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Research Article
Synthesis, Vibrational and Optical Studies of Indeno Quinoxaline Pyrrolothiazole Derivative Crystal

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Abstract

Background and Objective: The indeno quinoxaline pyrrolothiazole derivative crystal of ethyl 6'-cyano-7'-(p-tolyl)-1',5a,6',7',7a',9a-hexa hydro-3'H-spiro [indeno [1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c] thiazole]-6'-carboxylate (ECPTHSIPTC) was crystallized from slow evaporation method at room temperature. The grown crystal was characterized by the FT-IR, FT-Raman and UV-Visible spectroscopy techniques. The complete vibrational spectra of various functional groups wavenumber assignment for title crystal were interpreted in the present work. **Materials and Methods:** Ethyl cyano acetate, thioproline, benzaldehyde, indeno quinoxaline, ethyl acetate and chloroform were the raw materials used to synthesis the title compound. The synthesized compound was recrystallized from chloroform solution by the slow evaporation method. **Results:** FT-IR and FT-Raman spectrometers were used to record the vibrational spectra of title crystal at room temperature in the wavenumber range 4000- 400 cm^{-1}. The optical property was performed by double beam spectrophotometer in the wavelength range 200–1100 nm. **Conclusion:** The both spectroscopy studies confirmed the various functional groups present in the title compound. The UV-Visible spectroscopy study showed that the grown crystal has high transparency in the entire visible region and the optical band gap was found as 3.25 eV. The ECPTHSIPTC crystal was taking into account to study and investigated in this present work due to the wide-ranging applications in biological and pharmaceutical fields.

Key words: Methyl substituted indeno quinoxaline, FT-IR, FT-Raman, UV-Visible spectroscopy, Vibrational spectra

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Quinoxaline derivatives are biological important class of benzo heterocycles which are found to have anti-bacterial, antiviral and anti-cancer activities against various pathogens[1,2]. Also, the pyrrolothiazoles belong to a class of heterocyclic that possess two fused rings, a pyrrole and a thiazolidine ring, which share a common nitrogen atom and its derivatives play an important role in medicinal chemistry as herbicidal, fungicidal, bacterial, anti-tumor agents[3]. It has wide range of pharmacological applications, such as anti-cancer, anti-viral, anti-bacterial, anti-fungal and anti-inflammatory activities[4,5]. Pyrrolidine derivatives are found to have anti-convulsant, anti-microbial and anti-fungal activities[6]. In addition to the quinoxaline derivatives play an effective role as anti- HIV and anti-depression in pharmaceutical fields which increases the biological activity of the compound[7-10]. Drugs containing a quinoxaline core are under clinical trial for anti-cancer therapeutic purposes[11]. Muthuselvi *et al.*[12-14] have reported similar structures related to title compound. Also, the spectroscopy analyzes for those compounds were already reported[15,16]. The motivation of present work is to synthesis the new indeno quinoxaline derivative drug compounds by substitution of various functional groups such as methyl, Br, Cl, CN and NO_2. The structure modification of indeno quinoxaline compounds provides development of new drugs with medicinal and biological activity in biological pharmaceutical fields. In view of enormous biological importance of indeno quinoxaline fused system, the detailed experimental FT-IR, FT-Raman, UV-Visible spectroscopy techniques were presented here in order to establish its conformation.

MATERIALS AND METHODS

The raw materials used for this crystallization were indeno quinoxaline, thioproline, ethyl cyano (p-tolyl) acrylate, benzaldehyde, ethyl acetate and chloroform which were purchased from Sigma Aldrich Company. The title crystal was crystallized using the slow evaporation technique. In this method, an equimolar amount of 11H-indeno[1, 2-b]quinoxalin-11-one thiazolidine-4-carboxylic acid was dissolved in a round bottom flask containing 20 mL of methanol and refluxed under water bath for 2 min. Then an equimolar amount of propyl (E)-2-cyano-3-(p-tolyl) acrylate was added to the reaction mixture and continued for refluxing until completion of the reaction. The reaction progress was monitored intermittently using thin-layer chromatography (TLC). As evident from the TLC the reaction attained completion after 4 h of continuous refluxing. The precipitated solid was filtered and washed with methanol to obtain the ECPTHSIPTC compound in good yields (94-98%). The colorless block shaped crystals were obtained from the slow evaporation method after re-crystallization with chloroform solution. The FT-IR vibrational spectrum was recorded by using SHIMADZU FT-IR spectrometer in the range 4000-400 cm^{-1}. Also, the FT-Raman spectrum was recorded by using the BRUKER: RFS 27 Raman spectrometer in the wave number range 4000-400 cm^{-1}. These vibrational spectral data was recorded at SAIF, IIT Madras, Chennai. The optical absorbance spectrum of title compound has been recorded at Research Department of Chemistry, V.H.N.S.N. College, Virudhunagar with SHIMADZU-UV1800 double beam spectrometer in the wavelength range 200-1100 nm insteps of 1 nm. The crystal was grown by us at the Research Department of Physics, Devanga Arts College, Aruppukottai and work was completed during 3 months duration of year 2018.

RESULTS AND DISCUSSION

Vibrational analyzes: The vibrational spectra of ECPTHSIPTC crystal were analyzed by the FT-IR and FT-Raman spectroscopy techniques to identify presence of the various functional groups wavenumber assignments. The title compound has C-H, CH_2, CH_3, C = O, C-O, C-N, C = N, C ≡ N, C-S, C-C functional groups. The chemical diagram of ECPTHSIP crystal was shown in Fig. 1. The FT-IR and FT-Raman spectra of title compound were depicted in Fig. 2 and 3, respectively. The detailed wave number assignments for this compound were shown in Table 1.

P-tolyl ring vibrations: In the past years, the vibrational spectra of toluene and its derivatives had been extensively studied and analyzed by Varsanyi[17], Ramalingam *et al.*[18,19] and Wang *et al.*[20]. The benzene ring has C-H stretching vibrations but the toluene has both aromatic C-H and methyl C-H stretching vibrations. The aromatic C-H stretching vibrations normally appeared[21,24] at 3100-3050 cm^{-1}. Anbarasan *et al.*[25]

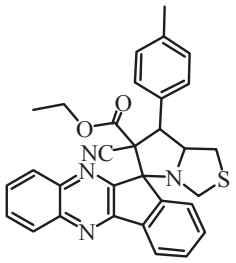

Fig. 1: Molecular structure of ECPTHSIPTC crystal

Table 1: FT-IR and FT-Raman wavenumbers and their assignments for ECPTHSIPTC crystal

FT-IR ($\bar{\upsilon}$ cm^{-1})	FT-Raman ($\bar{\upsilon}$ cm^{-1})	Assignments
3166 (w)	3169 (w)	υ (C-H)$_{Pyrrole}$, υ_{as} (C-H)$_{P\text{-}tolyl}$
3053 (m)	3057 (m)	υ (C-H)$_{Indeno\ quinoxaline}$, υ (C-H)$_{Thiazole}$, υ_s(C-H)$_{P\text{-}tolyl}$
3020 (m)	3015 (m)	υ (C-H) $_{Indeno\ quinoxaline}$, υ (C-H)$_{Thiazole}$, υ_s(C-H)$_{P\text{-}tolyl}$
2983 (m)	2983 (m)	υ_{as} (CH_3) $_{Ethyl\ cyano\ acetate}$, υ_{as} (CH_3) $_{P\text{-}tolyl}$
-	2947 (m)	υ_{as} (CH_2) $_{Pyrrolothiazole}$, υ_{as} (CH_2) $_{Ethyl\ cyano\ acetate}$
2912 (m)	2915 (w)	υ_s (CH_3) $_{Ethyl\ cyano\ acetate}$, υ_s (CH_3) $_{P\text{-}tolyl}$
2867 (w)	2890 (m)	υ_s (CH_2) $_{Ethyl\ cyano\ acetate}$, υ_s (CH_2)$_{Pyrrolothiazole}$
-	2267 (w)	υ (C≡N)$_{Ethyl\ cyano\ acetate}$
-	1786 (w)	υ (C=O) $_{Ethyl\ cyano\ acetate}$
1711(w)	-	υ (C=O) $_{Ethyl\ cyano\ acetate}$
1617 (m)	1609 (w)	υ (C=C) $_{P\text{-}tolyl}$, υ (C=N) $_{Indeno\ quinoxaline,}$ υ (C=C) $_{Indeno\ quinoxaline}$
1546 (s)	1583 (s)	υ (C-C)$_{Pyrrolothiazole,}$ υ (C-C) $_{Indeno\ quinoxaline,}$ υ (C=C) $_{P\text{-}tolyl}$
1514 (m)	1508 (s)	υ (C-C) $_{Indeno\ quinoxaline}$, υ (C-C)$_{Pyrrolothiazole}$
-	1476 (m)	υ (C-C)$_{Pyrrolothiazole}$
1460 (m)	1463 (m)	υ (C-N)$_{Pyrrolothiazole}$, δ_{as}(CH_3) $_{P\text{-}tolyl}$, ρ(CH_2) $_{Ethyl\ cyano\ acetate}$, υ (C-C)$_{Pyrrolothiazole,}$ ρ(CH_2)$_{Pyrrolothiazole}$, δ_{as}(CH_3) $_{Ethyl\ cyano\ acetate}$
-	1394 (s)	δ_s(CH_3) $_{P\text{-}tolyl,}$ δ_s(CH_3) $_{Ethyl\ cyano\ acetate}$, υ (C-C) $_{P\text{-}tolyl}$, υ (C-C)$_{Pyrrolothiazole}$
1370 (m)	1371 (s)	υ (C-C) $_{P\text{-}tolyl,}$ ω (CH_2)$_{Pyrrolothiazole,}$ ω (CH_2) $_{Ethyl\ cyano\ acetate}$, υ (C-C)$_{Pyrrolothiazole}$
1337 (s)	1337 (w)	υ (C-C) $_{P\text{-}tolyl,}$ ω (CH_2)$_{Pyrrolothiazole}$, ω (CH_2) $_{Ethyl\ cyano\ acetate}$
1270 (s)	1263 (w)	β (C-H) $_{Indeno\ quinoxaline}$, t (CH_2)$_{Pyrrolothiazole}$, β (C-H)$_{Pyrrolothiazole}$, β (C-H) $_{P\text{-}tolyl}$, t (CH_2) $_{Ethyl\ cyano\ acetate,}$ υ (C-O) $_{Ethyl\ cyano\ acetate}$
-	1210 (w)	β (C-H) $_{Indeno\ quinoxaline}$, t (CH_2)$_{Pyrrolothiazole}$, β (C-H)$_{Pyrrolothiazole}$, t (CH_2) $_{Ethyl\ cyano\ acetate}$, υ (C -CH_3) $_{P\text{-}tolyl}$
1166 (m)	1174 (m)	β (C-H) $_{Indeno\ quinoxaline}$, β (C-H) $_{P\text{-}tolyl,}$ β (C-H)$_{Pyrrolothiazole}$
1123 (s)	1136 (w)	β (C-H) $_{Indeno\ quinoxaline}$,u (C-N) $_{Indeno\ quinoxaline}$, β (C-H)$_{Pyrrolothiazole}$, υ_{as}(C-O-C), β (C-H) $_{P\text{-}tolyl}$
1101(m)	1100 (w)	β (C-H) $_{Indeno\ quinoxaline}$, β (C-H)$_{Pyrrolothiazole}$, β (C-H) $_{P\text{-}tolyl}$
1070 (m)	1097 (w)	β (C-H) $_{P\text{-}tolyl}$, β (C-H)$_{Pyrrolothiazole}$
1053 (m)	1055 (w)	β (C-H) $_{Indeno\ quinoxaline}$, υ_{as}(C-O-C) $_{Ethyl\ cyano\ acetate}$, τ (CH_3) $_{Ethyl\ cyano\ acetate}$, β (C-H) $_{P\text{-}tolyl}$, τ (CH_3) $_{P\text{-}tolyl,}$ β (C-H)$_{Pyrrolothiazole}$
939 (m)	936 (w)	γ (C-H) $_{Pyrrolothiazole,}$ υ_s(C-O-C) $_{Ethyl\ cyano\ acetate}$, τ (CH_2) $_{Ethyl\ cyano\ acetate}$, τ (CH_3) $_{P\text{-}tolyl}$, Five membered ring breathing mode
878 (m)	849 (w)	γ (C-H) $_{P\text{-}tolyl,}$ γ(C-H) $_{Pyrrolothiazole,}$ γ(C-H) $_{Indeno\ quinoxaline}$
827 (w)	-	γ (C-H) $_{Indeno\ quinoxaline,}$ γ(C-H) $_{P\text{-}tolyl}$
809 (w)	-	γ (C-H) $_{Indeno\ quinoxaline,}$ γ(C-H) $_{P\text{-}tolyl}$
-	781(w)	(Ring breathing mode) $_{P\text{-}tolyl}$
754 (s)	-	γ (C-H) $_{Indeno\ quinoxaline}$
-	748 (w)	τ (CH_2)$_{Pyrrolothiazole,}$ γ (C-H) $_{Indeno\ quinoxaline}$
712 (s)	718 (w)	γ (C-H) $_{Indeno\ quinoxaline}$, υ (C-S)$_{Pyrrolothiazole}$, τ (CH_2)$_{Pyrrolothiazole}$
673 (w)	-	β (C=O) $_{Ethyl\ cyano\ acetate,}$ γ(C-H) $_{Indeno\ quinoxaline,}$ δ(C-C-N) $_{Indeno\ quinoxaline}$,
656 (m)	641 (w)	δ (C-C-N) $_{Indeno\ quinoxaline}$, β(C=O) $_{Ethyl\ cyano\ acetate,}$ υ (C-S)$_{Pyrrolothiazole}$
572 (w)	-	γ (C=O) $_{Ethyl\ cyano\ acetate,}$ δ(C-C-N) $_{Indeno\ quinoxaline}$
516 (m)	522 (w)	δ (C-C-N) $_{Indeno\ quinoxaline}$, γ (C=O) $_{Ethyl\ cyano\ acetate}$

s: Strong, w: Weak, m: Medium, br: Broad, υ: Stretching, υ_s: Sym. stretching, υ_{as}: Anti sym. stretching, δ: Bending, γ: Out-of-plane bending, β: In-plane bending, τ: Rocking, ω: Wagging, ρ: Scissoring, t: Twisting

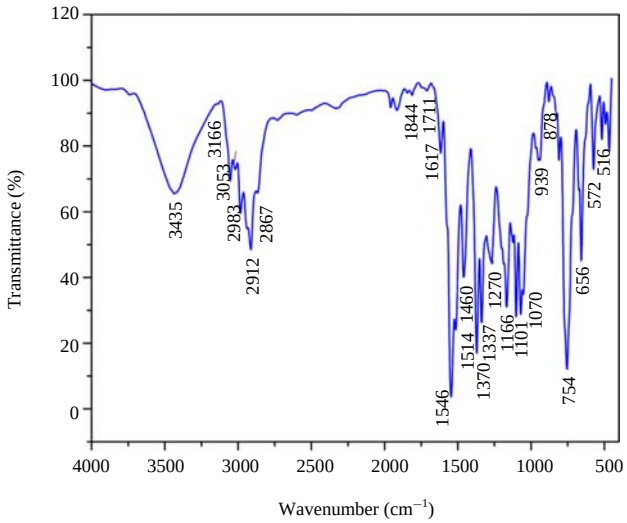

Fig. 2: FT-IR spectrum for ECPTHSIPTC crystal

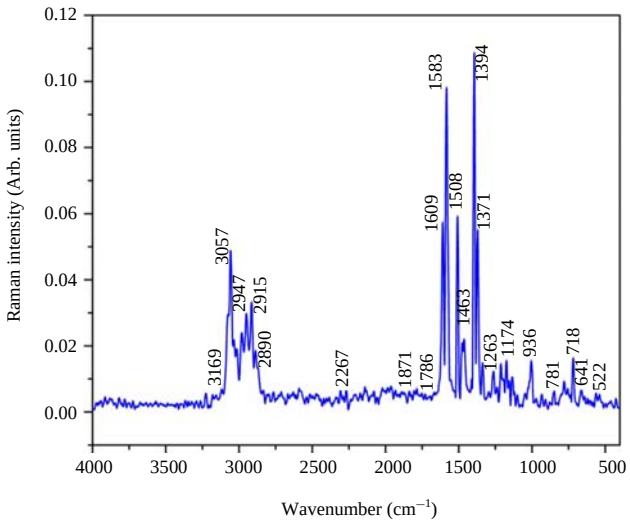

Fig. 3: FT-Raman spectrum for ECPTHSIPTC crystal

observed the bands at 3139 cm^{-1} and at 3080, 3064, 3060, 3047 cm^{-1} for C-H anti-symmetric and symmetric stretching modes, respectively to 4-chlorotoluene molecule. Also, Sebastian *et al.*[26] reported the C-H stretching vibrations by B3LYP method in the range 3121-3055 cm^{-1} for 6-Methyl-1-({[(2E)-2-methyl-3-phenyl-prop-2-en-1-yl]oxy}methyl)-1,2,3,4-tetra-hydro quinazoline-2,4-dione. Accordingly, the peaks appeared at 3166, 3169 cm^{-1} in IR and Raman spectra was assigned to aromatic antisymmetric stretching vibrations whereas the medium peaks at 3053 and 3020 cm^{-1} in FT-IR and the peaks at 3057 and 3015 cm^{-1} in FT-Raman are assigned to aromatic C-H symmetric stretching vibrations for the title molecule. The aromatic C-H in-plane bending modes of benzene and its derivatives were observed in the region 1300-1000 cm^{-1} and out- of- plane bending vibration arises in the range[27] of 1000-750 cm^{-1}. Anbarasan *et al.*[25] reported theoretically calculated value of C-H in-plane bending vibrations by DFT method at 1277-1057 cm^{-1} and also experimentally observed for this mode at 1140 and 1209 cm^{-1} for 4-chlorotoluene molecule. In the present study, the aromatic C-H in-plane bending modes of title compound was identified at 1270, 1166, 1123, 1101, 1070 and 1053 cm^{-1} in IR and at 1263, 1174, 1136, 1100 and 1097 cm^{-1} in Raman spectra, respectively. The calculated frequencies for the C-H out-of-plane bending mode of 4-chlorotoluene molecule were reported by Anbarasan *et al.*[25] at 933-787 cm^{-1}. Also the bands observed at 879, 611 and 606 cm^{-1} in FT-IR were assigned to this mode[21]. Based on the literature data, this mode was attributed at 878, 827 and 809 cm^{-1} in IR and 849 cm^{-1} in Raman spectra, respectively for the title compound. For the benzene ring, the C = C stretching mode was normally occurred in the range 1660-1580 cm^{-1} while the theoretically computed C = C vibrations were seen in the range 1674-1504 cm^{-1} and 1437-1428 cm^{-1} as suggested by Anbarasan *et al.*[25]. The wavenumbers observed by Babu *et al.*[28] in the FT-IR spectrum at 1687, 1612 and 1435 cm^{-1} and in FT-Raman spectrum at 1669, 1614 and 1566 cm^{-1} have been assigned to C = C stretching vibrations of Irinotecans molecule. For the title compound ν(C = C) vibrations was observed at 1617, 1546 (IR), 1609 and 1583 cm^{-1} (Raman). In all substituted benzenes, C-C stretching mode was usually observed in the region[25] 1650-1400 cm^{-1}. For 4-chlorotoluene molecule this mode was assigned by Anbarasan *et al.*[25] at 1605, 1477 and 1390 cm^{-1}. In the present study, this mode was identified at 1370 and 1337 cm^{-1} in IR and at 1394, 1371 and 1337 cm^{-1} in Raman spectra for title compound. The ring breathing mode for para substituted benzene ring is normally observed in the interval[17,25] 840-680 cm^{-1}. For the para-substituted benzene, ring breathing mode was reported by Mary *et al.*[29] at 795 and 782 cm^{-1} theoretically and experimentally at 804 in IR and 792 cm^{-1} Raman spectra, respectively. This mode was observed in Raman spectrum as weak band at 781 cm^{-1} for title compound of p-tolyl ring. The CH_3 stretching vibrations of the p-tolyl group were expected in the range[30,31] of 3050-2900 cm^{-1}. The anti-symmetric stretching modes of the methyl group were calculated by Sebastian *et al.*[26] at 3023, 3011, 2976 and 2971 cm^{-1} and the symmetric modes at 2927 and 2926 cm^{-1}. The bands observed at 2977 and 2925 cm^{-1} in the infrared spectrum and at 3005, 2980, 2966 and 2920 cm^{-1} in the Raman spectrum were assigned as stretching modes of the CH_3 group[26]. The $\nu_{as}(CH_3)$ mode was attributed at 2983 cm^{-1} in both spectra for the title

compound. Also, the $\nu_s(CH_3)$ mode was assigned at 2912 cm^{-1} in IR and at 2915 cm^{-1} in Raman spectra, respectively. The anti-symmetric and symmetric bending vibrations of the methyl group normally appeared in the region[30,31] of 1485-1400 and 1420-1380 cm^{-1}. Sebastian *et al.*[26] reported the bands observed at 1455 cm^{-1} in the IR spectrum and at 1464 cm^{-1} in the Raman spectrum were assigned as CH_3 anti-symmetric bending mode. In the present case, the anti-symmetric and symmetric bending modes of CH_3 group was assigned as a medium bands at 1460 cm^{-1} (IR), 1463 cm^{-1} (Raman) and as a strong band at 1394 cm^{-1} (Raman), respectively. The CH_3 rocking wavenumber normally occurred in the region[32] of 1050-790 cm^{-1}. Sebastian *et al.*[26] predicted the rocking mode of methyl group at 1045, 1037, 1024 and 992 cm^{-1} by B3LYP method and were experimentally observed at 1048 cm^{-1} in the IR spectrum and at 1027 cm^{-1} in the Raman spectrum. For the title compound, this mode was assigned as medium bands at 1053 and 939 cm^{-1} in the IR spectrum and as weak bands at 1055 and 936 cm^{-1} in Raman spectrum, respectively. The C-CH_3 stretching mode in a number of methyl benzenes was observed at around[25] 1200 cm^{-1}. The band observed at 1210 cm^{-1} in Raman spectrum was assigned to the C-CH_3 stretching mode of title compound.

Pyrrolothiazole ring vibrations: The wavenumber assignments of pyrrolothiazole ring were examined on the basis of the vibrations of substituted cyclopentane five membered ring (CH_2, C-C and C-H), C-N and C-S modes. Normally, the C-H stretching bands for hetero aromatics such as furans, pyrroles and thiophenes occurred in the region of 3180-3090 and 3120-3060 cm^{-1}, respectively[31,33]. Magdaline and Chithambarathanu[34] computed the C-H stretch for 2-thiophene carboxylic acid compound in the range 3117-3080 cm^{-1} by B3LYP method. In the present study, C-H stretch for pyrrole ring was assigned as weak bands at 3166 and 3169 cm^{-1} in both spectra. For thiazole ring this mode was attributed at 3053, 3020 and at 3057, 3015 cm^{-1} in IR and Raman spectra, respectively. The C-H in-plane bending and out-of plane bending wave numbers appeared in the range 1300-1000 and 1000-750 cm^{-1}, respectively[35]. Also, Magdaline *et al.*[34] reported bands at 1283, 1105 and 1041 in FT-IR and at 1114 cm^{-1} in FT-Raman were described to C-H in plane bending mode. The C-H out-of -plane bending vibrations were assigned to the medium bands observed at 910 and 858 cm^{-1} in FT-IR and to a weak band at 862 cm^{-1} in FT-Raman for the 2-thiophene carboxylic acid[36]. The β(C-H) mode was attributed on the basis of literature data at 1270, 1166, 1123 , 1101, 1070 and 1053 cm^{-1} in IR and at1263, 1210, 1174, 1136, 1100, 1097 and 1055 cm^{-1} in Raman spectra, respectively for the title compound. Moreover, the γ(C-H) mode was assigned as medium bands at 878 and 849 cm^{-1} in both spectra, respectively. Rao[33] observed band at 1425 cm^{-1} which could be assigned to the C-N stretching vibration of 1,2,4 triazole ring and the calculated value of this comment mode was found at 1440 cm^{-1}. In the current study, observed medium bands at 1460 cm^{-1} and 1463 cm^{-1} in both spectra was assigned to C-N stretching modes of pyrrolothiazole ring of present compound. The C-C stretching vibrations occurred generally in the region of 1600-1350 cm^{-1}. But for the five membered heterocyclic rings, position and intensity of the bands were more sensitive than the corresponding bands of benzene to changes in the substituent. So that wide wave number variation can occur. For 2-substituted thiophenes, four bands were observed at 1532-1514, 1454-1430 and 1367-1347 cm^{-1} in the region[33]. Rao[33] observed in the FT -IR spectrum at 1528 and 1352 cm^{-1} were assigned to C-C stretching vibrations. Magdaline *et al.*[34] theoretically predicted the C-C stretching vibrations at 1526, 1410 and 1356 cm^{-1} by DET/B3LYP method. In the present study, the stretching of the C-C bonds in the pyrrolothiazole ring was identified at 1546, 1514 and 1370 in IR and at 1583, 1508, 1394 and 1371 cm^{-1} in Raman spectra, respectively which are good agreement with the reported spectral data[33,34]. Coats[36] and Nogueira *et al.*[37] observed C-S stretching modes between 710 and 687 cm^{-1} and at 839 and 608 cm^{-1}, respectively. Magdaline *et al.*[34] observed theoretically the stretching of C-S bond in the thiophene ring at 852 and 649 cm^{-1} but only one peak was observed at 647/637 cm^{-1} in the experimental FT-IR/FT-Raman spectra. For the title compound, a strong band occurs at 712 and 656 cm^{-1} in IR and at 718 and 641 cm^{-1} in Raman spectra are assigned to C-S stretching mode of thiazole ring. The small wavenumber changes for this mode resulting from the mixing of two rings and substituent group. The CH_2 antisymmetric stretching vibrations were generally observed in the region 3000-2900 cm^{-1}, while the CH_2 symmetric stretch appeared between[38,39] 2900 and 2800 cm^{-1}. Babu *et al.*[28] observed the CH_2 symmetric stretching vibration at 2943 cm^{-1} in FT-IR spectrum for Irinotecan molecule.

The calculated anti-symmetric and symmetric CH_2 stretching vibrations of the Irinotecan molecule were seen in the range 3008-2951 cm^{-1} and 2948-2903 cm^{-1} respectively. In the present study, anti-symmetric stretching mode of CH_2 is identified at 2947 cm^{-1} in Raman spectrum only. Also, the symmetric stretching mode of the CH_2 group

of five membered rings was assigned at 2867 cm^{-1} in IR and 2890 cm^{-1} in Raman spectra respectively for the title compound. The general wavenumber assignment order for the CH_2 bending modes were identified from the literatures is given as follows: CH_2scis> CH_2wag >CH_2 twist > CH_2 rock[28]. Babu *et al.*[28] reported computed values of CH_2 scissoring modes fall in the range 1482-1437 cm^{-1} and also observed FT-IR and FT-Raman bands at 1435 and 1449 cm^{-1}, respectively for Irinotecan molecule. It was attributed as medium bands at 1460 cm^{-1} and 1463 cm^{-1} in both spectra respectively in the present study. The CH_2 wagging and twisting vibrations were observed in the region[31] 1390-1180 cm^{-1}. The CH_2 wagging and twisting modes were already assigned by Babu *et al.*[28] at 1373, 1323, 1233 and 1222 cm^{-1} (B3LYP), 1373 and 1329 cm^{-1} (IR), 1376, 1236 and 1223 cm^{-1} (Raman), respectively. The absorption bands at 1370, 1337 and 1270 cm^{-1} (IR), 1371, 1337, 1263 and 1210 cm^{-1} (Raman) on pyrrolothiazole ring of title compound have been interpreted as due to CH_2 wagging and twisting vibrations respectively. Due to the crystallinity, the rocking vibration of cyclopentane group was splitting which appears[31] at 730 and 720 cm^{-1}. Babu *et al.*[28] calculated the rocking modes of CH_2 group by B3LYP method at 968 and 914 cm^{-1}. In this present study, the bands present in Raman spectrum at 748 and 718 cm^{-1} was assigned to the rocking modes of CH_2 group of pyrrolothiazole ring. The ring breathing mode for pyrrolidine five membered ring appeared[31] at 902 cm^{-1}. This mode was acknowledged at 939 cm^{-1} in IR spectrum and at 936 cm^{-1} in Raman spectra for pyrrolothiazole ring in the present study.

Ethyl cyano acetate group vibrations: The IR region of 2270-2210 cm^{-1} was assigned normally to the characteristic C≡N stretching mode[40]. The cyano stretching vibration was assigned by Zeng *et al.*[41] at 2233 cm^{-1} for 3,5-bis(3,4-dicyanophenoxy) aniline. In this study, this mode was observed at 2267 cm^{-1} in Raman spectrum only. In aromatic rings, the appearance of strong bands in IR and weak bands in Raman spectra around 1800-1650 cm^{-1} was most salient feature of the presence of carbonyl group and was due to the C=O stretching modes [42]. Inkaya *et al.*[43] theoretically reported at 1851 cm^{-1} and at 1745 cm^{-1} by HF and B3LYP methods for this mode. Also, C=O stretching mode was experimentally assigned at 1730 cm^{-1} in FT-IR spectrum[43]. For the title compound, C=O stretching mode is attributed as weak bands at 1711 and 1786 cm^{-1} in both spectra. The in-plane and out-of- plane deformation vibration of C=O group was appear in the regions 680-630 $cm^{-1}$and 580-570 cm^{-1}, respectively[44]. In our case, weak bands observed at 673 and 572 cm^{-1} in IR are assigned to β (C = O) and γ (C = O) modes, respectively. The carboxyl group have strong band in the region 1395-1200 cm^{-1} for C-O stretching mode[20]. This mode was recently reported by Sert *et al.*[40] by B3LYP method at 1267 cm^{-1} and experimentally at 1259 cm^{-1} in IR spectrum for ethyl (2E)-2-cyano-3-(4-methoxyphenyl)-acrylate molecule. For the title compound, C-O stretching mode was attributed as strong band at 1270 cm^{-1} in FT-IR and as a weak band at 1263 cm^{-1} in Raman spectra respectively. The C-O-C anti-symmetric and symmetric stretching vibrations were identified by Inkaya *et al.*[43] at 1083 and 945 cm^{-1}, respectively. Bhagyasree *et al.*[45] reported C-O-C stretching modes at 1144, 1063 (IR), 1146 and 1066 cm^{-1} (Raman) and at 1153 cm^{-1} theoretically. For the title compound as expected the anti-symmetric C-O-C stretching vibration was assigned at 1123 and 1053 cm^{-1} (IR), 1136 and 1055 cm^{-1} (Raman) and the symmetric stretching mode at 939 and 936 cm^{-1} in both spectra. The anti-symmetric stretch, symmetric stretch and scissoring vibrations of CH_2 group appeared in the regions 2945±45, 2885±45 and 1445±35 cm^{-1}, respectively[31]. Joseph *et al.*[46] predicted the modes for $\nu_{as}(CH_2)$ at 3029, 2974 and $\nu_s(CH_2)$ at 2950, 2884 cm^{-1}, respectively by B3LYP methods. The bands observed at 3035 and 2868 cm^{-1} (IR) and 2945 and 2882 cm^{-1} (Raman) are assigned to CH_2 stretching mode[46]. In the present study, $\nu_{as}(CH_2)$ mode was assigned at 2947 cm^{-1} (Raman) and ν_s (CH_2) is assigned at 2867 cm^{-1} (IR), 2890 cm^{-1} (Raman), respectively for the title compound. The scissoring vibration of CH_2 group was identified as medium bands at 1460 and 1463 cm^{-1} in both spectra in the present study. The wagging and twisting vibrations of CH_2 group were observed in the region[43,31] 1390-1180 cm^{-1}. Inkaya *et al.*[43] reported the CH_2 wagging and twisting modes of ethyl cyano acetate group at 1373, 1323, 1233, 1222 (B3LYP), 1373, 1329 (IR), 1376, 1236 and 1223 cm^{-1} (Raman), respectively. The bands observed at 1370, 1337 and 1270 cm^{-1} in IR and at 1371, 1337, 1263 and 1210 cm^{-1} in Raman spectra were assigned to the wagging and twisting modes of CH_2 group for the title compound. Also, the bands calculated at 968 and 914 cm^{-1} were assigned as the rocking modes[43] of CH_2. In the present study, this mode was identified as a weak intensity bands at 939 and 936 cm^{-1} in IR and Raman spectra, respectively. The stretching vibrations of the CH_3 group were expected in the range[26,31] of 3050-2900 cm^{-1}. Sebastian *et al.*[26] calculated the anti-symmetric stretching modes of the methyl

group at 3023, 3011, 2976 and 2971 cm^{-1} and the symmetric modes at 2927 and 2926 cm^{-1} by B3LYP method respectively. The bands observed at 2977 and 2925 cm^{-1} in the Infrared spectrum and at 3005, 2980, 2966 and 2920 cm^{-1} in the Raman spectrum were assigned as stretching modes of the CH_3 group[26]. In the present case, the antisymmetric and symmetric stretching modes of the CH_3 group was attributed at 2983 cm^{-1} (IR), 2983 cm^{-1} (Raman) and at 2912 cm^{-1} (IR), 2915 cm^{-1} (Raman), respectively. The anti-symmetric and symmetric bending vibrations of the methyl group normally perform in the region[45,46] of 1485-1400 and 1420-1380 cm^{-1}. Bhagyasree *et al.*[45] observed the bands at 1455 cm^{-1} in the IR spectrum and at 1464 cm^{-1} in the Raman spectrum were assigned as CH_3 bending modes. The anti-symmetric bending modes of CH_3 group was assigned as a medium bands at 1460 cm^{-1} in the IR spectrum and at 1463 cm^{-1} in the Raman spectrum respectively for the title compound. A strong band observed in Raman spectrum at 1394 cm^{-1} was assigned to the symmetric bending mode of CH_3 group in the present study. Joseph *et al.*[46] calculated the rocking modes of methyl group by B3LYP method to be at 1045, 1037, 1024 and 992 cm^{-1} and were observed at 1048 cm^{-1} in the IR spectrum and at 1027 cm^{-1} in the Raman spectrum. This mode was presented at 1053 and 1055 cm^{-1} in both spectra for the title compound.

Indeno quinoxaline vibrations: The C-H stretching, C-H in-plane bending, C-H out-of-plane bending, C-C, C = C, C-N and C = N stretching vibrations were observed in indeno quinoxaline fused rings. The C-H stretching vibrations of hetro aromatic ring showed the characteristic bands in the region of 3100-3000 cm^{-1} which were not affected during appreciably by the nature of the substituent[47]. Subramanian *et al.*[48] reported the C-H stretching vibrations of quinoline ring in B3LYP method at 3062, 3052, 3038, 3029 and 3026 cm^{-1}. In the present study, the C–H stretching vibration for indeno quinoxaline ring was observed at 3053, 3020 cm^{-1} in FT-IR and at 3057 and 3015 cm^{-1} in FT-Raman spectra for title compound, respectively. The in-plane and out-of-plane aromatic C-H deformation vibrations befall in the region[47] 1300-1000 cm^{-1}. Babu *et al.*[28] predicted C-H in-plane bending vibrations by B3LYP at 1406, 1394, 1344,1308, 1293, 1278, 1259 , 1231, 1164, 1128 and 1117 cm^{-1}. For the title compound, β(C-H) mode was identified at 1270, 1166, 1123, 1101, 1053 in IR and at 1263, 1210,1174, 1136, 1100 and 1055 cm^{-1} in Raman spectra, respectively. The out-of-plane bending mode of C-H group was seen in the region[31] 900-667 cm^{-1}. Li and Zhang[49] observed the out- of -plane bending mode of C-H group at 816 cm^{-1} and also calculated at 960, 934, 835 and 803 cm^{-1} by DFT/B3LYPmethod. The vibrations due to γ (C-H) of title compound were assigned at 878, 827, 809, 754 and 673 cm^{-1} in IR spectrum. In Raman spectrum this mode is observed at 849 and 748 cm^{-1}.The carbon-carbon stretching vibration of benzene ring appeared in the region[31] 1625-1430 cm^{-1}. This mode has been observed by Rofouei *et al.*[50] at 1589 and 1516 cm^{-1} in FT-IR and at 1596 and 1541 cm^{-1} in FT-Raman spectra. For the title compound, the wave numbers were observed in IR spectrum at 1546 and 1514 cm^{-1} and at 1583 and 1508 cm^{-1} in Raman spectrum was assigned to C-C stretching modes. The C=C stretching vibrations arrived on range[31] of 1674-1504 cm^{-1}. In the present study it was observed as medium bands at 1617 cm^{-1} in IR and at 1609 cm^{-1} in Raman spectra, respectively for title compound. The appearance of strong absorption band in the region 1630-1600 cm^{-1} corresponds to υ C=N stretching frequency. The bands present in the range 1150-1130 cm^{-1} were assigned due to ν(C-N) vibration[51,52]. Al-Jibouri *et al.*[53] reported υ (C=N) mode at 1610 cm^{-1} for amide pyrazine compound. Gulluoglu *et al.*[51] reported the C-N stretching mode at 1135 cm^{-1} for piperidine molecule. Based on the literature data, the C=N and C-N stretching modes of indeno quinoxaline ring were attributed at 1617, 1609 cm^{-1} and at 1123, 1136 cm^{-1} in both spectra respectively in the present work. Generally the strong band in the region nearly around 500 cm^{-1} was due to C-C-N group deformation mode [54]. For piperazine compound, Gunasekaren *et al.*[55] reported the deformation mode for C-C-N group 669, 612, 601 and 565 cm^{-1}. The medium bands observed at 673, 572 and 516 cm^{-1} in IR and at 522 cm^{-1} in Raman spectra respectively was attribute to C-C-N deformation mode in the present investigation.

Optical analysis: The absorbance spectrum of title crystal was recorded using SHIMADZU-UV1800 double beam spectrometer in the wavelength range 300-1100 nm which was shown in Fig. 4. It was showed that the crystal had the maximum absorbance peaks at 271, 351 and 373 nm. The lower cut-off wavelength was found to be at 315 and 388 nm. The title crystal has 100% transmittance in the entire visible region which makes usefulness of this material in optical application. The Tauc's relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ was used to determine the energy gap value E_g of title crystal by plotting $(\alpha h\nu)^2$ vs. photon energy. The linear portion of $(\alpha h\nu)^2$

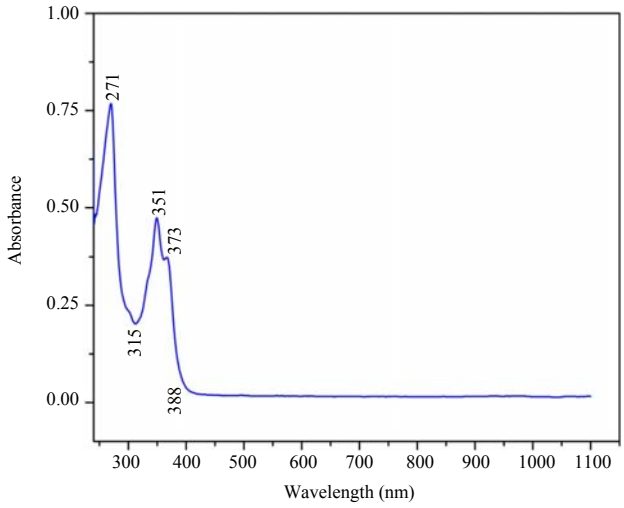

Fig. 4: Absorbance spectrum for ECPTHSIPTC crystal

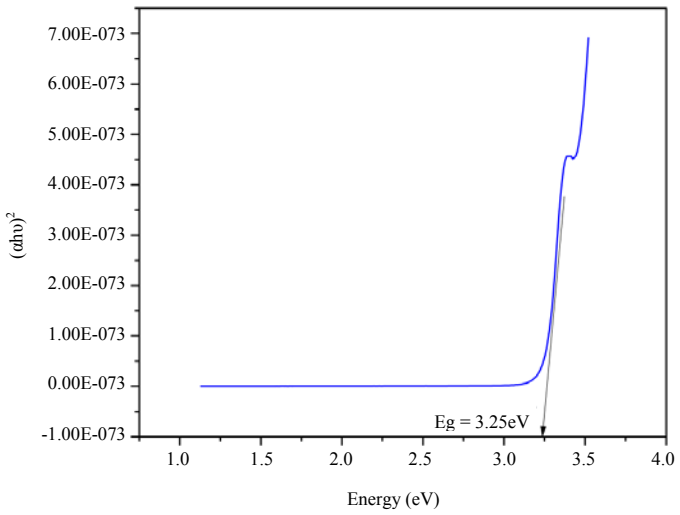

Fig. 5: Optical band gap for ECPTHSIPTC crystal

was extrapolated to the photon energy axis gave the energy gap values of title crystal. From the Fig. 5, the energy gap value was determined as 3.25 eV for title crystal.

CONCLUSION

The block shaped single crystal of ECPTHSIPTC was synthesized and crystallized using the slow evaporation method successfully at room temperature. It was analyzed through the spectroscopic techniques such as FT-IR, FT-Raman and UV-Visible spectroscopy. The wavenumber assignment of various functional groups present in the molecule was interpreted and which has been seen to be in good agreement with the corresponding results in the literature. The optical band gap, maximum absorbance and lower cut-off wavelength of title crystal were determined using UV-Visible spectroscopy analyzes.

SIGNIFICANCE STATEMENT

This study discovers the methyl substituted indeno quinoxaline pyrrolothiazole derivative crystal that can be play considerable roles in the biological and medicinal fields. Also, modified crystal structure of indeno quinoxaline moiety by

fusions of various compounds provides the development of biological diversities and future drug discovery. This study will help the researcher to develop and synthesis of new heterocycles with medicinal and biological activity for research in organic and medicinal chemistry. Thus a new attempt was made on the growth of indeno quinoxaline derivative crystal by substitution of methyl and ethyl cyano acetate groups which are analyzed by spectroscopic approach may be arrived at.

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