), 130.4 (C_2), 140.7 (C_1), 144.1 (C_5) ppm. UV–vis (CH_2Cl_2): λ_{max}=462 nm (ε = 9780); 340 nm (ε = 6180); 272 nm (ε = 7425); 265 nm (ε = 7260).

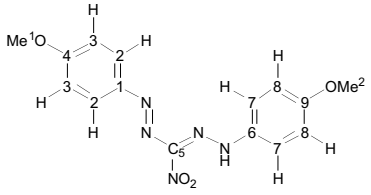
3-nitro-1,5-(4-butylphenyl) formazan (2c). Dark red microcrystalline solid. Yield: 81%. Mp= 116 °C; Mp^{lit}= 114-115 °C [16]; FT-IR (KBr): 3437, 2956, 2927, 2856, 1549, 1458, 1384, 1286, 1180, 1044, 831, 780, 693, 609, 584, 468 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.94 (t, 6H, J=7.28 Hz, C_9-H), 1.37 (dq, 4H, J_1=7.39 Hz, J_2=7.39 Hz, J_3=7.31 Hz, J_4=14.66 Hz, C_8-H), 1.63 (dt, 4H, J_1=7.52 Hz, J_2=7.52 Hz, J_3=15.15 Hz, C_7-H), 2.67 (t. 4H, J=7,73 Hz, C_6-H), 7.30 (d, 4H, J=8.21 Hz, C_3-H), 7.64 (d, 4H, J=8.23 Hz, C_2-H), 15.4 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0 (C_9), 22.4 (C_8), 33.5 (C_7), 35.6 (C_6), 120.0 (C_3), 129.9 (C_2), 144.4 (C_4), 145.6 (C_5), 145.8 (C_1) ppm. UV–vis (CH_2Cl_2): λ_{max}=462 nm (ε = 18150); 339 nm (ε = 11945); 270 nm (ε = 9950); 261 nm (ε = 11295).

3-nitro-1,5-(4-methoxyphenyl) formazan (2d). Dark violet microcrystalline solid for TASC conformation, dark red microcrystalline solid for TSSC conformation after flash-chromatography on dry column (silica, n-hexane / AcOH = 150 : 1 as eluent). Total yield: 82%. Anal. calcd. for $C_{15}H_{15}N_5O_4$: C, 54.71; H, 4.59; N, 21.27. Found: C, 54.65; H, 4.55; N, 21.20. FT-IR (KBr): 3385, 1598, 1546, 1501, 1350, 1282, 1257, 1156, 1032, 826 cm^{-1}.

TSSC isomer ^1H NMR ($CDCl_3$, 300 MHz): δ 3.89 (s. 6H, OMe), 7.00 (d, 4H, J=9 Hz, C_3-H), 7.68 (d, 4H, J=9 Hz,), 15.45 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.45 (OMe), 114.19 (C_3), 124.75 (C_2), 146.0 (C_5), 147.01 (C_1), 162.4 (C_4) ppm. UV–vis (CH_2Cl_2): λ_{max}=509 nm (ε = 36210); 365 nm (ε = 24060); 272 nm (ε = 16930).



TASC isomer ^1H NMR ($CDCl_3$, 300 MHz): δ 3.92 (s. 3H, OMe^2), 3.94 (s. 3H, OMe^1), 7.04 (d, 2H, J=9.3 Hz, C_8-H), 7.34 (d, 2H, J=9.6 Hz, C_3-H), 8.23 (d, 2H, J=8.7 Hz, C_7-H), 8.33 (d, 2H, J=9.3 Hz, C_2-H), 15.66 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.45 ($OMe^{1,2}$), 114.11 (C_8), 114.69 (C_3), 124.51(C_7), 124.75 (C_2), 146.29 (C_6), 146.92 (C_5), 147.01 (C_1), 164.41 ($C_{4,9}$) ppm. UV–vis (CH_2Cl_2): λ_{max}=516 nm (ε = 1830); 382 nm (ε = 1640); 256 nm (ε = 1470).



3-nitro-1,5-(4-bromophenyl) formazan (2e). Coral microcrystalline solid. Yield: 80%. Mp= 194 °C; Mp^{lit}= 156-158 °C [10]; FT-IR (KBr): 3013, 1553, 1351, 1289, 1278, 1070, 1005, 824, 786 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, 4H, J=9.15 Hz, C_3-H), 7.65 (d, 4H, J=9.13 Hz, C_2-H), 15.13 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 121.5 (C_3), 124.4 (C_4), 133.2 (C_2), 145.2 (C_1), 142.4 (C_5) ppm. UV–vis (CH_2Cl_2): λ_{max}=461 nm (ε = 13810); 338 nm (ε = 7485); 237 nm (ε = 6770). Anal. calcd for $C_{13}H_9Br_2N_5O_2$: C, 36.56; H, 2.12; Br, 37.42; N, 16.40. Found: C, 36.45; H, 2.16; Br, 37.40; N, 16.42.

3-nitro-1,5-(4-cyanophenyl) formazan (2f). Rufous microcrystalline solid. Yield: 87%. Mp= 205 °C; FT-IR (KBr): 3430, 2228, 1550, 1508, 1361, 1336, 1287, 1232, 1005, 847 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, 4H, J=8.93 Hz, C_3-H), 7.87 (d, 4H, J=8.93 Hz, C_2-H), 14.89 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 117.6 (CN), 129.1 (C_3), 132.2 (C_2), 145.7 (C_1), 148.6 (C_5) ppm. UV–vis (CH_2Cl_2): λ_{max}=455 nm (ε = 18530); 316 nm (ε = 12885); 258 nm (ε = 14735); 241 nm (ε = 14750). Anal. calcd for $C_{15}H_9N_7O_2$: C, 56.43; H, 2.84; N, 30.71. Found: C, 56.42; H, 2.85; N, 30.69.

3-nitro-1,5-(4-nitrophenyl) formazan (2g). Carmine microcrystalline solid. Yield: 85%. Mp= 207 °C; Mp^{lit}= 202 °C [28]; FT-IR (KBr): 3116, 1555, 1517, 1341, 1279, 1224, 1111, 864 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, 4H, J=9.01 Hz, C_2-H), 8.42 (d, 4H, J=8.93 Hz, C_3-H), 14.85 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 129.9 (C_2), 132.5 (C_3), 141.4 (C_1), 146.6 (C_5), 148.5 (C_4) ppm. UV–vis (CH_2Cl_2): λ_{max}=458 nm (ε = 11130); 311 nm (ε = 10085). Anal. calcd for $C_{13}H_9N_7O_6$: C, 43.46; H, 2.53; N, 27.29. Found: C, 43.61; H, 2.50; N, 27.34.

3-nitro-1,5-(4-(methoxycarbonyl)phenyl) formazan (2h). Maroon microcrystalline solid. Yield: 67%. Mp=193 °C; FT-IR (KBr): 3509, 2925, 2854, 1725, 1557, 1514, 1355, 1286, 1110, 854, 765 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.96 (s. 6H, CH_3), 7.80 (d, 4H, J=8.4 Hz, C_3-H), 8.18 (d, 4H, J=8.8 Hz, C_2-H), 15.12 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.6 (Me), 120.0 (C_3), 131.5 (C_2), 131.6 (C_4), 146.0 (C_5), 149.2 (C_1), 166.1 (C=O) ppm. UV–vis (CH_2Cl_2): λ_{max}=457 nm (ε = 12395); 320 nm (ε = 9295); 256 nm (ε = 11230). Anal. calcd for $C_{17}H_{15}N_5O_6$: C, 52.99; H, 3.92; N, 18.17. Found: C, 52.95; H, 3.90; N, 18.19.

3-nitro-1,5-(2-methylphenyl) formazan (2i). Maroon microcrystalline solid. Yield: 72%. Mp= 152 °C; Mp^{lit}= 153-154 °C [10]; FT-IR (KBr): 3172, 1550, 1470, 1358, 1338, 1270, 1090, 860, 775, 750, 712 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.55 (s. 6H, CH_3), 7.29-7.36 (m, 6H, C_{Ar}), 7.87 (d, 2H, J=6.9 Hz, C_6-H), 14.31 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.3 (Me), 117.5 (C_3), 127.6 (C_4), 129.8 (C_5), 130.9 (C_6), 131.3 (C_2), 145.3 (C_1), 146.3 (C_7) ppm. UV–vis (CH_2Cl_2): λ_{max}=45 nm (ε = 46950); 332 nm (ε = 26050); 249 nm (ε = 18580). Anal. calcd for $C_{15}H_{15}N_5O_2$: C, 60.60; H, 5.09; N, 23.56. Found: C, 60.50; H, 5.07; N, 23.54.

3-nitro-1,5-(4-iodophenyl) formazan (2j). Maroon microcrystalline solid. Yield: 71%. Mp= 190 °C; Mp^{lit}= 161 °C [29]; FT-IR (KBr): 3488, 1549, 1402, 1350, 1331, 1287, 1054, 1002, 821, 783 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, 4H, J=8.77 Hz, C_3-H), 7.84 (d, 4H, J=8.76 Hz, C_2-H), 15.1 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 100.3 (C_4), 127.3 (C_2), 133.5 (C_1), 139.6 (C_3), 145.8 (C_5) ppm. UV–vis (CH_2Cl_2): λ_{max}=470 nm (ε = 21820); 351 nm (ε = 12220); 241 nm (ε = 13135). Anal. calcd for $C_{13}H_9I_2N_5O_2$: C, 29.97; H, 1.74; I, 48.71; N, 13.44. Found: C, 30.04; H, 1.71; I, 48.79; N, 13.40.

3-nitro-1,5-((1,1'-biphenyl)-4-yl) formazan (2k). Rosewood microcrystalline solid. Yield: 96%. Mp= 173 °C; Mp^{lit}= 168-170 °C [10]; FT-IR (KBr): 3568, 2925, 2854, 1654, 1541, 1457, 1092, 799, 700, 469 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.4 (t. 2H, J=6.9 Hz, C_8-H), 7.46-7.51 (m. 4H, C_7-H), 7.64 (d, 4H, J=7.5 Hz, C_6-H), 7.73 (d, 4H, J=8.1 Hz, C_3-H), 7.81 (d, 4H, J=7.8 Hz, C_2-H), 15.8 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 127.3 (C_8), 127.6 (C_7), 128.5 (C_6), 129.0 (C_5), 130.2 (C_4), 135.2 (C_3), 139.6 (C_2), 139.8 (C_1), 148.1 (C_9) ppm. UV–vis (CH_2Cl_2): λ_{max}=485 nm (ε = 39110); 362 nm (ε = 25195); 270 nm (ε = 39085). Anal. calcd for $C_{25}H_{19}N_5O_2$: C, 71.25; H, 4.54; N, 16.62. Found: C, 71.15; H, 4.51; N, 16.69.

3-nitro-1,5-(4-(phenyldiazenyl)phenyl) formazan (2l). The resulting precipitate was purified *via* column chromatography (silica gel and dichloromethane as eluent). The eluate was concentrated in vacuo to afford **2l**. Black microcrystalline solid. Yield: 58%. Mp= 193 °C; FT-IR (KBr): 3401, 2926, 2853, 1549, 1385, 1282,

1230, 848, 769, 687 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.55 (m. 6H, C_7-H, C_8-H), 7.90-7.98 (m. 8H, C_3-H, C_6-H), 8.08 (d, 4H, J=8.4 Hz, C_2-H), 15.4 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 122.8 (C_7), 123.3 (C_3), 124.2 (C_6), 126.2 (C_8), 129.3 (C_2), 132.4 (C_5), 152.1 (C_9), 152.6 (C_1), 153.8 (C_4) ppm. UV–vis (CH_2Cl_2): λ_{max}=509 nm (ε = 22610); 363 nm (ε = 24800); 323 nm (ε = 26020). Anal. calcd for $C_{25}H_{19}N_9O_2$: C, 62.89; H, 4.01; N, 26.40. Found: C, 62.93; H, 4.02; N, 26.32.

CONCLUSION

In conclusion, the high reactivity of arenediazonium tosylates allowed us developing a simple and effective procedure for the synthesis of 3-nitrofromazans with various substituents in the benzene ring under mild conditions. The new representatives of 3-nitroformazans synthesized by this procedure can find practical application as reagents for analytical chemistry and biochemistry.

The detailed study of 3-nitroformazan **2d** showed the possibility of formation of TSSC (*trans-syn, s-cis*) and TASC (*trans-anti, s-cis*) isomers. The quantum-chemical calculation showed that the TASC (*trans-anti, s-cis*) isomer is more stable than TSST (*trans-syn*, *s-trans*) form. These investigations can potentially open the new directions in formazan application as molecular sensors.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's web site along with the published article.

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