SPECTROSCOPIC STUDIES OF SOME N-HETEROCYCLIC COMPOUNDS

R. G. Bavane, Y. N. Khairnar and G. N. Jethave*

Dr. Annasaheb G. D. Bendale Mahila Mahavidyalaya, Jalgaon, Maharashtra, India, 425001

Abstract:

Fourier Transform Infrared (FTIR) spectroscopy is a versatile analytical technique widely employed in the investigation of various chemical compounds. This study focuses on the FTIR spectroscopic characterization of a series of N-heterocyclic compounds, namely 2-bismethyl thiomethelene Malononitrile, 2-(methylthio)(phenylamino)methylene Malononitrile, 2-(methylthio)(4-nitrophenyl)amino)methylene Malononitrile, 3-(methylthio)(3-phenylamino)-2-(1H-tetrazolyl) acrylonitrile, and (z) 3-(methylthio)(4-phenylamino)-2-(1H-tetrazolyl)-5-acrylonitrile. The FTIR spectra for each compound provided valuable information regarding their molecular structures and functional groups. Characteristic peaks corresponding to the N-heterocyclic moieties and other functional groups were identified. Additionally, the influence of substituents on the vibrational frequencies and intensities of the observed bands was examined. The result demonstrates the significant potential of FTIR spectroscopy as a rapid and non-destructive tool for the structural elucidation of N-heterocyclic compounds. Furthermore, the obtained FTIR spectra data can be employed for the development of spectral libraries and the establishment of reference fingerprints for these compounds. Spectrometric analytical technique provides insights into the electronic transitions and absorption characteristics of these compounds. This study helps to determine the compound's absorption spectrum, revealing important information about its electronic structure and the nature of the conjugated systems present within the molecule. This work contributes to the understanding of the spectroscopic properties of N-heterocyclic compounds and provides essential groundwork for their future identification and quantitative analysis in various research and industrial applications.

Keywords: N-heterocyclic Compound, FTIR analysis.

Introduction

FTIR spectroscopy is a valuable tool for studying the molecular vibrations and functional groups present in various compounds, including N-heterocyclic compounds. By analyzing the FTIR spectra of these compounds, we can gain insights into their molecular structure and bonding patterns. N-

heterocyclic compounds hold significant importance in various scientific and industrial fields due to their unique structural properties and diverse functionalities. Some of the key significance and importance of N-heterocyclic compounds are as follows:

Medicinal Chemistry: Many N-heterocyclic compounds exhibit promising biological activities, making them essential in drug discovery and medicinal chemistry. Numerous pharmaceutical drugs, such as antibiotics, antivirals, and antifungals, are derived from N-heterocyclic structures. Their ability to interact with specific biological targets makes them valuable in treating various diseases and medical conditions.

Agriculture: N-heterocyclic compounds are widely used in the development of agrochemicals, including pesticides and herbicides. Their targeted activity against pests and weeds ensures effective crop protection, leading to increased agricultural productivity and food security.

Material Science: N-heterocyclic compounds are essential in the development of advanced materials. Polymers and organic materials containing N-heterocycles offer unique properties such as high thermal stability, conductivity, and light-emitting capabilities. These materials find applications in electronics, optoelectronics, and sensors.

Coordination Chemistry: N-heterocyclic ligands form stable complexes with metal ions, leading to the development of metal-organic frameworks (MOFs) and coordination complexes. These compounds have diverse applications, including catalysis, gas storage, and drug delivery.

Organic Synthesis: N-heterocyclic compounds serve as versatile building blocks in organic synthesis. They can undergo various transformations and reactions to produce a wide range of functionalized compounds, enabling the synthesis of complex organic molecules.

Environmental Chemistry: Some N-heterocyclic compounds have applications in environmental remediation and monitoring. They can be employed as chelating agents for heavy metal ion removal and as indicators for specific environmental pollutants.

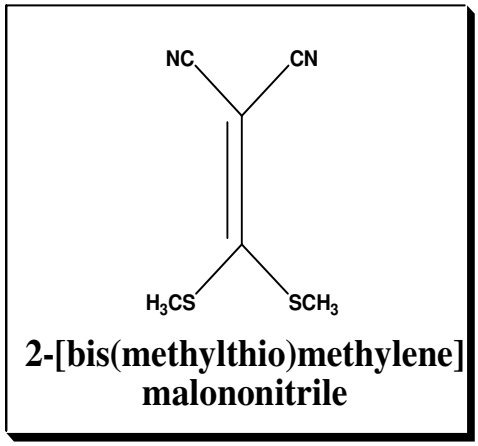
Pharmacology and Biochemistry Research: N-heterocyclic compounds are valuable tools for studying biological processes and drug interactions. They are used as pharmacological probes and enzyme inhibitors in biochemical research.

Industrial Chemistry: N-heterocyclic compounds find applications in the production of dyes, pigments, and other industrial chemicals. They contribute to the coloration of textiles, plastics, and paints.

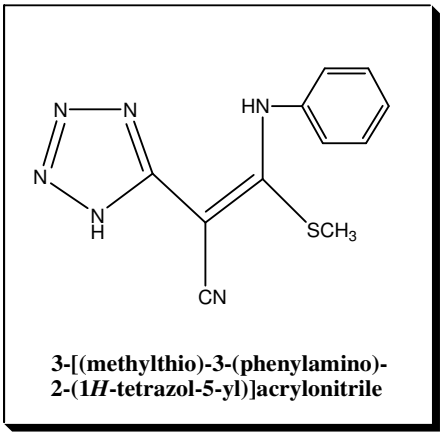
Coordination and Transition Metal Chemistry: N-heterocyclic compounds are often utilized as ligands to stabilize and control the reactivity of transition metal complexes, leading to the development of novel catalysts and catalytic processes.

Overall, N-heterocyclic compounds play a crucial role in various scientific disciplines, providing the foundation for new drug discoveries, materials development, and advanced technologies. Their versatility and diverse functionalities make them indispensable components of modern chemistry and scientific research. It's worth mentioning that the successful interpretation of FTIR spectra requires experience and expertise in vibrational spectroscopy and organic chemistry. The N-heterocyclic compounds prepared by using ketene dithioacetal has its own importance in organic synthesis.

Structure of ketene dithioacetal- Structure of N-heterocyclic compounds-



2-[bis(methylthio)methylene] malononitrile



3-[(methylthio)-3-(phenylamino)-2-(1*H*-tetrazol-5-yl)]acrylonitrile

N-heterocyclic compounds have attracted much attention due to their pronounced biological activities and pharmacological properties. N-heterocyclic compounds have been the subject of chemical and biological studies due to their interesting pharmacological activities. These compounds show antifungal and antiviral activity. This work aimed to synthesize some N-heterocyclic compounds and their spectroscopic study.

Edgar A. Steck et al reported the Absorption Spectra of Heterocyclic Compounds and some Benzimidazole Derivatives. He studied the ultraviolet absorption spectra of isomeric amino derivatives

of pyridine and quinoline and for several amino isoquinolines. From spectroscopic evidence, he studied the physical and chemical data and assigned the structures of molecules.

FTIR - [Fourier Transform Infrared] - spectroscopy analysis and testing identify chemical compounds in a wide range of capacities.

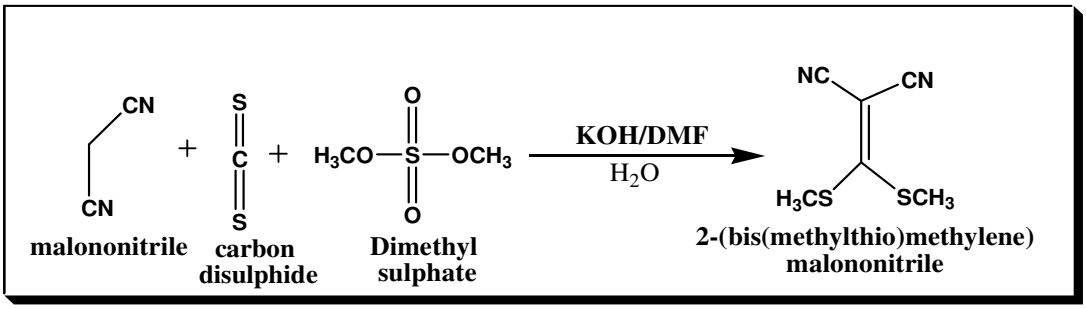
Based on the aforesaid importance of the FTIR spectroscopy, we planned to characterize the samples of a few heterocyclic compounds by FTIR technique.

Experimental Work

Synthesis of 2-[Bis(methylthio)methylene]malononitrile

To an ice-cold solution of 5.18 g of KOH in 10 ml of water and 15 ml of DMF was added with cooling and stirring, 3.0 g of malononitrile followed by 2.73 ml of CS_2 was stirred for 1 hour at room temperature and treated dropwise with 8.6 ml dimethyl sulphate maintaining temperature about 0-5 ˚C. The reaction mixture was allowed to stand at room temperature for 12 hours. The progress of reaction was monitered by TLC. Whole reaction mixture was poured into ice cold water. The obtained solid were filtered and washed with water. Dried and recrystalized by using methanol.

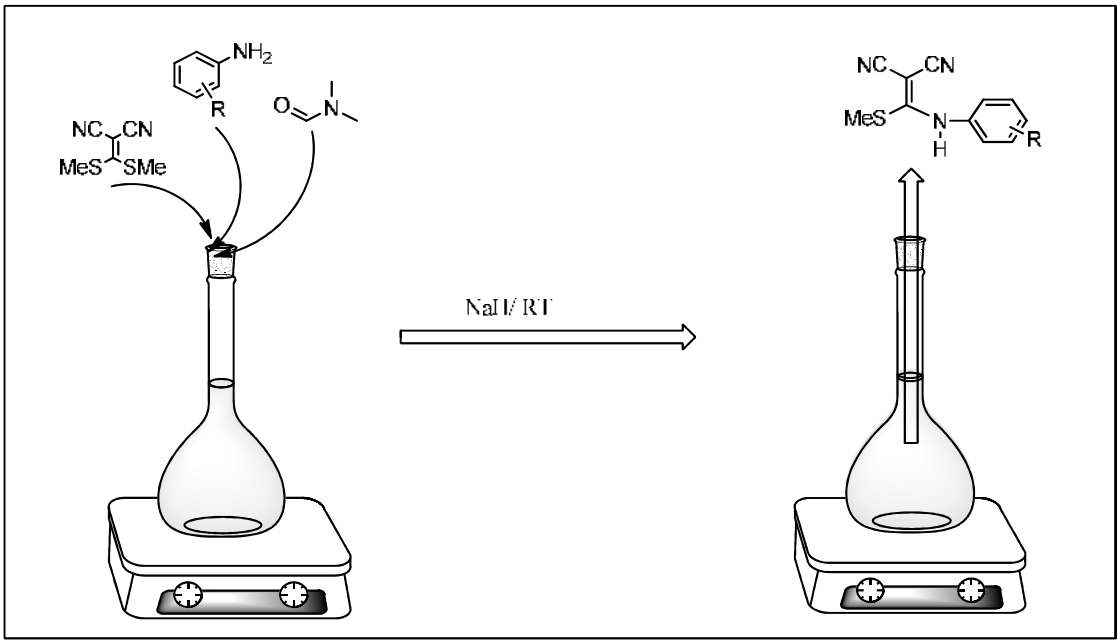
Reaction



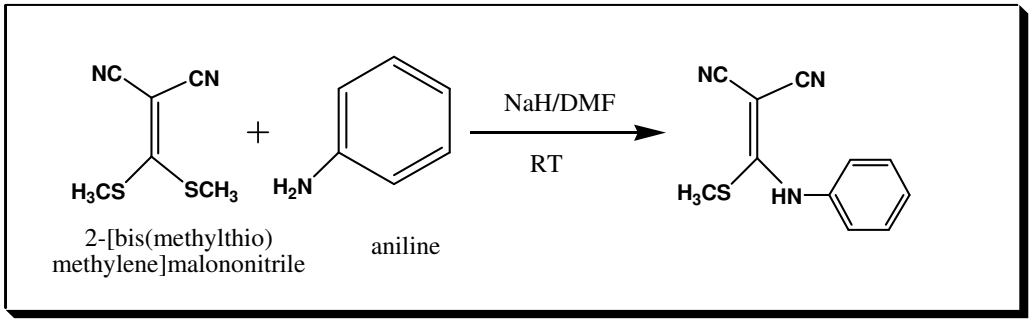
The main heterocyclic compound **2-[bis(methylthio) methelene] Malononitrile** [$C_6H_6N_2S_2$] numbered as **1** is used and further subsequent heterocyclic compounds labelled as **1-a, 1-b, 2-a, 2-b** were derived from the main heterocyclic compound Malononitrile.

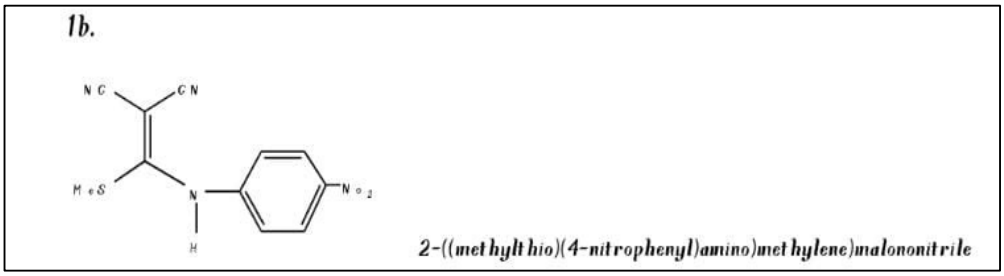
Synthesis of 2-[(phenylamino)(methylthio)methylene] malononitrile (1a)

Synthesis of 2-[(phenylamino)(methylthio)]malononitrile was carried from substituted aniline and ketene dithioacetal using NaH as base and DMF or THF as solvent by stirring the reaction mixture for several hours. The progress of reaction is monitored by TLC.



Reaction:

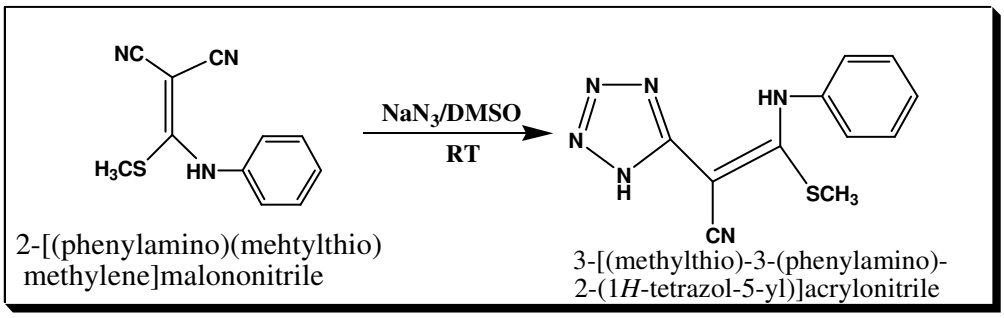




Synthesis of 3-[(methylthio)-3-(phenylamino)-2-(1H-tetra-zole-5-yl)] acrylonitrile (2a)

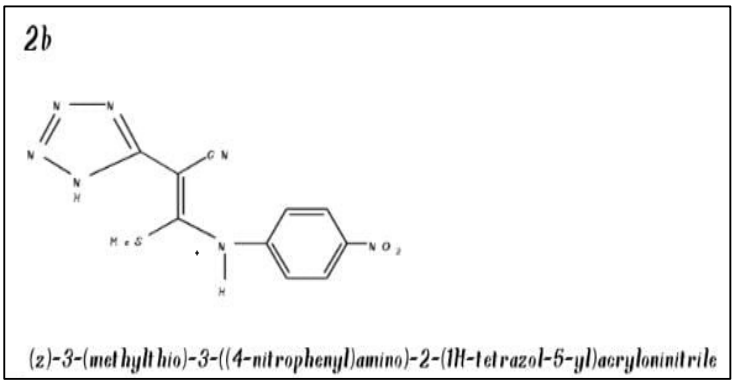
The product obtained in step second was reacted with NaN_3 to obtain 1,2,3,4-tetrazole. The product formation was favored when the reaction was carried out by reflux for 2 hours in DMSO solvent. The progress of reaction was monitored by TLC.

Reaction



2-[(phenylamino)(mehtylthio) methylene]malononitrile

3-[(methylthio)-3-(phenylamino)-2-(1*H*-tetrazol-5-yl)]acrylonitrile



All the above 5 samples in powder form were tested with FTIR spectroscopy.

Discussion and Analysis of the Results

FT-IR Characterization of the samples

The FTIR spectra of the 5 different heterocyclic compounds have been studied as follows: Spectral Evidence of heterocyclic Compounds are-

FTIR- Identification of Heterocyclic Compounds: The bands of functional groups in spectra gave strong evidence for new synthesized compound via disappearance of bands and appearance other new bands that indicate to preparation of the new compounds that represented by:

Compound 1: 2-bismethyl thiomethelene Malononitrile

The appearance of band at 3496 cm^{-1} due to -N-H stretching of primary amine group, band at 2926 cm^{-1} due to -C-H aliphatic, band at 2210 cm^{-1} is due to -C-N stretching, band at 1410 cm^{-1} due to -C-H bending.

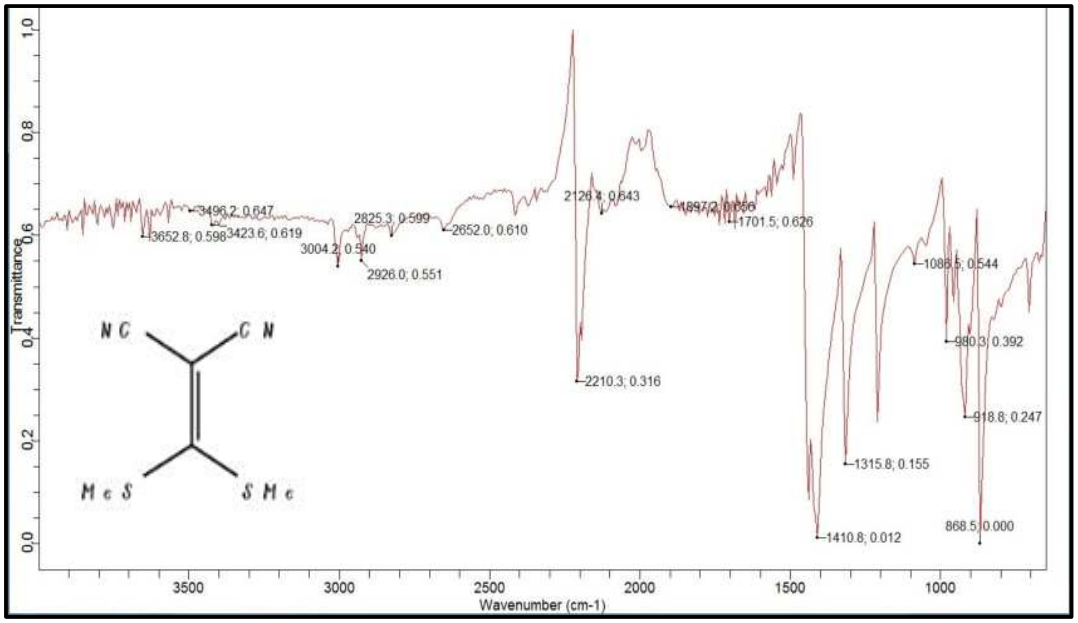


Figure 1: IR Spectrum of the Heterocyclic Compound 1

Compound 2: 2-(methylthio)(phenylamino) methylene Malononitrile

The appearance band at 3289 cm^{-1} due to N-H of amine group, band at 2926 cm^{-1} due to C-H aliphatic, band at 2182 cm^{-1} is due to C-N stretching, band at 1371 cm^{-1} due to C-H bending, band at 1315 cm^{-1} is due to C-N stretching for Aromatic.

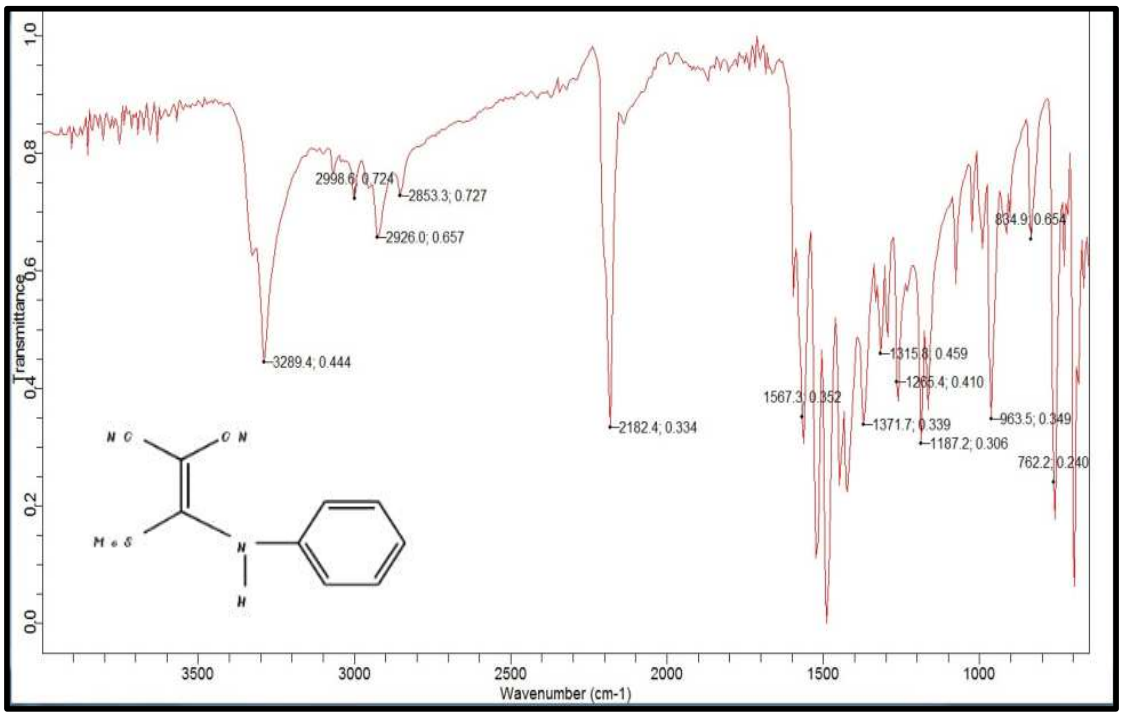


Figure 2: IR Spectrum of the Heterocyclic Compound 1a

Compound 3:- 2-(methylthio)(4-nitrophenyl)amino) methylene Malononitrile

The appearance band at 3356 cm^{-1} due to N-H stretching of amine group, band at 2920 cm^{-1} due to C-H aliphatic, band at 2115 cm^{-1} is due to C-N stretching, band at 1628 cm^{-1} due to C=C stretching, band at 1299 cm^{-1} is due to C-N stretching for Aromatic.

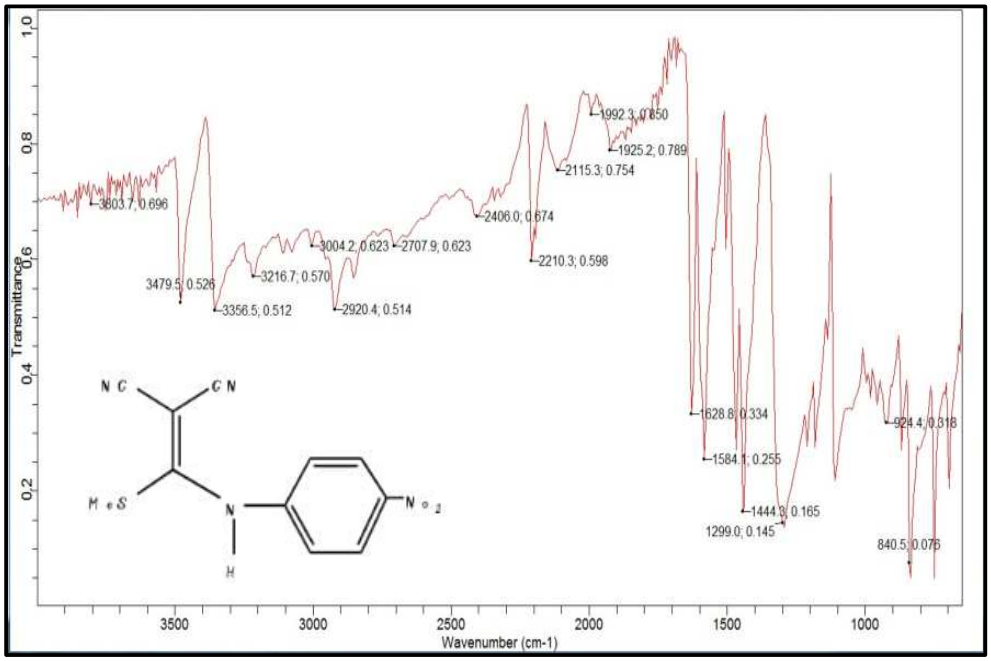


Figure 3: IR Spectrum of the Prepared Compound 1b

Compound 4: 3-(methylthio) (3-phenylamino)-2-(1H-tetrazolyl) acrylonitrile

The appearance band at 3289 cm^{-1} due to N-H stretching of amine group, band at 2926 cm^{-1} due to C-H aliphatic, band at 2182 cm^{-1} is due to C-N stretching, band at 1656 cm^{-1} due to C=N stretching, band at 1595 cm^{-1} due to C=C stretching, band at 1259 cm^{-1} is due to C-N stretching for Aromatic.

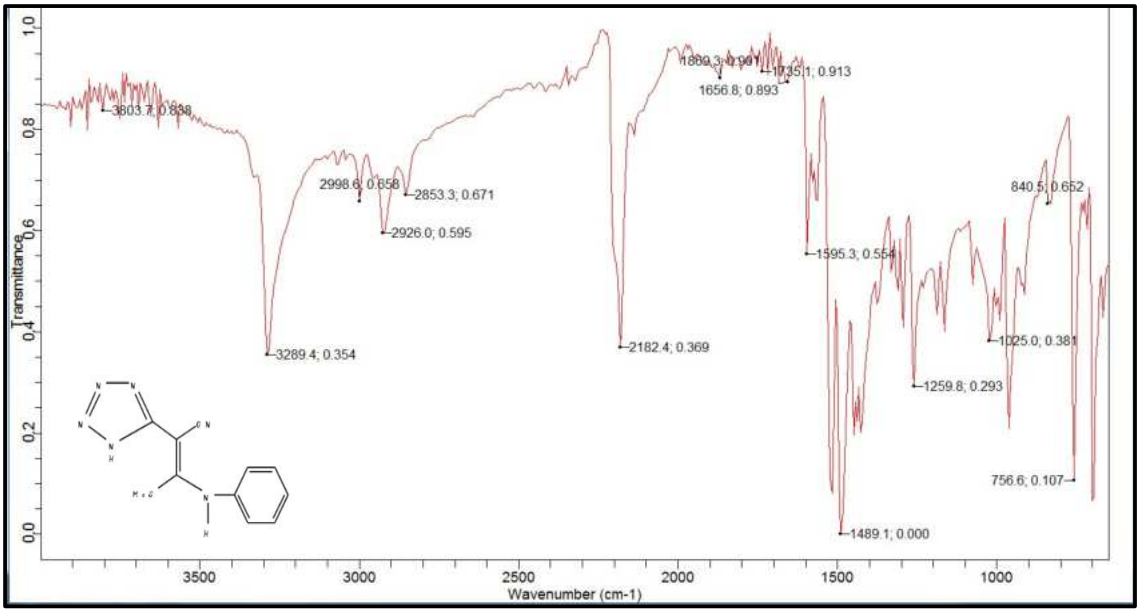


Figure 4: IR Spectrum of the Prepared Compound 2a

Compound 5: (z) 3-(methylthio) (4-phenylamino)-2-(1H-tetrazolyl)-5- acrylonitrile

The appearance band at 3356 cm^{-1} due to N-H stretching of amine group, band at 2920 cm^{-1} due to C-H aliphatic, band at 2115 cm^{-1} is due to C-N stretching, band at 1656 cm^{-1} due to C=N stretching, band at 1628 cm^{-1} due to C=C stretching, band at 1293 cm^{-1} is due to C-N stretching for Aromatic.

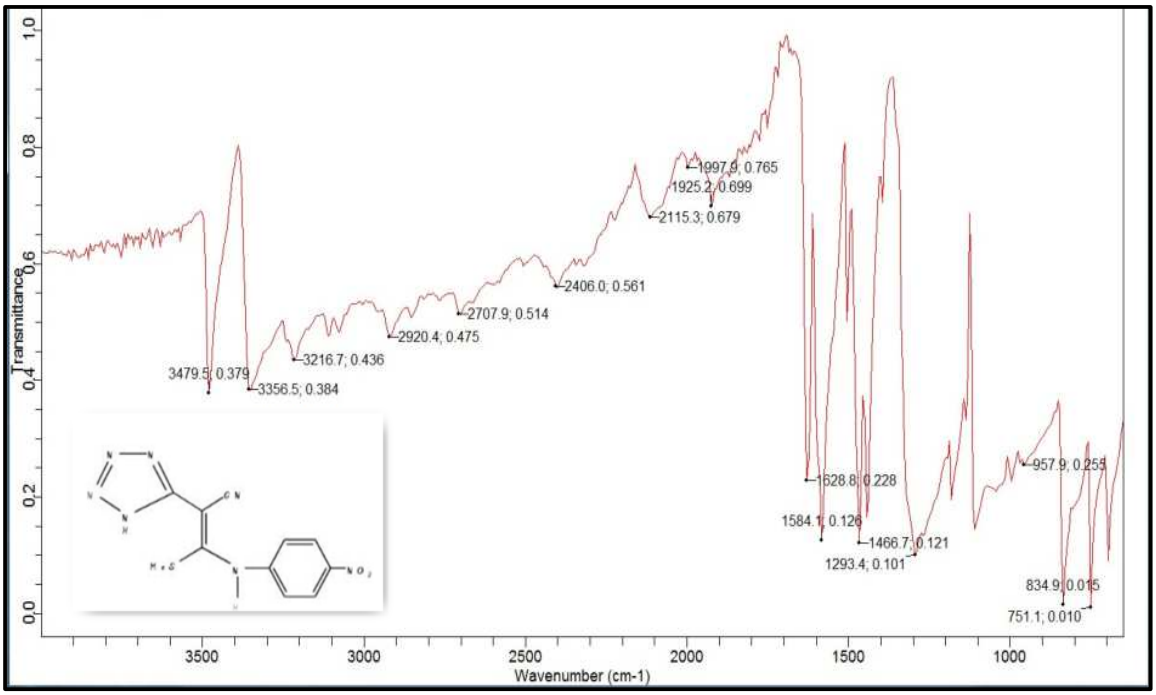


Figure 5: IR Spectrum of the Prepared Compound 2b

UV-Vis Analysis:

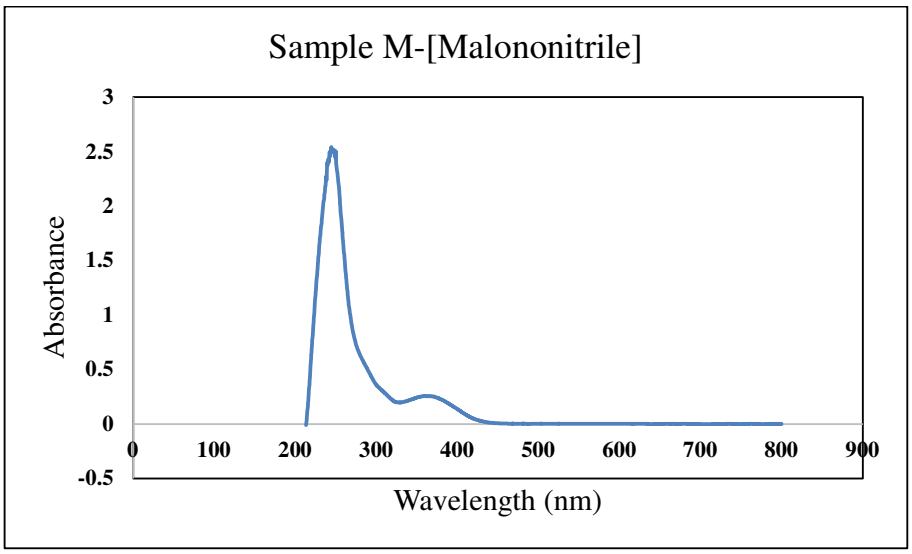


Figure 6: UV-Vis Spectrum of the 2-bismethyl thiomethelene Malononitrile (Compound 1)

Optical properties of the (Compound-1) 2-bismethyl thiomethelene Malononitrile were investigated by UV-vis spectroscopy using suitable solvent (Figure 6). As expected, the aqueous solution of the starting complex in figure 6 exhibits a single absorption in the UV-visible regions.

Conclusion

The spectral values obtained from the FTIR spectra of the 5 samples of heterocyclic compounds, shows the stretching bands which are matches with the reported values of different functional groups in the backbone of the compound. This confirms the formation of the concern heterocyclic compounds. N-heterocyclic compounds hold significant importance and versatility in various scientific fields. Their unique chemical properties and diverse structural characteristics make them invaluable building blocks for the design and synthesis of biologically active compounds and functional materials. As demonstrated in this research, the study and characterization of N-heterocyclic compounds using techniques like FTIR spectroscopy provide crucial insights into their molecular structures and functional groups. This work contributes to the understanding of the spectroscopic This knowledge is instrumental in understanding their chemical behavior and reactivity, aiding in the development of new pharmaceuticals, agrochemicals, and advanced materials. Moreover, N-heterocyclic compounds'

presence in natural products highlights their importance in drug design, as nature serves as a valuable source of inspiration for novel therapeutic agents.

ACKNOWLEDGEMENT

Authors are thankful to Principal, Dr. Annasaheb G. D. Bendale Mahila Mahavidyalaya, Jalgaon for the kind cooperation and guidance.

DACLARATIONS

Competing interests:

The authors have no competing interests.

Funding

Department of Science and Technology, New Delihi-India funded this work under the research grant, (Sanction No. DST/CURIE-PG/2022/35(C))

Availability of data and materials

Not Applicable

References

1. H. Iqbal, V.Prabhakar, A.Sangitha, B.Chandrika, R.Balasubramanian. "Synthesis, anti-inflammatory and antioxidant activity of ring-A- monosubstituted chalcone derivatives". Med.Chem.Res., 2014, 23(10), 4383-4394.
2. Md.Amir, H.Kumar, S.A.Khan. "Synthesis and pharmacological evaluation of pyrazoline derivatives as new anti-inflammatory and analgesic agents". Bio.Med.Chem.Lett., 2008,18,918-922.
3. Yadav, R.; Srivastava, S. D.; Srivastava, S. K.; Indian J. Chem. 2005, 44B, 1262.
4. Cacic, M.; Trkovnik, M.; Cacic, F.; Has-Schon, E. Molecules, 2006, 11, 13
5. S. R. Deshpande, P. S. Chavan, S. N. Nagarale, M. V. Patil, Synthesis, Spectral Characterization and Antimicrobial Studies of New Hybrid Heterocyclic Compounds Bearing 1H-benzimidazol-2-yl Thiomethyl Motif, Indian J Pharm Sci; 79(3):385-394, 2017.
6. Edgar A. Steck, Frederick C. Nachod, Galen W. Ewing, and Nancy H. Gorman, Absorption Spectra of Heterocyclic Compounds. III. Some Benzimidazole Derivatives, J. Am. Chem. Soc. 1948, 70, 10, 3406–3410.
7. Li, M. M., Chen, X., Deng, Y., & Lu, J. (2021). Recent advances of N-heterocyclic carbenes in the applications of constructing carbo-and heterocyclic frameworks with potential biological activity. RSC advances, 11(60), 38060-38078.
8. Üstün, E., Özdemir, N., & Şahin, N. (2021). Activity analysis of new N-heterocyclic carbenes and silver N-heterocyclic carbene molecules against novel coronavirus by UV-vis, fluorescence spectroscopy and molecular docking. Journal of Coordination Chemistry, 74(21-24), 3109-3126.
9. Froese, R. D., Lombardi, C., Pompeo, M., Rucker, R. P., & Organ, M. G. (2017). Designing Pd–N-heterocyclic carbene complexes for high reactivity and selectivity for cross-coupling applications. Accounts of Chemical Research, 50(9), 2244-2253.
10. Bellotti, P., Koy, M., Hopkinson, M. N., & Glorius, F. (2021). Recent advances in the chemistry and applications of N-heterocyclic carbenes. Nature Reviews Chemistry, 5(10), 711-725.
11. Hopkinson, M. N., Richter, C., Schedler, M., & Glorius, F. (2014). An overview of N-heterocyclic carbenes. Nature, 510(7506), 485-496.
12. De Sarkar, S., Biswas, A., Samanta, R. C., & Studer, A. (2013). Catalysis with N-heterocyclic carbenes under oxidative conditions. Chemistry–A European Journal, 19(15), 4664-4678.
13. Kandepi, V. K. M., & Narender, N. (2012). Synthesis of N-heterocyclic compounds over zeolite molecular sieve catalysts: an approach towards green chemistry. Catalysis Science & Technology, 2(3), 471-487.