engineering proceedings

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Proceeding Paper

Quinoline-Based Hydrazone Derivative as a Biocide Chemosensor: Synthesis and Sensing Studies †

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† Presented at the 9th International Electronic Conference on Sensors and Applications, 1–15 November 2022; Available online: https://ecsa-9.sciforum.net/.

Abstract: Tributyltin (TBT) is an organic biocide used on antifouling paints to avoid biofouling on boats and submersed structures. It is toxic to a variety of aquatic organisms and was banned by the Rotterdam Convention in 1998. TBT sensing is an important issue as the biocide is still affecting aquatic environments as some countries did not sign the convention and are still using it. Currently, TBT monitoring methods are based on sampling and laboratory analysis, which is expensive, time-consuming, and require expert users. Therefore, a new simple and fast TBT sensing method would be of high interest. In this work, a new quinoline-based hydrazone derivative was synthesized by a condensation reaction in 67% yield. The new compound was characterized by the usual spectroscopic and spectrometric techniques. The preliminary chemosensory study of the hydrazone derivative in the presence of TBT in acetonitrile solution resulted in a color change from colorless to red together with the appearance of fluorescence. This interaction was confirmed by spectrophotometric and spectrofluorimetric titrations, which revealed that 17 equivalents of TBT led to the maximum optical signal in terms of fluorescence intensity and absorbance.

Keywords: optical chemosensor; quinoline; hydrazone; TBT; biocide

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Citation: Sousa, R.P.C.L.; Costa, S.P.G.; Figueira, R.B.; Raposo, M.M.M. Quinoline-Based Hydrazone Derivative as a Biocide Chemosensor: Synthesis and Sensing Studies. *Eng. Proc.* **2022**, *27*, 13. https://doi.org/10.3390/ecsa-9-13199

Academic Editor: Stefano Mariani

Published: 1 November 2022

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1. Introduction

Antifouling paints are used on ships and submerged structures to mitigate biofouling development. This process is a major drawback for many structures in aquatic environments due to the damage induced on the submerged constructions and the decrease in the hydrodynamic performance of ships and vessels. Antifouling compounds are generally used in paints and act as biocides to mitigate the excessive growth of microorganisms. The most used antifouling compound is tributyltin (TBT), an organotin that has been found to be toxic to a wide diversity of aquatic living beings, such as algae, bacteria, fish, and even mammals [1–7].

TBT was banned in 1998 by the Rotterdam Convention. However, it is still used in some countries that did not sign the convention, and its effects are still being felt in aquatic environments [8–10]. Furthermore, only the use of TBT as a biocide was banned, so its consumption as a paint component is still free of restrictions and has not yet been regulated. The currently used monitoring methods for TBT include sampling and laboratory analysis, which are time-consuming techniques that require long procedures and expensive equipment. The development of simple and fast monitoring systems is of utter importance to monitor aquatic environments. The use of optical chemosensors for TBT detection can be an interesting and promising solution.

Hydrazones are a class of compounds that are considered as both proton donor and proton acceptor, which is a promising structural characteristic in the design of chemosensors [11–17]. The versatile triatomic group C=N-N includes a nucleophilic imine with more reactive nitrogen, imine carbon that has both electrophilic and nucleophilic character, and

additionally a configurational isomerism stemming from the intrinsic nature of the C=N double bond [18].

This work reports the synthesis, characterization, and chemosensory study of a new quinoline-based hydrazone derivative **1**, which was found to be an optical chemosensor in the presence of TBT. Their interaction was analyzed by spectrophotometric and spectrofluorimetric titrations. A change of color of the solution of the compound in acetonitrile (ACN) from colorless to red and the appearance of fluorescence occurred in the presence of TBT. It was observed that 17 equivalents (equiv.) of this analyte were necessary to achieve the absorption and fluorescence plateaus.

2. Experimental Section

2.1. Materials

Melting points were measured on a Stuart SMP3 melting point apparatus. TLC analysis was carried out on 0.20 mm thick precoated silica plates (Macherey-Nagel), and spots were visualized under UV light on a CN-15 camera (Vilber Lourmat). Infrared spectra were obtained on a PerkinElmer Spectrum Two instrument with ATR accessory in the 450–4000 cm^{-1} range with 32 scans. The solid compound was applied directly on the ATR crystal with pressure applied with the incorporated press. UV–vis absorption spectra (200–700 nm) were obtained using Shimadzu UV/3101PC spectrophotometer and fluorescence spectra with a Fluoromax-4 spectrofluorometer. NMR spectra were obtained on a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H and 100.6 MHz for ^{13}C using the solvent peak as internal reference at 25 °C. All chemical shifts are given in ppm using δ_H Me_4Si = 0 ppm as reference, and J values are given in Hz. Assignments were supported by spin decoupling–double resonance and bidimensional heteronuclear correlation techniques. Mass spectrometry analysis were performed at the Mass Spectrometry Facility at CQE, Node IST/RNEM, Campus Alameda, Portugal. All commercial reagents and solvents were used as received.

2.2. Synthesis of Hydrazone Derivative 2-((2-(pyridin-2-yl)hydrazineylidene)methyl)quinoline 1

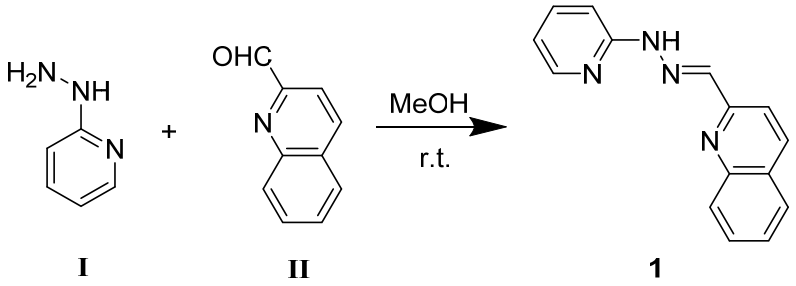
Equal amounts (0.318 mmol) of the hydrazine derivative **I** and quinoline-2-carbaldehyde **II** were dissolved in 10 mL of MeOH at room temperature. The reaction mixture was stirred for 8 h. The precipitated yellow solid was filtered and dried in the oven at 40 °C overnight. No additional purification was required to obtain the pure hydrazone derivative **1** in 67% yield. Mp: 211 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.84 (dq, J = 5.2 and 1.2 Hz, 1H, H5), 7.39 (dd, J = 8.4 and 1.2 Hz, 1H, H3), 7.56 (dt, J = 7.2 and 1.2 Hz, 1H, H6′), 7.68-7.76 (m, 2H, H4 + H7′), 7.95 (dt, J = 7.2 and 1.2 Hz, 2H, H5′ + H8′), 8.13-8.16 (m, 2H, H6 + H3′), 8.20 (s, 1H, N=CH), 8.32 (d, J = 8.8 Hz, 1H, H4′), 11.34 (s, 1H, NH) ppm.

2.3. Preliminary Chemosensing Studies

In the preliminary study, 50 equiv. of TBT (50 µL, 1×10^{-1} M) were added to an ACN solution of compound **1** (1 mL, 1×10^{-4} M). The color/fluorescence changes were evaluated by naked eye and in a UV–vis chamber under ultraviolet light at 312 nm. TBT chloride solution was prepared in UV-grade ACN. Spectrophotometric and spectrofluorimetric titrations were performed with sequential addition of TBT (10^{-2} M) to an ACN solution of compound **1** (3 mL, 1×10^{-5} M). Absorbance and fluorescence spectra were collected until a plateau was reached.

3. Results and Discussion

A new quinoline-based hydrazone derivative **1** (Scheme 1) was synthesized by the reaction of 2-hydrazinopyridine **I** with quinoline-2-carbaldehyde **II** in methanol at room temperature for 8 h. The reaction mixture was filtered, and the hydrazone derivative was isolated with 67% yield as a yellow solid. The structure of the compound was confirmed by ^{1}H NMR. The spectra showed the characteristic singlet signal of hydrazone NH at 11.34 ppm as well as the imine signal of the N=CH proton as a sharp singlet at 8.20 ppm.



Scheme 1. Synthesis of hydrazone derivative **1**.

Heterocyclic hydrazone derivative **1** was then submitted to a preliminary chemosensory ability analysis in the presence of different anions and cations. First, 50 equiv. of each ion were added to an ACN solution of **1,** and the optical response was then analyzed under visible light and under UV light (312 nm). In the presence of TBT, a change of color of the solution of the compound from colorless to red and the appearance of fluorescence occurred (Figure 1).

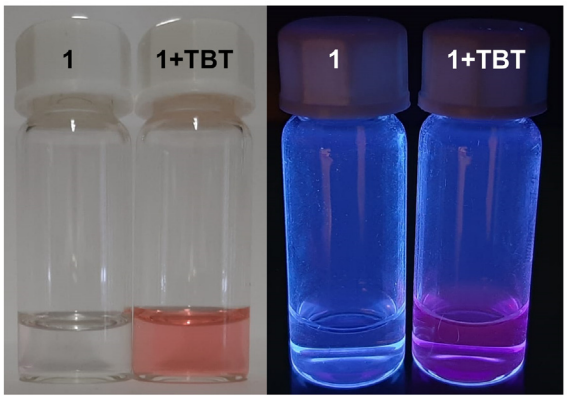


Figure 1. Optical changes of hydrazone derivative **1** in ACN solution (10^{-5} M) in the presence of 50 equiv. of TBT under visible light (**left**) and under UV light of 312 nm (**right**).

Spectrophotometric and spectrofluorimetric titrations were performed to obtain more complete information about the interaction between hydrazone **1** and TBT (Figure 2). A sequential addition of TBT (10^{-2} M) to an ACN solution of compound **1** (3 mL, 1×10^{-5} M) was performed. Absorbance and fluorescence spectra were collected until a plateau was reached.

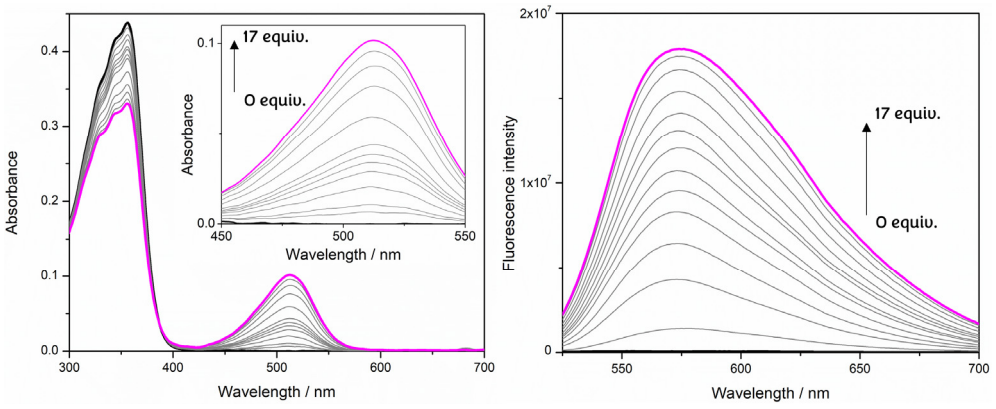


Figure 2. Spectrophotometric titrations of the interaction between compound **1** and TBT: absorption (**left**) and fluorescence, λ_{exc}: 512 nm (**right**).

The spectra of compound **1** showed an absorption band with a maximum absorption wavelength at 356 nm. The addition of TBT induced a decrease in this band and resulted in the appearance of a new band at 512 nm. The appearance of fluorescence was also observed with the addition of TBT. It was found that 17 equiv. of TBT led to the maximum absorbance band at 512 nm and the maximum fluorescence intensity at 576 nm.

4. Conclusions

A new hydrazone derivative **1** was successfully synthesized in 67% yield and showed sensitive colorimetric/fluorimetric changes in the presence of TBT. A change of color from colorless to red and the appearance of fluorescence were confirmed by spectrophotometric titrations. Spectrophotometric and spectrofluorimetric titrations revealed that 17 equiv. of TBT led to the maximum optical signal in terms of fluorescence intensity and absorbance. Therefore, hydrazone derivative **1** shows promising properties to be applied as a transducer to monitor TBT in real samples of aqueous nature.

Author Contributions: Conceptualization, R.P.C.L.S., S.P.G.C. and M.M.M.R.; methodology, R.P.C.L.S., S.P.G.C. and M.M.M.R.; formal analysis, R.P.C.L.S., S.P.G.C. and M.M.M.R.; investigation, R.P.C.L.S.; resources, S.P.G.C., R.B.F. and M.M.M.R.; writing—original draft preparation, R.P.C.L.S.; writing—review and editing, S.P.G.C., R.B.F. and M.M.M.R.; supervision, S.P.G.C., R.B.F. and M.M.M.R.; project administration, S.P.G.C., R.B.F. and M.M.M.R.; funding acquisition, S.P.G.C., R.B.F. and M.M.M.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fundação para a Ciência e Tecnologia (FCT) and FEDER (European Fund for Regional Development)-COMPETE-QRENEU through the Chemistry Research Centre of the University of Minho (Ref. CQ/UM UID/QUI/00686/2020) as well as a PhD grant to R. P. C. L. Sousa (SFRH/BD/145639/2019).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

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