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8-Hydroxyquinoline based push-pull azo dye: Novel colorimetric chemosensor for anion detection

Ömer Arslan ^a, Burcu Aydıner ^a, Ergin Yalçın ^a, Banu Babür ^a, Nurgül Seferoğlu ^b, Zeynel Seferoğlu ^{a, *}

^a Gazi University, Department of Chemistry, 06500, Ankara, Turkey

^b Gazi University, Advanced Technology Department, Inst. Sci. &Technol., Ankara, Turkey

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ABSTRACT

A novel colorimetric chemosensor based on push-pull dye (**8HQA**) was synthesized and characterized by using IR, ¹H/¹³C NMR and HRMS for the purpose of recognition of anions and cations in DMSO. The absorption maxima of the chemosensor were determined in different solvents. The selectivity and sensitivity of **8HQA** to anions were determined with spectrophotometric and ¹H NMR titration techniques. The selectivity of **8HQA** for studied anions (CN⁻, F⁻, Cl⁻, I⁻, AcO⁻, HSO₄ and H₂PO₄) was determined in DMSO. There is no selectivity between competing anions such as CN⁻, F⁻ AcO⁻ and H₂PO₄ at the stoichiometric ratio of 1:1 in UV-vis titrations experiments however, it was observed different color changes upon addition of CN⁻, F⁻, AcO⁻ and H₂PO₄ to the DMSO solution. In addition, the chemosensor showed no colorimetric response for the following anions; Cl⁻, I⁻ and HSO₄ in DMSO. The colorimetric sensing ability of **8HQA** was studied in the presence of chloride salts of different cations such as Ca²⁺, Mg²⁺, Cu²⁺, Sn²⁺, Ni²⁺, Cd²⁺ and Hg²⁺. Upon the addition of 4 equiv of each of the cations showed bathochromic shifts except for Ca²⁺and Cu²⁺. Interestingly, no selectivity was observed in interaction with metal cations. In addition, the molecular and electronic structures of **8HQA**, as well as the molecular complexes of **8HQA**, formed with the anions, were obtained theoretically and confirmed by DFT and TD-DFT calculations.

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1. Introduction

In recent years, sensing and recognition of anions, cations and biomolecules have become a highly hot topic of interest to scientist whose research studies on supramolecular and organic chemistry [1–25]. The anions like F^- , Cl^- , I^- , AcO^- , and $H_2PO_4^-$ are quite significant in human health [26–28]. In addition, metals and their ions especially toxic metals such as Hg^{2+} , Cd^{2+} and Pb^{2+} play an important role in many biological and environmental processes. Therefore, determination of anions and cations in real sample is quite important with simpler, faster and cheaper methods than conventional techniques. Till now, the determination of anions and cations and cations can be achieved by several analytical methods using spectroscopic techniques. However, simpler methods for practical applications of detection of any analyte of interest are desirable. Colorimetric and fluorimetric chemosensors can be alternative

Corresponding author.
 E-mail address: znseferoglu@gazi.edu.tr (Z. Seferoğlu).

techniques instead of the traditional analytical methods for determination of anions and cations in real sample. Therefore, the development of chromogenic chemosensors for anions and cations recognition has become an attractive research field and synthesis of new additional chemosensor is still required. Recently, we reported syntheses and spectroscopic properties of 8-hydroxyquinoline based carbocyclic and heterocyclic azo dyes [29-31]. Here, we developed a 8-hydroxyquinoline based push-pull azo dye as chemosensor containing dicyanovinylene as an electron acceptor group at the 4-position of phenyldiazenyl moiety, and the OH group in the quinoline heterocyclic moiety acts as a H-bond donor site. The structure of the chemosensor (8HQA) was characterized by FT-IR, ¹H NMR, ¹³C NMR and HRMS techniques. The effect of solvents with different polarities on the UV-vis absorption spectra of 8HQA were investigated. In addition, the anion recognition properties of the receptor of 8HQA towards the anions CN⁻, F⁻, Cl⁻, I⁻, AcO⁻, HSO_{4}^{-} and $H_{2}PO_{4}^{-}$ were studied experimentally by colorimetric response, UV-Vis, and ¹H NMR spectroscopic titration methods. The nature of the interactions between 8HQA and the anions were investigated by the quantum mechanical calculations at the level of







density functional theory (DFT and TD-DFT). In addition, the interactions between **8HQA** and the cations (Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, Sn²⁺, Ni²⁺, Cd²⁺ and Hg²⁺) were also investigated by UV-Vis and naked-eye. Based on our study, we were surprised to find that no significant selectivity was observed towards cations.

2. Experimental

2.1. Materials and instrumentation

The chemicals used in the syntheses of all compounds were obtained from Sigma-Aldrich Chemical Company (USA) and were used without further purification. All solvents used were of analytical grade. The solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin layer chromatography (TLC), using Merck silica gel (60 F254) plates (0.25 mm) and visualized under Ultraviolet light (UV). FT-IR (ATR) spectra were recorded on Perkin-Elmer Spectrum 100 FT-IR spectrophotometer (ν , are in cm⁻¹). NMR spectra were recorded on a Bruker Avance 300 Ultra-Shield in DMSO-d₆. Chemical shifts are expressed in δ units (ppm). Ultraviolet–Visible (UV-vis) absorption spectra were recorded on Shimadzu Corporation, Kyoto Japan UV-1800 240V spectrophotometer (Gazi University Department of Chemistry, Turkey). Mass spectra were recorded on Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments: in m/z(rel. %) (Gazi University Laboratories, Department Pharmacological Sciences). Chemical shifts are expressed in δ units (ppm) with tetramethylsilane (TMS) as the internal reference. Coupling constant (*I*) is given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; triplet, t, multiplet, m. The melting points were measured on Electrothermal IA9200 apparatus and uncorrected. Thermal analyses were performed with a Shimadzu DTG-60H system, up to 600 °C (10 °C min⁻¹) under a dynamic nitrogen atmosphere (15 mL min⁻¹). Typically, aliquots of a freshly prepared standard solutions of the alkylammonium salt of the anions (CN⁻, F⁻, Cl⁻, I⁻, AcO⁻, HSO $_{4}^{-}$ and H₂PO $_{4}^{-}$) and of chloride salt of cations $(Ca^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Sn^{2+}, Ni^{2+}, Cd^{2+} and Hg^{2+})$ were added, and their various UV-vis spectra were recorded. ¹H NMR titrations for anions were carried out in DMSO-*d*₆ solution.

2.2. Synthetic procedures

2-(1-(4-aminophenyl)ethylidene)malononitrile (1) was synthesized by using literature method [32].

2.3. The synthesis of (E)-2-(1-(4-((8-hydroxyquinolin-5-yl) diazenyl)phenyl)ethylidene)malononitrile (**8HQA**)

2 mmol 2-(1-(4-aminophenyl)ethylidene)malononitrile (1) was dissolved in hot glacial acetic acid-propionic acid mixture (2:1, 9.0 mL) and was rapidly cooled in an ice/salt bath to -5 °C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulphuric acid (prepared from sodium nitrite (0.15 g) and

concentrated sulphuric acid (3 mL at 50 °C)). The mixture was stirred for an additional 2 h at 0 °C. Excess nitrous acid was consumed by the addition of urea. The resulting diazonium salt was cooled in salt/ice mixture. After diazotization was complete the diazo liquid was slowly added to vigorously stirred solution of 8hydroxyquinoline (2 mmol) in potassium hydroxide (2 mmol in 4 mL methanol and 2 mL and water). The solution was stirred at 0–5 °C for 2 h. After 2 h. the pH of the reaction mixture was maintained at 4-6 by the addition of saturated sodium carbonate solution. The mixture was stirred for one hour at room temperature. After that, the resulting solid was filtered, washed with cold water and dried. Recrystallization from ethanol gave dark brown solid. Yield 50%; mp 232 °C; FT-IR (ATR) v/cm⁻¹ 3249 (N-H), 2960 (C-H), 2218 (C=N), 1732 (C=O); ¹HNMR (DMSO-*d*₆, 300 MHz) δ 9.37 $(d, J = 8.56 \text{ Hz}, 1\text{H}), \delta 9.00 (d, 2.60 \text{ Hz} 1\text{H}), \delta 8.14 (d, J = 8.53 \text{ Hz}, 2\text{H}),$ δ 8.06 (d, J = 8.59 Hz, 1H), δ 7.92 (d, J = 8.53 Hz, 2H), δ 7.80 (m, J = 8.52 Hz, 1H), δ 7.26 (d, J = 8.56 Hz, 1H), δ 2.71 (s, 3H) ppm; ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 176.5, 159.1, 154.7, 149.6, 139.2, 138.3, 138, 132.4, 129.7, 129.3, 128.6, 128.3, 123.9, 123.1, 115.9, 113.8, 113.7, 112.3, 84.3, 24.7 ppm; HRMS (ESI, CH₃CN) (C₂₀H₁₄N₅O) found. 340.1200, calc.340.1198.

2.4. Computational methods

All calculations were carried out using the Gaussian09 program package [33]. The molecule geometry was optimized at HF/631 g with the rotations C8-C10-C13-C15 torsion angles by 20° intervals in the range of 0-360° to find the most possible conformation. Then, this conformation was taken as a starting geometry and reoptimized using B3LYP/631 + g(d,p) [34,35] in gas phase and different solvents. It is confirmed that no imaginary vibrational frequencies at the optimized geometries to indicate true minima of the potential energy surface. The absorption spectra of the molecule and its deprotonated forms were calculated by using the time-dependent density functional method (TD-DFT) and using self-consistent reaction field (SCRF) method, based on the polarizable continuum model (PCM) [36,37].

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of **8HQA** was performed by stepwise procedure as illustrated in Scheme 1.1 was synthesized using Microwave Irradiation Method (MWI) with excellent yield. In addition, **8HQA** was prepared by coupling 8-hydroxyquinoline with diazotized 1 in nitrosyl sulphuric acid. The structure of **8HQA** was confirmed by FT-IR, ¹H NMR, ¹³C NMR and HRMS techniques. The spectral data were consistent with the proposed structure (Supplementary data, Figs. S1–S4). The prepared dye may show two possible tautomeric forms, namely azo form **A** and hydrazone **B** as shown in Scheme 2. After deprotonation of two tautomeric forms, it may be stable as common anion mesomeric structure **C** (Scheme 2). In some



Scheme 1. Synthesis of (E)-2-(1-(4-((8-hydroxyquinolin-5-yl)diazenyl)phenyl)ethylidene)malononitrile (8HQA).



Scheme 2. Azo-hydrazone tautomeric and anionic forms of 8HQA.

previous studies were suggested that 8-hydroxyquinolines and their heteroaryl/phenylazo derivatives are stable in azo form due to intramolecular and intermolecular H-bond in solid state [29,30]. In this study, the infrared spectra of the prepared dye showed weak band within the range 3249–3180 cm⁻¹ and strong sharp band in 1732 cm⁻¹ corresponding to hydrazone NH and carbonyl C=O. In addition, ¹H NMR spectroscopy can be useful in the determination of the most stable tautomeric form. The ¹H NMR spectra of aromatic protons of dye **8HQA** in the 8-hydroxyquinoline ring appeared at 9.37 (doublet), 9.0 (doublet), 8.14 (doublet), 7.80 (multiplet) and 7.26 (doublet). The OH proton of 8-hydroxyquinoline ring was observed at around 11.07 ppm in DMSO-*d*₆ as a weak broad peak. This result suggested that **8HQA** exists predominantly in azo form in DMSO.

3.2. Photophysical properties

Recently, the azo dyes are the most important commercial coloring materials [31] and many chemosensors which have been synthesized including azo chromophore. In this paper, a novel chromogenic azo dye was designed and synthesized as $D-\pi$ -A type push-pull system. It consists 8-hydroxyquinoline moiety as a donor part, and dicyanovinylene at the 4-position of phenyldiazenyl moiety as an acceptor part of the synthesized dye. 8-hydroxyquinoline based azo dyes theoretically may be involved in azo-hydrazone tautomerism (Scheme 2) in solution phase depending on solvent polarity.

To investigate the effect of solvent polarity on tautomeric structure of dye, we used different solvents with various polarities



Fig. 1. Absorption spectra of 8HQA in various solvents.

such as DMSO, DMF, methanol, ethanol, CHCl₃, and toluene. The visible absorption spectra of **8HQA** showed one absorption maximum in all solvents used. Effects of solvent polarity on absorption of **8HQA** are shown in Fig. 1. The absorption maxima of the dye were found to be independent of polarity of the solvents used. These results showed that the dye is in favor of the predominantly single tautomeric form (azo) in solvents used.

3.3. UV-vis absorption titrations of chemosensor **8HQA** with various anions

8HQA has two acidic part, one of them is active methyl protons attaching dicyanovinylene, second one is hydroxyl group attaching

hydroxyquinoline moiety. However, hydroxyl group has better deprotonation ability than active methyl protons. Thus, before investigation of anion sensitivity of chemosensor, effect of basicity on the absorption maxima of the **8HQA** was evaluated and the result is shown in Fig. 2.

There was a significant change in the spectra of the dye when equivalent amount of piperidine was added to its solution in DMSO. In the first equivalent amount addition of piperidine the main absorption maxima 418 nm of the chemosensor didn't change significantly, however a second band was observed in long wavelength (624 nm). The longest wavelength absorption maximum is attributed to the anionic form which obtained after deprotonation of hydroxyl group (–OH) on hydroxyquinoline part. In addition, the



Fig. 2. Spectrophotometric titration of piperidine to 8HQA (2×10^{-5} M) in DMSO.



Fig. 3. Absorption spectra of 8HQA 1:1 various anion in DMSO.



Fig. 4. Color changes of **8HQA** (1×10^{-4} M in DMSO) before and after the addition of 10 equiv of F⁻, H₂PO₄⁻, CN⁻ and AcO⁻ (1×10^{-2} M in DMSO) ions, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Changes in the absorption spectrum of 8HQA (2×10^{-5} M) in DMSO upon addition of anions in chloride salts form 4 equiv of various cations.

absorption band of this dye shifted hypsochromically and a new one dominant absorption band appeared with the increasing addition of equivalent amount piperidine. These data indicate that during the addition of the first equivalent amount of piperidine, more acidic proton (-OH) was deprotonated. With the more equivalent amount of the piperidine added, active methyl proton was then deprotonated. After determination of acidic properties of **8HOA**, the anion binding and the sensing ability of chemosensor against F⁻, Cl⁻, I⁻, AcO⁻, CN⁻, H₂PO₄ and HSO₄ anions with tetrabutylammonium (TBA) as the counter cation was performed in DMSO using spectrophotometric titration technique. In order to avoid anion-solvent interactions, we chose DMSO as aprotic, polar and water miscible solvent for anion titrations. The anion titrations were performed with different molar equiv of TBA salts of the anions. Fig. 3 shows the changes in the absorption spectrum of 8HQA $(2 \times 10^{-5} \text{ M})$ in DMSO in the absence and presence of studied anions at room temperature. Upon addition of one equiv of F⁻, AcO⁻, CN⁻ and $H_2PO_4^-$ the main band of dye **8HQA**, which was observed at 418 nm, decreased gradually and new absorption band was appeared and observed at 622 nm (Supplementary data, Figs. S5–S8). In addition, the absorption band of this dye shifted hypsochromically and a new one dominant absorption band appeared with the increasing addition of equivalent amount of F⁻, AcO⁻, CN⁻ and H₂PO₄⁻. It indicated that the dye interacts with F⁻ by hydrogen bonding at solution phase and then deprotonated during the addition of fluoride. This result shows that an equilibrium between neutral (8HQA) and deprotonated (8HQA⁻) has been formed which can be attributed to the hydroxyquinoline moiety (Scheme 2). In this deprotonated form, the negative charge on the hydroxyquinoline oxygen is completely delocalized from negatively charged oxygen on hydroxyquinoline part to dicyanovinylene group and the new absorption maximum was observed at 622 nm. The observed bathochromic shift is 204 nm.

The optical response on interaction with F⁻ can be explained by the fact that ICT process occurred between the negative charged hydroxyguinoline oxygen and the electron withdrawing dicyanovinylene part, with the formation deprotonated form via hydrogen bonded complex between the F⁻ and the chemosensor. The same spectral responses were observed towards AcO⁻, CN⁻ and H₂PO₄ ions (Fig. 3). However, other anions, such as Cl⁻, I⁻ and HSO₄ did not cause any significant changes in the absorption maximum of 8HQA in DMSO (Supplementary data, Figs. S9-S11). Also, the interaction of 8HQA with F⁻, AcO⁻, CN⁻ and H₂PO₄⁻ can be distinguished by the naked eye. The addition of F⁻ and AcO⁻ resulted in a yellow-to-purple color change, whereas a yellow-to-pink and a yellow-to-green color changes were observed in the case of CN⁻ and $H_2PO_4^-$, respectively (Fig. 4). No significant color changes were observed by the naked eye upon the addition of other ions (Cl⁻, I⁻ and HSO₄). This result indicates that **8HQA** in DMSO could be used as a highly selective colorimetric sensor for CN⁻ and H₂PO₄⁻ anions in DMSO over other competing anions such as F⁻ and AcO⁻.

8-Hydroxyquinoline and its derivatives are one of the most important derivatives of quinoline moiety because of its chelator properties for important metal ions. Therefore, we evaluated chemosensor **8HQA** affinity towards some metal ions. The colorimetric sensing ability of **8HQA** was studied in the presence of chloride salts of different cations such as Ca^{2+} , Mg^{2+} , Cu^{2+} , Co^{2+} , Sn^{2+} , Ni^{2+} , Cd^{2+} and Hg^{2+} (Figs. 5 and 6). Upon the addition of 4 equiv of each of the cations showed bathochromic shifts except for Ca^{2+} and Cu^{2+} . Interestingly, no selectivity was observed in interaction with metal cations.

3.4. ¹H NMR titrations study

The nature of interaction between **8HQA** and different anions (F⁻, Cl⁻, I⁻, HSO₄, CN⁻, AcO⁻ and H₂PO₄, 1.0 × 10⁻² M) were probed with ¹H NMR in DMSO-*d*₆. F⁻, AcO⁻, H₂PO₄ and CN⁻ showed significant and interesting spectral changes however, other anions such as Cl⁻, I⁻ and HSO₄ anions are showed no spectral changes (Fig. 7). The significant shift of the signals of **8HQA** is observed upon addition of AcO⁻ from 0 to 6 equiv, F⁻ from 0 to 7 equiv and H₂PO₄ from 0 to 6 equiv.

With deprotonation of OH, Ha protons shift to upper field from 7.26 to 6.24, 6.35 and 6.38, respectively. The signal for OH proton at 11.07 ppm began to shift toward downfield each the addition of F^- , which is attributed to the strong hydrogen bonding interaction between OH and F^- , FHF⁻ (J = 120 Hz) peak was located at 16.39 ppm after addition of 7 equiv. of F^- which indicates complete deprotonation of OH (Fig. 8). On the other hand, the chemical shift changes by AcO⁻ and H₂PO₄⁻ anions are similar to addition F^- but OH signals are not observed after the addition of 1 equiv of AcO⁻ and H₂PO₄⁻ anion in the titration. Also after the addition of these anions, methyl signal was disappeared at 2.71 and two new signals appeared at about 4.2 and 4.0 ppm. These new signals show deprotonation of methyl hydrogen and formation of methylene. These results indicate that the di-deprotonation process of compound from both OH and CH₃ hydrogens.

Interestingly, upon addition of CN^- showed similar Ha shift from 7.76 to 6.30 ppm while methyl signal shifted to upper field from 2.71 to 1.59 ppm and no new signal was observed about



Fig. 6. Color changes of **BHQA** (1×10^{-4} M in DMSO) before and after the addition of 4 equiv of cations (1×10^{-2} M in DMSO), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Partial ¹H NMR (300 MHz) spectra obtained via titrations of 8HQA (1×10^{-2} M in DMSO) with different amounts of studied anions solution (1 M) in DMSO- d_6 .



Fig. 8. Partial ¹H NMR (300 MHz) spectra obtained via titrations of 8HQA (1×10^{-2} M in DMSO) with different amounts of TBAF solution (1 M) in DMSO-d₆.



Scheme 3. Proposed mechanisms on anions-chemosensor interactions.

4 ppm which are quite different from those of addition F^- , AcOand $H_2PO_4^-$. This result can only be explained by the monodeprotonation mechanism of OH hydrogen (Scheme 3) (Fig. 9). As a result of deprotonation, the electron distribution in the conjugated system is changed and it causes increased the electron density on the methyl group. For this reason, the methyl signal is shifted to the upper field. Both mono- and di-deprotonation process show that only the deprotonation of the OH caused distinct upper field shifts compared with the free sensor due to an overall change of the electron distribution while the deprotonation of methyl hydrogen had no noticeable effect at chemical shifts.

3.5. Theoretical calculations

The ground state optimization of **8HQA** and its two possible tautomeric forms (azo and hydrazone) were optimized in gas phase and different solvents. In Table 1, the relative stability obtained from the sum of electronic and thermal energies (E_t) and sum of electronic and thermal free energies (G) are given in Table 1. According to the obtained values, the dye existed as its azo tautomeric form, with the relative energy values $\Delta E_t = 10.81$ kcal/mol and $\Delta G = 10.50$ kcal/mol. In addition, for this dye, the azo form is also preferable in different solvents in consistent with the experimental results.



Fig. 9. Partial ¹H NMR (300 MHz) spectra obtained via titrations of 8HQA (1×10^{-2} M in DMSO) with different amounts of TBACN solution (1 M) in DMSO-d₆.

Table 1

Relative stability obtained from the sum of electronic and thermal energies (E_t) and sum of electronic and thermal free energies (G) for the azo and hydrazon tautomers of **8HQA** in gas phase and different solvent.

		Et (a.u)	ΔEt (kcal/mol)	G (a.u)	ΔG (kcal/mol)
Gas	azo	-1118.61908	0.00	-1118.69516	0.00
	hid	-1118.60185	10.81	-1118.67843	10.50
Chloroform	azo	-1118.63180	0.00	-1118.70773	0.00
	hid	-1118.62376	5.05	-1118.69957	5.12
DMSO	azo	-1118.63709	0.00	-1118.71340	0.00
	hid	-1118.63375	2.10	-1118.70928	2.58
DMF	azo	-1118.63692	0.00	-1118.71331	0.00
	hid	-1118.63341	2.20	-1118.70895	2.74
Ethanol	azo	-1118.63650	0.00	-1118.71305	0.00
	hid	-1118.63260	2.45	-1118.70818	3.06
Ethylacetate	azo	-1118.63293	0.00	-1118.70890	0.00
	hid	-1118.62584	4.45	-1118.70185	4.42
Methanol	azo	-1118.63680	0.00	-1118.71325	0.00
	hid	-1118.63318	2.27	-1118.70873	2.84
Toluene	azo	-1118.62739	0.00	-1118.70371	0.00
	hid	-1118.61579	7.28	-1118.69166	7.56
Aceticacid	azo	-1118.63311	0.00	-1118.70908	0.00
	hid	-1118.62618	4.35	-1118.70226	4.28
Acetonitrile	azo	-1118.63688	0.00	-1118.71329	0.00
	hid	-1118.63334	2.22	-1118.70888	2.77

In order to obtain a further information about the mechanism of the colorimetric chemosensor **8HQA** (azo form) in the presence of F^- , CN^- , AcO^- and $H_2PO_4^-$, the DFT and TD-DFT calculations were done for **8HQA** and its mono and di-deprotonated forms (**8HQA**⁻ and **8HQA**²⁻). The ground state geometries and selected geometrical parameters are illustrated in Fig. 10 and Table 2, respectively. As seen from the table, significant differences in the bond distances are seen after both deprotonations. The biggest decrease is observed in C30–O37 bond distance from 1.343 Å to 1.255 Å (for **8HQA**⁻) and in C13–C14 from 1.507 Å to 1.359 Å (for **8HQA**²⁻) while the biggest increase is seen in C30–C28 bond distance with 0.059 Å for mono-deprotonation (**8HQA**⁻) and in C13–C15 bond distance with 0.080 Å after di-deprotonation (**8HQA**²⁻). On the other hand, when we examine the dihedral angles given in Table 2,

we obtained that the dicyanovinilene part is not coplanar with the rest of the molecule after and before deprotonations. But, the C8–C10–C13–C15 and C8–C10–C13–C14 dihedral angles changed from 142.7° to 153.2° and –36.6° to –25.3° after occurring **8HQA**⁻, that show that the planarity increase for **8HQA**⁻. According to this, an increase in ICT from hydroxyquinoline to the dicyanovinilene part and as a result, a bathochromic shift in absorption spectra are expected. On the other hand, when **8HQA**⁻ and **8HQA**²⁻ are compared, it is seen that C8–C10–C13–C15 and C8–C10–C13–C14 dihedral angles change from 153.2° and –25.3° to 134.8° and –46.5° for **8HQA**⁻ and **8HQA**²⁻, respectively. As a result of **8HQA**²⁻ being less planar than **8HQA**⁻, the decreasing in ICT from hydroxyquinoline to the dicyanovinilene part and the hypsochromic shift occur.



Fig. 10. The ground state geometries obtained B3LYP/631 + g(d,p) a) 8HQA, b) 8HQA⁻ and c) 8HQA²⁻.

Table 2 The selected geometrical parameters $8HQA,\,8HQA^-$ and $8HQA^{2-}.$

	8HQA	8HQA-H ⁺	8HQA-2H ⁺
Bond lengths			
C30-037	1.343	1.255	1.264
C30-C26	1.431	1.488	1.484
C30-C28	1.388	1.447	1.439
C25-C28	1.401	1.371	1.379
C26-N39	1.360	1.356	1.359
C23-N1	1.401	1.354	1.373
N1-N2	1.265	1.300	1.284
N2-C3	1.413	1.388	1.409
C3–C4	1.403	1.416	1.408
C4–C6	1.391	1.384	1.393
C10-C13	1.475	1.454	1.493
C13–C14	1.507	1.508	1.359
C13–C15	1.374	1.391	1.471
C15-C16	1.435	1.429	1.405
C15–C17	1.436	1.430	1.405
Bond angles			
C37-C30-C28	121.2	121.7	122.1
C23-N1-N2	115.9	117.7	117.8
N1-N2-C3	115.0	114.2	114.7
N2-C3-C4	115.7	116.4	116.2
C10-C13-C15	122.7	123.7	117.7
C14-C13-C15	119.8	118.2	122.9
Dihedrals			
C24-C23-N1-N2	177.3	-179.4	178.9
C23-N1-N2-C3	179.1	-179.4	179.4
N1-N2-C3-C4	174.9	-178.9	176.8
C8-C10-C13-C15	142.7	153.2	134.8
C8-C10-C13-C14	-36.6	-25.3	-46.5

In TD-DFT calculations, the absorption spectra of **8HQA**, **8HQA**⁻ and **8HQA**^{2–} were obtained in DMSO in parallel to the experimental part. For **8HQA**, the main absorption band occurred at

445 nm with the oscillator strength f = 0.9709, and 600 nm with f = 1.5225 and 482 nm with f = 0.9927 for **8HQA**, **8HQA**⁻ and **8HQA**²⁻, respectively. This trend observed in our calculation results, in which the bathochromic shift when mono-deprotonation via –OH and the hypsochromic shift after di-deprotonation via –CH₃ with respect to mono-deprotonation are in consistent with experimental results. These bands were due to the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) for **8HQA** and **8HQA**⁻ and from HOMO-1 to the LUMO for **8HQA**²⁻ (Fig. 11).

3.6. Thermal analysis

The thermal stability of the dye **8HQA** has a fundamental character which decides its suitability for application as a probe, dyeing of textile fibers and electro-optical (EO) devices. The thermogravimetric studies have been conducted at 30–500 °C under nitrogen gas at a heating rate of 10 °C min⁻¹. TGA result indicated that the dye **8HQA** is stable up to 220 °C (decomposed 12%) as shown in Fig. 10. TGA revealed the onset decomposition temperature (Td) 218 °C of **8HQA** whose thermogravimetric curve showed a major loss in weight (Supplementary data, Fig. S12). The dye in particular showed good thermal stabilities up to 218 °C, which is high enough for industrial applications field when it is used as a chemosensor or an optic dye.

4. Conclusions

In this study a novel azo dye was synthesized as D- π -A type push-pull system. The visible absorption spectra of **8HQA** showed one absorption maximum in all solvents used. The solvent effect on absorption maxima showed that the absorption maxima of the dye



Fig. 11. Frontier molecular orbitals a) 8HQA, b) 8HQA⁻ and c) 8HQA²⁻.

were found to be independent of polarity of the solvents used and did not have a correlation with the polarity of the solvents. This results showed that the dye was stable a single tautomeric form (azo) in all solvent used. The anion binding and the sensing ability of a novel push-pull chemosensor (**8HQA**) against F^- , Cl^- , I^- , AcO^- , CN^- , $H_2PO_4^-$ and HSO_4^- anions. The chemsensor show a highly selective colorimetric sensor for CN^- and $H_2PO_4^-$ anions in DMSO over other competing anions such as F^- and AcO^- . The interaction of **8HQA** with F^- , AcO^- , CN^- and $H_2PO_4^-$ can be easily distinguished by the naked eye. However, F^- and AcO^- gave same colorimetric response thus, **8HQA** may be used as chromogenic colorimetric chemosensor for discrimination of only F^- , CN^- and $H_2PO_4^-$. In addition, the two different deprotonation mechanisms between the F^- , AcO^- , CN^- and $H_2PO_4^-$ anions and chemosensor were clearly confirmed by NMR spectroscopy.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.08.001.

References

- [1] H.D. Ali Paduka, E.K. Paul, G. Thorfinnur, Colorimetric 'naked-eye' and fluorescent sensors for anions based on amidoureafunctionalised 1,8naphthalimide structures: anion recognition via either deprotonation or hydrogen bonding in DMSO, New J. Chem. 32 (2008) 1153–1161.
- [2] M. Arvind, M. Shahid, P. Dwivedi, An efficient thiourea-based colorimetric chemosensor for naked-eye recognition of fluoride and acetate anions: UV-vis and 1H NMR studies, Talanta 80 (2009) 532–538.
- [3] E.A. Katayev, Y.A. Ustynyuk, LJ. Sessler, Receptors for tetrahedral oxyanions, Coord. Chem. Rev. 250 (2006) 3004–3037.
- [4] T. Gunnlaugsson, M. Glynn, G.M. Tocci, P.E. Kruger, F.M. Pfeffer, G.M. Thorfinnur, Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors, Coord. Chew. Rev. 250 (2006) 3094–3117.
- [5] S.O. Kang, R.A. Begum, K. Bowman-James, Amide-based ligands for anion coordination, Angew. Chem. Int. Ed. 45 (2006) 7882–7894.
- [6] N. Kaur, S. Kumar, A differential receptor for selective and quantitative multiion analysis for Co 2+ and Ni 2+/Cu 2+, Tetrahedron Lett. 49 (2008) 5067–5069.
- [7] A.P. De Silva, H.N. Gunaratne, T. Gunnlaugsson, A.J. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Signaling recognition events with fluorescent

sensors and switches, Chem. Rev. 97 (1997) 1515-1566.

- [8] A.H. McKie, S. Friedland, F. Hof, Tetrazoles are potent anion recognition elements that emulate the disfavored anti conformations of carboxylic acids, Org. Lett. 10 (2008) 4653–4655.
- [9] D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, Why, on interaction of urea-based receptors with fluoride, beautiful colors develop, Org. Chem. 70 (2005) 5717–5720. H.M.
- [10] Y.H. Zhou, P.C. Zheng, X.P. Bao, Selective recognition and discrimination of H₂PO₄- and F- based on a cleft-shaped anion receptor incorporating bisamide and bispyrrole groups, Supramol. Chem. 26 (2014) 761–768.
- [11] E.J. Cho, J.W. Moon, S.W. Ko, J.Y. Lee, S.K. Kim, J. Yoon, K.C. Nam, A new fluoride selective fluorescent as well as chromogenic chemosensor containing a naphthalene urea derivative, J. Am. Chem. Soc. 125 (2003) 12376–12377.
- [12] D.S. Kim, K.H. Ahn, Fluorescence "turn-on" sensing of carboxylate anions with oligothiophene-based o-(carboxamido) trifluoroacetophenones, J. Org. Chem. 73 (2008) 6831–6834.
- [13] T. Gunnlaugsson, A.P. Davis, G.M. Hussey, J. Tierney, Design, synthesis and photophysical studies of simple fluorescent anion PET sensors using charge neutral thiourea receptors, Org. Biomol. Chem. 2 (2004) 1856–1863.
- [14] S.E. García-Garrido, C. Caltagirone, M.E. Light, P.A. Gale, Acridinone-based anion receptors and sensors, Chem. Commun. 14 (2007) 1450–1452.
- [15] J. Shao, A novel colorimetric and fluorescence anion sensor with a urea group as binding site and a coumarin group as signal unit, Dyes Pigments 87 (2010) 272–276.
- [16] D.H. Lee, J.H. Im, S.U. Son, Y.K. Chung, J.I. Hong, An azophenol-based chromogenic pyrophosphate sensor in water, J. Am. Chem. Soc. 125 (2003) 7752–7753.
- [17] J.Y. Lee, E.J. Cho, S. Mukamel, K.C. Nam, Fluoride-selective fluorescent host: experiment and theory, J. Org. Chem. 69 (2004) 943–950.
- [18] L. Nie, Z. Li, J. Han, X. Zhang, R. Yang, W. Liu, F. Wu, J. Xie, Y. Zhao, Y. Jiang J, Development of N-benzamidothioureas as a new generation of thioureabased receptors for anion recognition and sensing, Org. Chem. 69 (2004) 6449–6454.
- [19] V. Thiagarajan, P. Ramamurthy, D. Thirumalai, V.T. Ramakrishnan, A novel colorimetric and fluorescent chemosensor for anions involving PET and ICT pathways, Org. Lett. 7 (2005) 657–660.
- [20] B. Liu, T. He, A ratiometric fluorescent chemosensor for fluoride ions based on a proton transfer signaling mechanism, J. Mater. Chem. 15 (2005) 2681–2686.
- [21] R. Nishiyabu, A. Pavel, Sensing of antipyretic carboxylates by simple chromogenic calix[4]pyrroles, J. Am. Chem. Soc. 127 (2005) 8270–8271.
- [22] R. Martínez-Máñez, F. Sancenón, Fluorogenic and chromogenic chemosensors and reagents for anions, Chem. Rev. 103 (2003) 4419–4476.
- [23] B. Babur, N. Seferoglu, M. Ocal, G. Sonugur, H. Akbulut, Z. Seferoglu, A novel fluorescence turn-on coumarin-pyrazolone based monomethine probe for biothiol detection, Tetrahedron 72 (2016) 4498–4502.
- [24] G. Chaoxia, L. Ping, P. Meishan, Z. Guangyou, Sensors Actuators B 221 (2015) 1223-1228.
- [25] B. Babür, N. Seferoğlu, Z. Seferoğlu, A ratiometric fluorescence chemosensor based on a coumarin–pyrazolone hybrid: the synthesis and an investigation of the photophysical, tautomeric and anion binding properties by spectroscopic techniques and DFT calculations, Tetrahedron Lett. 56 (2015) 2149–2154.
- [26] W. Huang, Z. Chen, H. Lin, A novel thiourea-hydrazone-based switch-on fluorescent chemosensor for acetate, J. Lumin 131 (2011) 592–596.
 [27] J. Shao, H. Lin, M. Yu, Z. Cai, H. Lin, Study on acetate ion recognition and
- [27] J. Shao, H. Lin, M. Yu, Z. Cai, H. Lin, Study on acetate ion recognition and sensing in aqueous media using a novel and simple colorimetric sensor and its analytical application, Talanta 75 (2008) 551–555.

- [28] Z. Ying, J.F. Zhang, J. Yoon, Fluorescence and colorimetric chemosensors for fluoride-ion detection, Chem. Rev. 114 (2014) 5511–5571.
- [29] A. Saglam, Z. Seferoglu, N. Ertan, Synthesis and spectroscopic properties of new hetarylazo 8-hydroxyquinolines from some heterocyclic amines, Dyes Pigments 76 (2008) 470–476.
- [30] A. Saglam, Z. Seferoglu, N. Ertan, Azo-8-hydroxyquinoline dyes: the synthesis, characterizations and determination of tautomeric properties of some new phenyl- and heteroarylazo-8-hydroxyquinolines, J. Mol. Liq. 195 (2014) 267–276.
- [31] H. Zollinger, Color Chemistry Syntheses, Properties and Applications of Organic Dyes and Pigments, third ed., Wiley-VCH, Zurich, 2003, pp. 165–241.
- [32] E. Yalçın, S. Achelle, Y. Bayrak, N. Seferoğlu, A. Barsella, Z. Seferoğlu, Styrylbased NLO chromophores: synthesis, spectroscopic properties, and theoretical calculations, Tetrahedron Lett. 56 (2015) 2586–2589.
- [33] M.J. Frisch, et al., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
- [34] C.T. Lee, W.T. Yang, R.G. Parr, Development of the colle–salvetticorrelationenergy formula into a functional of the electron-density, Phys.Rev. B 37 (1988) 785–789.
- [35] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.
- [36] M. Cossi, V. Barone, R. Cammi, J. Tomasi, Ab initio study of solvated molecules: a new implementation of the polarizable continuum model, Chem. Phys.Lett. 255 (1996) 327–335.
- [37] V. Barone, M. Cossi, J. Tomasi, Geometry optimization of molecular structures in solution by the polarizable continuum model, J. Comput. Chem. 19 (1998) 404–417.