RESEARCH PAPER

Synthesis of 5-Nitrovanillin in Low Temperature as Cyanide Anion Sensor

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Abstract: In terms of organic sensor, the molecular structure affects a compound's ability to be used as a colorimetric chemosensor. Here, we present a simple synthesis technique for 5-nitrovanillin sensor. It has been successfully synthesized using nitric acid as a source of nitro groups. Dichloromethane DCM was used as a solvent, and the synthesis was carried out at low temperatures (under 5°C). The method produces a good yield. The nitro group attached to the chemosensor plays a role in prolonging the electron delocalization. Its effect is in the process of anion recognition by the chemosensor. The formation of a sensor-analyte complex between the chemosensor and anion produces a color change in the solution.

Keywords: synthesis, 5-nitrovanillin, cold temperature, chemosensor

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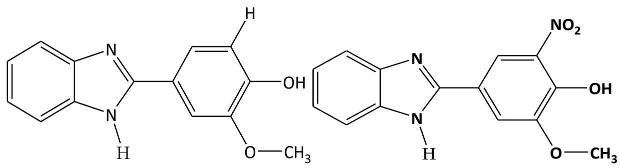
INTRODUCTION

In the synthesis of sensor compounds, the molecular structure will affect the ability of a compound to be used as a color or fluorescent sensor. One of the conditions for a compound to be used as a chemosensor is to have an electron donor substituent group such as an OH group, methoxy, NO_2, or others directly attached to the π bonding system [1]. The π bonding system connects the electron donor groups that can be used as sensor trigger. The compound should have π bonding system, lone pair, and a heterocyclic aromatic structure with heteroatoms (S, N, O) to have a strong chemosensor property. The ring formation improves fluorescent quality.

Previoulsy, we synthesized a chemosensor compound derived from benzimidazole (S1) [2] and benzoxazole (S3) derivatives from vanillin [3]. We attached a nitro group into the ring of S1 and S2 compounds at position 5 to obtain chemosensor compounds S2 and S4 (figure 1), which gives a more potent (in the form of color change and fluorescent) signal [4,5].

However, the synthesis of S2 and S4 directly from S1 and S3 experienced difficulties because the nitro group was difficult to attach to C ring number 5. We attached the nitro group to vanillin to get a 5-nitrovaniliin compound (Figure 2).



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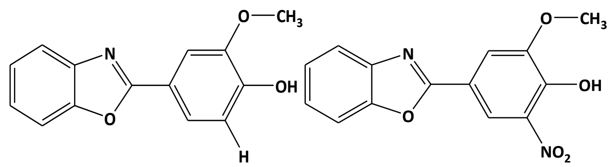


B.

Figure 1. Comparison of the sensor structure: A) S1 with S2; B) S3 with S4.

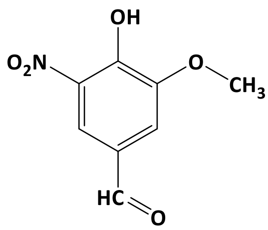


Figure 2. 5-nitrovanillin compound structure

The synthesis of nitrovanillin compounds is carried out through the nitration on the benzene ring. Many methods are used in the nitration reaction. Mondal et al., Used yttrium nitrate, $Y(NO_3)_3.6H_2O$, in glacial acetic acid solvent as an intermediate medium for phenol nitration at room temperature. Nitration of vanillin at position 6 was carried out by Yadav et al., Through acetyl vanillin intermediates using DCM, acetic anhydride, and dry pyridine [7,8]; and Rakshit et al., [9] carried out the nitration of vanillin via the o-Bn-vanillin intermediate. 5-nitrovanilin compounds can also be synthesized in cold conditions using HNO_3 and acetic acid [10]. The 5-nitrovanillin synthesis in this study was carried out using a combination of these methods.

MATERIALS AND METHODS

Materials

Vanillin, DCM, HNO_3 absolute, ice water, ethanol, beaker glass, dropper pipette, stirring glass.

Method

Introducing NO_2 groups into the ring system of vanillin refers to the method of synthesizers with some modifications. A total of 75 mmol of vanillin was dissolved in 55 mL dichloromethane at 0-5^{o}C. Then dripped with 12 mL HNO_3 until it runs out, then stirred at room temperature for 20 minutes. Then added 25 mL of ice water and left for 2 hours. The precipitate formed is recrystallized with ethanol. The synthesis results were then determined for the melting point and then characterized by FT-IR instruments and mass spectra.

RESULTS AND DISCUSSION

The nitro group on 5-nitrovanillin is synthesized by the electrophilic substitution reaction of HNO_3 with vanillin in dichloromethane at cold temperatures. Synthesis of 5-nitrovanilin compound was carried out by vanillin and nitric acid reaction. The synthesis path is shown in Figure 3.

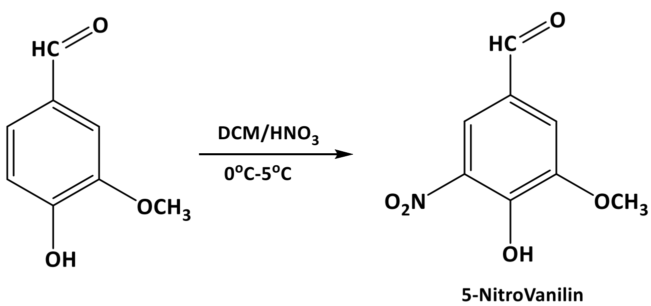


Figure 3. 5-nitrovanillin synthesis pathway

The product formed is a bright yellow powder with a molecular weight of 107 mol/gram, 64% yield and a melting point is 175.4-177.5^{o}C (ref. 175-178^{o}C, Chemicalbook, 2017). The characterization of the synthesis results was carried out using an infrared spectrometer.

Figure 3 shows that the nitration reaction was carried out successfully. It is evidenced by the emergence of a strong absorption from the strain of the nitro group at 1550 cm^{-1}. The confirmation of the formation of this compound was strengthened by the mass spectrum data in Figure 4.

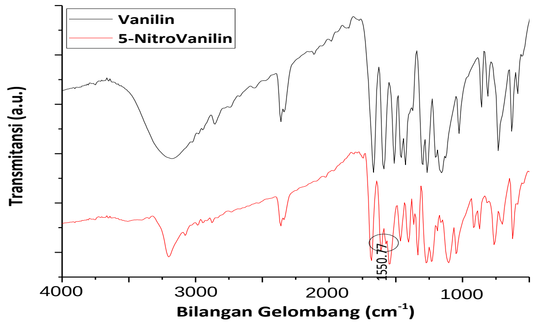


Figure 4. FTIR spectra of 5-nitrovanilin compound

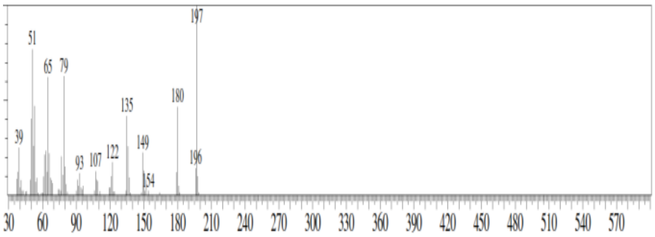


Figure 5. Mass spectrum of the compound 5-nitrovanilin

The appearance of the spectral peak of the molecular ion in 197 is the molecular mass of the 4-hydroxy-3-methoxy-5-nirobenzaldehyde. It indicated that the compound had been formed. The fragmentation pattern of the 4-hydroxy-3-methoxy-5-nirobenzaldehyde can be predicted as in Figure 6.

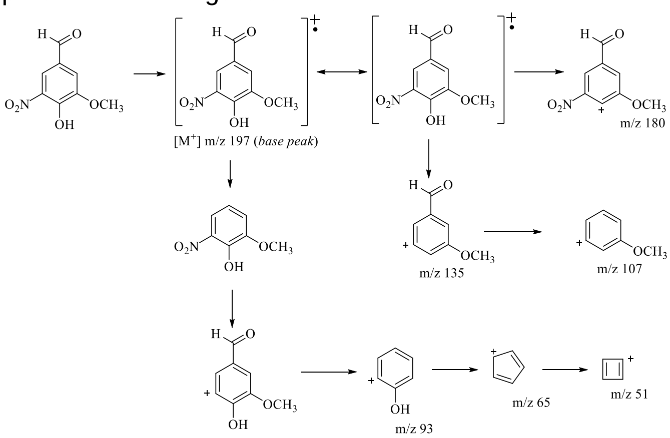
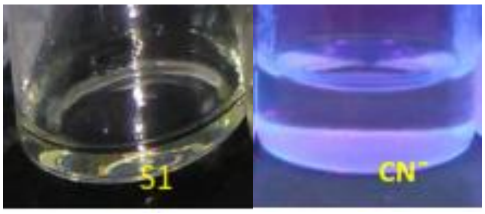


Figure 6. The fragmentation pattern of 5-nitrovanilin compound

Effects of Nito Clusters on 5-Nitrovanilin on Chemosensory Detection Ability. The nitro group incorporated into the vanillin compound as the basic material for making S2 and S4 sensor compounds had a different effect on the ability of these chemosensor compounds to recognize the presence of anions.

Chemosensor S1, synthesized from vanillin directly without nitro groups, only responds in the form of fluorescent changes when interacting with CN anions. The addition of a nitro group on the S2 chemosensor, which was synthesized using 5-nitro aniline, only gave a response in the form of a color change with CN, phosphate, and F anions. The fluorescent response and selectivity were lost.



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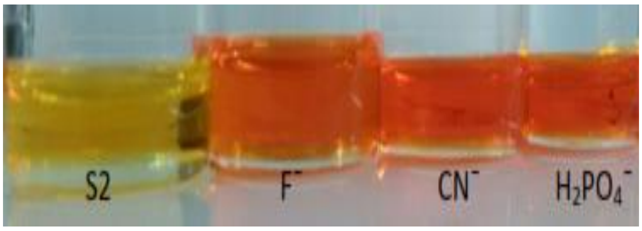
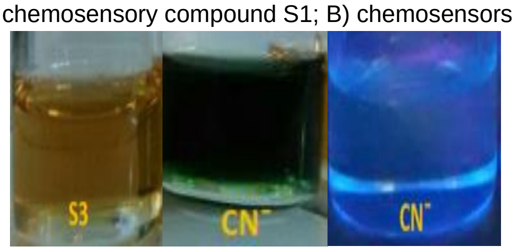


B

Figure 7. The difference in the color of the solution and the response of the sensor compound to anion recognition: A) the chemosensory compound S1; B) chemosensors S2



A

B

Figure 8. The difference in the color of the solution and the response of the sensor compound to anion recognition: A) the chemosensor compound S2; B) S4 . chemosensor

The same thing happened to the S3 chemosensor, which was synthesized from vanillin. Its response to anion recognition was a color change and a fluorescent change (dual sensor) and was selective only for the CN anion. The S4 chemosensor with the inclusion of a nitro group gave a response only in a change in fluorescence. Its selectivity could be maintained, the color property was lost.

CONCLUSION

1. Attaching the nitro group to the C number 5 ring of the vanlin compound through the nitration reaction in the cold reaction gives a 5-nitrovanilin with a good yield.
2. The nitro group at the S2 and S3 compound ring system results in changes in the response of the sensor toward anions.

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