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SYNTHESIS, SPECTRAL CHARACTERIZATION, NLO, AND DFT STUDIES OF 3 -THIOMETHYL ANILINE-BASED AZO DYES

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ABSTRACT

3-thiomethyl aniline-based azo dyes were prepared by conventional diazotization and followed by coupling reactions with various coupling components such as α-naphthol, β-naphthol, and 6-bromonaphthol under suitable experimental conditions. The isolated azo dyes are primarily confirmed by their orange-red color. Further via spectroscopic methods dyes are characterized and confirmed by various analytical techniques, such as IR, UV-visible, and NMR spectroscopic methods. Along with synthesis and characterization, computational studies and theoretical properties of the azo dyes are calculated and tabulated. DFT studies are also performed for the synthetic compounds. Optimized structures and electrostatic potential maps of azodyes are displayed and in addition, with the help of E-homo and Elumo various quantum chemical parameters relevant to nonlinear optical properties (NLO) properties are calculated and results are interpreted.

Keywords:. Azo Dyes; Synthesis -Spectral Characterization; NLO and DFT- Studies

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INTRODUCTION

Azo dyes are synthetic organic dyes that were prepared by diazotizing an aromatic primary amine and coupling with the coupling agents. In 1863, Peter Griess developed Bismarck brown, the first azo dye [1]. Azo dyes have become more intriguing compounds in synthetic chemistry as a result of their applications in numerous domains of research and technology.[2] Azo dyes are being used as colorants in a variety of sectors, including paper, leather, textiles, and food industries[3-5], and as non-colorants in optical and other electronic devices as well.[6-7] Azo dyes are also used in several bio-medical practices[8-11], due to their wide range of applications azo dye has become a vast class of synthetic organic molecules/dyes. Azo dyes are categorized based on a number of azo group moiety and functional groups, structure, etc.[12] From the literature survey, it is clear that vast research and review on azo compounds have been reported and many have miscellaneous applications.[13] Though no reports are available on thiomethyl aniline-based azo dyes. Hence, we have focused on synthesizing the thiomethyl aniline-based azo dyes to explore their wide range of applications in various fields. 3-Thiomethyl aniline-based azo dyes were synthesized by diazotization and coupling of amines with α-naphthol, β-naphthol, and 6-bromo naphthol. The synthesized dyes are characterized by IR, UV-visible, and NMR spectral techniques, theoretical data has been studied and reported.

EXPERIMENTAL

Materials and Methods

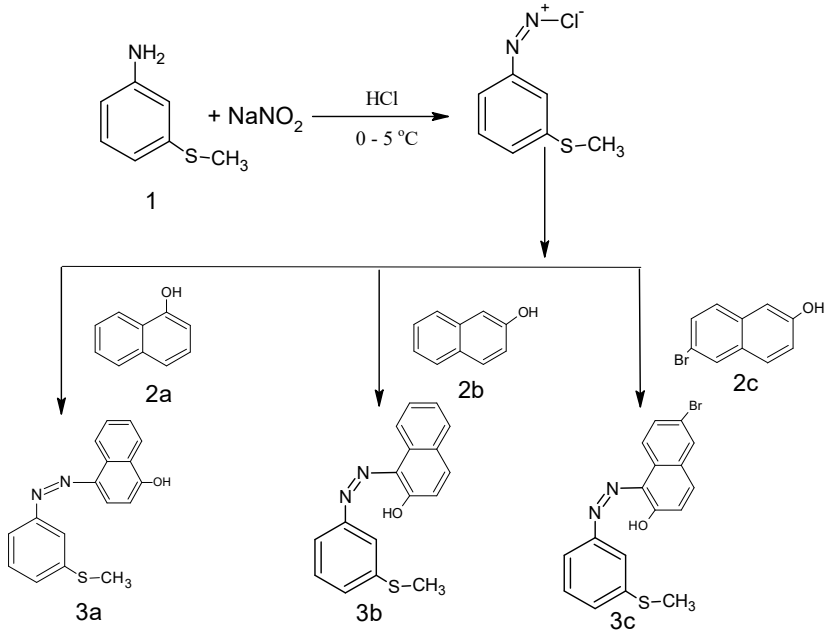
3-Thiomethyl aniline was procured from 'Sigma Aldrich's chemical suppliers, in India. Other chemicals are obtained from 'Nice' chemical suppliers in India. All the chemicals obtained were put to use as such obtained. The compounds' UV-visible absorption spectra were captured using a SHIMADZU UV-visible spectrometer in the 200–800 nm wavelength range.

The Infrared spectra of synthetic azo dyes in KBr pellets were captured using an FTIR-Spectrometer in the 400 $cm^{-1}$to 4000 cm-1 range.^{1}H NMR spectra in d6-DMSO at 400MHz were recorded. TMS was used as

the internal standard an LC-MS-trap-XCT plus mass spectrometer was employed to capture the mass spectra.

Synthesis of Azo Dyes

A 0.3g of 3-thiomethyl aniline was taken in a beaker containing 3 mL of dilute hydrochloric acid (1:1) and kept for stirring for about 30 minutes under ice-cold conditions till the solution became homogeneous clear. An equivalent weight of $NaNO_2$ was added to the soluble aniline solution gradually with constant stirring. The reaction mixture was stirred continuously for 15 minutes by maintaining the temperature between 0 – 5 ^oC, resulting in the formation of intermediate diazonium salt in the form of ions. To the obtained diazonium salt, coupling components are added while being stirred. The resultant azo dye obtained was filtered, washed with cold water and with alcohol, dried, and purified.
The general chemical pathway is displayed in the given scheme-1.



Scheme-1: Synthesis of Azo dyes (3a-3c)

RESULTS AND DISCUSSION

Electronic Spectral Studies

UV-visible spectroscopy is an important tool for chemical compounds that exhibit color. Azo dyes with the typical functional groups -C=N, -N=N- typically exhibit $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ transitions in the visible spectrum (wavelength range 400–800 nm), and a transition $\sigma\rightarrow\sigma^*$ is also anticipated in the ultraviolet spectrum (wavelength range 200–400 nm). These transitions are what cause the peaks to appear in the electronic spectrum. For the azo dye compound 3A, the peak at 350nm in the ultra-violet is assigned for $\sigma\rightarrow\sigma^*$ transition, whereas the peak at 504nm in the visible region was attributed for $n\rightarrow\pi^*$transition respectively shown in Fig.-1. Figure-2 displays UV the visible spectrum of compound 3B, wherein we observed $\sigma\rightarrow\sigma^*$ transition at 349nm and $n\rightarrow\pi^*$ transition at 499nm respectively.

IR Spectral Studies

Major chemical functional groups of synthesized azo dyes are determined by using the IR spectroscopic technique as different functional groups absorb particular IR radiation frequencies. For elucidating structure and identifying functional groups in the compounds, IR spectroscopy is a crucial and well-liked instrument. Due to carbon-carbon stretching vibrations in the aromatic ring, aromatic hydrocarbons exhibit absorptions in the ranges of 1600–1585 cm^{-1} and 1500–1400 cm^{-1}. The O-H stretch of alcohols is a very prominent, broadband that can be seen in the 3600–3200 cm^{-1} range. The C-O stretch is visible between 1260 and 1050

cm^{-1}. α, β-unsaturated C=O at 1685-1666 cm^{-1}, -CN shows an intense band around 2250 cm^{-1}, N-H bond stretch in the range of about 3200 - 3600 cm^{-1}. peaks appear as a weak to the medium, somewhat broad band, -N=N- stretch is in the between 1500-1630 cm^{-1}.[14] The IR spectrum of compound 3A (displayed in figure-5), the sharp peak at 1511 cm^{-1} is assigned for the diazo group (-N=N-) which is a major functional group in azo compounds. 3012 cm^{-1} was meant for -OH functionality and other peaks are connected to other skeletal vibrations of the molecule. Figure-5 displays the IR spectrum of compound 3C, the sharp peak at 1493 cm^{-1} was assigned for the diazo group (-N=N-), 3120 cm^{-1} was expected for -OH functionality and other peaks are connected to other skeletal vibrations of the molecule.

NMR Studies

The spectral studies of ^{1}H and ^{13}C NMR are carried out which helps to confirm the structure of synthesized azo molecules. Azo compounds showed three types of protons i.e., aromatic protons which are expected to be at 6-8.5 ppm, aliphatic protons at 2-3 ppm, and functional protons which are variable in nature. The compound 3A has ten aromatic protons, three aliphatic protons, and one functional Proton. Figure-3 shows ten aromatic protons between 6.7-8.5ppm, aliphatic protons at 1.6-2.8ppm, and -OH at 5.4ppm. The compound 3C has nine aromatic hydrogen atoms, three aliphatic hydrogen atoms, and one -OH which is observed at 6.8-8.5, 1.6-1.8, and 5.5ppm respectively according to Fig-4.Thus based on UV-visible spectroscopy, IR spectroscopy, and NMR spectroscopy we confirmed the synthesized compounds.

DFT Studies and NLO Studies

DFT (density functional studies) are carried out by using the Gaussian software PM3 method. Frontier Molecular Orbitals of Azo dyes (3A,3B and 3C) from optimized geometries were displayed in Fig.-7, and Optimized structures and electrostatic potential surfaces of 3A-3C are shown in Fig.-8.By calculating the HOMO and LUMO energies a few quantum chemical characteristics, including electrophilicity(χ), electrophilicity index(ω), chemical hardness(η), chemical softness(σ), chemical potential(μ), electron affinity (I), ionization potential (A), and energy gap ΔE, the relative stability of the azo dye was assessed by using equations (1-11).[15] The NLO materials have grown significantly in both theoretical and experimental fields of advanced study. These resources are very helpful for the telecoms industry and technology. Nearly all NLO materials exhibit a direct correlation between their optical characteristics and the intensity of incident light.[16] Hence we are correlating the energy gap obtained in DFT studies and the optical softness of the material required NLO materials. The optical Softness(σ_o) of compounds 3A and 3C was found to be 0.191 and 0.194, the synthetic compounds can also be used as NLO materials.

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

$$E_{Gap} = E_{HOMO} - E_{LUMO} \quad (3)$$

$$\eta = \frac{I-A}{2} \quad (4)$$

$$\sigma = \frac{1}{\eta} \quad (5)$$

$$\sigma_0 = \frac{1}{E_{Gap}} \quad (6)$$

$$\chi = \frac{|I+A|}{2} \quad (7)$$

$$CP = -\chi \quad (8)$$

$$\omega = \frac{CP^2}{2\eta} \quad (9)$$

$$N = \frac{1}{\omega} \quad (10)$$

$$S = \frac{1}{2\eta} \quad (11)$$

Table-1: Calculated Quantum Chemical Parameters of Dyes (3a, 3c)

Electronic parameters	3A	3C
E_{HOMO} (eV)	-6.73	-7.01
E_{LUMO} (eV)	-1.51	-1.87
E_{HOMO}-E_{LUMO} (eV)	-5.21	-5.14
Electronegativity (δ)	4.12	4.44
Chemical potential (α)	-4.12	-4.44
Hardness (η)	2.61	2.57
Electrophilicity index (ω)	3.251	3.835
Electron affinity (I)	6.73	7.01
Ionization potential (A)	1.51	1.87
Absolute softness(σ)	0.383	0.389
Optical Softness(σ_o)	0.191	0.194
Global softness(S)	0.191	0.194
Nucleophilicity index (N)	0.307	0.260

Table -2: Theoretical Data of Compound 3a

S. No.	Parameters	Calculated data
	Molecular Formula	$C_{17}H_{14}N_2OS$
	Formula Weight	294.37086
	Composition	C(69.36%), H(4.79%), N(9.52%), O(5.44%), S(10.89%)
	Molar Refractivity	87.83 ± 0.5 cm^3
	Molar Volume	241.0 ± 7.0 cm^3
	Parachor	633.5 ± 8.0 cm^3
	Index of Refraction	1.649 ± 0.05
	Surface Tension	47.6 ± 7.0 dyne/cm
	Density	1.22 ± 0.1 g/cm^3
	Polarizability	34.81 ± 0.5 $10^{-24}cm^3$
	Monoisotopic Mass	294.082683 Da
	Nominal Mass	294 Da

Table-3: Theoretical Data of Compound 3c

S. No.	Parameters	Calculated data
	Molecular Formula	$C_{17}H_{13}BrN_2OS$
	Formula Weight	373.26692
	Composition	C(54.70%) H(3.51%) Br(21.41%) N(7.50%) O(4.29%) S(8.59%)
	Molar Refractivity	95.38 ± 0.5 cm^3
	Molar Volume	253.6 ± 7.0 cm^3
	Parachor	677.0 ± 8.0 cm^3
	Index of Refraction	1.675 ± 0.05
	Surface Tension	50.7 ± 7.0 dyne/cm
	Density	1.47 ± 0.1 g/cm^3
	Polarizability	37.81 ± 0.5 $10^{-24}cm^3$
	Monoisotopic Mass	371.993188 Da
	Nominal Mass	372 Da

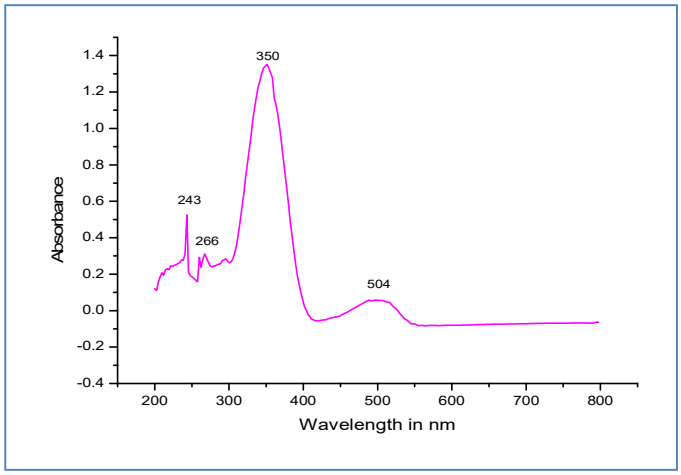


Fig.-1: UV-Visible Spectrum of 3a

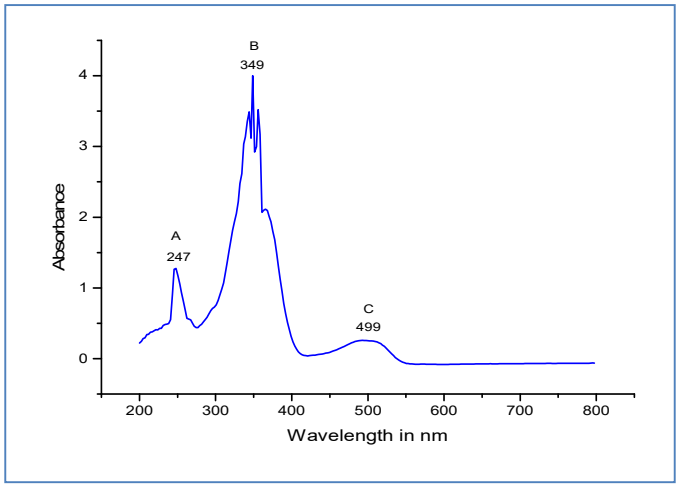


Fig.-2: UV- Visible Spectrum of Compound 3b

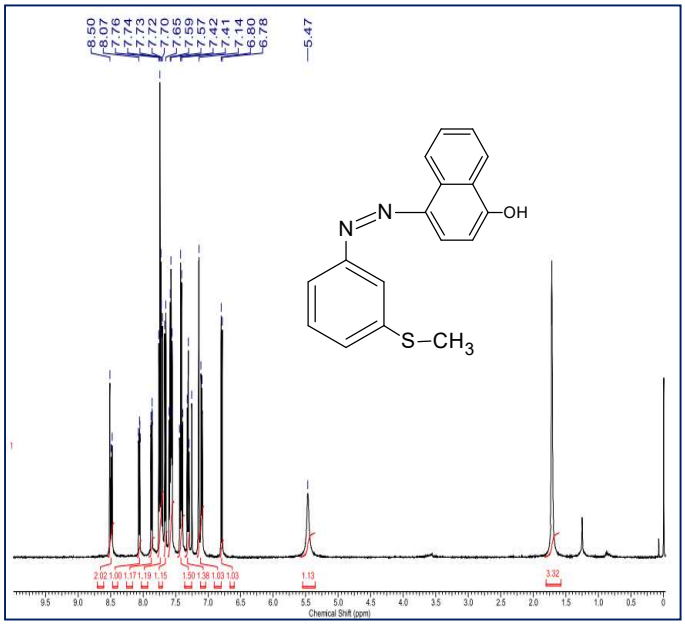


Fig.-3: ^{1}H-NMR Spectrum of Compound 3a

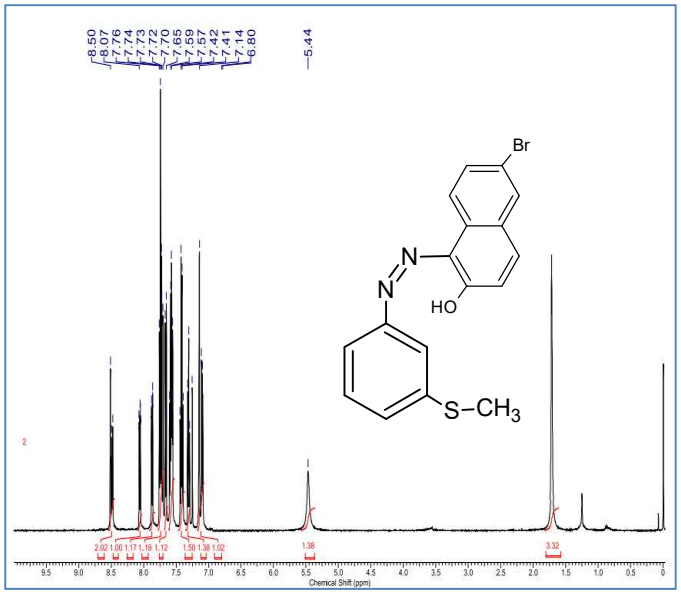


Fig.-4: ^{1}H-NMR Spectrum of Compound 3c

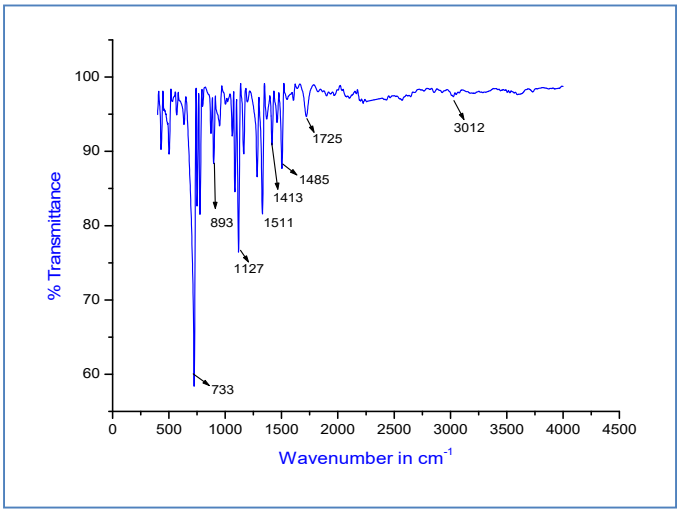


Fig.-5: IR Spectrum of Compound 3a

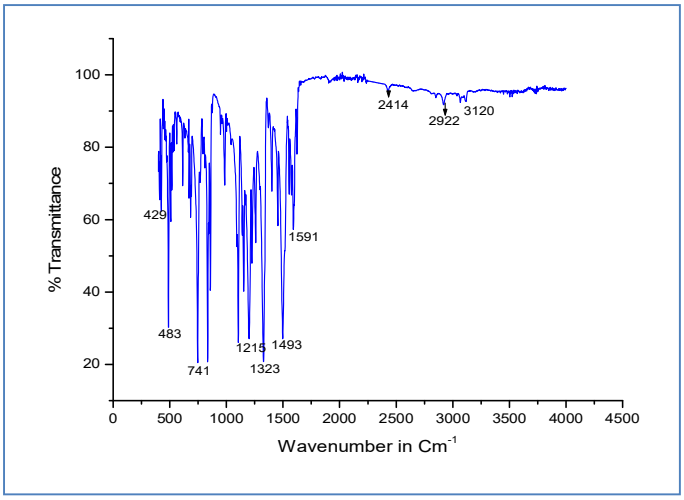


Fig.-6: IR Spectrum of Compound 3b

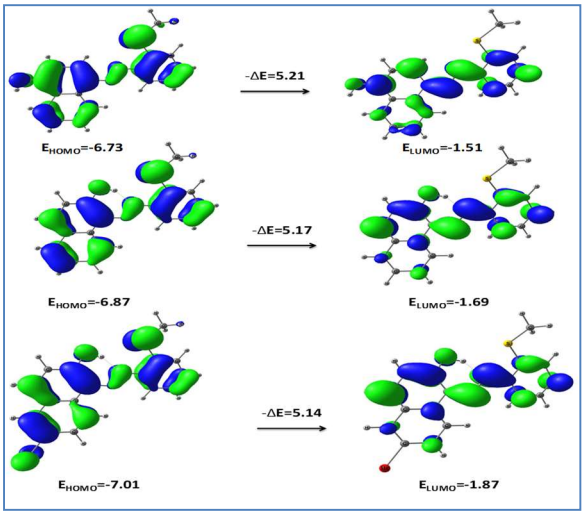


Fig.-7: Frontier Molecular Orbitals of Azo Dyes(3a,3b and 3c) from Optimized Geometries

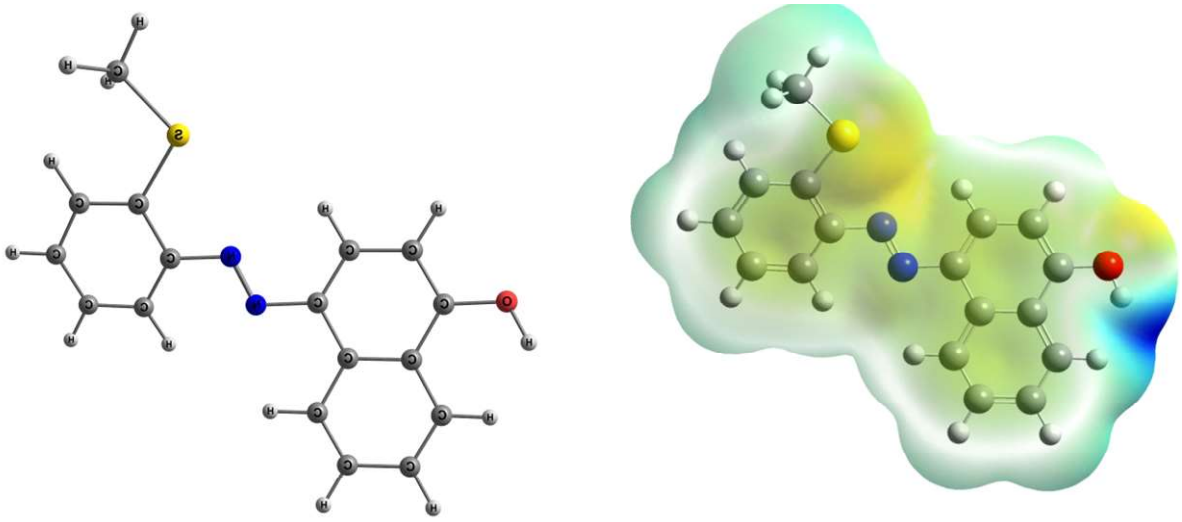


Fig.-8a: Optimized Structures and Electrostatic Potential Surfaces of 3a

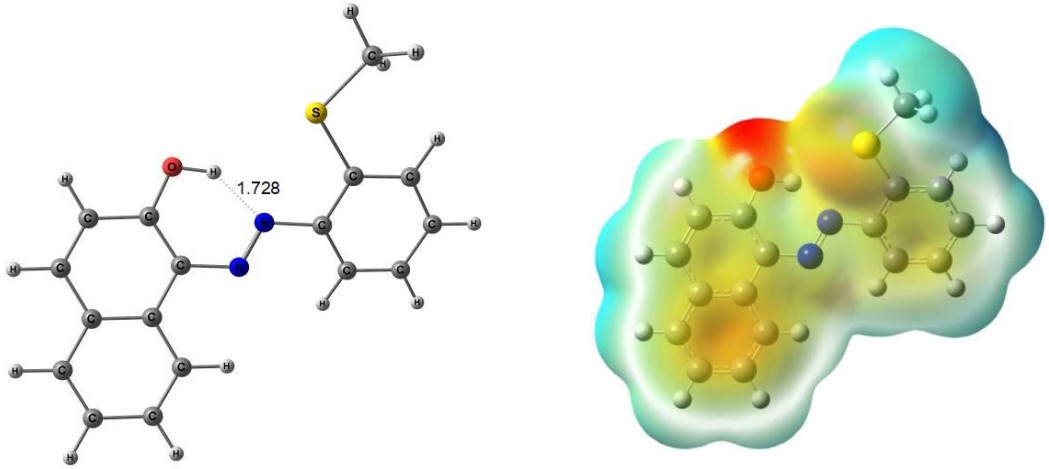


Fig.-8b: Optimized Structures and Electrostatic Potential Surfaces of 3b

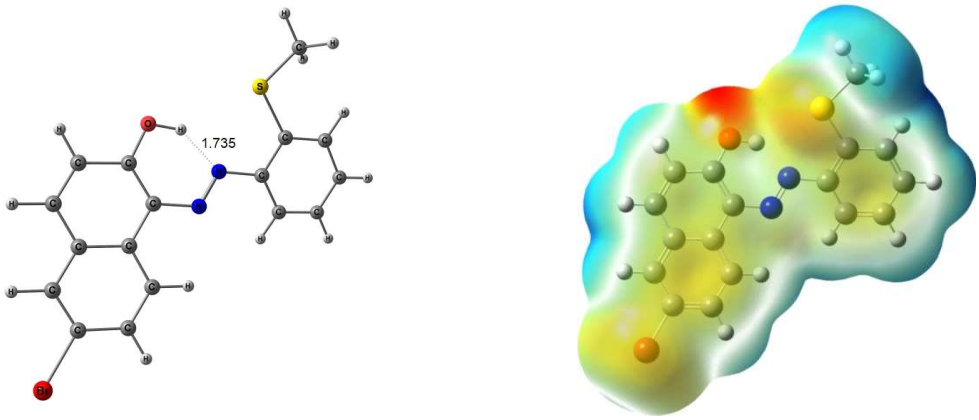


Fig.-8c: Optimized Structures and Electrostatic Potential Surfaces of 3c

CONCLUSION

This research work mainly focuses on novel 3-thiomethylaniline based azo dyes. Which were synthesized by diazotization and coupling methods. The synthesized azo dye is structurally characterized and confirmed by spectral techniques like UV-visible, IR, and NMR spectroscopy. Further based on density functional theory by PM3 method energy of HOMO-LUMO, various quantum chemical parameters like EHOMO-ELUMO (eV), EHOMO-ELUMO (eV), Electronegativity (δ), Hardness (η), Electrophilicity index (ω), Electron affinity (I), Ionization potential (A), Absolute softness(σ), Optical Softness(σo), Global softness(S), Nucleophilicity index (N), were calculated and correlated to a nonlinear optical property of synthetic azo dyes. Results are interrelated and data were tabulated.

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CONFLICT OF INTERESTS

The authors hereby declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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