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Spectroscopic and computational study of a new thiazolylazonaphthol dye 1-[(5-(3-nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol



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spectroscopic and computational study of a new imazory azonaphinor dye 1-l(5-

(3-nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol

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Арыгасі

A new thiazolylazo structure, 1-[(5-(3-nitrobenzyl)-1,3-thiazol-2yl)diazenyl]naphthalen-2-ol (NBnTAN), has been synthesized for the first time. The geometric parameters and properties of the new dye were studied using spectroscopic, DFT and semiempirical methods through the computation of different electronic descriptors (aromaticity, frontier molecular orbitals, dipole moments, partial atomic charges). The solvation effect of different organic liquids on the absorption spectra of the reagent has been studied. ¹H, ¹³C, COSY, HSQC and HMBC NMR, UV-Vis and IR spectra were used to confirm the reagent structure. It has been shown that NBnTAN forms complex compounds with a number of transition metals, allowing the development of selective methods for the determination of these metals.

Keywords:

Azo dye; metal complex; spectroscopic characterization; partial charge; dipole moment; aromaticity.

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1. ингоансион

Azo dyes are a family of scientifically and commercially important organic compounds widely used in spectrophotometric analysis and, owing to their color fastness and fairly low price, in a variety of industrial applications [1]. The main common structural feature of these compounds is the presence of a chromophoric azo group (-N=N-) offering a wide spectrum of colors.

Thiazolylazo dyes, a subset of the azo dyes containing the thiazolyl group, have been extensively used in analytical chemistry for spectrophotometric determinations, because of good selectivity and sensitivity of these reagents over a wide pH range, and also due to the relative simplicity of their synthesis and purification. It must be noted, however, that for the conventional spectrophotometric analysis in aqueous solution the typically low solubility of these azo compounds and their complexes could be a serious problem [2]; so adding of some organic solvents or surfactants could be necessary in order to overcome this problem. On the other hand, the low solubility of the above compounds can be an advantage when the solid phase spectrophotometry (SPS) technique is applied, as the reagent can be immobilized through physical sorption on a properly selected support [3].

The list of applications of thiazolylazo dyes in the chemical operations includes spectrophotometry, solid phase extraction, liquid chromatography, electrochemistry, and liquid and cloud point extraction. The applications of thiazolylazo dyes in spectrophotometry are based on the colored compounds resulting from their reaction with most (especially with some transition) metals [1-5]. The simplest and most

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popular representative of the unazorylazo uyes family is a spectrophotometric reagent 1-(2-thiazolylazo)-2-naphthol (TAN) which, despite its relatively low selectivity, is commonly used for the spectrophotometric determination of various metal ions [6-20]. TAN has also been successfully utilized in the extraction [14] and separation [15, 16] of metal ions. Thus, water samples of Mn(II), Ni(II), and Co(II) ions were reportedly successfully determined via the flame atomic absorption spectrometry using TAN as an extracting agent [17, 18]. Furthermore, the flow-injection solid phase technique was successfully used for the determination of Ni(II), and Zn(II) ions, where TAN was acting as a chelating agent [19, 20].

In order to continue the search for a new selective and sensitive chromogenic thiazolylazo dye, and to study the influence of the substituent positions of a benzyl group on the thiazole ring upon the characteristics of the reagent, earlier we introduced a benzyl group into the 5-position of the thiazole ring of the TAN reagent and thus synthesized a new compound, 1-[(5-benzyltiazol-2-yl)diazenyl]naphtalen-2-ol (BnTAN) [21]. Thiazolylazonaphthol BnTAN was found to be an efficient complexing reagent for the spectrophotometric and extraction-photometric determination of a number of metals [22-24]. In view of the reactivity, selectivity and sensitivity of the BnTAN reagent, a new derivative of this azo compound, 1-[(5-(3-nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol (NBnTAN), was synthesized in which the nitro group was attached to the benzyl group. The decision about introduction of the nitro group was dictated by the powerfulness, importance and simplicity of this approach in molecular design [25, 26] for modification of chemical

and physic-chemical properties [27, 26]. Thus, the main goar of the present work is (i) to study the structure and spectral properties of the new dye obtained; (ii) to determine the effect of nitro group on the physico-chemical and electronic properties of this azo dye; and (iii) to test the ability of this new reagent to form complex compounds with certain transition and heavy metals, and thus its further potential applicability in spectrophotometric analysis.

2. Experimental details

2.1. Synthesis

3-(3-Nitrophenyl)-2-chloropropanal (**2**, $C_9H_8CINO_3$) was prepared by the method described earlier [29]. A three-necked flask equipped with a stirrer, a dropping funnel, and a gas-outlet tube (attached to a bubble counter) was charged with 0.2 mol (13.5 cm³) of acrolein, 10 g of CuCl₂·2H₂O, and 50 cm³ of acetone. A cold aqueous solution of 3-nitrophenildiazonium chloride **1** (prepared by diazotization of 27.6 g (0.2 mol) of 3-nitroaniline) was added dropwise under vigorous stirring. The temperature was maintained within 0-5 °C. When the reaction was complete, the organic layer was separated, and the aqueous layer was extracted with chloroform. The extract was combined with the organic phase, dried over MgSO₄, evaporated and the residue was distilled under reduced pressure. Yellow viscous oil, yield 41% (17.50 g), bp 150-153 °C (at pressure 3 mmHg).

Caution: Overheating of the product 2 can lead to an explosion, so the distillation of2 should be carried out with care!

2-Amino-5-(3-nitrobenzyl)thiazole (**3**, $C_{10}H_9N_3O_2S$) was synthesized according to Scheme 1. A mixture of 8.36 g (0.11 mol) thiourea and a3-(3-nitrophenyl)-2chloropropanal **2** 21.36 g (0.1 mol) in 20 cm³ of ethanol was heated for 2 h under reflux. The mixture was cooled, diluted with 500 cm³ of water, and made alkaline by adding aqueous ammonia. The precipitate was filtered off and recrystallized from toluene. Yellow crystals, yield 81% (18.80 g), mp 108-109 °C. ¹H NMR (DMSO-*d*₆, 400 MHz), δ (in ppm) 7.72-7.58 (4H, m, C₆H₄), 6.88 (1H, s, thiazole), 6.77 (2H, s, NH₂), 4.08 (2H, s, CH₂). The spectroscopic data are in agreement with those reported in the literature [30].



Scheme 1. Two-step synthesis of compound 3.

1-[(5-(3-Nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol (**5**, $C_{20}H_{15}N_3OS$) was synthesized according to Scheme 2. 2-Amino-5-(3-nitrobenzyl)-1,3-thiazole **3** (2.35 g, 10 mmol) was dissolved in concentrated H₂SO₄ (6 cm³) at -5 °C. The solution was diluted with 3 cm³ water. The suspension was warmed to 80 °C and a clear solution was formed. The mixture was cooled to -15 °C, and crystalline sodium nitrite (1.73 g, 25 mmol) was added portion wise while keeping the temperature below -10 °C. After 10 min, the resinous sediment was filtered and the clear solution was added slowly with intensive stirring to the mixture of naphthalen-2-ol (1.44 g, 10 mmol), NaOH (0.40 g, 10 mmor), Na₂CO₃ (20 g) and 50 cm⁻ or water. The temperature was kept below 5 °C. After diazonium salt was added, the mixture was stirred 2 h at the room temperature and diluted of water (200 cm³). The precipitate was filtered off and recrystallized from EtOH-DMF (2:1). Purple-black crystals, yield 40 % (1.56 g,), mp 205-206 °C.

NMR signals of all atoms were assigned to individual protons and carbons of benzene (B), naphthalene (N), and thiazole (T) subunits. ¹H NMR of NBnTAN (DMSO-*d*₆, 600MHz), δ (in ppm): 4.41 (s, 2H, CH₂), 7.02 (N, d, 1H, J = 9.3, H-3'), 7.44 (N, dd, 1H, J = 7.8, 7.2, H-6'), 7.59 (N, dd, 1H, J = 7.8, 7.2, H-7'), 7.66 (B, t, 1H, J = 7.8, H-5), 7.79 (T, s, 1H, H-4'', 7.80 (N, d, 1H, J = 7.8, H-5'), 7.83 (B, d, 1H, J = 7.8, H-6), 7.98 (N, d, 1H, J = 9.3, H-4'), 8.12 (B, dd, 1H, J = 7.8, 1.5, H-4), 8.24 (B, d, J = 1.5, 1H, H-2), 8.45 (N, d, 1H, J = 7.8, H-8'), 14.25 (N, br s, 1H, OH). ¹³C NMR (DMSO-*d*₆, 151 MHz), δ (in ppm): 32.04 (CH2), 121.35 (N, CH-8'), 121.79 (B, CH-4), 122.58 (N, CH-3'), 123.11 (B, CH-2), 125.53 (N, CH-6'), 127.89 (N, C-4a'), 128.82 (N, CH-5'), 129.13 (N, CH-7'), 130.02 (N, C-1'), 130.22 (B, CH-5), 131.84 (N, C-8a'), 135.37 (B, CH-6), 137.37 (T, C-5''), 139.54 (N, CH-4'), 140.91 (T, CH-4''), 141.95 (B, C-1), 147.94 (B, C-3), 162.69 (N, C-2'), 173.18 (T, C-2'').

Elemental analysis, Found: C, 61.39; H 3.54; N 14.26%; molecular formula $C_{20}H_{14}N_4O_3S$ requires C, 61.53; H, 3.61; N, 14.35%.

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Scheme 2. Two-step synthesis of compound 5.

2.2. Materials and instrumentation

The stock solution of 1-[(5-(3-Nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol was prepared by dissolving the reagent in ethanol (96%). The reagent's working solutions were prepared by diluting the stock solution in the ethanol–water mixture.

All used chemicals were of analytical grade purity. Transition metals' stock solutions were prepared by dissolving their soluble salts in distilled water. To prevent metal salts hydrolysis, a small amount of the acid corresponding to the salt anion was added. The stock and working solutions were prepared using distilled water.

To maintain the desired p*H* values, the following solutions were used: HCl (pH = 1.0-3.0), CH₃COOH and CH₃COONa (pH = 4.0-7.0), NH₄OH and NH₄Cl (pH = 8.0-9.0), NaOH (pH>10.0). The control of acidity was carried out by a p*H*-meter InoLab p*H* Level 1 equipped with a combined glass electrode (WTW, Germany).

The measurements of absorbance were carried out on a computerized spectrophotometer WPA Lightwave II UV/VIS (Biochrom, England) in 1.0 cm

quartz cens in the wavelenguns range of 550-900 mm with a resolution of 1 mm. The organic solvents used for the extraction of the reagents were also used as the blanks. For measurements of protolytic constants, a spectrophotometer Specord[®] S 600 with an optical probe (661,000 Hellma Analytics, Germany) was employed in the wavelengths range of 400-900 nm with the step of 0.5 nm.

IR spectra were obtained by a FT-IR spectrometer model Nicolet 6700 from Thermo SCIENTIFIC in ATR mode.

In the case of compound 2, NMR spectra were measured on NMR spectrometer Bruker Avance 400 MHz spectrometer (at 400 MHz for ¹H NMR). In the case of compound 5, NMR spectra were measured on a 600 MHz Varian VNMRS spectrometer (Palo Alto, USA) at 599.861 MHz (¹H) and 150.835 MHz (¹³C) at room temperature at a concentration of 16 mg of NBnTAN sample in DMSO- d_6 (0.5 mL, Sigma-Aldrich). ¹H and ¹³C 1D NMR and 2D NMR methods (gCOSY, gHSQCAD, gHMBCAD) were used to assign chemical shifts. The chemical shifts (δ scale, ppm) were referenced to solvent signals (¹H – 2.50 ppm, ¹³C – 39.50 ppm). Coupling constants are given in Hz.

2.3. Computational methods

The structure of NBnTAN molecule was modelled based on previous XRD [21] and DFT [31] studies of BnTAN molecule. DFT geometry optimizations and Hessian calculations were performed at the PBE/6-311G(d,p) level of theory [32-34], as it was shown that this method can accurately describe similar dyes [35, 36]. Total

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energy was computed at the who-2A/0-511+O(20,p) level [57], as this functional is known to be superior for thermochemistry and non-covalent interactions (NCI) [38-40]. Intramolecular NCI were analyzed using electron density calculated with the PBE0/6-31++G(d,p) method [41]. NMR chemical shifts and NICS(0) aromaticity indexes [42] were calculated with the gauge-independent atomic orbital (GIAO) approach [43] at three different levels of theory: PBE/ $\Lambda 2$ [44] in gas phase, B3LYP/6-31G(d,p) [45] and PBE0/6-31G(d,p) with employment of the CPCM solvent (DMSO) [46]. Choosing of the PBE functional was stipulated by the previous successful NMR calculations [47-49]. In numerous works, it was shown that the theoretical NMR shifts computed with the PBE [47-49], B3LYP [50] and PBE0 [51] functionals demonstrate a good correlation with the experimental data; also, consideration of the solvent effects is sometimes desirable [52, 53]. Dipole moments, frontier molecular orbitals, Hirshfeld population analysis [54], ADCH [55], and CM5 [56] net atomic charges were computed at the PBE0/6-31++G(d,p) level. Mulliken [57], Löwdin [58], and NPA [59] partial charges, which are good in prediction of some physicochemical properties, such as partitioning coefficient logP [61], are known for their inconsistency with the diffuse functions [60], so the non-augmented 6-31G(d,p) basis set was used in these calculations. The choice of PBE0 functional was dictated by its adequate representation of dipole moments [62] and electron density [63]. Taking into account the popularity of semiempirical quantum models [64-67], we have studied the Mulliken [57] and Coulson [68] net charges calculated with the FWF [09] and KWFF [70, 71] methods in gas phase and in the COSIVIO [72] water solution.

All gas phase calculations employing the PBE functional were performed using the PRIRODA 17 code [73]. Other DFT computations were done with the ORCA 4.1 package [74]. AIM critical points, reduced density gradient (RDG) [75] isosurface and ADCH partial charges were calculated with the MultiWFN 3.6 software [76]. The JANPA 2.02 program was used for natural population analysis [77]. CM5 charges were calculated with the CM5charges code [78]. MOPAC2016 was used for all calculation related to the semiempirical methods [79]. All manipulations with geometric parameters and input files preparation were done using the Avogadro [80] and the Gabedit [81] programs, respectively. Visualization and figures rendering were performed with the VMD [82] and Jmol [83] programs. Resolution of identity [84] and chain-of-spheres [85] techniques were used for speed-up the DFT computations.

3. Results and discussion

3.1. Synthesis

Our syntheses of the target 1-[(5-(3-nitrobenzyl)-1,3-thiazol-2yl)diazenyl]naphthalen-2-ol **5** (NBnTAN) are illustrated in Schemes 1 and 2. At the first step the acrolein was chloroarylated by diazonium salt in the presence of copper (II) chloride under Meerwein arylation conditions. As mentioned above, distillation of **2** requires care because overheating of this product can lead to an explosion. 3-(3formed 2-amino-5-(3-nitrobenzyl)-1,3-thiazole **3** with a good yield (Scheme 1) [86]. Previously we have discussed the synthetic possibilities of 5-benzyl-2-aminothiazoles during the synthesis of some derivatives as potential biologically active compounds [87-90] and analytical reagents [21-23, 31, 91].

Herein we describe novel advantages of 2-amino-5-(3-nitrobenzyl)-1,3-thiazole diazotization and the application of obtained diazonium salt in diazocoupling. 5-(3-Nitrobenzyl)-2-aminothiazole is a weak base, so efficient diazotization can be achieved only by using nitrosylsulfuric acid obtained from NaNO₂ and concentrated H_2SO_4 .

5-(3-Nitrobenzyl)-1,3-thiazole-2-diazonium salt is unstable and readily participates in the diazocoupling reaction. Diazocoupling of 5-benzyl-1,3-thiazole-2-diazonium with naphthalen-2-ol was carried out in alkaline conditions forming 1-[(5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol with a good yield (Scheme 2). It should be concluded that the above described method can be an excellent synthetic route to new azo dyes of the thiazolyl series.

3.2. General DFT computations of NBnTAN structure

Taking into account high similarity of NBnTAN with the previously described thiazolylazo dye [21], starting geometry of NBnTAN was modeled based on BnTAN. The four conformations related to *m*-nitrobenzyl fragment was checked at the M06-2X/6-311+G(2d,p)//PBE/6-311G(d,p) level of theory (see Figure 1). The relative



Choos nee energies calculated for the four structures \mathbf{a} , \mathbf{b} , \mathbf{c} , and \mathbf{u} are 0.0, 0.5, 0.8, and 0.7 kcal/mol, respectively. Off course, the difference is marginal and testifies about the presence of all proposed structures simultaneously; however, to save computational resources, it was necessary to choose one structure. Hence, the \mathbf{a} conformation was used as a basic structure in our further investigations.



Figure 1. Four considered conformations of NBnTAN with different position of *m*-nitrobenzyl fragment.

In previous works related to the BnTAN molecule [31], four possible tautomeric forms caused by possible different location of the hydrogen atom were investigated. The same picture can be observed in the case of the NBnTAN molecule (Figure 2). The non-covalent interactions (NCI) were studied with the RDG function and bond critical points. Blue areas of the RDG isosurface on Figures 2A and 2B indicate the presence of OH…N and O…HN hydrogen bonds, respectively.

Furthermore, CP68 and CP71 critical points also show the presence of strong electrostatic attraction. Critical points CP70 and CP76 on Figures 2C and 2D are



Figure 2. Bond critical points (orange dots) and RDG function of four tautomeric forms of NBnTAN. Blue areas of the RDG isosurface correspond to strong attraction, green areas to weak interactions, and red areas to strong repulsion.

In order to find more accurate data about the stability of the tautomers, we have carried out the calculation of thermodynamic properties at the M06-2X/6-311+G(2d,p)/PBE/6-311G(d,p) level of theory (see Table 1). As can be seen, the computed relative Gibbs free energy values and the relative enthalpy values are very close for each considered tautomer-phase combination. Consequently, respective Boltzmann distribution values relatively the same. We have to notice, that with the increase of the solvents polarity (dielectric constant), the quantity of the forms **B**, **C**,

and **D** is also increased, but the structure **A** is the most stable one in the an modeled media; so all further calculations in the present work were based on this form.

Table 1. Relative Gibbs free energies of the A-D tautomeric forms of NBnTAN in

Tautomer Gas phase Chloroform DMSO Water Ethanol 15.3 3.4 0.5 0.2 0.0 Relative Α Gibbs free 17.2 4.6 B 1.6 1.2 1.0 С 7.5 30.8 12.3 energy, 6.8 6.6 kcal/mol D 34.9 16.8 12.0 11.4 11.1 95.99 88.53 85.49 85.05 Boltzmann A 84.86 14.51 distribution B 4.01 11.47 15.14 14.95 according С 4.2E-10 2.8E-05 7.0E-4 1.1E-3 1.3E-3 to ΔG , % 4.3E-13 1.4E-08 3.2E-07 4.9E-07 6.0E-07 D 15.3 3.4 0.5 0.2 0 Α Relative В 17.1 4.6 1.5 1.1 1.0 enthalpy, С 32.2 13.7 8.9 8.2 8.0 kcal/mol 35.6 17.6 12.8 12.2 D 11.9 84.18 A 95.58 87.46 83.72 83.51 Boltzmann distribution 4.42 12.54 15.82 16.28 B 16.49 according С 4.1E-11 2.7E-06 6.6E-05 1.0E-4 1.2E-4 to ΔH , % 1.1E-13 1.3E-07 3.6E-09 8.4E-08 1.6E-07 D

different media, and Boltzmann distribution of each tautomer.

3.3. IR spectroscopy study

The experimental and calculated (at the PBE/6-311(d,p) level) IR spectra of NBnTAN are presented on Figure 3. A full list of the calculated vibrations in the NBnTAN molecule is presented in Supplementary Materials.



Figure 3. Experimental (blue curve) and calculated (purple drop lines) IR spectra of NBnTAN.

As the NBnTAN IR spectrum was overloaded with many bands, it was analyzed by comparison with the IR spectra of the model compounds, 1-(5-benzyltiazol-2-yl)azonaphtalen-2-ol and 1-(2-thiazolylazo)-2-naphthol. The assignment of selected peaks in the IR spectrum of NBnTAN was supported by analysis of theoretical calculations and corresponding types of vibrations listed in Table 2. A broad band in the range of 2500–3500 cm⁻¹ in the IR spectra of solid NBnTAN corresponds to the v(C–H) and v(O–H) vibrations. Sharp medium peak at 3066 cm⁻¹ corresponds to the v(C–H) vibrations of the methylene group. The v(C–C) vibrations are observed as medium peak in the range of 1596-1615 cm⁻¹. The strong band at 1523 cm⁻¹ corresponds to the asymmetric v(N–O) vibrations of the nitro group. Medium bands in the range of 1433-1478 cm⁻¹ are related to the v(C=N), v(C=C) and δ (C–O–H) vibrations of 1,3-thiazole and naphthalen-2-ol moieties. Symmetrical N-O vibrations of the nitro group appear as the strong band at 1344 cm⁻¹. The medium band at 1247

cm can be assigned to the v(C-O) vibration in the naphthalen-2-or magnent. In general, the rest of the NBnTAN IR spectrum is very similar to the spectra of other thiazolylazonaphthol dyes (e.g., TAN) [92].

As seen, there is a good correlation between the experimental and theoretical wavenumbers, which additionally testifies the correctness of the selected computational method. Some non-triviality of the O-H vibration observed for system under study could be explained by the possible coexistence of a few tautomeric NBnTAN forms, which was discussed earlier in detail for a similar molecule [6].

Experimental	Type of	Functional group	Calculated
wavenumbers, cm ⁻¹	vibration and		wavenumbers, cm ⁻¹
	bond		
2500-3500w	ν(O–H)	naphthalen-2-ol	2966-3158 (C-H)
3066m	ν(C–H)	benzyl	2967, 3009 (CH ₂)
			2560 (OH)
1596-1615m	v(C-C)	naphthalen	1588-1623
		benzyl	
1523s	$v_{as}(N-O)$	nitro	1544
1433-1478m	ν (C=N)	1,3-thiazole	1492-1506
	ν (C=C)	naphthalen-2-ol	
	δ(C–O–H)		
1344s	$v_{s}(\overline{N-O})$	nitro	1314
1247m	$\nu(C-O)$	naphthalen-2-ol	1294

Table 2. Selected assigned experimental and theoretical IR vibrations of NBnTAN.

3.4. NMR spectroscopy study

The structure of the NBnTAN sample was unambiguously proven by NMR spectroscopy. The 1H and ¹³C NMR signals of all atoms were assigned to individual protons and carbons of benzene (B), naphthalene (N), and thiazole (T) subunits based

on men chemical sinns, multiplicities, COST, HSQC, and HNIBC cross-peaks, and substituent effects of the nitro, azo and hydroxyl substituents on the chemical shifts in accord with literature and chemical expectations.

In the ¹H NMR spectrum, four signals were observed for the benzene nucleus, including two doublets H-4 and H-6, one triplet H-5 and one singlet H-2 as a result of spin-spin interactions through 3-bonds (atom numbering according to Scheme 2). The signals H-2 (8.24 ppm) and H-4 (8.12 ppm) were significantly deshielded by the ortho-electron acceptor effect of the nitro group. Six aromatic signals were detected for the naphthalene nucleus, of which 4 doublets belonged to protons 3', 4', 5' and 8' and two triplets belonged to protons 6' and 7'. The high chemical shift value of the OH proton at 14.25 ppm indicates its involvement in a strong hydrogen bond or tautomerization. As expected, the OH group with a strong +M effect significantly shifted the H-3' doublet to a higher field, 7.02 ppm. The markedly deshielded H-8' signal in naphthalene (8.45 ppm) appears to be due to the magnetic anisotropy of the adjacent azo bond (N=N) on the C-1' naphthalene carbon.

In the ¹³C NMR spectrum, all signals were observed at the expected chemical shifts, similar to model spectra of *m*-nitrobenzyl, 2-naphthol and thiazole. It was easy to assign more intense aromatic CH signals in a typical region of 121.35-139.54 ppm and a CH₂ group (32.04 ppm) using twelve one-bond HSQC correlations with the identified protons. Quaternary carbon signals were mainly assigned using strong HMBC cross peaks with protons spaced through 3 bonds (${}^{3}J_{CH} \approx 8$ Hz). Within the thiazole ring, the HSQC and HMBC transfers to all three carbons, N=C-2" (173.18)

ppm), Cn-4 (140.91 ppm) and C-3 (157.57 ppm) nom the proton n-4, together with ¹³C FID exponentially multiplied with a large line-broadening constant LB = 20, allowed detection of the both quaternary carbons of a very low intensity (Figure 4). Similarly, we found a very weak signal of the naphthalene HO-C-2' carbon (162.69 ppm) by recording a spectrum with LB = 50.



Figure 4. 2D NMR HSQC spectra of the NBnTAN.

Comparison of the experimental and calculated chemical shifts was done for different levels of theory. Particularly, the PBE/ Λ 2 method without solvent model, the

boline bo

Table 3. Comparison of experimental and theoretical ¹H chemical shifts (in ppm).Numbering of atoms corresponds to Scheme 2.

Hydrogen	Experimental	CPCM-B3LYP/6-	CPCM-PBE0/6-	$PBE/\Lambda 2$
atom	shift	31G(d,p)	31G(d,p)	
CH ₂	4.41	4.41	4.41	4.41
H-3'	7.02	7.31	7.43	7.35
H-6'	7.44	7.75	7.86	7.66
H-7'	7.59	7.87	7.98	7.72
H-5	7.66	7.79	7.88	7.70
H-4"	7.79	8.03	8.11	8.00
H-5'	7.80	7.98	8.11	7.83
H-6	7.83	7.94	8.02	7.72
H-4'	7.98	8.19	8.33	7.95
H-4	8.12	8.43	8.50	8.59
H-2	8.24	8.53	8.62	8.69
H-8'	8.45	8.78	8.86	8.88
OH	14.25	16.87	16.89	17.78
	Slope	0.7675	0.7707	0.6996
	Intercept	1.5570	1.4650	2.1098
	R^2	0.9906	0.9922	0.9803

It must be noted that inclusion of solvents influence considerably improve the accuracy of predicted ¹H shifts. Thus, the coefficient of determination R^2 in the case of PBE/ $\Lambda 2$ model is only 0.9803, whereas the use of the CPCM approach with the B3LYP/6-31G(d,p) and PBE0/6-31G(d,p) levels results in the R^2 values of 0.9906 and 0.9922, respectively (see Table 3). For the best tested method, CPCM-PBE0/6-

calculated chemical shifts can be written as $\delta(\exp) = 0.7707 \times \delta(\operatorname{calc.}) + 1.4650$.

Table 4. Comparison of experimental and theoretical ¹³C chemical shifts (in ppm).Numbering of atoms corresponds to Scheme 2.

Carbon	Experimental	CPCM-B3LYP/6-	CPCM-PBE0/6-	$PBE/\Lambda 2$
atom	shift	31G(d,p)	31G(d,p)	
CH ₂	32.04	32.04	32.04	32.04
CH-8'	121.35	112.35	113.83	108.85
CH-4	121.79	113.92	115.77	116.60
CH-3'	122.58	110.59	112.35	114.37
CH-2	123.11	115.17	116.93	117.45
CH-6'	125.53	116.55	118.42	118.66
C-4a'	127.89	119.05	119.67	126.18
CH-5'	128.82	121.59	123.31	120.92
CH-7'	129.13	121.05	123.11	121.84
C-1'	130.02	124.76	125.54	128.82
CH-5	130.22	120.91	122.76	123.94
C-8a'	131.84	123.82	124.70	127.42
CH-6	135.37	128.00	130.00	129.42
C-5"	137.37	140.54	140.00	140.74
CH-4'	139.54	133.67	135.92	133.43
CH-4"	140.91	132.33	134.09	135.30
C-1	141.95	135.13	135.90	140.47
C-3	147.94	141.58	142.51	146.35
C-2'	162.69	149.57	150.81	153.86
C-2"	173.18	171.43	171.73	170.62
	Slope	1.0179	1.0185	1.0010
	Intercept	4.7601	3.3917	4.6795
	R^2	0.9804	0.9853	0.9814

For computed ¹³C NMR chemical shifts, the solvent's influence is less tremendous (see Table 4). Thus, the best correlation ($R^2 = 0.9853$) was again got for the CPCM-PBE0/6-31G(d,p) method. The PBE/A2 level of theory outperforms the popular



3.5. Comparison of electronic structure of NBnTAN and BnTAN

Figure 5. Frontier molecular orbitals and dipole moments (purple vectors) of NBnTAN (left) and BnTAN (right).

Taking into account structural similarity of the NBnTAN and BnTAN molecules, we decided to compare their electronic structures. The geometry of BnTAN was optimized at the PBE/6-311G(d,p) level of theory [31]. Dipole moments vectors and frontier molecular orbitals calculated for the above molecules at the PBE0/6-31++G(d,p) level in gas phase are presented in Figure 5. Despite the different vector directions found, the absolute values of the dipole moments are 2.72 D and 2.93 D for

indiffair and diffair, respectively. nowever, the difference is more obvious for the

CPCM water solutions, with 3.05 D for NBnTAN and 4.16 D for BnTAN.

Frontier molecular orbitals of the two aforementioned dyes are quite similar. Thus, the gas phase computed HOMO energies are -6.3 eV and -6.1 eV for NBnTAN and BnTAN, respectively, while the respective LUMO energies are -3.2 eV and -3.0 eV. In turn, in the water solution the difference between the energies of HOMOs and LUMOs of the both dyes becomes negligible within the round-off error: in both cases $E_{HOMO} = -6.2 \text{ eV}$ and $E_{LUMO} = -3.2 \text{ eV}$.

Unfortunately, comparison of electronic structures of the above dyes through the direct subtracting of electron densities is not possible due to the difference in their geometries. Hence, it was decided to employ various population analysis schemes in order to highlight the differences in the electron densities. The Hirshfeld, ADCH, and CM5 partial charges calculated with the PBE0/6-31++G(d,p) method for gaseous and water-dissolved states of NBnTAN and BnTAN are presented in Table 5. In all cases, the differences between corresponding NBnTAN and BnTAN atomic partial charges are less than 0.005 e, except the *m*-nitrobenzyl and benzyl fragments, where differences in atomic partial charges values are about 0.01-0.02 e. This can be explained by the relatively localized influence of the nitro group on the benzyl moiety, rather than thiazole or naphthalene rings due to the absence of conjugation between the benzyl and thiazole fragments. We have to emphasize the stable small decrease in the partial charge of the N5 atom of NBnTAN in comparison to BnTAN, which testify the lower nucleophilicity and lower proton-affinity of the N5 atom in Journal Pre-proof me muo-uye. Consequentiy, me basicity (pk value) of indiffait is expected to be

lower in comparison with BnTAN, which was proven experimentally.

Table 5. PBE0/6-31++G(d,p) Hirshfeld, ADCH, CM5 partial charges of BnTAN (Bn) and NBnTAN (NBn) in the gas phase and in water. Numbering of atoms is consistent with Figure 5.

	Gas phase				Water							
Atom	Hirsh	nfeld	AD	СН	CN	/15	Hirsł	nfeld	AD	СН	CM	15
	Bn	NBn	Bn	NBn	Bn	NBn	Bn	NBn	Bn	NBn	Bn	NBn
S 1	0.048	0.047	0.060	0.059	0.031	0.030	0.048	0.050	0.063	0.065	0.030	0.033
O2	-0.189	-0.186	-0.268	-0.264	-0.359	-0.357	-0.208	-0.207	-0.302	-0.300	-0.379	-0.377
H3	0.113	0.114	0.175	0.176	0.317	0.318	0.111	0.112	0.176	0.176	0.315	0.315
N4	-0.058	-0.060	0.021	0.019	-0.191	-0.193	-0.065	-0.066	0.016	0.014	-0.198	-0.199
N5	-0.199	-0.198	-0.298	-0.296	-0.374	-0.373	-0.235	-0.234	-0.367	-0.365	-0.410	-0.409
N6	-0.074	-0.072	-0.142	-0.139	-0.179	-0.178	-0.077	-0.076	-0.145	-0.143	-0.182	-0.182
C7	0.112	0.114	0.122	0.123	0.136	0.138	0.109	0.110	0.124	0.125	0.133	0.134
C8	0.013	0.014	0.053	0.054	0.089	0.090	0.012	0.012	0.054	0.054	0.087	0.088
C9	0.003	0.003	-0.018	-0.018	0.005	0.005	-0.005	-0.004	-0.030	-0.030	-0.003	-0.003
C10	-0.039	-0.038	-0.120	-0.120	-0.088	-0.088	-0.048	-0.048	-0.133	-0.132	-0.098	-0.097
H11	0.040	0.040	0.114	0.114	0.101	0.101	0.041	0.041	0.117	0.118	0.102	0.102
C12	-0.032	-0.030	-0.111	-0.109	-0.087	-0.085	-0.034	-0.034	-0.117	-0.116	-0.089	-0.088
H13	0.045	0.047	0.136	0.138	0.100	0.101	0.055	0.056	0.153	0.153	0.110	0.110
C14	-0.044	-0.042	-0.133	-0.132	-0.099	-0.097	-0.046	-0.046	-0.141	-0.141	-0.100	-0.100
H15	0.044	0.045	0.134	0.136	0.098	0.100	0.054	0.055	0.152	0.152	0.109	0.109
C16	-0.036	-0.034	-0.121	-0.120	-0.088	-0.086	-0.035	-0.035	-0.126	-0.126	-0.087	-0.087
H17	0.043	0.044	0.131	0.132	0.099	0.099	0.056	0.057	0.152	0.152	0.112	0.112
C18	-0.011	-0.010	-0.022	-0.023	-0.018	-0.017	-0.015	-0.015	-0.031	-0.031	-0.022	-0.022
C19	-0.012	-0.009	-0.094	-0.091	-0.063	-0.060	-0.004	-0.003	-0.088	-0.087	-0.055	-0.054
H20	0.051	0.053	0.142	0.144	0.107	0.108	0.067	0.068	0.168	0.168	0.123	0.123
C21	-0.051	-0.050	-0.149	-0.148	-0.100	-0.099	-0.052	-0.052	-0.155	-0.155	-0.101	-0.101
H22	0.054	0.055	0.144	0.146	0.112	0.113	0.062	0.062	0.157	0.158	0.120	0.120
C23	0.089	0.092	0.107	0.110	0.257	0.260	0.082	0.084	0.107	0.108	0.250	0.252
C24	-0.007	-0.005	-0.053	-0.053	0.017	0.018	-0.009	-0.006	-0.050	-0.048	0.015	0.018
H25	0.053	0.054	0.145	0.147	0.116	0.117	0.065	0.067	0.165	0.167	0.129	0.130
C26	-0.009	-0.013	-0.026	-0.034	0.000	-0.004	-0.001	-0.003	-0.011	-0.017	0.008	0.006
C27	-0.036	-0.034	-0.133	-0.125	-0.130	-0.128	-0.033	-0.029	-0.091	-0.081	-0.127	-0.123
H28	0.041	0.046	0.106	0.115	0.097	0.101	0.053	0.058	0.125	0.132	0.108	0.113
H29	0.046	0.049	0.122	0.128	0.101	0.105	0.057	0.063	0.141	0.151	0.113	0.118
C30	-0.001	0.009	-0.049	-0.048	-0.015	-0.004	-0.005	0.012	-0.186	-0.148	-0.018	-0.001
C31	-0.043	-0.023	-0.038	0.060	-0.095	-0.075	-0.051	-0.017	0.449	0.492	-0.103	-0.069
H32	0.039	0.048	0.073	0.032	0.095	0.104	0.045	0.058	-0.203	-0.214	0.101	0.115
C33	-0.037	-0.025	-0.132	-0.113	-0.092	-0.079	-0.046	-0.023	-0.194	-0.138	-0.101	-0.077

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1134	0.044	0.055	0.155	0.131	0.070	0.100	0.050	0.000	0.155	0.177	0.105	u .120
C35	-0.041	-0.024	-0.139	-0.131	-0.096	-0.070	-0.050	-0.024	-0.198	-0.177	-0.104	-0.070
H36	0.043	0.055	0.133	0.141	0.097	0.118	0.050	0.060	0.145	0.147	0.104	0.122
C37	-0.040	0.034	-0.128	0.019	-0.094	0.083	-0.047	0.031	-0.144	0.022	-0.101	0.080
C38	-0.046	-0.031	-0.139	-0.134	-0.098	-0.075	-0.050	-0.028	-0.191	-0.180	-0.102	-0.072
H39	0.039	0.050	0.124	0.130	0.094	0.114	0.049	0.057	0.142	0.140	0.104	0.120
H40/N40	0.043	0.231	0.133	0.373	0.098	0.071	0.051	0.235	0.147	0.392	0.105	0.076
O41		-0.204		-0.273		-0.166		-0.232		-0.317		-0.194
O42		-0.205		-0.275		-0.168		-0.232		-0.317		-0.195

Additionally, we have performed calculations of atomic partial charges through the Mulliken, Löwdin, and natural population analyses at the PBE0/6-31G(d,p) level, and the Mulliken and Coulson partitioning schemes with the PM7 and RM1 semiempirical methods. Selections of these semiempirical methods is dictated by their good performance in the prediction of heterocycles reactivity [93]. In all these cases, we have observed the same influence of the nitro group and very similar partial charges in the thiazolylazo-2-naphthol fragments of the two dyes. Tables with the PBE0/6-31G(d,p), PM7, and RM1 partial charges can be found in Supplementary Materials.

Taking into account that NBnTAN and BnTAN contain few aromatic moieties (benzyl substituent, thiazolyl cycle, and naphthalene fragment), aromaticity is an important property of these two dyes. To quantitatively analyze and compare aromaticity of the aforementioned parts of NBnTAN and BnTAN, we have calculated the NICS(0) indexes at the three levels of theory: CPCM-PBE0/6-31G(d,p), CPCM-B3LYP/6-31G(d,p), and PBE/A2 (see Table 6). The more negative NICS(0) values of benzyl (C30-C31-C33-C35-C37-C38), thiazole (S1-C23-N5-C24-C26), non-substituted naphthalene (C9-C10-C12-C14-C16-C18) rings means the more evident

aromaticity in comparison to naphthalene-2-of ring (C7-Co-C9-C10-C19-C21). We have to notice that at all tested computational methods the aromaticity of benzyl ring is higher in NBnTAN than in BnTAN.

Table 6. Values of NICS(0) aromaticity indexes (in ppm) of NBnTAN (NBn) and BnTAN (Bn). Numbering of atoms is consistent with Figure 5.

Ring	CPCM-B3L	.YP/6-31G(d,p)	CPCM-PBE	0/6-31G(d,p)	PBE	Ε/Λ2
	NBn	Bn	NBn	Bn	NBn	Bn
C30-C31-C33-C35-C37-C38	-9.97	-9.41	-10.06	-9.40	-8.76	-8.06
S1-C23-N5-C24-C26	-8.75	-8.71	-9.06	-9.02	-8.39	-8.36
C7-C8-C9-C18-C19-C21	-5.99	-6.13	-6.03	-6.17	-4.89	-4.97
C9-C10-C12-C14-C16-C18	-9.08	-9.09	-9.12	-9.13	-7.45	-7.49

3.6. Investigation of UV-Vis properties

NBnTAN is an amorphous powder of red color, poorly soluble in water, but well soluble in many organic solvents.



Figure 6. Absorption spectra of NBnTAN in different solvents. $C(NBnTAN) = 2.4 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. 1 – amyl acetate, 2- acetone, 3 – amyl alcohol, 4 – triethylamine, 5 – hexane.

Absorption maxima in most solvents were found at 485-493 nm.

The molar absorption coefficients in different solvents ranges from 7.4×10^3 L × mol⁻¹ × cm⁻¹ (hexane) to 12.6×10^3 L × mol⁻¹ × cm⁻¹ (amyl acetate). Increasing the polarity of the solvent as a whole causes a bathochromic shift of the absorption maximum and an increase in the value of ε , however, it is difficult to talk about the regular nature of this tendency. In addition to polarity, the ability of polar in nature solvents to deprotonate the dye and thus shift the equilibrium to the formation of anionic form of NBnTAN. This is followed, for example, by a significant bathochrome shift of the maxima to 505-511 nm as was observed after addition of triethylamine, N,N-dimethylcyclohexylamine, dimethylformamide, which can be explained by their strong basic properties. A less characteristic signal in the form of a "shoulder" was observed in the long-wave region at 570-590 nm. In low-polar solvents such a "shoulder" is not observed.

Organic solvent		$\varepsilon \cdot 10^{-3}$,	Organic solvent		$\varepsilon \cdot 10^{-3}$,
	λ, nm	$L \cdot mol^{-1} \cdot cm^{-1}$		λ , nm	$L \cdot mol^{-1} \cdot cm^{-1}$
hexane	486	7.4	1-nonanol	493	8.9
cyclohexane	487	8.6	ethyl acetate	486	7.2
dichloromethane	492	9.0	<i>n</i> -butyl acetate	486	8.8
chloroform	492	9.1	acetonitrile	488	9.2
1,2-dichloroethane	492	9.1	isobutyl acetate	485	9.9
tetrachlorethylene	488	8.0	amyl acetate	487	12.6
methanol	492	8.1	aceton	488	9.2
ethanol	491	8.3	methyl isobutyl ketone	486	9.1
1-propanol	492	8.9	diethyl ether	485	9.3
<i>n</i> -butanol	493	8.8	methyl tert-butyl ether	485	9.4
amylalkohol	492	8.8	tributyl phosphate	487	8.8

Table 7. Spectral characteristics of NBnTAN in various organic solvents.

		Journal	Pre-proof		
1-octano1	492	0.0	totuene	491	10.0

NBnTAN is well soluble in ethanol. There is a linear correlation between the concentration of NBnTAN and absorption of solutions at maximum wavelength of 492 nm. The ethanol-water solutions allow avoiding the use of toxic organic solvents. The results of the study of water-ethanol solutions of different composition showed that increasing content of water in the water-alcohol solution decreased the molar absorption coefficient (Table 8). In all cases, the dependence between NBnTAN concentration and absorption of solutions is linear, with the correlation coefficient close to 1.0, but the angle of inclination of the line (slope) and the intervals of linearity are significantly different, probably due to different solubility of NBnTAN in the respective media.

Volume fraction of ethanol	96%	50%	10%
Spectral maximum, nm	491	492	492
Molar absorbtion coefficient, $L \cdot (mol \cdot cm)^{-1}$	8300	6500	4580
Limits of linear dependence, $mol \cdot L^{-1}$	(2.1-8.6) ·10 ⁻⁵	(3.2-8.6) ·10 ⁻⁵	$(0.8-4.4) \cdot 10^{-5}$
Calibration curve equation	$A = 0.0043 + 0.831 \cdot 10^4 \cdot C$	$A = 0.0024 + 0.649 \cdot 10^4 \cdot C$	$A = 0.0030 + 0.458 \cdot 10^4 \cdot C$
Correlation coefficient, R	0.9997	0.9998	0.9996

Table 8. Spectral characteristics of NBnTAN water-ethanol mixtures.

3.7. Investigation of acid-base properties

Depending on the acidity of the medium, NBnTAN can exist in several forms. The dissociation processes of BnTAN, on the basis of which this reactant was

synthesized, are described in [21]. The intro group effect significantly affects the values of the NBnTAN acidity constants.

Depending on the acidity of the medium, NBnTAN in water-ethanol solutions can exist in three forms. In a strongly acidic medium (pH<1), NBnTAN exists in the form of a yellow compound with a maximum absorption at 446 nm. In a wide range of acidities of the medium (pH = 1-9), NBnTAN dominates in the form of a compound of orange-red color, with a maximum at 492 nm. In an alkaline medium (pH>9), a purple colored compound with a maximum at 540 nm is formed.

Formation of these forms is conditioned by the protolytic equilibrium, which in general can be written as shown in Scheme 3. Figure 7 shows the absorption spectra of these forms in ethanol–water mixture (1:9, v/v) at different acidity values.



Scheme 3. Protonation and deprotonation of the NBnTAN molecule.



Figure 7. Absorption spectra of NBnTAN in ethanol-water mixture (1:9, v/v) at different acidity values. pH = 0.20 (1), 4.00 (2), 12.60 (3); C(NBnTAN) = $5.17 \cdot 10^{-5}$ mol·L⁻¹.

The acid-base properties of NBnTAN were investigated using the spectrophotometric method in solutions with different acidity of the medium. The measured data from the absorption spectra showed that absorbance was dependent on the acidity of the medium ($A = f(\lambda)$, Figure 8). The three maxima visible in the spectra correspond to the different forms of the dye. The work was carried out by titration with solutions of sulfuric acid or sodium hydroxide. The absorbance was measured using an optical probe, and the pH was controlled potentiometrically with a glass electrode. The development of the absorption curve was dependent on the conditions under which the reaction equilibrium had been reached. The curves went through the isosbestic point if only one absorbing component was present in the system. The unprotonated form of the dye absorbed at 492 nm. Decreasing the pH caused the absorbance at 492

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nni to decrease and a new peak to appear sinunaneously at 440 nm. This new peak in the absorption spectra was due to protonation at the nitrogen center of the 1,3-thiazol-2-yl moiety. This peak is the equivalent to the protonated form of the dye (see Figure 8a). The appearance of a new peak at 540 nm upon increasing the pH was due to a deprotonated form of the dye. As the pH of the solution increased, the equilibrium shifted towards the deprotonated form. Absorbance of the unprotonated form of the dve at 492 nm was simultaneously decreased (see Figure 8b). The presence of an isosbestic point showed the equilibrium between the protonated, unprotonated, and deprotonated form. At this point, absorbance A, transmittance T, and ε were invariable with a pH change (Figure 8). The equilibrium protolytic constants, determined spectrophotometrically, were found to be: 0.39 ± 0.05 for the dissociation constant pK₁ and 8.74 \pm 0.08 for the constant pK₂. It should be noted that the values of pK for NBnTAN are higher than for BnTAN [21], probably due to the influence of the nitro group which exhibits strong acidic properties.



Figure 6. Ground state fination of INDITARY by Π_2 504 (a) and INAOT (b) in emanolwater mixture (1:9, v/v). (a): pH = 0.20, 0.39, 0.48, 0.56, 0.75, 1.04, 1.25, 1.53; (b): pH = 7.60, 8.13, 8.62, 9.11, 9.58, 10.40, 11.01.

3.8. Perspectives of analytical applications

BnTAN forms stable complex compounds with some metal ions, which are the basis of their spectrophotometric determination [21-24, 31]. Since the nitro group significantly influence on the acidity constant value, the reaction between NBnTAN and metal ions was studied.

It has been established that in a weakly acid medium (pH 5.1), NBnTAN formed complex compounds with the Cu (II), Cd (II), and Pd (II) ions, characterized by absorption maxima at 570, 590, and 650 nm, respectively (Figure 9a). Other ions (Ca (II), Al (III), Ni (II), Co (II), Fe (III), Mn (II), and Pb (II)) did not exhibit the ability to form complexes with NBnTAN. In a more acidic medium (pH 1), the formation of complexes was observed only with the Cu (II) and Pd (II) ions (Figure 9b). Taking into account the results obtained, a highly selective spectrophotometric determination of Pd is possible, since none of the ions studied (Ca (II), Al (III), Ni (II), Co (II), Fe (III), Mn (II), Pb II), Cu (II), Cd (II)) interfered with its definition.



Figure 9. Absorption spectra of NBnTAN and it complexes with transition metals in ethanol-water mixture (1:1, v/v) in solution at pH = 5.1 (a) and pH = 1.0 (b). $C(NBnTAN) = 2.27 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; $C(Me(II)) = 1.0 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; l = 1.0 cm.

4. Conclusions

A new reagent 1-[(5-(3-Nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol based on BnTAN was synthesized and investigated. The introduction of the nitro group into BnTAN significantly changed its properties. Quantum chemical calculations have shown that, despite different dipole moments and lower partial charge on the thiazole nitrogen atom, the aromaticity, HOMO, LUMO and redistribution of the electronic density of NBnTAN is quite close to the non-nitro analog, BnTAN. The transition to the protonated NBnTAN form occurs at higher values of the acidity of the medium and the pK value of NBnTAN is higher than that of BnTAN. In water-ethanol solutions, NBnTAN forms complex compounds with the Cu(II) and Pd(II) ions, and the palladium reaction is highly selective. The prospect of using NBnTAN as an anarytical reagent, in particular for spectrophotometric determination of panadium with high sensitivity and selectivity, is shown. The determination does not require the use of toxic extragents, and thus it meets the requirements of modern green chemistry.

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☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract

Highlights

- synthesis of 1-[(5-(3-nitrobenzyl)-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol, NBnTAN

- NICS(0) indexes show the same aromaticity of NBnTAN and the non-nitro analog

- analyzed partial charges testify similar redistribution of dyes' electron densities

- structure, spectrophotometric and protolytic behavior of the new thiazolylazo dye
- possibility of high selective spectrophotometric determination of Pd