A Novel Quinoxaline-Rhodamine Conjugate for a Simple and Efficient Detection of Hydrogen Sulphate Ion

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Abstract: This work presents the development of a quinoxaline and rhodamine conjugate system that acts as a colorimetric chemosensor for hydrogen sulfate (HSO₄⁻) ions in methanol media. This sensor has been characterized both theoretically and experimentally. The detection limits for HSO₄⁻ are small as 0.71 µM and 3.8 µM for the absorption and emission experiments, respectively. The effectiveness of the probe in recognizing HSO₄⁻ both in gel and solid phase is evaluated as well. Thus, this work presents a simple strategy to detect the environmental HSO₄⁻ pollutant event at tiny concentrations.

Keywords: quinoxaline-rhodamine conjugate; HSO₄⁻ sensing; visual detection; spirolactum ring opening

1. Introduction

The exponential increase of environmental pollution has forced researchers to rethink the modes of identification of the hazards through quick yet accurate methods [1,2]. In this framework, the emergence of fluorescent/colorimetric chemosensors for cations/anions/neutral molecules has recently driven groundbreaking advances in the field by providing a plethora of efficient sensing systems with sometimes exceptional selectivity and sensitivity [3–16]. Among the various anions that need to be detected, hydrogen sulfate (HSO₄⁻) ions are of particular interest because: (i) they play major roles in biological systems; (ii) they impart toxicity as pollutant; and (iii) they are essential as sulphate binding proteins in the physiological transport system [17–21]. In addition, HSO₄⁻ ions have numerous applications in industrial sectors such as agricultural fertilizers, industrial raw materials, nuclear fuel wastes, etc. [22,23]. It is also notable that HSO₄⁻ dissociates at high pH to generate toxic sulfate (SO₄²⁻), which can cause skin and eye irritations and even respiratory paralysis or other severe disorders [24–29]. The large standard Gibbs energy of hydration (−1080 kJ·mol⁻¹) and small pKₐ value of 1.99 (in aqueous medium) of the HSO₄⁻ anion also imply major constraints for its recognition and separation from an aqueous media [30–32]. Accurate and easy detection of HSO₄⁻ is consequently essential to monitor and control several hazardous effects.

Recent research efforts to target HSO₄⁻ have been mostly focused on chemosensors based on various fluorophores and chromophores, e.g., oxindole, boron-dipyromethene (BODIPY), diarylethene, azomethine, indolium, naphthalimide, benzothiazolein, as well as different media, e.g., acetonitrile:water, ethanol and tetrahydrofuran (see Table S1). However, only a few probes have been reported in the literature for the detection of HSO₄⁻ [33–51]. New strategies are therefore required to fill that gap in the currently available methods of detection. Among all possible alternatives, colorimetric detection is one of the most preferable alternatives as it allows an easy and rapid detection by the...
naked eye without any expensive instruments. Accordingly, we have chosen an effective colorimetric signaling unit, rhodamine derivative, for the anion. Rhodamine moiety has already proved its potential in the field of chemosensors due to the signature photophysical outcomes of the fragmented spirolactum ring \([52]\). Herein, we propose a novel synthetic route by integrating quinoxaline and rhodamine moieties to generate the probe molecule, QRH, for selective detection of the anion \(\text{HSO}_4^−\) in methanol. We have also been able to reproduce the sensing phenomenon in gel droplet and paper strip formats.

2. Experimental Section

Synthesis of the novel ligand (hereafter labeled as QRH) used indeno \([1,2−b\)quinoxalin-11-one (compound 1) and Rhodamine B hydrazide (compound 2) as starting materials (see Scheme 1). The resulting product was completely characterized by spectroscopic and X-ray crystallography techniques. The nature of the main excited states was also assessed by means of theoretical calculations within the framework of the density functional theory (DFT). See Appendix A for further experimental and computational details.

![Scheme 1. Synthetic procedure of novel QRH probe.](image)

3. Results and Discussion

3.1. Synthesis and Characterization

Simple condensation of compound 1 and compound 2 yielded QRH as illustrated in Scheme 1. The resulting product is fully characterized by FTIR, \(^1\)H, \(^{13}\)C NMR, ESI−MS spectra (Figures S1–S3, S5) and single crystal XRD method before its application. The FTIR data confirmed the generation of Schiff base by the appearance of the characteristic peak of C=\(\equiv\)N at 1609 cm\(^{-1}\). From \(^1\)H and \(^{13}\)C NMR data the aromatic proton signals appeared at \(\delta_H 8.06–6.1\). The ESI−MS spectra shows 671.32 amu as the same as the calculated value for \([\text{C}_{43}\text{H}_{39}\text{N}_6\text{O}_2]\)^+ species. Characterization was continued with single crystal X-ray diffraction experiment to determine the structure of the probe. The red colored single crystal was obtained by layering technique using the solvents chloroform and ether. As illustrated in Figure 1, QRH crystallizes in triclinic space group \(P\)-1 with a chloroform molecule as solvent of crystallization.

3.2. Crystal Structure Description

The crystal structure depicts the spirolactum ring and three rings in the xanthene moiety are non-planar due to the presence of sp\(^3\) spiro carbon. The five-member lactum ring and the six-member xanthene rings are nearly perpendicular (87.20°) \([53]\). Here the condensed planar quinoxaline conjugate makes an angle of 59.82° with the lactum ring. Due to the presence of a large number of π-rings, the molecule undergoes intermolecular π···π stacking interaction between two naphthalene−phenyldiammine moieties in reverse. The two stacking interactions take place between phenazine···phenazine ring (distance 3.899(3) Å, slippage 1.592 Å) and phenyl···cyclopentane ring (distance 3.756(3) Å, slippage 1.272 Å) along \(b\)-axis. The C-H···π between the molecule forms pseudodimeric structure along \(c\)-axis (Figure S14).
3.3. Naked Eye Sensing

The developed sensor, QRH, was examined in the presence of several metal ions (M$^{n+}$ = Na$^+$, K$^+$, Ca$^{2+}$, Cr$^{3+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Al$^{3+}$) available in their chloride and perchlorate salts (Figure S10) and anions (terabutylammonium (TBA) salts of F$^-$, OAc$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$, SCN$^-$, PF$_6^-$, ClO$_4^-$) in methanol at room temperature. The sensor shows a distinct amount of response in bare eyes for HSO$_4^-$ ion from yellow to pink in methanol and shows a pink fluorescence under UV light irrespective of other anions in the respective solution phase (Figure 2). Based on these preliminary results, the response of the probe towards HSO$_4^-$ was investigated in detail by means of the absorption and emission spectral outputs in methanol at room temperature.

3.4. Photophysical Studies of QRH towards HSO$_4^-$

We observed that the absorption spectral output of QRH (10$^{-6}$ M) shows peaks at 357 nm and 275 nm, and upon addition of HSO$_4^-$, a new peak generated at 558 nm along with a clear isosbestic point at 456 nm. QRH (10$^{-5}$ M) also responded selectively towards HSO$_4^-$ by switch-on fluorescence enhancement at 609 nm ($\lambda_{ex} = 357$ nm) in methano-
lic solution (Figures S6 and S7). These spectral outputs are mainly governed by the opening of spirolactum ring in presence of $\text{HSO}_4^-$, resulting in ring conjugation that is responsible for generation of absorption band at 558 nm and emission band at 609 nm (Figures S6 and S7) [54]. That ring opening phenomenon and the resultant conjugation increases the electron density throughout the rhodamine moiety and this can be monitored by NMR titration in CDCl$_3$ where the related aromatic proton peaks of the probe show a somewhat downfield shift (Figure S13).

Figures 3 and 4 summarize the results of titration experiments using both absorption and emission spectroscopic techniques to determine the sensitivity of the probe towards $\text{HSO}_4^-$. The absorption titration experiment was carried out by preparing a solution ($1 \times 10^{-6}$ M) of QRH in methanol and followed by the addition of tetrabutylammonium salt of hydrogen sulfate (TBAHS) solution. The addition of $\text{HSO}_4^-$ solution to the probe gradually developed a new band at 558 nm and the peak saturated upon the addition of 20 equivalents of $\text{HSO}_4^-$. The emission experiment was carried out by preparing a solution ($1 \times 10^{-5}$ M) of the probe in methanol, followed by the addition of tetrabutylammonium salt of hydrogen sulfate (TBAHS) solution. The addition of $\text{HSO}_4^-$ solution into the probe gradually developed a new band at 609 nm and the peak saturated upon the addition of 6 equivalents of $\text{HSO}_4^-$. QRH also exhibited high selectivity for $\text{HSO}_4^-$ in the presence of other anions in solution, as depicted in Figures S8 and S9. We then sought to scale up the detection limit of QRH towards $\text{HSO}_4^-$ according to the International Union of Pure and Applied Chemistry (IUPAC) protocol (LOD = 3σ/slope) [55] and it was estimated to be $7.1 \times 10^{-7}$ M (from absorption spectroscopy) and $3.8 \times 10^{-6}$ M (from emission spectroscopy) suggesting high selectivity (Figures S11 and S12). Sahoo et al. reported a rhodamine 6G hydrazide sensor for $\text{HSO}_4^-$ but the detection limit was 16.70 μM in absorbance which is higher than our probe (see Table S1). Therefore, due to the presence of the quinoxaline moiety, the sensitivity towards $\text{HSO}_4^-$ has improved. The fluorescence quantum yields were calculated to be 0.004 and 0.32 in the absence and presence of $\text{HSO}_4^-$ ions (6 equiv.) by using rhodamine B as the standard (Φ, 0.64 in methanol), respectively.

![Figure 3. UV–Vis spectra of QRH ($10^{-6}$ M) in methanol in the presence of various concentrations of $\text{HSO}_4^-$ (upto 20 equiv.). Upward arrow indicates gradual increase of absorption at 558 nm with increasing concentration of externally added $\text{HSO}_4^-$. Inset: Absorbance of QRH at 558 nm as a function of $\text{HSO}_4^-$.](image-url)
Figure 4. Emission spectra of QRH (10^{-5} M) in methanol in the presence of various concentrations of HSO_{4}^{-} (upto 6 equiv.). Upward arrow indicates gradual increase of emission at 609 nm with increasing concentration of externally added HSO_{4}^{-} (λ_{ex} = 357 nm). Inset: Emission of QRH at 609 nm as a function of HSO_{4}^{-}.

3.5. Theoretical Study and the Elucidation of a Proposed Model

Figure 5 summarizes the numerical outcomes of the performed theoretical calculations. The left panel shows the computed absorption profile for the neutral-closed spirolactum ring form of QRH (black line). As one can see, the theoretical profile matches the experimental measures, with an intense peak at ca. 300 nm and a clean spectrum beyond 500 nm. On the contrary, if calculations are carried out with the protonated-open spirolactum ring, a new band appears at that region, which is consistent with our experimental observations. Such dissimilarity can be analyzed through the nature of the first excited state. According to the time dependent (TD) DFT calculations, the parent QRH presents the first S_{0}→S_{1} excitation at 526 nm. However, such allowed transit is associated with a very low absorbance, which is characterized by the oscillator strength value (f = 0.0043). However, when QRH adopts the protonated-open spirolactum ring form, the first excitation is largely activated (f = 0.2333), and eventually produces the observed change in the absorption spectrum. That first excitation corresponds to the HOMO→LUMO transition. The frontiers orbitals are displayed on the right panel of Figure 5. A close inspection reveals that the S_{0}→S_{1} gap can be interpreted as a π→π* transition with a charge transfer contribution; the HOMO is mainly located in the bottom aromatic entity while LUMO spreads in both system aromatic systems. The computed absorption spectra consequently confirm that the new band arises from the opening of the spirolactum ring due to the activation of the charge transfer phenomena; overall the structure of them is the QRH ligand.

As the preceding section describes, the experimental results have already pointed towards the existence of open spirolactum ring to form the probe, QRH, due to the presence of absorbance and fluorescence peaks at 558 and 609 nm, respectively. The precursor compound 1 and compound 2 also checked in the presence of HSO_{4}^{-} and neither showed any characteristic peaks in both absorbance and emission as QRH at experimental concentration. Rhodamine undergoes lactum opening in the presence of acidic protons. Although hydrogen sulfate is an anion, it still is pretty acidic (pK_{a} ~1–2). Thus, the ring-opening of
rhodamine is sensitive to the acidity of the proton, not the anion per se, which is why there is no emission turn-on in the presence of other anions. From the theoretical study, we also found that the protonated-open spirolactum ring form of QRH exists where the HSO$_4^-$ can pair up as a counter anion but not in direct interaction with the probe (Scheme 2). This proposed model can be further reinforced by the ESI—MS spectrum where we got the peak for the protonated-open spirolactum form of the probe, [C$_{43}$H$_{39}$N$_6$O$_2$]$^+$ along with HSO$_4^-$, Na$^+$ and solvent methanol molecule at 823.96 amu (Figure S4). Therefore, we may presume that the generation of protonated-open spirolactum ring form of QRH in association with HSO$_4^-$ counter anion produces a stable ensemble and consequently results in the visual color change (Scheme 2).

**Figure 5.** The left panel shows the computed absorption spectra for the QRH sensor in its parent and protonated-protonated-open spirolactumring forms, plotted with black and red lines, respectively. The right panel displays the frontiers orbitals (HOMO and LUMO) involved in the first excitation $S_0 \rightarrow S_1$ process for the QRH in the presence of HSO$_4^-$.

**Scheme 2.** Mechanistic representation of the spirolactum ring opening upon the addition the HSO$_4^-$ anion to the probe.

**4. Application**

Encouraged by the colorimetric visual HSO$_4^-$ detection ability of the probe, QRH$_1$, in methanol solution, we decided to assess the performance of QRH in mediums other than the solution phase. The sensing property of QRH was evaluated in solid and gel forms [56]. The preparation methods are discussed in Appendix A. As shown in Figure 6c, a significant color change occurs on test paper from yellow to pink. In Figure 6a,b, both in daylight and under UV light, after addition of HSO$_4^-$, the probe undergoes a noticeable change implying suitability of the methods.
Figure 6. Visual change of QRH in the presence of HSO$_4^-$ in gel droplet under (a) normal light and (b) UV light. (c) Color change of the test paper containing QRH in the presence of HSO$_4^-$.

5. Conclusions

In this work, a quinoxaline-rhodamine integrated colorimetric sensor for selective detection of HSO$_4^-$ is reported. We demonstrated the detailed characterization of the probe by FTIR, $^1$H, $^{13}$C NMR, ESI-MS and single crystal XRD method. The probe shows effective recognition towards HSO$_4^-$ aside from the other anions. The experimental as well as theoretical results provided evidence in favor of the spirolactum ring opening in the presence of HSO$_4^-$ anion, for example, by exhibiting the signature spectroscopic outputs for the open form. We have, therefore, proposed a model consisting of a stable [probe-HSO$_4^-$] ensemble. The detection limit of the probe is $7.1 \times 10^{-7}$ M in methanol medium. In addition to solution phase detection, the probe shows its versatility in both gel droplet and solid paper strip forms. All accumulated data confirm the wide applicability of the proposed probe for detecting hydrogen sulphate ion in real life samples at a reduced cost.

Supplementary Materials: The following are available online at https://www.mdpi.com/ article/10.3390/compounds1010004/s1, $^1$H, $^{13}$C NMR, ESI-MS, FTIR spectrum of probe QRH, spectrophotometric study, NMR studies, crystal data and supramolecular figures.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Appendix A.1. Materials and Physical Methods

Ninhydrin, o-phenylenediamine, rhodamine B and hydrazine hydrate were purchased from Sigma-Aldrich and used as received. The tetrabutylammonium salts of anions were also purchased from Sigma Aldrich. Solvents for the syntheses were purchased from commercial sources and used as received. 1H and 13C NMR spectra were recorded in CDCl3 with TMS as internal standard on a Bruker, AV300 Supercon Digital NMR system with dual probe. The FTIR spectra were recorded from KBr pellets in the range of 400–4000 cm−1 on a Perkin-Elmer Spectrum 100 spectrometer (Perkin-Elmer, Shelton, CT, USA). Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 II analyzer (Perkin-Elmer, Waltham, MA, USA). The ES-MS experiments were performed on Waters Xevo G2-S QTof mass spectrometer (Waters, Milford, CT, USA). The crystallographic data were recorded on a Bruker Nonius Apex II CCD diffractometer (Bruker, Karlsruhe, Germany). The absorption and emission spectral studies were performed on a Hitachi UV–Vis U–3501 spectrophotometer (Hitachi, Fukuoka, Japan) and Perkin-Elmer LS55 fluorometer (Perkin-Elmer, Boston, MA, USA), respectively.

Appendix A.2. Single-Crystal X-ray Crystallography

A good quality, single crystal of QRH was chosen and mounted on a Bruker Nonius Apex II CCD diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. The diffraction data were collected with an exposure time of 5 s/frame and at 296 K. The structure was solved by direct methods and refined by full-matrix, least-squares techniques based on F2, using SHELXL–2017/1 software package [57]. A multi-scan empirical absorption correction was applied using SADABS program [57]. All non-hydrogen atoms were refined in the anisotropic approximation against F2 of all reflections and determined from the difference Fourier maps. All the hydrogen atoms were isotropically refined. The crystallographic figures were generated using Mercury 3.9 and Diamond 3.0 codes [58]. The structure refinement parameters and crystallographic data of ligand QRH is listed in Table S2. CCDC 1957625 contains the crystallographic data in CIF format. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix A.3. Computational Details

Theoretical calculations were conducted to assess the optical signatures of ligand QRH in both its parent structure (neutral electronic configuration with the spirolacatum ring in closed condition) and in the proposed structure once in the presence of HSO4− (protonated form concomitant with the opening of spirolactum ring). To this end, we used the density functional theory (DFT) and its time dependent formulation (TD-DFT) at the PBE0/6–31++G(d,p) level [59–62], which was shown to correctly mimic the photochemical phenomena associated with the development of novel sensors [63]. Our model systems were initially built using experimental X-ray data. The geometrical parameters resolved in the crystal structures are therefore relaxed without any symmetry restrain. The stability of the optimized structures was confirmed by computing the vibrational frequencies; for example, the absence of normal modes with imaginary wavelength ensures that the calculations yield to a real minimum in the potential energy surface rather than to a saddle
point. The resulting geometries are used to compute the vertical transition energies and finally yield to the theoretical absorption spectra. Solvent effect was accounted for in all these calculations by using methanol within the Polarizable Continuum Model approach (PCM) [64], as implemented in the Gaussian 16 suite of programs [65].

Appendix A.4. Synthesis of the Ligand (QRH)

Indeno[1,2–b]quinoxalin–11–one (compound 1) and Rhodamine B hydrazide (compound 2) was prepared from literature procedure [66–68]. In methanolic solution (10 mL) of Indeno[1,2–b]quinoxalin–11–one (116 mg, 0.5 mmol), Rhodamine B hydrazide (228 mg, 0.5 mmol) in methanol was added dropwise and refluxed with stirring for 4 h (Scheme 1). The yellow product was filtered through suction filtration and air dried, yield = 62% (210 mg, 0.31 mmol). Anal. calc. for C_{43}H_{38}N_{6}O_{2}: C, 76.99; H, 5.71; N, 12.53; O, 4.77; Found: C, 76.85; H, 5.65; N, 12.51; O, 4.72; \text{H} NMR (300 MHz, CDCl_{3}, 290 K, TMS) \delta: 7.91–8.06 (m, 4H), 7.73–7.76 (d, 1H), 7.65–7.69 (t, 1H), 7.52–7.60 (t, 1H), 7.44–7.45 (m, 3H), 7.43 (s, 1H), 7.31–7.37 (t, 1H), 7.13–7.16 (m, 1H), 6.85 (d, 2H), 6.36 (s, 2H), 6.154 (d, 1H), 3.22–3.24 (q, 8H), 1.04–1.08 (m, 12H); \text{C} NMR (75 MHz, DMSO–d_{6}) \delta: 161.45, 156.86, 155.46, 154.60, 153.17, 152.59, 148.57, 147.43, 142.40, 141.51, 139.13, 136.92, 132.86, 131.84, 131.33, 130.93, 130.67, 129.08, 128.84, 128.70, 128.06, 123.79, 123.69, 123.53, 121.75, 107.78, 106.89, 97.56, 46.04, 44.21, 12.59; FTIR (KBr): 3425, 2964, 1706, 1609, 1512, 1237, 1103, 977, 754; ESI–MS (m/z) Calculated: 671.31 Found: 671.32 (QRH + H+).

Appendix A.5. Sample Preparation for Spectroscopic Studies

All the stock and working solutions were prepared using spectroscopy graded methanol. The stock solutions of the anions were prepared by terabutylammonium (TBA) salts. In UV–V is and fluorometric titration experiment, a stock solution of 10^{-4} (M) QRH was filled in a quartz optical cell of 1.0 cm optical path length to achieve a final concentration of the solution of QRH (10^{-6} (M) and 10^{-5} (M), respectively) in 2000 \mu L. After 1 min, each spectral data was recorded with the addition of HSO_{4}^{-} solution by using a micropipette. NMR titration experiments were carried out in CDCl_{3} solvent.

Appendix A.6. Sample Preparation for Application

We soaked the methanolic solution of QRH in a test paper and dried it. Then we dropped the methanolic solution of the HSO_{4}^{-} on the dried paper. The result is depicted in Figure 6c. The gel droplet was obtained by using Poloxamer 407 as described in the literature [56,69]. The poloxamer-407 solution was prepared using the cold method. The poloxamer dissolved in cold deionized water with continuous stirring. Then in this solution QRH and QRH with HSO_{4}^{-} were added. Then it was stored in a refrigerator at 4 \degree C until a clear solution formed. After refrigeration, the solutions were kept at room temperature. After the gel was completely formed, the color change was observed, as depicted in Figure 6a,b.

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