Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 07, July-2019

A New Electron Transport Conjugated Compound: Vinyl Benzaldehyde Capped Quinoxaline Derivatives for Photoluminescence and Antibacterial Applications

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***Abstract*: Organic compounds containing π-conjugated structures are best known for their electroluminescence (EL) and photoluminescence (PL) characteristics and thus used for making OLED materials. Introduction of suitable organic moiety in those materials make them multifunctional. A similar kind of such materials containing electron withdrawing groups like pyrazine and quinoxaline rings were synthesized. Quinoxaline finds many pharmacological activities and electron transport properties. The quinoxaline moiety, which contains electron-withdrawing nitrogen atoms is highly electron deficient and thus serves as an efficient electron acceptor. The present study involves to synthesis vinyl benzaldehyde containing quinoxaline derivatives by Wittig route. The synthesized compounds were characterized by UV, FT-IR, ^{1}H, ^{13}C, ^{31}P-NMR and Mass spectra. The result of fluorescent spectral investigation reveals that vinyl benzaldehyde containing quinoxaline derivatives exhibited photoluminescence with bluish-green emission. The Phosphonium compound and p-vinyl benzaldehyde capped quinoxaline derivatives were subjected to four different bacteria viz., *Staphylococcus aureus*, *Bacillus substilis*, *Escherichia Coli*, *Pseudomonas auroginosa*. A result of the antibacterial studies reveals that compounds acquire substantial activity in assessment with Ampicillin.**

Keywords: Quinoxaline derivatives, photoluminescence, benzopyrazine, Wittig reaction.

1. INTRODUCTION

Quinoxaline is commonly called as 1,4- diazanaphthalene or benzopyrine. Quinoxaline derivatives are an important class of fused heterocycles that display a wide range of biological, pharmacological, and medicinal properties involving antiviral, antibacterial, anti-inflammatory, and antiprotozoal and as kinase inhibitors [1-5]. Many quinoxaline derivatives have a wide application as dyes, electroluminescent materials, organic semiconductors, chemically controllable switches, and DNA cleaving agents [6-11]. The elaboration of electro-optical (EO) and nonlinear optical (NLO) materials has attracted considerable attention because of their wide range of potential applications in optical data processing technologies. The synthesis of extended π-conjugated systems has been the key to provide organic materials with such properties. These compounds are often based on a push-pull system, which is constituted by an electron-donating group (D) and an electron withdrawing group (A) linked through a π-conjugated spacer. The molecular properties of the chromophores depend on the strength of the "push-pull" effects which are function of the ability of the donor to provide electrons and the acceptor to withdraw electrons. Pyrazine and quinoxaline, which are highly π-deficient aromatic heterocycles, can be used as electron withdrawing part in push-pull structures for intramolecular charge transfer (ICT) such important ICT along the backbone of the molecule can induce luminescence properties [12]. For efficient green emission, core chromophores such as coumarin, quinacridone, quinolone, quinoxaline and carbazole are usually equipped with donor-acceptor (D-A) structural features along the main conjugated backbone[13]

Hence, vinyl benzaldehyde capped quinoxaline derivatives, containing electron donor-acceptor units, were synthesized via condensation and Wittig reaction in hope of combining light-emitting properties and antibacterial activity and were characterized.

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2. EXPERIMENTAL

2.1 Materials

All the chemicals were obtained from Avra chemicals, Hyderabad, India and were used as supplied. Solvents used were purified and dried according to the standard procedure.

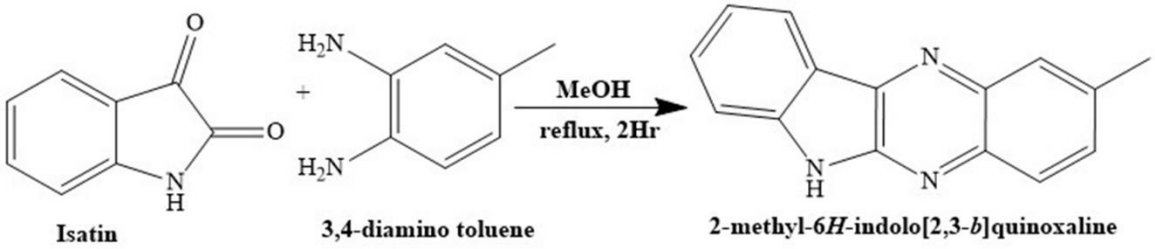
2.2 Characterization Methods

The UV-Visible spectra were recorded on an Alpha-Bruker UV spectrophotometer equipped in the range between 200-800nm. Room temperature FTIR spectra were recorded as KBr pellet with an Alpha-Bruker FTIR spectrophotometer in the range of 4000-400cm^{-1}. Nuclear magnetic resonance spectra with different core viz., ^{1}H NMR, ^{13}C NMR and ^{31}P NMR were recorded in either DMSO-d_6 or $CDCl_3$ on Bruker ADVANCE III 500mHz spectrometer. The fluorescence spectra of the synthesized compound in ethanol were recorded on fluorescence spectrophotometer, FP-8500, JASCO. Mass spectroscopy was recorded on ES-FIGIEAN ionization mass spectrometer.

2.3 Synthesis

A. Synthesis of 2-methyl-6-indolo-2,3-quinoxaline

As shown in scheme 1, equimolar quantities of Isatin (2mmol) and 3,4-diaminotoluene (2mmol) were refluxed in alcohol for 2 hours. The progress of the reaction was monitored by TLC. The contents of the reaction mixture were cooled down to separate out the yellow sponge. The crude yellow sponge was recrystallized from a mixture of ethanol and chloroform (1:1). The melting point of the compound was found to have 280˚ - 282˚ C. Observed Spectral data: **UV (λmax, nm)**: 230, 269 and 354. **FTIR (KBr, cm^{-1})**: 2837 (C-H, st), 1583 (C=N, st), 1402 (C=C, st), 1324 (C-N, st), 3300 (N-H, st). **^{1}H NMR ($CDCl_3$, ppm):** 2.78 δ (3H, s), 9.69δ (1H, s) 8.41 δ(2H, s) 7.84 δ(1H, d) 7.58 δ(1H, m) 7.46 δ (1H, m) 7.26 δ (1H, m). **Mass(m/z):** Calculated M.W 233.1, Observed M.W 234.2(M+1).



Scheme 1. Synthesis of 2-methyl-6H-indolo[2,3] quinoxaline

B. Synthesis of 2-bromomethyl-2,3-indoloquinoxaline

The reddish brown crystals of 2-bromomethyl-2,3-indoloquinoxaline was synthesized by refluxing the mixture of compounds, 2-methyl-indolo-2,3-quinoxaline (0.2333g, 1mmol), *N*-bromosuccinimide (0.1780g, 1mmol) in 30ml of CCl_4 and 0.08g (0.0003mol) benzoyl peroxide were added as radical initiator. The reaction was carried out for 8 hours. Then the reaction mixture was filtered and the solvent was evaporated to get the reddish brown crystal compound**.** The melting point of the compound was found to be 128˚- 130˚ C. **FT-IR (KBr, cm^{-1})**: 2720 (C-H, st), 1570 (C=N, st) 1466 (C=C, st) 1337 (C-N, st) 678 (C-Br, st), 3054 (N-H, st). **^{1}H-NMR (DMSO, ppm):** 3.35 δ (2H, s) 12.05 δ(1H, s) 7.36 – 8.37 δ(7H, m)

C. Synthesis of 2-triphenylphosphonium-bromomethyl-2,3-indoloquinoxaline

1mmol (0.3122g) of 2-bromomethyl-indolo-2,3-quinoxaline and 1mmol (0.2623g) of triphenylphosphine were dissolved in 20ml of acetonitrile. The reaction was carried out for 12 hours at 40˚C. Then, the reaction mixture was filtered and the solvent was evaporated. The brown coloured crude solid was recrystallized from toluene-methanol (2:1) mixture to get yellow sticky product of 2-triphenylphosphonium-bromomethyl-2,3-indoloquinoxaline**. FT-IR (KBr, cm^{-1}):** 2920 (C-H, st), 1590 (C=N, st) 1436 (C=C, st) 1332 (C-N, st), 721 (C-Br, st), 694 (C-P, st), 540 (P-Br, st), 3406 (N-H, st). **^{1}H-NMR (DMSO, ppm):** 2.76δ (2H, s), 7.68 – 7.72 δ (3H, m), 7.50-7.58 δ(4H, m), 7.28-7.48 δ(15H, m) 9.47 δ(1H, s). **^{31}P-NMR (DMSO, ppm):** 23.17 δ(1P, s)

D. Synthesis of vinyl benzaldehyde capped quinoxaline derivative.

The phosphonium salt (1mmol) and terephthaldicarboxaldehyde (1mmol) were dissolved in a mixture of absolute ethanol and dry chloroform (12ml, 3+1 v/v) under N_2 atmosphere. Further, stoichiometric amount of sodium methoxide (25wt% in methanol, 1.3ml, 5.6mmol) was added and the resulting solution was stirred at 50^{o} C overnight. The product was washed with methanol and reprecipitated from dichloromethane-methanol (1:1) followed by dissolving in acetonitrile – chloroform mixture (1:1) and dried under vacuum to yield 85 % of pale yellow colour solid product as vinyl benzaldehyde capped quinoxaline derivative. **UV(λ_{max}, nm):** 230.50nm (π-π*), 269, 355nm (n-π*); **FT-IR (KBr, cm-1):** 2921 (C-H, st), 1693 (C=O, st), 1550 (C=N, st), 1416 (C=C), 1353 (C-N, st**),** 3403(N-H, st) **;** (S Fig. 8)^{1}H-NMR ($CDCl_3$, ppm): 10.03 δ(1H, s), 7.91 δ(1H, s) 5.51 – 5.57 δ(2H, d) 7.65 – 7.88 δ(3H, m) 7.68 – 7.69 δ(2H, m), 7.56 - 7.58 δ(2H, m) 7.28 – 7.54 δ(4H, m); **^{13}C-NMR ($CDCl_3$, ppm):** 178.30δ, 112.01 – 145.13 δ **Mass(m/z):** Calculated M.W 349.1, Observed M.W 349.3; **PL** : 484nm Emission

Scheme 2 illustrates the conversion of 2-methyl-6-indolo-2,3-quinoxaline to vinyl benzaldehyde capped quinoxaline via three steps as explained above:

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Scheme 2. Synthesis of vinyl benzaldehyde capped quinoxaline

3. RESULTS AND DISCUSSION

The four compounds (labeled 1-4) were synthesized as shown in the scheme 1 and scheme 2. The vinyl benzaldehyde capped quinoxaline derivatives were prepared by following the procedure reported earlier[14-16].

Compound 1: 2-methyl-6-indolo-2,3-quinoxaline was synthesized by condensation between the precursors isatin and 3,4-diamino toluene.

Compound 2: Obtained by brominating compound 1 using NBS as brominating agent via free radical mechanism.

Compound 3: It is the Phosphonium salt of compound 2 and was obtained by treating it with triphenyl phosphine.

Compound 4: Vinyl benzaldehyde capped quinoxaline derivative was synthesized through Wittig reaction.

The structures of the compounds were characterized by UV, FT-IR, ^{1}H, ^{31}P NMR. The optical properties including absorption and luminescence of these VB-QUI were measured with UV-Vis and PL systems.

The structure of the compound 1 were confirmed by UV, FTIR, ^{1}H NMR and Mass spectral interpretation. The FTIR spectrum of 2-methyl-6*H*-indolo-2,3-quioxaline have shown in Fig. 1. The transmittance peaks at 3300 and 2837 cm^{-1} related to stretching frequencies of N-H and C-H. The peaks at 1583 and 1402 cm^{-1} were attributed to C=N and C=C stretching vibrations. The peak at 1324 $cm^{-1}$was related to C-N stretching vibration. ^{1}H NMR spectrum showed a The compound 2 bromomethylated quinoxaline was confirmed by FTIR, ^{1}H NMR spectroscopy. Fig. 2 illustrates peak at 2.78 δ due to methyl proton ($-CH_3$). A singlet peak at 9.69 δ ppm indicated the NH proton in the ring system. A multiplet at 7.26 – 8.14 δ ppm for 7H, indicated aromatic protons present in two phenyl rings. In the mas spectrum, the molecular ion peak appeared at m/z = 234.2 (M+1) which has good agreement with calculated mass of the compound m/z = 233.1

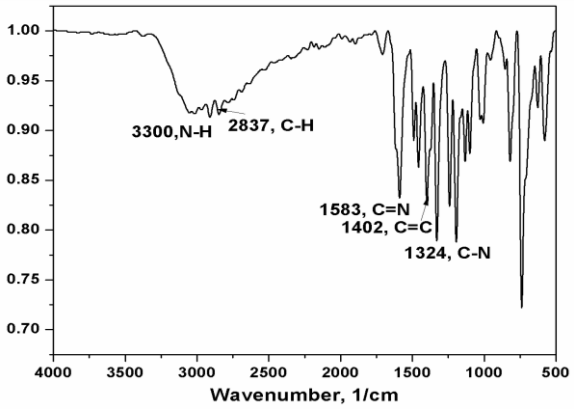

Figure 1: FTIR spectrum of 2-methyl-6*H*-indolo-2,3-quinoxaline

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 07, July-2019

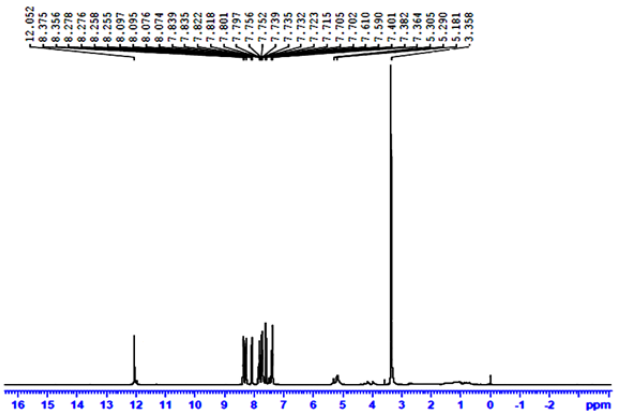

Figure 2: [1]H NMR spectrum of 2-bromomethyl-6H-indolo-[2,3-b] quinoxaline

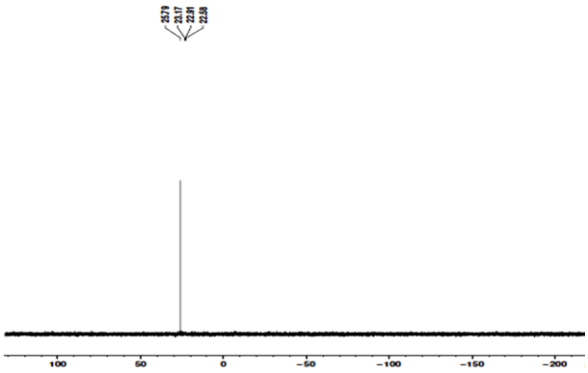

Figure 3: [31]P NMR spectrum of 2-triphenylphosphonium-bromomethyl-2,3-indoloquinoxaline

the [1]H NMR spectrum of compound **2.** In the NMR spectrum, the downfield proton resonates at 3.35 δ ppm due to bromo methyl protons in quinoxaline ring which is a singlet. A multiplet at 7.36 – 8.37 δ ppm (7H), indicates aromatic protons in quinoxaline ring. A singlet at 12.05 δ ppm (1H) designated NH proton present in a indolo ring respectively.

The compound 3 Phosphonium ylide was obtained from bromomethylated quinoxaline. Fig. 3 shows the [31]P NMR spectrum of phosphonium compound. They displayed singlet signal at 23.17 ppm due to single phosphorous appeared in the compound.

The target compound 4 Vinylbenzaldehyde capped quinoxaline derivative was obtained from phosphonium salt. The FTIR spectrum of 2,3-indoloquinoxalin-2-vinyl benzaldehyde have shown a broad peak at 3403 assigned to N-H stretching vibration. A transmittance peak at 2921 cm^{-1} indicated the C-H stretching vibration. The peak at 1693 cm^{-1} related to the carbonyl stretching. The two strong peaks at 1550 and 1416 cm^{-1}corresponding to C=N and C=C stretching respectively. The peak at 1353 cm^{-1} have assigned to C-N vibration. In the [1]H NMR spectrum, a singlet peak appeared at downfield region at 10.03 δ ppm, 1H, pointed out aldehyde proton (-CHO) of C-H. A singlet at 7.91 δ ppm, equivalent to 1H, for N-H proton. A doublet appeared at 5.5.1 – 5.57 δ, ppm for 2H, assigned to vinyl protons. The multiplet peaks from 7.56 – 7.88 δ have assigned to corresponds to aromatic protons in which 7.56 – 7.69 δ ppm may be given to 4H of benzaldehyde ring protons. Similarly, 7.65 – 7.88 δ for 3H of benzene ring of quinoxaline ring moiety. Another multiplet peak appeared at 7.28 – 7.54 δ ppm, 4H, corresponds to aromatic protons in indoloquinoxaline ring moiety. [13]C NMR spectrum: A peak at 178.30 and 128.28 δ ppm, were indicated the carbonyl carbon and vinyl carbon respectively. The peaks that appear at 128.97, 125.77, 136.89 and 140.38 δ ppm, were related to aromatic carbons in benzaldehyde ring. The peaks at 137.55, 125.04, 128.55 and 130.22 δ ppm, were associated with aromatic carbons in quinoxaline ring. The peaks at 139.07, 140.49, 145.13, 143.15 and 133.46 δ ppm assigned for heterocyclic ring carbons. The signals at 119.75, 112.07, 121.64 and 122.73 were pointed out the aromatic carbons of indolo ring moiety. Fig. 4 shows the LC-Mass of the compound **4.** The expected mass of the compound found to have 349.3 m/z value which was accompanied with observed 349.1 m/z value.

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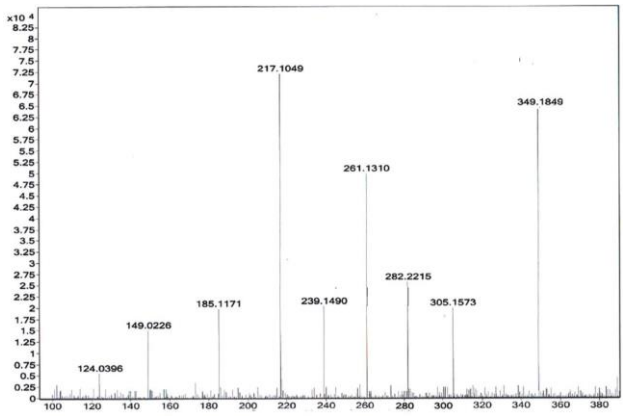

Figure 4: Mass spectrum of 2,3-indoloquinoxalin-2-vinyl benzaldehyde

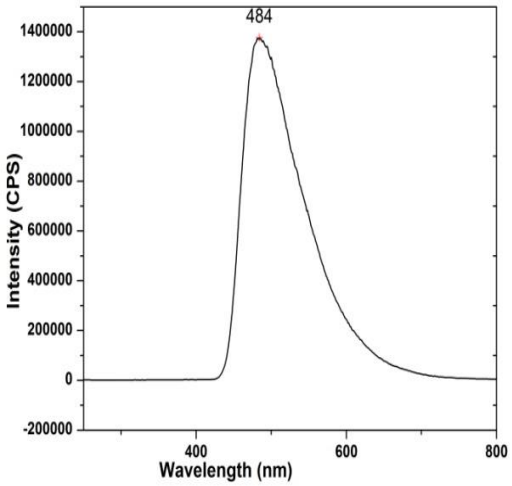

Figure 5: PL spectrum of 2,3-indoloquinoxalin-2-vinyl benzaldehyde

Photoluminescence properties

Fig. 5 displays PL spectra of VB-QUI compound in the ethanol solution. In the PL spectra the compound showed a strong bluish green emission approximately 484nm.

Anti-bacterial activity

The anti-bacterial activity of vinyl benzaldehyde substituted quinoxaline was evaluated using two Gram positive (*Bacillus substilis and Staphylococccus aureus*) and two Gram negative (*Escherichia coli and Pseudomonas auroginosa*) bacteria. Ampicillin was used as positive control. The MIC values of the compound were determined by broth dilution method[17]. Among the tested micro-organism both the compounds the phosphonim ylide and vinyl benzaldehyde capped quinoxaline derivatives exhibited the best antibacterial activity except *Escherichia coli* organism of VB-QUI.

Table 2. MIC (Minimum Inhibitory Concentration) values (in ppm) of phosphonium ylide and VB-QUI compound

Compound	*Bacillus substilis* (MTCC 441)	*Staphylococccus aureus* (MTCC 6908)	*Escherichia Coli* (MTCC 406)	*Pseudomonas auroginosa* (MTCC 2453)
Phosphonium ylide	0.12	0.12	0.12	0.12
Vinyl benzaldehyde containing quinoxaline derivatives	0.12	0.12	0.25	0.12
Ampicillin	0.12	0.12	0.12	0.12

4.CONCLUSION

The vinyl benzaldehyde capped quinoxaline derivative compound was synthesised through Wittig reaction using Phosphonium salt and terephthaldehyde. The resulting compound was characterized by UV, FTIR, ^{1}H, ^{13}C, ^{31}P NMR and GC-MASS spectral studies. The vinyl benzaldehyde introduced into the quinoxaline derivatives in the conjugation unit showed strong bluish green emission at 484nm in the Photoluminescene spectra. Anti-bacterial activities of the synthesized compound were studied using Gram positive and Gram negative bacteria. In comparison with positive control ampicillin, the phosphonium ylide compound and vinyl benzaldehyde containing quinoxaline derivatives show good anti-bacterial activity against tested micro-organism except *Escherichia coli* organism of VB-QUI.

5. ACKNOWLEDGMENT

The authors gratefully acknowledge Muthurangam Govt Arts College (Autonomous) for providing laboratory facilities and acknowlege SIF-VIT and SAIF-IIT Madras for recording spectral analysis.

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