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Synthesis, Characterization and Investigation of Some Photophysical Properties of Novel Benzothiazole Based Pyridine Derivative

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Benzothiazole, Picolinoyl chloride, Fluorescence, Organic synthesis

Abstract: Benzothiazole derivates have been play important role in chemical, biological and pharmacological reactions because of heterocyclic structure. In this study, fluorescent active novel benzothiazole substitute picolinoyl chloride derivate 6-((2-(benzothiazol-2 yl)phenyl)carbamoyl)picolinoyl chloride **(**BTPCP**)** successfully synthesized and characterized. BTPCP structure was identified by classic spectroscopic methods (FT-IR, ^{1}H-NMR and ^{13}C-NMR). BTPCP photophysical properties was investigated by using UV-Vis spectroscopy and Fluorescence spectroscopy. Benzothiazole substitute picolinoyl chloride derivate **(**BTPCP**)** has been shown fluorescence activity. The novel fluorescence active BTPCP is expected to find potential application studies in different biological, pharmacological and especially toxic heavy metal ion detection sensor as Hg^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}…etc.

Yeni Benzotiyazol Bazlı Piridin Türevinin Sentezi, Karakterizasyonu ve Bazı Fotofiziksel Özelliklerinin Araştırılması

Anahtar Kelimeler
Benzotiyazol, Pikolinoil klorür, Floresans, Organik sentez

Öz: Benzotiyazol türevleri, heterosiklik yapıları nedeniyle kimyasal, biyolojik ve farmakolojik reaksiyonlarda önemli rol oynamaktadır. Bu çalışmada, floresans aktif yeni benzotiyazol substitue pikolinoil klorür türevi 6-((2-(benzotiyazol-2il)fenil)karbamoil)pikolinoil klorür (BTPCP) başarıyla sentezlenmiş ve karakterize edilmiştir. Sentezlenen BTPCP'nin molekül yapısı klasik spektroskopik yöntemler (FT-IR, ^{1}H-NMR ve ^{13}C-NMR) kullanılarak belirlenmiştir. BTPCP molekülünün fotofiziksel özellikleri Uv-Vıs spektroskopisi ve Fluoresans spektroskopisi kullanılarak incelenmiştir. Yapılan incelemeler sonucunda benzotiyazol substitue pikolinoyil klorür türevi BTPCP floresans aktivitesi gösterdiği belirlenmiştir. Yeni floresans aktif BTPCP'nin Hg^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}… gibi ağır metal iyonlarının belirlenmesi kullanılabilecek sensör çalışmaları başta olmak üzere, farklı biyolojik ve farmakolojik çalışmalarda uygulama bulması beklenmektedir.

1. INTRODUCTION

Toxic heavy metals are harmful to environmental and human life and the most significant damage caused the environment occurred in soil and water. Nowadays, developing new methods for the detection of heavy metal ion pollution caused by industrial activities an important field of studies [1-6]. Heavy metal ions wastewater, which released uncontrollably into the environment from many different industrial areas such as leather, textile and paint, poses a danger to the environment and human life [7-9]. Detection and disposal of these metals constitute an important field of work. It has known that toxic heavy metals cause diseases in humans, especially the immune system, nervous system, digestive system, heart, kidney and neurological diseases [10-12]. Today, heavy metal analyzes of pollution are generally carried out using different analytical methods such as voltammetry, chromatography or spectroscopy. However, since all methods require expensive devices and involve complex, time-consuming procedures that can only be carried out by well-trained technical personnel, instrumental analysis methods used for the qualitative and quantitative detection of heavy metal ions, especially in water samples. However, studies continue to develop new methods with simple devices, cheap, fast and high

sensitivity [13-15]. Among the methods used to detect heavy metal ions, applications of fluorescent sensors are preferred over other common analytical methods due to their advantages such as high sensitivity, good selectivity, fast response and local observation [16]. The molecular structure modifications of chemosensors have been triggered the ability to selectively complex selective against the metal ions. [17-21].

Benzothiazole molecules have high quantum yields and large Stokes shifts due to their stable conjugated structures. Benzothiazole compounds constitute an interesting field of study for researchers who want to synthesize fluorescence sensors and chemosensors due to their excellent photophysical properties such as photostability [21-24].

The last decade, synthesis of new benzothiazole based fluorescence active compounds for detection of heavy metal ions have been an important research area. The synthesis and determination of photophysical properties benzothiazole based amide derivatives fluorescence sensor applications such as Hg^{2+}, Cu^{2+}, Cr^{3+}, CN^{-} have been in the literature [14, 25-26].

Benzothiazole based molecules are an important group of heterocyclic compounds that can exhibit various pharmacological activities such as anticancer, antibacterial, anti-inflammatory, analgesic and antidiabetic, as well as unique material properties due to their chemical and biological properties [27-29].

The aim of this study is to design, synthesize and characterize novel fluorescence active 6-((2-(benzothiazol-2-yl phenyl)carbamoyl)picolinoyl chloride **(**BTPCP**)** and BTPCP photophysical properties determined by using spectroscopic methods. (Uv-Vıs spectroscopy and Fluorescence spectroscopy). The novel fluorescence active BTPCP can be used in different fields as medicine, materials, toxic heavy metal ions detection sensors like Hg^{+2}, Cu^{+2}, Cr^{+3}, Fe^{+3}……etc.

2. MATERIAL AND METHOD

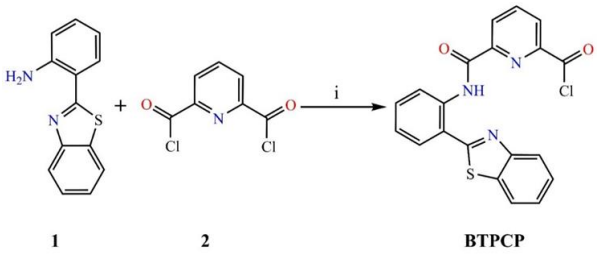
2.1. Reagents and Instruments

All chemical compounds and organic solvents were obtained from commercial sources (Merck, Sigma-Aldrich, and Alfa Aesar) without any purifications. For the column chromatography, silica gel 230–400 mesh was used and for thin layer chromatography (TLC) applications, pre-coated silica gel 60F254 aluminum sheets were used. The reaction was conducted in under inert (argon) atmosphere. FTIR spectra was performed on a Perkin Elmer Spectrum Two spectrophotometer equipped with ATR apparatus. The Bruker 400 MHz device was used for measuring the ^{1}H-NMR and ^{13}C-NMR spectra in chloroform solvent with the interior label of chemical shifts, tetramethyl silane. Fluorescence spectra were on the Agilent Cary Eclipse Spectrophotometer, while PerkinElmer Lambda 35 spectrophotometer was used to measure UV–Vis absorption spectra.

2.2. Synthesis of compound 6-((2-(benzothiazol-2-yl)phenyl)carbamoyl)picolinoyl chloride (BTPCP)

Na_2CO_3 (318 mg, 3 mmol) and 2-(2-aminophenyl)-benzothiazole (**1**) (226 mg, 1 mmol) were stirred for 1 h at room temperature in THF (25 ml) and then 2,6-pyridinedicarboxylic acid chloride (243,6 mg, 1,2 mmol) was added the mixture. The reaction mixture was refluxed for 8 h under Ar atmosphere. After the reaction mixture was cooled and poured into ice, the mixture was stirred for 1 h. The solid was filtered and the crude product was purified by column chromatography on silica gel. The synthesis of BTPCP is shown in Scheme 1.

White solid, Yield: 181,3 mg (45%). FT-IR (ATR, cm^{-1}) 3149 (NH), 1742 ($C=O_{acyl\ chloride}$) 1689 ($C=O_{amide}$), 752 (C-Cl). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.64 (s, 1H, N*H*-Ar), 8.95 (dd, *J*=7 Hz, 1H, $H_{1.}$), 8.64- 8.55 (m, 2H, $H_{2,}$ H_3), 8.35 (d, *J*=8 Hz, 2H, $H_{8,}$ H_{11}), 8.26–8.10 (m, 2H, $H_{4,}$ H_7), 7.60–7.38 (m, 2H, $H_{5,}$ H_{10}), 7.14–7.19 (m, 2H, $H_{6,}$ $H_{9.}$);^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5 (1C, *Cl-C=O*), 165.3 (1C, *-NH-C=O*), 164.3 *(-S-C=N-*), 162.6 (*-N-C=C-*), 154.3 (*-C-C=N-*), 152.5 (*-N-C=*C-),138.1, 130.4, 129.1, 127.8, 124.1, 121.5, 120.7 (*Aromatic C*)



Scheme 1. The synthesis of BTPCP**;** ***i***: THF, Na_2CO_3, inert atmosphere, 8 h reflux.

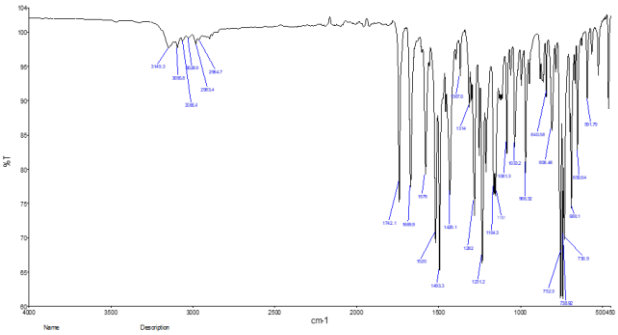


Figure 1. The FT-IR spectrum **o**f BTPCP

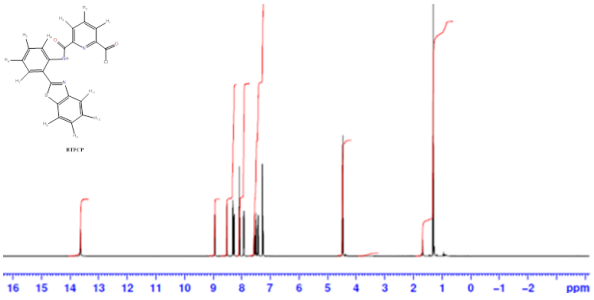


Figure 2. The ^{1}H-NMR spectrum of BTPCP

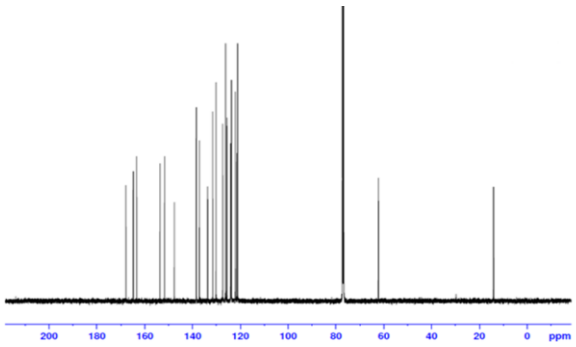


Figure 3. The ^{13}C-NMR spectrum of BTPCP

2.3.UV-Vis Spectroscopy

A novel benzothiazole substitute picolinoyl chloride derivate BTPCP was examined in UV-Vis spectrophotometer. In the UV-Vis spectrum, absorption bands were observed at wavelengths of 324 nm ($\lambda_{abs.}$) and 382 nm ($\lambda_{abs.}$), respectively, due to the influence of the chromophore C=C, C=N groups in the heterocycle and the C=O groups in the molecular structure. The Uv-Vis spectrum of BTPCP has been showed two absorbance bands: the π-π* transitions of the aromatic core are responsible for the absorbance band at 324 nm, while the n–π* electron transition, which results from the promotion of nonbonding electrons on the N atom of the pyridine and N ,S atoms of benzothiazole moiety to an anti-bonding orbital of BTPCP, is responsible for the bands at 382 nm. The UV-Vis spectrum of novel BTPCP shown in Figure 4.

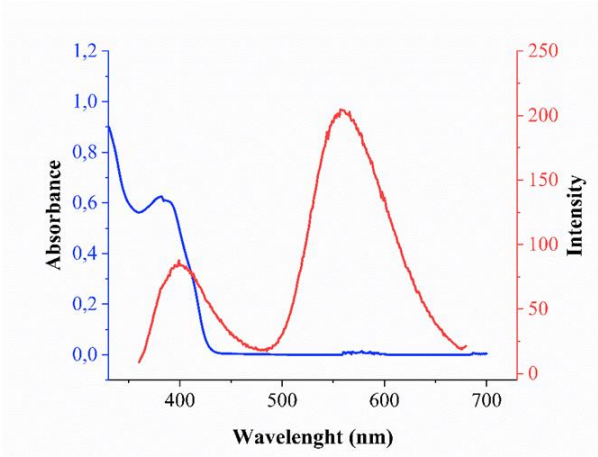


Figure 4. The UV-Vis spectrum of BTPCP

2.4. Fluorescence Spectroscopy

A novel benzothiazole substitute picolinoyl chloride derivate BTPCP's florescence properties was examined in two different solvents (Chloroform and H_2O) in Fluorescence Spectrophotometer. A novel benzothiazole derivate has been shown fluorescence properties in two solvents. Benzothiazoles have high quantum yields and large Stokes shifts due to their stable conjugated structure. The aromatic ring structure in the structure of benzothiazoles and the thiazole structure in the molecular skeleton provide the molecule with fluorescence properties. Excitation and emission wavelengths in the fluorescence spectrum of the BTPCP molecule were observed as 350 nm ($\lambda_{exc.}$) and 556 nm ($\lambda_{em.}$) in chloroform. The Fluorescence spectrum of novel BTPCP in chloroform is shown in Figure 5. Excitation and emission wavelengths in the fluorescence spectrum of the BTPCP molecule were observed as 350 nm ($\lambda_{exc.}$) and 564 nm ($\lambda_{em.}$) in H_2O. The Fluorescence spectrum of novel BTPCP in H_2O is shown in Figure 5.

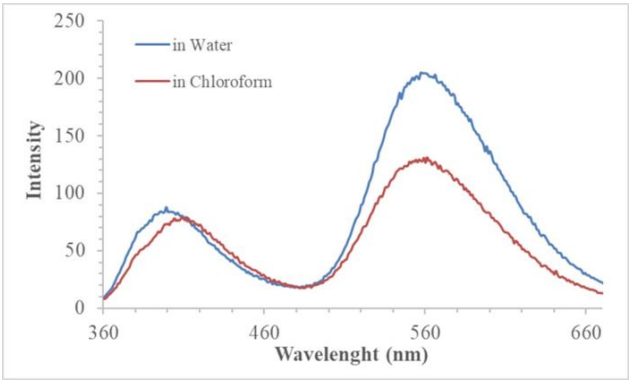


Figure 5. The Fluorescence spectrum of BTPCP in Chloroform and H_2O.

3. RESULTS

This study has two steps. In the first step of this study, novel benzothiazole substitute picolinoyl chloride derivate BTPCP's was synthesized by the condensation reaction of 2-(2-aminophenyl)-benzothiazole (1) with 2,6-Pyridinedicarboxylic acid chloride (2) (Scheme 1.). The chemical structure of compound BTPCP was characterized by spectroscopic methods (FT-IR, ^{1}H-NMR, ^{13}C-NMR) (Figure 1- Figure 3). The proposed structures are full agreement with the all spectroscopic data. In the FT-IR spectrum of BTPCP showed characteristic NH, C=N, C=O and C-Cl stretching bands at 3149, 1742, 1579, 1689 and 752 cm^{-1}, respectively [14]. (Figure 1.) In the ^{1}H-NMR spectrum, the low field singlet at 13.64 ppm was assigned to NH groups, doublet at 8.95 ppm ($H_{1.}$), multiplet at 8. 64-8.55 (H_2, H_3), 8.35 ppm doublet at (H_8, H_{11}), multiplet at 8.26–8.10 (m, 2H, H_4, H_7), 7.60–7.38 (m, 2H, H_5, H_{10}), 7.14–7.19 (m, 2H, H_6, H_9.) were assigned to the aromatic C-H. (Figure 2.) The carbonyl groups amide and acyl chloride peaks in the ^{13}C-NMR spectrum were confirmed at 168.5, 165.3 ppm respectively. The benzothiazole ring -*S*-*C*=*N*- aromatic carbon was confirmed at 164.3 ppm. The pyridine ring carbon atoms -*N*-*C*=*C*- peak at 162.6 ppm, -*C*-*C*=*N*- peak at 154.3 ppm, -*N*-*C*=C- peak at 152.5 ppm, the other aromatic carbons peaks between 164.3 and 120.7 ppm (Figure 3.).

The second step of this study, novel benzothiazole substitute picolinoyl chloride derivate BTPCP's the photophysical properties were determined by using UV-Vis spectrophotometer and Fluorescence spectrophotometer.

The absorption and fluorescence spectrums of BTPCP performed to its interaction in different solvents such as H_2O and chloroform. The UV-Vis spectrum of BTPCP is examined in chloroform, it has seen that it has two different absorbances at 324 and 382 nm wavelengths. (Figure 4.) Considering the UV spectra; when BTPCP was excited at 401 nm, emission of BTPCP was sighed at 556 nm with a large stokes' shift of 155 nm in the fluorescence spectrum in chloroform (Figure 5). And when BTPCP was excited at 350 nm, emission of BTPCP was monitored at 564 nm with a large stokes' shift of 158 nm in the fluorescence spectrum in H_2O (Figure 5).

Benzothiazole-based fluorescent sensor have emerged as powerful tools in chemosensor technology due to their photophysical properties and selective fluorescence quenching upon interaction with metal ions. The incorporation of electron-donating groups such as prydine heterocyle into an extended π-conjugated system enables benzothiazole heterocycles to function as efficient acceptors chromophores [25].

4. DISCUSSION AND CONCLUSION

Benzothiazole derivates have been play important role in chemical, biological and pharmacological reactions because of its heterocyclic structure that exhibit various important biological activities such as anti-inflammatory, antidiabetic, antibacterial, analgesic, anticancer, etc. Benzothiazole derivatives compounds are an important group of organic compounds with their properties that play an important role in chemical, biological and pharmacological reactions, as well as applications such as sensors and chemosensors for materials science. In this study, novel benzothiazole derivate potential chemosensor 6-((2-(benzothiazol-2-yl)phenyl)carbamoyl)picolinoyl chloride (BTPCP) has been successfully synthesized and characterized. The fluorescence properties of the synthesized molecule make into this molecule interesting in sensors studies. BTPCP is a compound that has the potential to be used in the detection of heavy metal pollution. It has been stated in the literature that compounds with similar molecular structures are sensitive and selective to Cu^{+2} ions, BTPCP a strong candidate for the detection of heavy metal ions. BTPCP is estimated that this new benzothiazole derivate will create a new perspective for research in many different fields such as material science, chemistry, biology, medicine, etc.

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REFERENCES

[1] J.H. Wang, M. Li, D. Li, Chem. Sci. 4 (2013) 1793–1801.
[2] M.K. Amini, B. Khezri, A.R. Firooz, Sensor Actuat B-Chem. 131 (2008) 470–478.
[3] A.D. McFarland, R.P.V. Duyne, Nano Lett. 3 (2003) 1507–1511.
[4] H.S. Jung, M.S. Park, J.H. Han, J.H. Lee, C. Kang, J.H. Jung, J.S. Kim, Chem. Commun. 48 (2012) 5082–5084
[5] K.R. Dalton, M. J. Orr, A. J. Kwong, K. K. Deibler, H. H. Munshi, C. S. Bridges, T. J. Chen, X. Zhang, H. D. Lacorazza, K.A. Scheidt, ACS Medicinal Chemistry Letters 2023 14 (5), 606-613.
[6] J.P. Vacca, J.P. Maxwell, B. Williams, J.H. Come, S. Throner, World Intellectual Property Organization, WO2023064586 A1 2023-04-20 | Language: English, Database: Caplus ESPACENET
[7] J. Ling, J. Liu, World Intellectual Property Organization, WO2014183300 A1 2014-11-20 | Language: English, Database: CAplus ESPACENET
[8] Ge, H. Zhang, P. Wang, Chem. Soc. Rev. 40 (2011) 3483–3495; L.-J. Fan, Y. Zhang, C.B. Murphy, S.E. Angell, M.F.L. Parker, B.R. Flynn, W.E. Jones Jr., Coord. Chem. Rev. 253 (2009) 410–422.
[9] E. Hrishikesan, C. Saravanan, P. Kannan, Ind. Eng. Chem. Res. 50 (2011) 8225– 8229.
[10] J. Chan, S.C. Dodani, C.J. Chang, Nat. Chem. 4 (2012) 973–984.
[11] Q. Zou, H. Tian, Sensor Actuat. B-Chem. 149 (2010) 20–27.
[12] X. Zhang, Y. Shiraishi, T. Hirai, Tetrahedron Lett. 48 (2007) 5455–5459.
[13] A. Misra, M. Shahid, J. Phys. Chem. C 114 (2010) 16726–16739.
[14] H. E. Gülbaş, S. Bozkurt, E. Halay, J. Heterocycl. Chem. 2023, 60(7), 1223.
[15] O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolamen,G. Gulseren, D. Nalbantoglu, H. Boyaci, E.U. Akkaya, *Journal of the American Chemical Society,* 132 (2010), 8029-8036.
[16] F.D. Natale, A. Lancia, A. Molino, M.D. Natale, D. Karatza, D. Musmarra, J. Hazard. Mater. 132 (2006), 220–225
[17] A. Renzoni, F. Zino, E. Franchi, Environ. Res. A 77 (1998) 68–72.
[18] J.M. Benoit, W.F. Fitzgerald, A.W.H. Damman, Environ. Res. A 78 (1998) 118–133.
[19] J. H. Wanga, Y. M. Liub, Z. M. Donga, J. B. Chaob, H. Wang, Y. Wanga, Journal of Hazardous Materials 382 (2020) 121056
[20] S. Das, H. K. Indurthi, P. Asati, P. Saha, D. K. Sharma, Dyes and Pigments 199 (2022) 110074.
[21] G. Dhaka, J. Singh, N. Kaur, Inorganica Chimica Acta 462 (2017), 152–157.
[22] R. Hussain, M. Ashraf, S. Khan, F. Rahim, W. Rehman, M. Taha, A. Sardar, Y. Khan, I. Khan, S.A.A. Shah, J. Mol. Struct. 1295 (2024) 136582.
[23] A. Sardar, O-ur-R. Abid, S. Daud, B.A. Shah, W. Shahid, M. Ashraf, M. Fatima, S. Ezzine, A.Shareef A.Wadood, H.A. Al-Ghulikah, S.A. Alissa, Arab. J. Chem. 15 (2022) 104300.
[24] A.K. Jain, S. Sharma, A. Vaidya, V. Ravichandran, R.K. Agrawal, Chem. Biol. Drug Des. 81 (2013) 557–576.
[25] Md. Mohasin, Z. Alam, S. Ahmad ,U. Salma , Q. Ullah , S. A. Khan, J.Mol.Struc.,1336 (2025), 142034.

[26] G.C. Santos, Y.G. Kappenberg, J.M. Rosa, A. Ketzer, M.A. Martins, G. Banacorsa, J. Photochem. Photobiol., A 444, (2023), 114900.
[27] T. Jabeen S. Aslam M. Yaseen, M.J. Saif, M. Ahmad, S.A. Al-Hussain M.E.A. Zaki, J. Saudi Chem. Soc. 27 (2023) 101679.
[28] Y. Khan, S. Khan, R. Hussain, A. Maalik, W. Rehman, M.W. Attwa, R. Masood, H. W. Darwish, H.A. Ghabbour, Pharmaceuticals, (Basel) 16 (2023) 1650.
[29] A. Khamitova, D. Berillo, A. Lozynskyi, Y. Konechnyi, D. Mural, V. Georgiyants, R. Lesyk, Mini. Rev. Med. Chem. 24 (2024).