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Spectroscopic Investigation of 7'-Nitro-6'-phenyl-1',6',7',7a'-tetrahydro-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c][1,3]thiazole] Crystal

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Abstract

Background and Objective: The crystal structure of 7'-Nitro-6'-phenyl-1',6',7',7a'-tetrahydro-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c][1,3]thiazole](NPTSIPT) crystal was recently reported by authors group. The main objective of the present study was to analyze the vibrational spectra of title compound. So it was crystallized by slow evaporation method and characterized by the single crystal XRD, FT-IR, FT-Raman and UV-Visible spectroscopy analysis. **Materials and Methods:** The raw materials used for this crystallization are benzene-1,2-diamine, 1H-indene-1,2,3-trione, thiazolidine-4-carboxylic acid, methanol, chloroform and trans-β-nitro styrene which were purchased from Sigma Aldrich Company through local scientific companies in Tamil Nadu, India. The crystals were obtained by the slow evaporation method using the chloroform as a solvent. **Results:** Using X-ray diffractometer, the unit cell parameters and space group of title crystal was obtained. The FT-IR and FT-Raman spectroscopic techniques have been used to identify the vibrational modes of compound. The optical property was analyzed by UV-Visible spectroscopy. **Conclusion:** The single crystal XRD study revealed that the title compound belongs to triclinic crystal system with centro symmetric space group $P\bar{1}$. The vibrational spectra have been investigated by FT-IR, FT-Raman spectroscopic techniques to elucidate the various functional groups present in the molecule. The optical property was analyzed by UV-Visible spectroscopy which showed that the grown crystal has high transparency in the entire visible region. Due to the wide variety of biomedical applications in biological and pharmaceutical fields, the modified quinoxaline structure of title compound is considered for study in this present research.

Key words: Indenoquinoxaline derivatives, FT-IR, FT-Raman, UV-Visible spectroscopy, single crystal XRD

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

INTRODUCTION

The important benzo hetero cyclic compound of quinoxaline and its derivatives were found in pharmaceutical applications as anticancer, antiviral and antibacterial agents^{1,2}. Also, the antimetabolism properties of indenoquinoxaline derivatives possess applications in dyes and synthesis of organic semiconductors^{3,4}. The naturally occurring substances of spiropyrrolidine derivatives were characterized by highly pronounced biological properties which act as potential antileukemic, anticonvulsant and anti-inflammatory agents⁵⁻⁹. The bioactivity of S,N-thiazoles and their derivatives were reported to exhibit diverse biological activities as antituberculous, bacteriostatic and fungi static agents^{10,11}. These heterocyclic compounds have been specifically identified with great synthesis effort in chemistry and studied widely for their different pharmaceutical and biological activities. Quinoxaline derivatives were an important class of hetero cycles which had been investigated in the recent years to discover new compounds owing to their both biological properties and pharmaceutical applications^{6,11}. Due to the potential medicinal properties of these compounds, attempt was made to synthesis quinoxaline fused ring derivatives which led to the title compound. Single crystal XRD, FT-IR, FT-Raman and UV-Visible spectroscopy techniques have been employed in order to establish its molecular structure and associated functional groups.

MATERIALS AND METHODS

The raw materials used for this crystallization are benzene-1,2-diamine, 1H-indene-1,2,3-trione, thiazolidine-4-carboxylic acid, methanol, chloroform and trans- β -nitro styrene which were purchased from Sigma Aldrich Company through local scientific companies in Tamil Nadu, India. Initially an equimolar amount of benzene-1,2-diamine, 1H-indene-1,2,3-trione and thiazolidine-4-carboxylic acid were dissolved in a round bottom flask containing 20 mL of methanol and refluxed in a water bath for 15 min. Then equimolar amount of substituted trans- β -nitro styrene was added to the reaction mixture and continued for refluxing until completion of the reaction. The reaction progress was monitored intermittently using TLC. As evident from the Thin Layer Chromatography (TLC), the reaction attained completion after 5 h of continuous refluxing. The precipitated solid was filtered and washed with methanol to obtain the title

compound in good yields (92-96%). Colorless block shaped crystals were obtained from slow evaporation method by recrystallization of synthesized compound with chloroform solution. The Bruker SMART APEX CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used to carry out the unit cell dimensions and space group. This data was taken from CSIR-Indian Institute of Chemical Technology, Hyderabad. The FT-IR vibrational spectrum was recorded using PERKIN ELMER SPECTRUM1FT-IR spectrometer in the range 4000-400 cm^{-1} . The FT-Raman spectrum was also recorded by BRUKER: RFS 27 Raman spectrometer in the wavenumber range 4000-400 cm^{-1} . These vibrational spectra recorded at SAIF, IIT Madras, Chennai. The optical absorbance spectrum has been recorded at V.H.N.S.N. College, Virudhunagar, with SHIMADZU-UV1800 double beam spectrometer in the wavelength range 200-1100 nm instead of 1 nm. The research work reported in this article was completed within 3 months.

RESULTS AND DISCUSSION

Single crystal XRD: Using Bruker SMART APEX CCD diffractometer, the unit cell parameters and space group of title crystal was obtained. Initially, these were checked with the Cambridge Structural Database (CSD) for confirmation. The report showed that the grown crystal was a new one. The preliminary crystallographic data of NPTS IPT crystal has been given in Table 1. From the recent X-ray study of the title crystal¹², its molecular structure was shown in Fig. 1.

Vibrational analyzes: The FT-IR and FT-Raman spectroscopic techniques have been used as an effective tool to identify the vibrational modes as well as the bonding and structural features of complex organic molecular compound. In this regard, the vibrational spectra of NPTS IPT crystal were analyzed using the FT-IR and FT-Raman spectroscopy techniques. The title compound has ring groups such as phenyl, pyrrolothiazole, Indenoquinoxaline and nitro groups which were associated with functional groups such as C-H, CH₂, C-N, C=N, C-S, C-C, C=C, NO₂ and C-NO₂. The FT-IR and FT-Raman spectra of title compound were depicted in Fig. 2 and 3, respectively. The detailed wavenumber assignment for various functional groups was shown in Table 2.

Mono substituted benzene ring vibrations: The presence of one or more aromatic rings in a structure having their C-H

Table 1: Preliminary crystallographic data of NPTS IPT crystal

Parameters	Details from X-ray study ¹²
Compound name	7'-Nitro-6'-phenyl-1',6',7',7a'-tetrahydro-spiro[indeno[1,2-b]quinoxaline-11,5'-pyrrolo[1,2-c][1,3]thiazole] (NPTS IPT)
Empirical formula	C ₂₆ H ₂₀ N ₄ O ₂ S
Molecular formula weight	452.52
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	a = 9.6591 (9) Å b = 10.5962 (11) Å c = 10.8001 (9) Å α = 80.389 (13)° β = 85.626 (15)° γ = 85.030 (14)°
Volume	1083.62 (18) Å ³
Density	1.387 Mg m ⁻³
Z	2

Table 2: FT-IR and FT-Raman wavenumbers and their assignments for NPTS IPT crystal

FT-IR ($\bar{\nu}$ cm ⁻¹)	FT-Raman ($\bar{\nu}$ cm ⁻¹)	Assignments
3164 (w)	-	ν (C-H) _{Pyrrolothiazole}
3052 (m)	3061 (m)	ν (C-H) _{Phenyl} ν (C-H) _{Pyrrolothiazole} ν (C-H) _{Indenoquinoxaline}
2970 (m)	2975 (m)	ν (C-H) _{Phenyl}
2921 (m)	2931 (m)	ν_{as} (CH ₂) _{Pyrrolothiazole}
2866 (m)	2866 (m)	ν_s (CH ₂) _{Pyrrolothiazole}
1603 (w)	1609 (m)	ν (C=C) _{Phenyl} ν (C=N) _{Indenoquinoxaline} ν (C=C) _{Indenoquinoxaline}
-	1582 (s)	ν (C=C) _{Phenyl} ν (C-C) _{Pyrrolothiazole} ν_{as} (NO ₂) _{Nitro group}
1545 (s)	-	ν (C=C) _{Phenyl} ν (C-C) _{Pyrrolothiazole} ν (C-NO ₂) _{Nitro group} ν (C=C) _{Indenoquinoxaline}
1503 (s)	1508 (m)	ν (C=C) _{Phenyl} ν (C-C) _{Pyrrolothiazole} ν (C-C) _{Indenoquinoxaline}
1455 (s)	1468 (m)	ν (C-N) _{Pyrrolothiazole} ν (C-C) _{Indenoquinoxaline} ν (C=C) _{Phenyl} ν (C-C) _{Pyrrolothiazole} ρ (CH ₂) _{Pyrrolothiazole}
-	1396 (s)	ν (C-C) _{Phenyl}
1373 (s)	1373 (m)	ν (C-C) _{Phenyl} ν (C-C) _{Pyrrolothiazole} ω (CH ₂) _{Pyrrolothiazole} ν_s (NO ₂) _{Nitro group}
1337 (s)	1338 (w)	ν (C-C) _{Phenyl} ω (CH ₂) _{Pyrrolothiazole}
1274 (m)	1260 (w)	β (C-H) _{Phenyl} β (C-H) _{Pyrrolothiazole} β (C-H) _{Indenoquinoxaline} τ (CH ₂) _{Pyrrolothiazole}
1202 (m)	1221 (w)	β (C-H) _{Indenoquinoxaline} β (C-H) _{Pyrrolothiazole}
1167 (s)	1179 (m)	β (C-H) _{Indenoquinoxaline} β (C-H) _{Pyrrolothiazole} β (C-H) _{Phenyl}
1128 (w)	1129 (w)	β (C-H) _{Indenoquinoxaline} β (C-H) _{Pyrrolothiazole} β (C-H) _{Phenyl} ν (C-N) _{Indenoquinoxaline}
1101 (m)	-	β (C-H) _{Pyrrolothiazole} β (C-H) _{Phenyl} β (C-H) _{Indenoquinoxaline}
-	1074 (w)	β (C-H) _{Pyrrolothiazole} β (C-H) _{Phenyl} β (C-H) _{Indenoquinoxaline}
1057 (s)	-	β (C-H) _{Pyrrolothiazole} β (C-H) _{Phenyl} β (C-H) _{Indenoquinoxaline}
-	1004 (w)	β (C-H) _{Pyrrolothiazole} β (C-H) _{Phenyl} β (C-H) _{Indenoquinoxaline}
959 (w)	976 (w)	γ (C-H) _{Phenyl} γ (C-H) _{Indenoquinoxaline}
939 (w)	946 (w)	γ (C-H) _{Phenyl} Five membered ring breathing mode
874 (w)	-	γ (C-H) _{Phenyl} γ (C-H) _{Pyrrolothiazole} γ (C-H) _{Indenoquinoxaline}
843 (w)	839 (w)	γ (C-H) _{Phenyl} γ (C-H) _{Indenoquinoxaline} γ (C-H) _{Pyrrolothiazole} ρ (NO ₂) _{Nitro group}
769 (m)	785 (w)	γ (C-H) _{Phenyl} γ (C-H) _{Indenoquinoxaline} ν (C-S) _{Pyrrolothiazole} ω (NO ₂) _{Nitro group}
740 (s)	754 (w)	γ (C-H) _{Phenyl} γ (C-H) _{Indenoquinoxaline} τ (CH ₂) _{Pyrrolothiazole}
-	717 (w)	τ (CH ₂) _{Pyrrolothiazole}
698 (w)	692 (w)	γ (C-H) _{Indenoquinoxaline} ν (C-S) _{Pyrrolothiazole}
667 (w)	651 (w)	γ (C-H) _{Indenoquinoxaline} δ (C-C-N) _{Indenoquinoxaline}
630 (w)	-	β (C-C-C) _{Phenyl} δ (C-C-N) _{Indenoquinoxaline}
568 (w)	-	γ (C-C-C) _{Phenyl} δ (C-C-N) _{Indenoquinoxaline}
538 (w)	548 (w)	δ (C-C-N) _{Indenoquinoxaline} τ (NO ₂) _{Nitro group}
509 (m)	-	γ (C-C-C) _{Phenyl}
493 (w)	-	γ (C-C-C) _{Phenyl}

s: Strong, w: Weak, m: Medium, ν : Stretching, ν_s : Symmetric stretching, ν_{as} : Anti symmetric stretching, δ : Bending, γ : Out-of-plane bending, β : In-plane bending, τ : Rocking, ω : Wagging, ρ : scissoring, τ : Twisting

stretching vibrations occur above 3000 cm⁻¹ and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretch¹³. Panicker *et al.*¹⁴ reported C-H stretching mode in the range 3037-2999 cm⁻¹ by

HF/6-31G* method and the bands observed experimentally at 3088, 3052, 3029 and 2985 cm⁻¹ in the IR spectrum and at 3099, 3068, 3033 and 2987 cm⁻¹ in the Raman spectrum for 2-Phenoxy methyl benzothiazole molecule. In the present

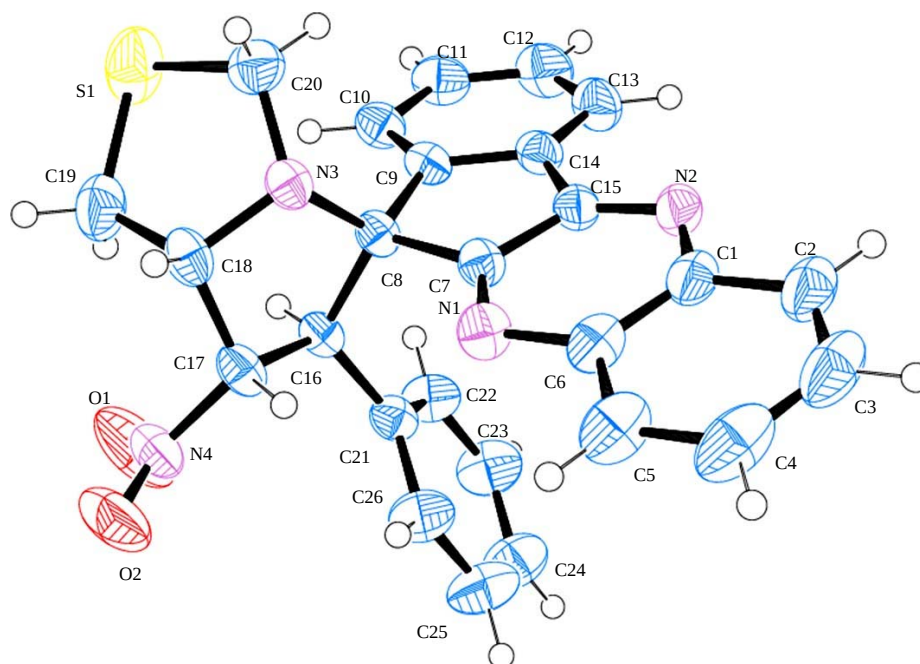


Fig. 1: Molecular structure of NPTS IPT crystal¹²

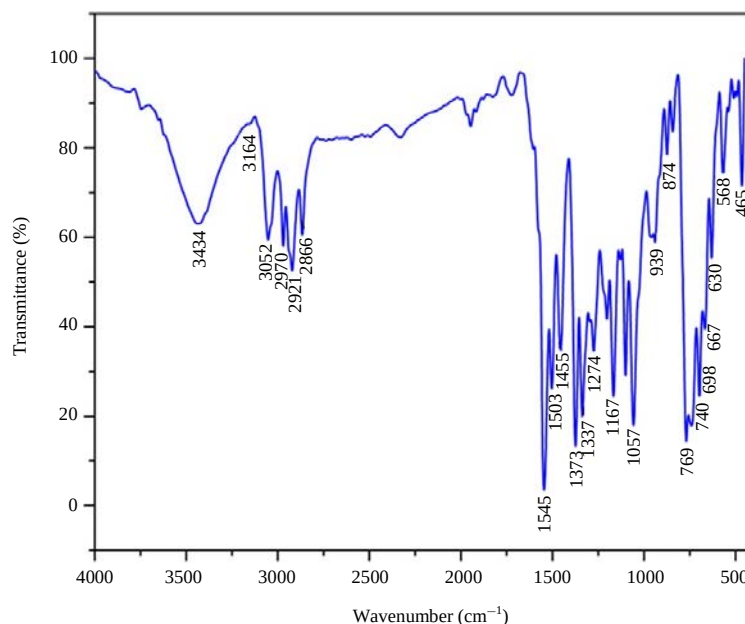


Fig. 2: FT-IR spectrum for NPTS IPT crystal

study, this mode was observed as medium intensity bands at 3052, 2970 cm^{-1} in IR and at 3061, 2975 cm^{-1} in Raman spectra for the title compound. Varsanyi¹⁵ have identified the C-H in-plane bending mode of the benzene ring at 1261, 1188, 1133, 1022 cm^{-1} in the IR spectrum and the wavenumbers at 1195, 1060, 1030 cm^{-1} in the Raman spectrum. The theoretically reported values for the same mode were 1290,

1188, 1176, 1067 and 1026 cm^{-1} . For the title compound, this mode was identified due to the wavenumbers at 1274, 1167, 1128, 1101, 1057 cm^{-1} in the IR spectrum and at 1260, 1179, 1129, 1074 cm^{-1} in Raman spectrum, respectively.

The C-H out-of-plane deformations were observed between 1000 and 700 cm^{-1} ¹⁴. The theoretically calculated values were identified at the wavenumbers 988, 960, 911, 828,

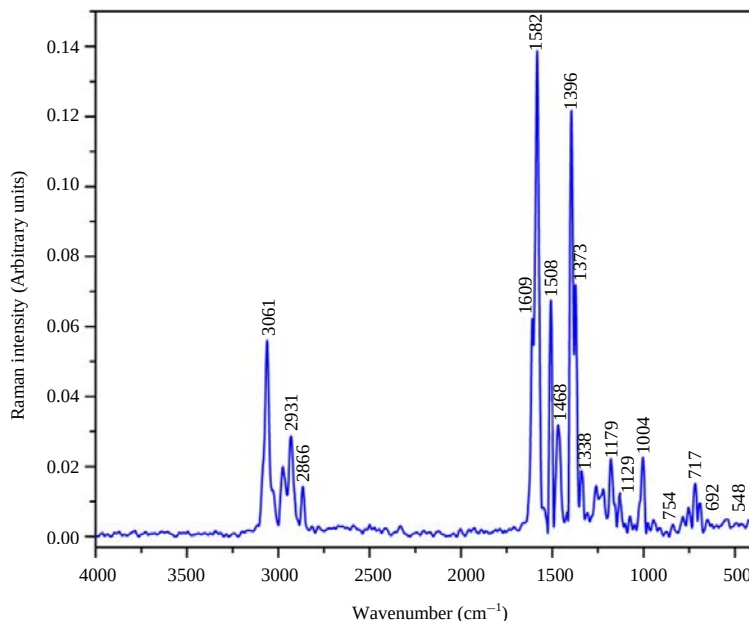


Fig. 3: FT-Raman spectrum for NPTS IPT crystal

726 cm^{-1} ¹⁵. The absorption peaks at 959, 939, 874, 843, 769, 740 cm^{-1} in IR and at 976, 946, 839, 785, 754 cm^{-1} in Raman spectra were attributed to C-H out-of-plane bending mode for the title compound. Generally the C=C stretching vibrations in aromatic compounds form bands in the region of 1650-1430 cm^{-1} and the C-C stretching vibrations occurs in the range 1400-1300 cm^{-1} ¹⁶. Varsanyi¹⁵ observed the in-plane C-C-C bending vibrations at 610 cm^{-1} and the corresponding out-of-plane bending modes at 590, 500 and 350 cm^{-1} in FT-IR. Based on these literature data, C=C stretching mode is attributed due to medium bands at 1603, 1545, 1503, 1455 cm^{-1} (IR) and at 1609, 1582, 1508, 1468 cm^{-1} (Raman). Also the C-C stretching mode was identified at 1373, 1338 cm^{-1} in IR and at 1396, 1373, 1338 cm^{-1} in Raman spectra, respectively. The in-plane and out-of plane C-C-C bending vibrations were assigned at 630 cm^{-1} and at 568, 509, 493 cm^{-1} in the IR spectrum for the title compound, respectively. The ring-breathing mode of mono substituted benzenes appears near 1000 cm^{-1} and Varsanyi¹⁵ theoretically identified the same at 1011 cm^{-1} . In the present study, this mode was identified as medium intensity band at 1004 cm^{-1} in Raman spectrum for the title compound.

Pyrrolothiazole ring vibrations: Vibrational assignments of the pyrrolothiazole ring were discussed on the basis of the cyclopentane five membered ring containing CH_2 , C-C, C-H, C-N and C-S functional groups. The furans, pyrroles and thiophenes hetero aromatics show C-H stretching bands in

the region 3180-3090 and 3120-3060 cm^{-1} , respectively^{17,18}. Magdaline and Chithambarathanu¹⁹ 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 due to a weak band at 3164 cm^{-1} in IR spectrum only. For thiazole ring, this mode is attributed at 3052 in IR and at 3061 cm^{-1} in Raman spectra, respectively.

The C-H in-plane bending wavenumbers appear in the range 1300-1000 cm^{-1} and C-H out-of plane bending in the range 1000-750 cm^{-1} ²⁰. Also Magdaline and Chithambarathanu¹⁹ reported IR bands at 1283, 1105, 1041 cm^{-1} and Raman bands at 1114 cm^{-1} to ascribed the C-H in plane bending modes. The C-H out-of-plane bending vibrations were assigned to the medium bands observed at 910, 858 cm^{-1} in FT-IR and to a weak band at 862 cm^{-1} in FT-Raman for the 2-Thiophene carboxylic acid¹⁹. Based on these literature data, the β (C-H) mode is attributed at 1274, 1202, 1167, 1128, 1101, 1057 cm^{-1} in IR and at 1260, 1221, 1179, 1129, 1074 cm^{-1} in Raman spectra, respectively for the title compound. The γ (C-H) mode is assigned due to bands at 874, 843 cm^{-1} in IR and at 839 cm^{-1} in Raman spectra, respectively.

The CH_2 antisymmetric stretching vibrations were generally observed in the region 3000-2900 cm^{-1} , while the CH_2 symmetric stretching will appear between 2900 and 2800 cm^{-1} ²¹⁻²³. For Irinotecan molecule Babu *et al.*²⁴ observed the CH_2 antisymmetric stretching vibration at 2943 cm^{-1} in

FT-IR spectrum. For the same compound the calculated antisymmetric and symmetric CH_2 stretching vibrations were seen in the range 3008-2951 and 2948-2903 cm^{-1} , respectively. In the present study, antisymmetric stretching mode of CH_2 is identified at 2921 cm^{-1} in IR and at 2931 cm^{-1} in Raman spectra, respectively. Also, the symmetric stretching mode of the CH_2 group of five membered rings is assigned at 2866 cm^{-1} in both spectra for the title compound. The general wavenumber assignments order for the CH_2 bending modes are given as follows: $\text{CH}_2\text{scis} > \text{CH}_2\text{wag} > \text{CH}_2\text{twist} > \text{CH}_2\text{rock}$ ²³. Babu *et al.*²⁴ have reported the theoretically computed values of CH_2 scissoring mode which falls in the range 1482-1437 cm^{-1} and their observed FT-IR and FT-Raman bands at 1435 and 1449 cm^{-1} , respectively for Irinotecan molecule. It is attributed as medium bands at 1455 and 1468 cm^{-1} in both spectra.

The CH_2 wagging and twisting vibrations were observed in the region 1390-1180 cm^{-1} ¹⁷. The CH_2 wagging and twisting modes were assigned by Babu *et al.*²⁴ at 1373, 1323, 1233, 1222 cm^{-1} (B3LYP), 1373, 1329 cm^{-1} (IR), 1376, 1236, 1223 cm^{-1} (Raman), respectively. The absorption bands at 1373, 1337, 1274 cm^{-1} (IR), 1373, 1338, 1260 cm^{-1} (Raman) on pyrrolothiazole ring of the title compound have been interpreted due to CH_2 wagging and twisting vibrations. The rocking vibration of cyclopentane group appeared at 730 and 720 cm^{-1} . This splitting is caused by crystallinity¹⁷. In this present study, the bands present in Raman spectrum at 754 and 717 cm^{-1} were assigned to the rocking mode of CH_2 group of pyrrolothiazole ring. The ring breathing mode for pyrrolidine five membered ring appeared at 902 cm^{-1} ¹⁷. This mode was identified at 939 cm^{-1} in IR spectrum and at 946 cm^{-1} in Raman spectrum for pyrrolothiazole ring.

The C-C stretching vibrations occur generally in the region 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 due to changes in the substituent. So that wide wavenumber variation can occur. For 2-substituted thiophenes four bands were observed in the ranges 1532-1514, 1454-1430 and 1367-1347 cm^{-1} ¹⁸. Rao¹⁸ observed IR bands at 1528 and 1352 cm^{-1} which was assigned to C-C stretching vibrations. Magdaline and Chithambarathanu¹⁹ theoretically predicted the C-C stretching vibrations at 1526, 1410 and 1356 cm^{-1} by DET/B3LYP method. In the present study, the stretching mode of the C-C bonds in the pyrrolothiazole ring were identified at 1545, 1503, 1455, 1373 cm^{-1} in IR and at 1582, 1508, 1468,

1373 cm^{-1} in Raman spectra, respectively which show good agreement with the reported spectral data^{18,19}. Coates *et al.*²⁵ observed C-S stretching modes between 710 and 687 cm^{-1} and Nogueira *et al.*²⁶ reported C-S stretching vibration at 839 and 608 cm^{-1} . Magdaline and Chithambarathanu¹⁹ observed theoretically the stretching of C-S bond in the thiophene ring at 852 and 649 cm^{-1} but only one peak is observed at 647-637 cm^{-1} in the experimental FT-IR/FT-Raman spectra. For the title compound, strong bands occurring at 769, 698 cm^{-1} in IR and 785, 692 cm^{-1} in Raman are assigned to C-S stretching mode of thiazole ring. The increase in wavenumber for this mode is due to mixing of pyrrolo ring and substituent nitro group. The observed band at 1425 cm^{-1} has been assigned to the C-N stretching vibration of 1,2,4-triazole ring by Rao *et al.*¹⁸ and the calculated value of this mode was at 1440 cm^{-1} . In the present study, observed bands at 1455 and 1468 cm^{-1} in both spectra are assigned to C-N stretching mode of pyrrolothiazole ring.

Nitro group vibrations: The antisymmetric and symmetric stretching vibrations of aromatic nitro compounds of NO_2 group give rise to bands in the regions 1570-1485 and 1370-1320 cm^{-1} , respectively²⁷⁻³⁰. In the case of 2-Bromo-5-nitro thiazole³¹ bands at 1570 cm^{-1} (IR), 1598 cm^{-1} (DFT, Density functional theory) have been assigned to antisymmetric stretching modes of NO_2 group. Also, the symmetric stretching mode for the same compound is assigned by Gobinath and Xavier³¹ at 1365 cm^{-1} (Raman), 1379 cm^{-1} (DFT). In the present study, the observed strong Raman band at 1582 cm^{-1} is attributed to the antisymmetric stretching mode of NO_2 of title compound and bands identified at 1373 cm^{-1} in both spectra have been assigned to the symmetric stretching mode.

In the aromatic nitro compounds, bands are usually seen at 855 ± 40 cm^{-1} (NO_2 scissoring), 760 ± 30 cm^{-1} (NO_2 wagging), 540 ± 30 cm^{-1} (NO_2 rocking) and 70 ± 20 cm^{-1} (NO_2 torsional)³². Panicker *et al.*³³ reported the bands at 800, 724, 534 cm^{-1} (theoretically) and at 809, 727, 717, 524 cm^{-1} (experimentally) for NO_2 scissoring, wagging and rocking modes, respectively. Mary *et al.*³² observed the bands for NO_2 scissoring mode at 778 cm^{-1} (DFT), 773 cm^{-1} (IR) 773 cm^{-1} (Raman) and the wagging mode of NO_2 group is at 692 cm^{-1} (DFT), respectively for 2-(p-fluorobenzyl)-6-nitrobenzoxazole molecule. Also, the rocking mode of NO_2 group for the same compound is assigned at 533 cm^{-1} (DFT), 522 cm^{-1} (IR), 528 cm^{-1} (Raman) and torsional mode of NO_2 is at 61 cm^{-1} (DFT). Based on these literature data, the scissoring,

wagging and rocking modes of NO₂ group were identified at 843, 769, 538 cm⁻¹ in IR and at 839, 785, 548 cm⁻¹ in Raman spectra, respectively for the title compound. Sundaraganesan *et al.*²⁹ theoretically reported the C-NO₂ stretching mode for 5-Bromo 2-nitropyridine molecule at 1540 cm⁻¹ and experimentally at 1545 cm⁻¹ in FT-Raman spectrum. The bands corresponding to the stretching vibration of C-NO₂ appears at 1545 cm⁻¹ in IR spectrum for the title compound.

Indenoquinoxaline ring vibrations: Indenoquinoxaline has four fused rings which have 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. The C-H stretching vibrations of hetro aromatic ring showed the characteristic bands in the region of 3100-3000 cm⁻¹ which are not affected appreciably by the nature of the substituent^{15,17,34}. Subramanian *et al.*³⁵ 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 Indenoquinoxaline ring is observed at 3052 cm⁻¹ in FT-IR and at 3061 cm⁻¹ in FT-Raman spectra for title compound respectively. The in-plane aromatic C-H deformation vibrations occur in the region 1300-1000 cm⁻¹³⁴. Babu *et al.*²⁴ have predicted C-H in-plane bending vibrations by B3LYP at 1406, 1394, 1344, 1308, 1293, 1278, 1259, 1231, 1164, 1128, 1117 cm⁻¹. For the title compound, β (C-H) mode is identified at 1274, 1202, 1167, 1128, 1101, 1057 cm⁻¹ in IR and at 1260, 1221, 1179, 1129, 1074 cm⁻¹ in Raman spectra, respectively. The out-of-plane bending mode of C-H group appears in the region 900-667 cm⁻¹¹⁷. Singh *et al.*³⁶ observed this mode at 816 cm⁻¹ and also calculated wavenumbers fall at 960, 934, 835 cm⁻¹ and 803 cm⁻¹ in DFT/B3LYP method. The wavenumbers due to γ (C-H) of Indenoquinoxaline are assigned by the weak bands at 874, 843, 769, 740, 698 and 667 cm⁻¹ in IR spectrum. In Raman spectrum, this mode was observed at 839, 785, 754, 692 and 651 cm⁻¹.

The ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm⁻¹¹⁷. By Rofouei *et al.*³⁷, the C-C stretching modes have been observed at 1589, 1516 cm⁻¹ in FT-IR and at 1596, 1541 cm⁻¹ in FT-Raman spectra. For the title compound, the wavenumbers observed in IR spectrum at 1503, 1455 cm⁻¹ and at 1508, 1468 cm⁻¹ in Raman spectrum are assigned to this C-C stretching modes. The C=C stretching vibrations appear in the range 1674-1504 cm⁻¹¹⁷. In the present study, it was attributed to medium bands at 1603, 1545 cm⁻¹ in IR and at 1609 cm⁻¹ in Raman spectra,

respectively. The appearance of strong absorption band in the region 1630-1600 cm⁻¹ corresponds to ν (C=N) stretching frequency. The bands present in the range 1150-1130 cm⁻¹ areas signed due to ν (C-N) vibration^{38,39}. The reported value of the (C=N) mode is at 1610 cm⁻¹ for amide pyrazine compound. Gulluoglu *et al.*³⁸ reported the C-N stretching mode at 1135 cm⁻¹ for piperidine molecule⁴⁰. Based on these literature data, the C=N and C-N stretching modes of Indenoquinoxaline ring are attributed at 1603, 1609 and at 1128, 1129 cm⁻¹ in both spectra respectively in the present study. Generally it has been observed that the strong band in the region nearly around 500 cm⁻¹ is due to C-C-N group deformation mode⁴¹. Gunasekaran *et al.*⁴² reported the deformation mode for C-C-N group nearly at 669, 612, 601 and 565 cm⁻¹ for piperazine compound. In the present investigation, the weak IR bands observed at 667, 630, 568, 538 cm⁻¹ and Raman bands at 651, 548 cm⁻¹ are attributed to C-C-N deformation mode.

Hydrogen bonding: The X-ray data revealed that title crystal has a three dimensional network formed through three C-H...N bonds and six C-H...O hydrogen bonds which stabilize the molecular structure¹². These two kinds of bonds are having D-H...A distances more than 3 Å indicating that they are weak hydrogen bonds. The emergence of these two weak hydrogen bonds plays an important role to stabilize the biological macromolecule crystal structures. However, they do not involve shifting the stretching and bending wavenumbers of related functional group frequencies.

Optical analysis: The UV-Vis absorbance spectrum of NPTSIPT crystal was recorded using SHIMADZU-UV1800 double beam spectrometer in the wavelength range 200-1100 nm. The observed UV-Vis absorbance spectrum of the title molecule was given in Fig. 4. It showed that the crystal has the maximum absorbance peaks at 267, 347 and 369 nm. The lower cut-off wavelength was found to be at 314 and 364 nm. The title crystal has 100% transmittance in the entire visible region which makes the crystal as useful material for optical application. The Tauc's relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ is 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 $(\alpha h\nu)^2$ is extrapolated to the photon energy axis to determine the energy gap value. From the Fig. 5, the energy gap value was determined as 4.36 eV, which showed that the grown crystal is a typical dielectric material.

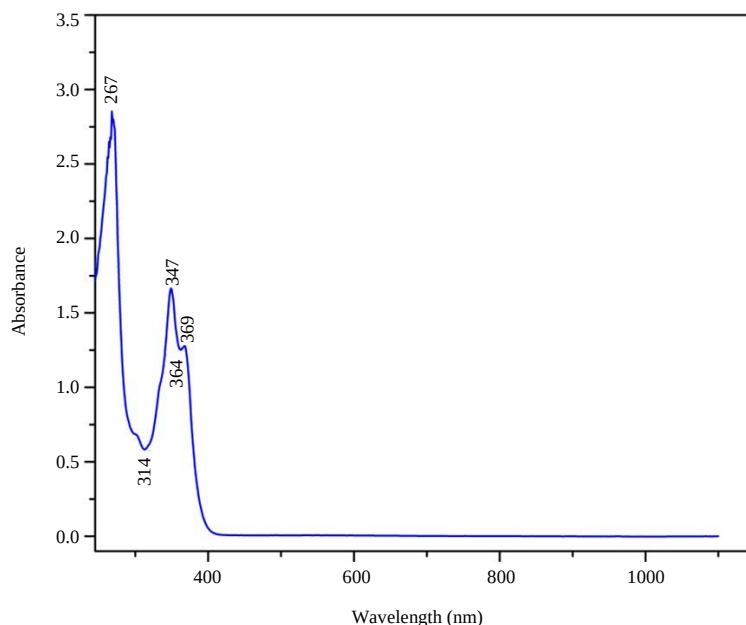


Fig. 4: Absorbance spectrum for NPTSIPT crystal

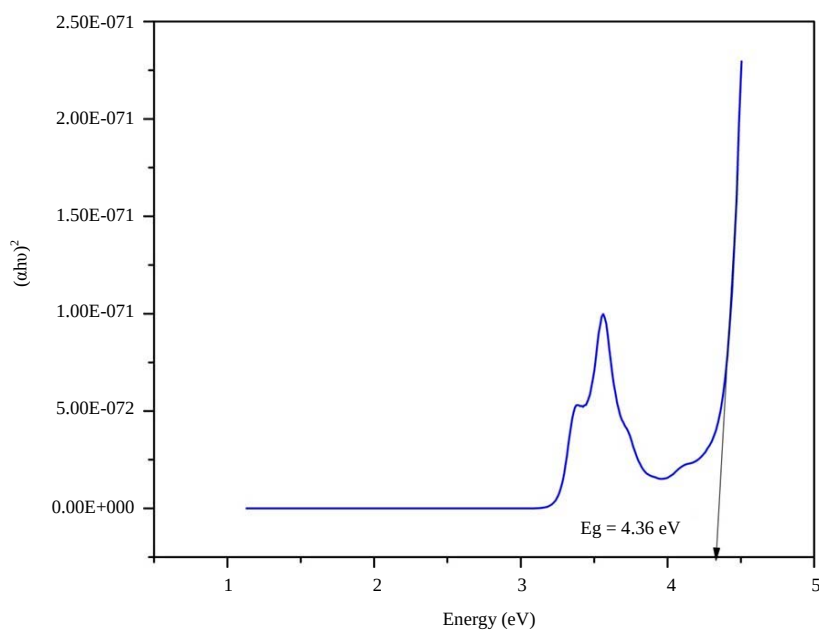


Fig. 5: Optical band gap for NPTSIPT crystal

CONCLUSION

For newly synthesized NPTSIPT crystal, the FT-IR and FT-Raman spectra have been recorded at room temperature to elucidate the various functional groups present in the compound. The wavenumber assignments have been made for phenyl, pyrrolothiazole, Indenoquinoxaline and nitro functional groups. These assignments have been seen to be in

good agreement with the similar compounds of recently published literature data. The title compound belongs to triclinic space group $P\bar{1}$ which was analyzed by the single crystal XRD technique. From the X-ray study, the presence of two kinds of hydrogen bonds is observed in the crystal. This observation revealed that these bonds do not involve for appreciable modification of stretching and bending wavenumbers of various functional groups. Using UV-Visible

spectroscopy analyzes the optical band gap was found to be as 4.36 eV. This large band gap shows that the grown crystal is a typical dielectric material. The structural modification of quinoxaline derivatives of present compound might provide a scope for further development of various biological activities through the formation of C-H...O and C-H...N intramolecular interactions.

SIGNIFICANCE STATEMENT

This study discovers the new drug compound that can be beneficial for human beings in medicinal field. This study will help the researchers to uncover the critical areas of crystal growth in indenoquinoxaline derivatives that many researchers were not able to explore. Thus a new attempt is made on the growth of indenoquinoxaline derivative crystal and analyzed by spectroscopic approach may be arrived at.

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