Journal of Molecular Structure 1010 (2012) 52–58

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

The tautomerization between keto- to phenol-hydrazone induced by anions in the solution

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ARTICLE INFO

Article history:
Received 21 September 2011
Received in revised form 6 November 2011
Accepted 17 November 2011
Available online 29 November 2011

Keywords:
Anion recognition
Tautomerization
Naked-eye
Theoretical investigation
Hydrazone derivative

ABSTRACT

Two simple anion receptors, 2-[(2-hydroxy-5-nitrophenyl)methylene]hydrazone (**1**) and 2-[(3,5-dibromo-2-hydroxyphenyl)methylene]hydrazone (**2**) with –OH binding sites, were synthesized and characterized. The anion binding ability of receptors **1** and **2** with halide anions (F^-, Cl^-, Br^- and I^-), AcO^- and $H_2PO_4^-$ was investigated using visual (naked-eye), UV–vis titration experiments in dry DMSO together with DFT theoretical calculation. The addition of F^-, AcO^- and $H_2PO_4^-$ to the host solution resulted in a red shift of the charge-transfer absorbance band accompanied by a color change from yellow to orange in the naked-eye experiments. Receptor **1** containing a nitro group at the para position and receptor **2** containing two bromine groups at the ortho and para positions both showed strong binding ability for $H_2PO_4^-$ ion in the form of phenol-hydrazone. Moreover, receptor **1**, induced by anion species in the solution, converted to the form of phenol-hydrazone from keto-hydrazone.

1. Introduction

Anion recognition by artificial receptors has received considerable attention in the field of host–guest chemistry due to the important roles of anions in biomedicinal and chemical processes [1–12]. The design of these receptors has been focused on having the ability to selectively recognize and sense the biologically important anions. Water-soluble anions (fluoride, chloride, bromide, phosphate, and etc.) play crucial role in a wide range of biological phenomena and are implicated in many disease states [13]. Especially, ubiquitous phosphates are biologically relevant anions. Phosphorylated species also play critical roles in a variety of fundamental processes such as energy transduction, signal processing, genetic information storage, and membrane transport [5]. In addition, phosphates can be found in many chemotherapeutic and antiviral drugs [14–16]. It is for sure that phosphate originating from the over use of agricultural fertilizers can also lead to eutrophication in inland waterways [17]. Hence, to recognize and sense phosphate ions and phosphorylated biomolecules is to be more and more important than other biologically functional anions [18–21].

In many cases, a colorimetric receptor for special anionic species is of particular interest due to its simplicity and high sensitivity [22,23]. In particular, colorimetric-based sensing is especially attractive, as it may allow naked-eye detection of the analyte without resorting to any expensive equipment [24,25]. In general, these chemosensors are constructed according to the receptor-chromophore general binomial, which involves the binding of a special anion substrate with receptor sites and a chromophore responsible for translating the receptor–anion association into an optical signal [26–28]. The color variation will occur when a charge-transfer complex is formed [29]. Although anion receptors containing phenol group as a binding site have been researched, recognition mechanism based on tautomeric phenol is rarely reported in the "naked-eye" detection of anions [30–32]. Therefore, it is necessary to develop a colorimetric anion receptor with anion-induced phenol-hydrazone as a signaling mechanism. By exploiting the optical properties of hydrazone group, many functional molecules have been reported in literatures [33,34]. Phenol group is among the most frequently used fragments to design neutral receptors for the selective recognition of anions as it is able to strongly bind anions using directional hydrogen bonding interactions even in the aqueous solution [31,3]. We reasoned that a simple colorimetric anion receptor would be obtained through coupling the phenol group as recognition site with nitro chromophore as a signal group. In this paper, we designed and synthesized a hydrazone derivative (**1**) containing phenol group (Scheme 1). According to the following theoretical investigation, compound **1** existed stable in the form of keto-hydrazone for one hydroxyl moiety in solid. We further anticipated that compound **1** with the NO_2 group in the para position could display tautomerization between keto- to phenol-hydrazone, stimulated by anionic species in the

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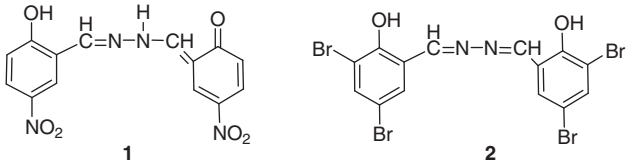
doi:10.1016/j.molstruc.2011.11.020



Scheme 1. Chemical structure for compounds.

solution. As a comparison, we also synthesized compound **2** (Scheme 1) containing two bromine groups in the ortho- and para-positions existing stable in the form of phenol-hydrazone in solid in order to elucidate the anion recognition mechanism of tautomerization between keto- and phenol-hydrazone in the solution.

2. Material and methods

2.1. Materials

Most of the starting materials were obtained commercially and all reagents and solvents used were of analytical grade. All anions, in the form of tetrabutylammonium salts [$(n\text{-}C_4H_9)_4NF$, $(n\text{-}C_4H_9)_4NCl$, $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_4H_9)_4NI$, $(n\text{-}C_4H_9)_4NAcO$, $(n\text{-}C_4H_9)_4NH_2PO_4$] were purchased from Sigma–Aldrich Chemical Co., and stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Tetra-n-butylammonium salts were dried for 24 h in vacuum with P_2O_5 at 333 K. Dimethyl sulfoxide (DMSO) was distilled in vacuum after dried with CaH_2. The hydrazine monohydrate is 80%.

0.1 mL DMSO solution of receptor (1×10^{-3} mol L^{-1}) was removed to a series of 5 ml colorimetric tube, various volume of tetra-n-butylammonium salts of anions in DMSO (1×10^{-3} mol L^{-1}) were added respectively. The mixtures were diluted with DMSO to the scale, mixed fully and stood for a night. Then, the absorption spectra were determined at 298 K (DMSO for reference).

2.2. Apparatus

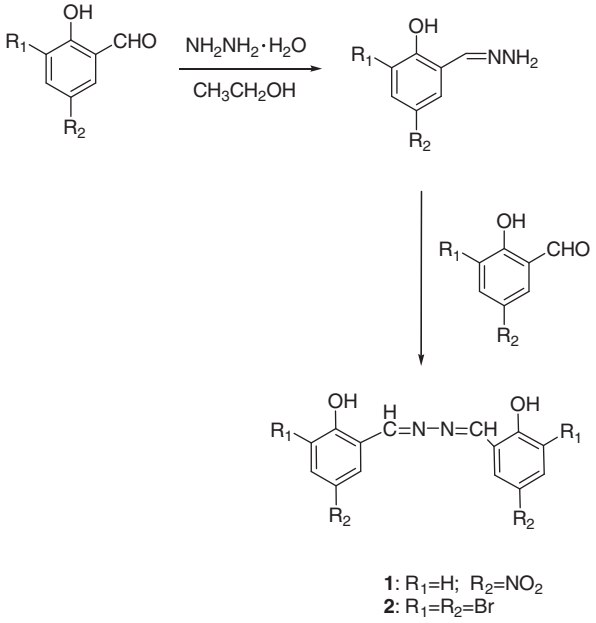
C, H, N elemental analyses were made on Vanio-EL. ^{1}H NMR spectra were recorded on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. UV–vis titration experiments were made on a Shimadzu UV2550 Spectrophotometer at 298.2 K. The affinity constant, K_s, was obtained by non-linear least square calculation method for data fitting.

2.3. Synthesis

(2-hydroxy-5-nitrophenyl)methylene-hydrazone and (3,5-Dibromo-2-hydroxyl- phenyl)methylene-hydrazone were obtained from the reaction of hydrazine monohydrate and 5-nitro-salicyaldehyde and 3,5-dibromo-salicyaldehyde in dry EtOH, respectively [32,35]. Compounds **1** and **2** were synthesized by Schiff base condensation between the corresponding hydrazine derivatives and 5-nitro-salicyaldehyde and 3, 5-dibromo-salicyaldehyde in dry EtOH, respectively (Scheme 2).

2.3.1. (2-Hydroxyl-5-nitrophenyl)methylene-hydrazone

A solution of hydrazine monohydrate (80%, 0.5 ml) in dry EtOH (30 mL) was added dropwise to a solution of 5-nitro-salicylaldehyde (167 mg, 1 mmol) in dry EtOH (15 mL) under stirring. The mixture was heated under refluxing for 8 h and the yellow precipitate was separated by filtration. The solid was washed with diethyl ether and dried under vacuum. m.p.>320 °C, 152 mg, (84%) yield. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ = 12.47 (s, 1H), 8.26 (d, 1H, J = 2.8), 7.78 (d, 2H, J = 8.4), 7.27 (s, 2H), 6.98 (t, 1H, J = 15.6). Elemental analysis: Calc. for $C_7H_7N_3O_3{\cdot}4H_2O$: C, 33.20; H, 5.97; N, 16.59; Found: C, 33.32; H, 6.13; N, 16.27.



Scheme 2. Synthesis route for compounds.

2.3.2. (3,5-Dibromo-2-hydroxyphenyl)methylene-hydrazone

Hydrazine monohydrate (80%, 0.5 ml) and 3,5-dibromo-salicylaldehyde (278 mg, 1 mmol) were used for the preparation. m.p. > 320 °C, 228 mg, (78%) yield. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ = 12.65 (s, 1H), 7.86 (s, 1H), 7.59 (d, 1H, J = 2.4), 7.48 (d, 1H, J = 2.4), 7.34 (s, 2H). Elemental analysis: Calc. for $C_7H_6Br_2N_2O{\cdot}2H_2O$: C, 25.48; H, 3.05; N, 8.49; Found: C, 25.81; H, 3.24; N, 8.36.

2.3.3. 2-[(2-Hydroxy-5-nitrophenyl)methylene]hydrazone (compound 1)

(2-Hydroxy-5-nitrophenyl)methylene-hydrazone (180 mg, 1 mmol) and 5-nitro-salicylaldehyde (167 mg, 1 mmol) were suspended in dry EtOH (40 mL). The mixture was refluxing for 12 h and the yellow precipitate was separated by filtration. The solid was washed with diethyl ether, recrystalled with EtOH, and dried under vacuum. m.p.>320 °C, 241 mg, (73%) yield. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ = 12.21 (s, 1H), 9.08 (s, 2H), 8.69 (d, 2H, J = 3.6), 8.26 (dd, 2H, J = 4.0, 4.0), 7.16 (d, 2H, J = 12). Elemental analysis: Calc. for $C_{14}H_{10}N_4O_6$: C, 50.92; H, 3.05; N, 16.96; Found: C, 50.73; H, 3.41; N, 16.99. ESI-MS (m/z): 329.12 (M-H)$^-$.

2.3.4. 2-[(3,5-Dibromo-2-hydroxyphenyl)methylene]hydrazone (compound 2)

Hydrazine monohydrate (80%, 0.5 ml) and 3,5-dibromo-salicylaldehyde (278 mg, 1 mmol) were used for the preparation, m.p.>320 °C, 337 mg, (61%) yield. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ = 11.98 (s, 1H), 9.08 (s, 1H), 7.99 (s, 1H), 7.89 (s, 1H). Elemental analysis: Calc. for $C_{14}H_8Br_4N_2O_2$: C, 30.25; H, 1.45; N, 5.04; Found: C, 30.47; H, 1.98; N, 5.29. ESI-MS (m/z): 550.48 (M-H)$^-$, 552.63 (M-H)$^-$.

3. Results and discussion

3.1. UV–vis spectral titrations and colorimetric signaling

The anion binding ability of receptors **1** and **2** with halide anions (F^-, Cl^-, Br^- and I^-), AcO^- and $H_2PO_4^-$ in dry DMSO was inves-

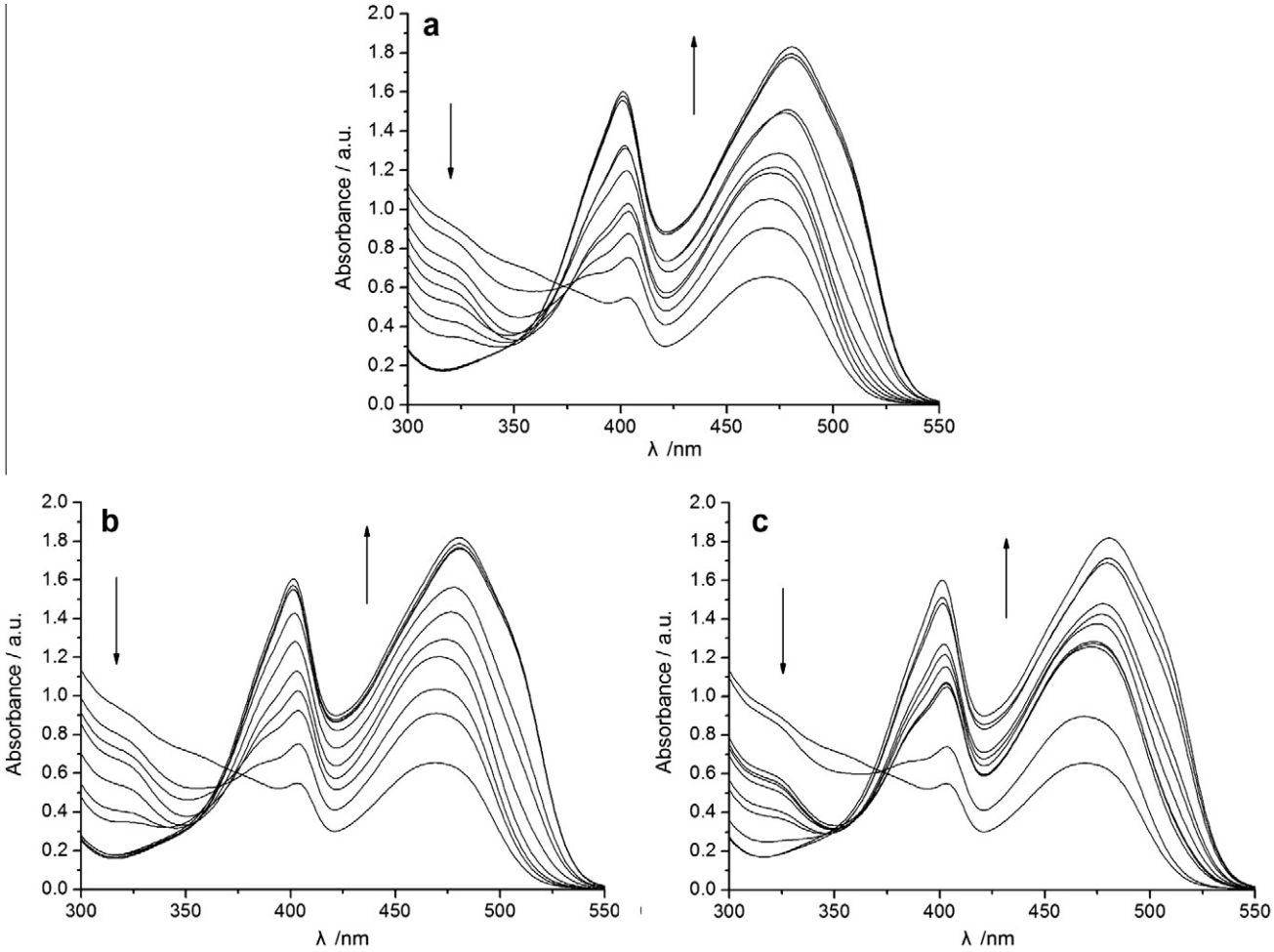


Fig. 1. UV–vis spectral changes of **1** (2.0×10^{-5} mol L^{-1}) upon the addition of anion (a) F^-, (b) AcO^-, (c) $H_2PO_4^-$, [anion] = 0–160×10^{-5} mol L^{-1}. Arrows indicate the direction of increasing anion concentration in DMSO.

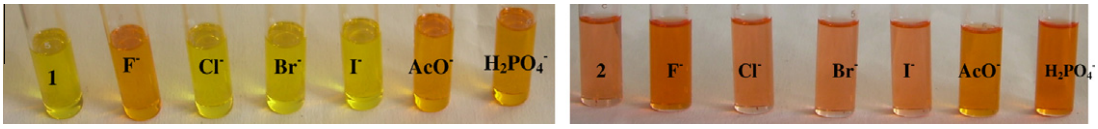
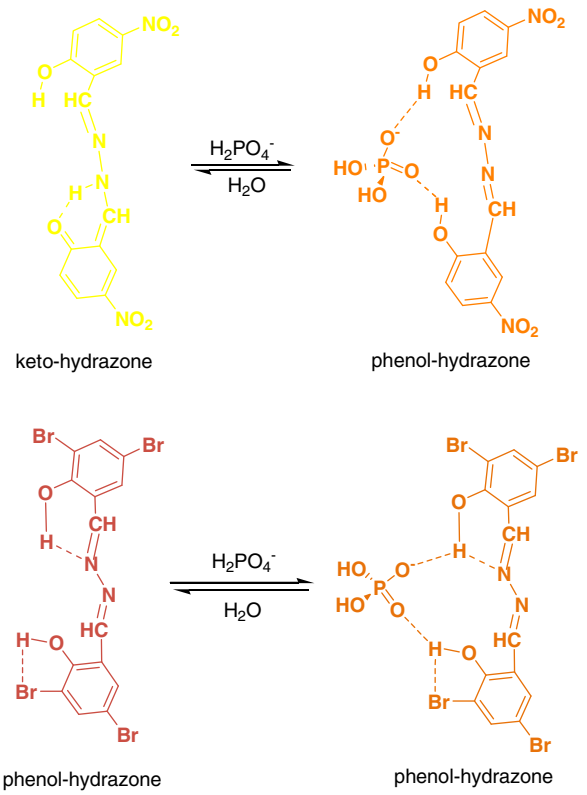


Fig. 2. Color changes inducted by the addition of anions (tetrabutylammonioum salts). From left to right: (A) compound **1**, **1** + F^-, **1** + Cl^-, **1** + Br^-, **1** + I^-, **1** + AcO^-, **1** + $H_2PO_4^-$; (B) compound **2**, **2** + F^-, **2** + Cl^-, **2** + Br^-, **2** + I^-, **2** + AcO^-, **2** + $H_2PO_4^-$. The concentration of anion is 5 equiv. of receptors **1** and **2**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tigated using UV–vis titration experiments. Solutions of 1×10^{-2} mol L^{-1} anions were added as tetrabutylammonium salts to 1×10^{-3} mol L^{-1} solutions of the receptors **1** and **2** at 298.2 ± 0.1 K.

Fig. 1 showed the significant UV–vis spectral changes of compound **1** upon addition of various anions. From the UV–vis absorption changes of **1** (Fig. 1), compound **1** displayed obvious absorption band at 470 nm with a small peak at 405 nm which was assigned to the charge transfer of hydroxyl moiety. The addition of F^-, AcO^- and $H_2PO_4^-$ to DMSO solution of **1** led to the similar spectral changes. After the anions were added gradually, the intensity of absorption peaks at 405 nm and 470 nm increased and the absorption bands shifted to the blue ($\Delta\lambda$ = 5 nm, from 405 nm to 400 nm) and red ($\Delta\lambda$ = 12 nm, from 470 nm to 482 nm), respectively. At the same time, the absorption peaks became sharper which was related to the decrease of the molecular conjugacy. The observed color changed from yellow to orange (Fig. 2). The results can be rationalized on the basis of the anion-induced tautomeric equilibrium between keto- and phenol-hydrazone in DMSO [30,31]. Prior to bonding with $H_2PO_4^-$, the phenol isomer of compound **1** dominates in the solution, to which can be attributed the strong absorption centered at 470 nm. After receptor **1** interacted with $H_2PO_4^-$, the H-bonding was formed between receptor **1** and $H_2PO_4^-$ ion in the form of phenol-hydrazone (Scheme 3). This will result in the red-shift phenomenon of absorption and visual color change. However, the presence of protic solvent such as H_2O, which will compete with anions for binding sites and disturb the H-bond interactions between the host and the anionic guest, will lead to a reversal of the visual color and the spectral changes. In the case of weak basic ions such as Cl^-, Br^- and I^-, the spectral changes were too small to calculate the corresponding affinity constants.

In order to elucidate the recognition mechanism of tautomerization between phenol- and keto-hydrazone, we also synthesized



Scheme 3. Proposed binding mode of compound **1** and **2** with $H_2PO_4^-$.

a similar compound **2**. Fig. 3 showed the remarkable UV–vis spectral changes of compound **2** upon addition of F^-, AcO^- and $H_2PO_4^-$. Obviously seen from Fig. 3, compound **2** was characterized by a broad strong absorption band centered at 375 nm and a weak absorption band centered at 500 nm which were assigned to the charge transfer of hydroxyl moiety. As the concentration of anion increased stepwise, the absorption intensity at 375 nm gradually decreased and disappeared thoroughly. At the same time, the absorption intensity at 500 nm increased and the significant red-shift ($\Delta\lambda$ = 125 nm) was occurred which demonstrated the H-bond interactions between **2** and the anionic guests affected the electronic properties of the chromophore, resulting in a new charge transfer interaction between the electron rich –OH moiety bond anion and the electron deficient –Br moiety along with a color change [11]. One clear isosbestic point appeared at 410 nm, which indicating the stable complex having a certain stoichiometric ratio between **2** and the anion formed [36]. In contrast, the addition of other anions (Cl^-, Br^-, I^-) did not trigger noticeable spectral change of compound **2**, indicating very weak or no interaction between these anions and compound **2**. The color of compound **2** deepened after the interaction with F^-, AcO^- and $H_2PO_4^-$, which was attributed to the clear increase of absorption intensity at 500 nm (Fig. 2). Nevertheless, compound **2** was insensitive to the addition of excess equiv. Cl^-, Br^- and I^- ions. So, a color change was not observed.

3.2. Affinity constant

The job-plot analysis indicated that the spectral change could be ascribed to the formation of 1:1 host–guest complexation. The

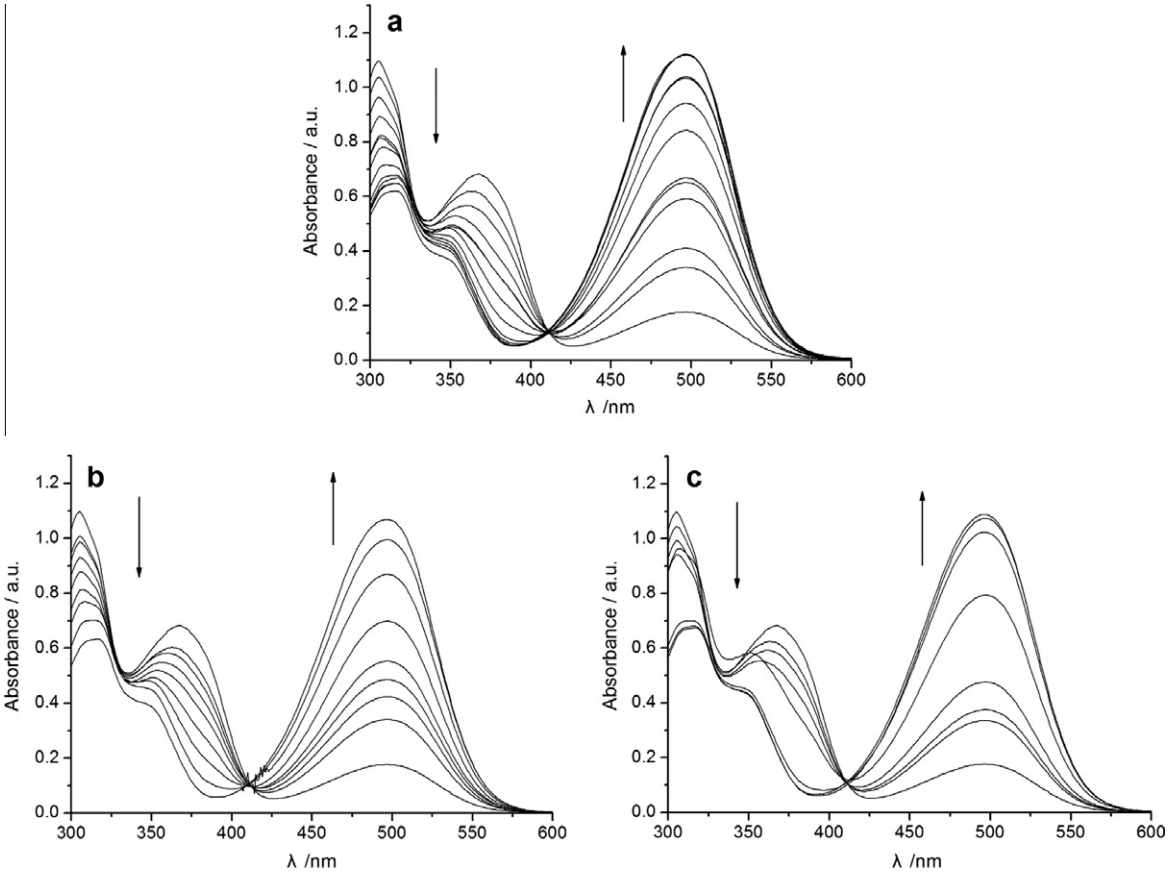


Fig. 3. UV–vis spectral changes of compound **2** (2.0×10^{-5} mol L^{-1}) upon the addition of anion (a) $H_2PO_4^-$, (b) AcO^-, (c) F^-, [anion] = 0–160×10^{-5} mol L^{-1}. Arrows indicate the direction of increasing anion concentration.

Table 1
Affinity constants of receptors with various anions.

Anions[a]	K_s(**1**)	K_s(**2**)
$H_2PO_4^-$	$(7.05 \pm 0.09) \times 10^4$	$(3.25 \pm 0.08) \times 10^5$
AcO^-	$(6.67 \pm 0.11) \times 10^4$	$(2.77 \pm 0.07) \times 10^5$
F^-	$(4.70 \pm 0.44) \times 10^4$	$(5.55 \pm 0.15) \times 10^4$
Cl^-	ND[b]	ND
Br^-	ND	ND
I^-	ND	ND

[a] All anions were added in the form of tetra-n-butylammonium (TBA) salts.
[b] The affinity constant could not be determined.

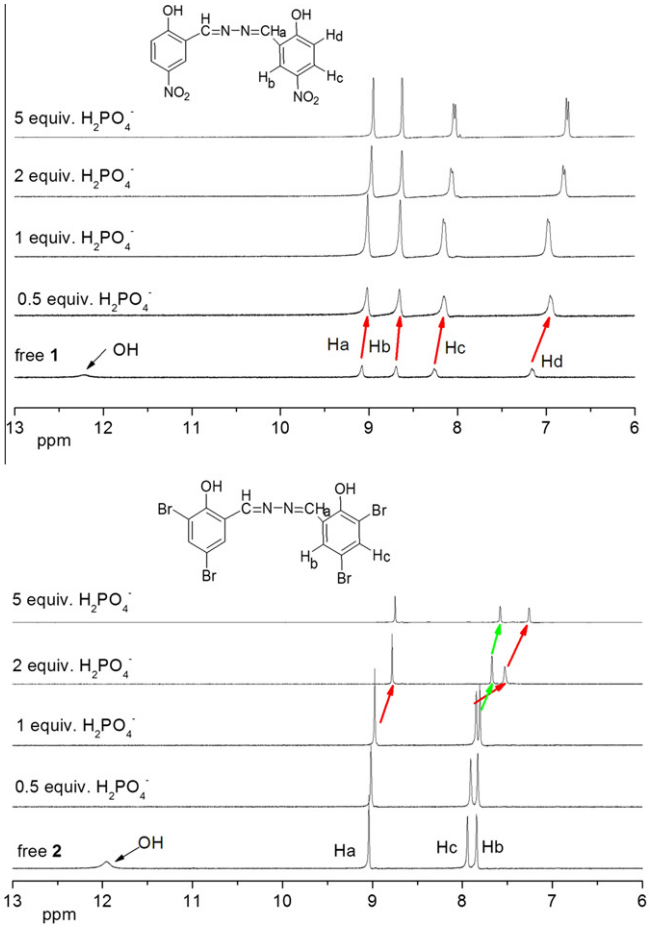


Fig. 4. Changes in the ^{1}H NMR spectra with gradual addition of anion in DMSO-d_6.

obtained affinity constants were listed in Table 1 using the method of non-linear least squares calculation according to the UV–vis data [37–39]. The selectivity trend of binding ability of receptors to anions followed the order of: $H_2PO_4^- > AcO^- > F^- \gg Cl^- \sim Br^- \sim I^-$. It is apparent that the selectivity for specific anions can be rationalized on the basis of the anion's basicity and the interactions between the host and the anionic guests. However, multiple hydrogen-bond interactions are also necessary in high-affinity anion binding sites [40]. As expected from their basicity, $H_2PO_4^-$, AcO^- and F^- will bind more strongly than the other anions studied; in addition, the tetrahedral configuration of $H_2PO_4^-$ ion may well match **1** and **2** in terms of shape and could form multiple hydrogen bonding interactions with receptors (Scheme 3). Consequently, $H_2PO_4^-$ ion can be selectively recognized from other anions based on its affinity constant. The electron-withdrawing ability of $-NO_2$ is stronger than that of –Br and then the anion binding ability of the former is higher than that of the latter in theory [41]. In fact, the binding ability of receptor **1** containing $-NO_2$ is weaker than that of receptor **2** containing –Br. The explanation is likely that **2** included two -Br and intramolecular hydrogen bonds, which may improve the anion binding ability.

Table 2
The total energy (E_T) and energy gap $\Delta E(E_{LUMO}-E_{HOMO})$ of **1** and its tautomer obtained at B3LYP/3-21G level.

Compound	**1**	tautomer of **1**
E_T (a.u.[a])	−1202.86317	−1202.89374
$E_{relative}$ (kJ mol^{-1})	0	−80.26
E_{LUMO} (a.u.)	−0.11468	−0.11650
E_{HOMO} (a.u.)	−0.24987	−0.23425
ΔE (kJ mol^{-1})	354.94	309.15

[a] 1 a.u. = 2625.5 kJ mol^{-1}.

3.3. ^{1}H NMR titrations

To further elucidate the nature of the intermolecular interactions between anions and receptors, the binding ability of receptors **1** and **2** toward selected anionic guests was investigated by standard ^{1}H NMR titrations, in which the host concentration was kept constant while the guest concentration was varied (Fig. 4). Two effects would be expected to result from the formation of hydrogen bond between the binding sites and the anion: (1) through-bond effects, which increase the electron density of the benzene ring and promote upfield shifts in ^{1}H NMR spectrum, and (2) through-space effects, which polarize C–H bond in proximity to hydrogen bond, create the partial positive charge on the proton and cause downfield shifts [42]. Obviously, for receptor **1**, the signal at 12.21 ppm, which was assigned to -OH, disappeared upon the addition of 0.5 equiv. of $H_2PO_4^-$ ion. In addition, the signals of Ha (9.08 ppm), Hb (8.69 ppm), Hc (8.26 ppm) and Hd (7.16 ppm) clearly shifted upfield with the addition of $H_2PO_4^-$ ion, indicative of the increase in the electron density of the phenyl ring owing to the through-bond effects. Thus, the results of ^{1}H NMR titration and spectrum titration implicated that the tautomeric equilibrium occurred during the anion recognition process. As mentioned above, the proposed anion recognition process in the solution is shown in Scheme 3. In the case of receptor **2**, the signal at 11.96 ppm, which was assigned to –OH, disappeared upon the addition of 0.5 equiv. of $H_2PO_4^-$ ion. In addition, the signals of Ha (9.04 ppm) and the phenyl protons Hc (7.95 ppm) and Hb

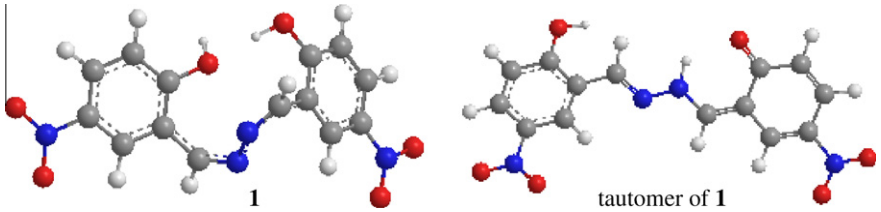


Fig. 5. Optimized geometry of compound **1**, and the tautomer of **1**.

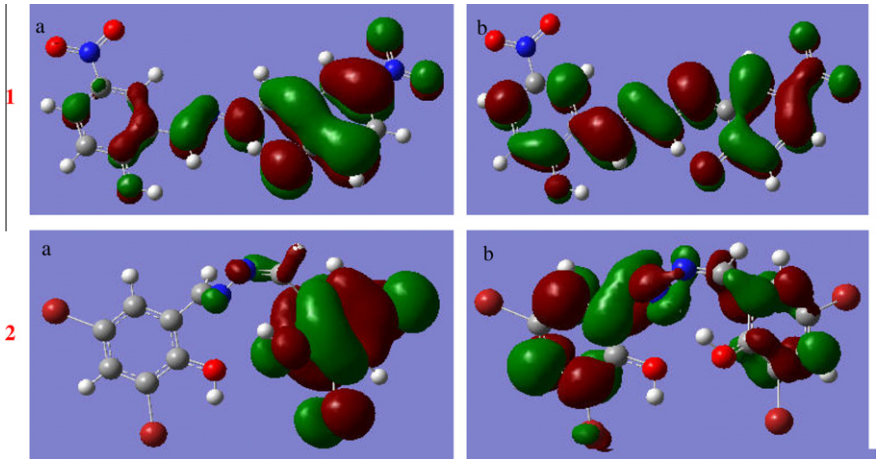


Fig. 6. Molecular orbital level of compound **1** and **2**, (a) HOMO; (b) LUMO.

(7.84 ppm) slowly shifted to the upfield when the anion concentration was less than 1 equiv. With the further addition of anion, the signals of Ha, Hb and Hc exhibited significant upfield shift. The above results observed likely indicated the $H_2PO_4^-$ ion exhibited a hydrogen-bonding interaction with **2**. Thus, the results of ^1H NMR titration also corroborated the above supposition of the interactions between the host and $H_2PO_4^-$ ion. The possible binding mode in the solution was shown in Scheme 3.

4. Theory

The geometries of compound **1** and its tautomer were optimized (Fig. 5) using Density functional theory at B3LYP/3-21G level with Gaussian03 program [43]. The calculation results on total energy and the energy gap of E_{LUMO}, E_{HOMO} of **1** and its tautomer were listed in Table 2. From Table 2, one can see that (1) the total energy of compound **1** is higher than that of its tautomer by 80.26 kJ mol^{-1}; (2) the energy gap $\Delta E(E_{LUMO}–E_{HOMO})$ of compound **1** is larger than that of its tautomer. The above results imply the tautomer of **1** (keto-hydrazone) is more stable than compound **1** in solid. Compound **1** (keto-hydrazone) converts to the tautomer (phenol-hydrazone), which participates the anion recognition process in the solution.

In addition, selected frontier orbitals for compounds are shown in Fig. 6. We introduced molecular frontier orbital in order to explain UV–vis absorption spectra in host–guest interacted process by electron transition of frontier orbital. The highest HOMO density and the highest LUMO density in compound **1** are both localized on the whole molecule, only the electron cloud density in one benzene ring of HOMO is less than LUMO. This demonstrates it is the electron transition of the highest HOMO to arouse the red shift phenomenon in UV–vis spectra of **1**-anion. In the case of compound **2**, the highest HOMO density is localized on one benzene ring and hydrazine, while, the highest LUMO density is localized on the whole molecule. Therefore, the result is as well as compound **1**: it is the electron transition of the highest HOMO to induce the red shift phenomenon in UV–vis spectra of **2**-anion. On the whole, the electron cloud density of compound **1** is stronger than that of compound **2**, which qualitative suggests the anion binding ability of the former containing $–NO_2$ is weaker than that of the latter containing -Br. This theoretical result is constituent with the previous text in affinity constant.

5. Conclusions

In summary, the presence of anions such as $H_2PO_4^-$ gave birth to changes in the color of solution of **1** from yellow to orange, as well as a red shift in the UV–vis spectrum. In particular, a tautomeric equilibrium occurred during the anion recognition process. The different electronic properties of the tautomer are responsible for the observed color and spectral changes. While, compound **2** containing two –Br groups at the ortho and para positions can bind $H_2PO_4^-$ ion in the form of phenol and the anion binding ability is stronger than compound **1**, exiting in the form of tautomerization, phenol-hydrazone, in recognition process.

Acknowledgment

This work was supported by the Nature Science Fund of Henan Province (2010B150024, 112300410104), Young Teacher Fund of Henan Province and Doctorial Starting Fund of Xinxiang Medical University.

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