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Synthesis, Spectroscopic and optical properties studies of new luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone)

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ABSTRACT

New azo dye was synthesized by coupling 1-(2,5 dichloro-4-sulfophenyl)-3- methyl-5- pyrazolone) with diazonium salt from luminol. The prepared dye was characterized by UV-Visible, FT-IR and ^{1}HNMR spectroscopic method. Spectroscopic analysis of this dye, dissolved in five polar solvents, were examined. The effect of temperature and amounts on the UV-Visible absorption spectra of the dye as well as measured. Polyvinylpyrrolidone (PVP) with prepared new azo dye films of thickness micrometer was prepared onto quartz substrate. The optical constant of the film by spectrophotometric measurements are also reported. The extinction coefficient and optical band gap (Eg) of the dye were examined by transmittance and reflectance in the spectra wavelength 300-780 nm.

Keywords: *luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone) , synthesis, spectroscopic, optical properties*

INTRODUCTION

The chemical name for pyrazole is C3H4N2, and it is a heterocyclic organic molecule. A five-membered aromatic ring with two nearby nitrogen atoms makes up the compound. (1,2) It is an adaptable component of organic synthesis. and is used as a precursor to a wide range of pharmaceuticals, agrochemicals, and other bioactive compounds.[3,4]

Pyrazole is also used as a ligand in coordination chemistry [5]. Pyrazole derivatives have a variety of pharmacological and biological activities, anti-inflammatory, analgesic, antipyretic, antitumor, and antifungal properties. [6,7]

Pyrazol has a planar structure and is commonly found as a colorless to yellowish liquid or solid.[7]

There are numerous uses for pyrazole and its derivatives in the sectors of medicines, agrochemicals, and other industries. [8,9] , dyes[10], and materials science. For example, some pyrazole derivatives are used as anti-inflammatory drugs[11], antitumor agents[12], and herbicides[13]. Pyrazole compounds are also used to synthesize other organic compounds, such as pyrazoles, which are an important class of heterocyclic compounds[14].

Optical exams donation transmittance and reflectance spectra supplied the information to determine optical constants such as the extinction coefficient, refractive index, dielectric constant, and direct and indirect transitions that take place in the compounds' band gaps [15].

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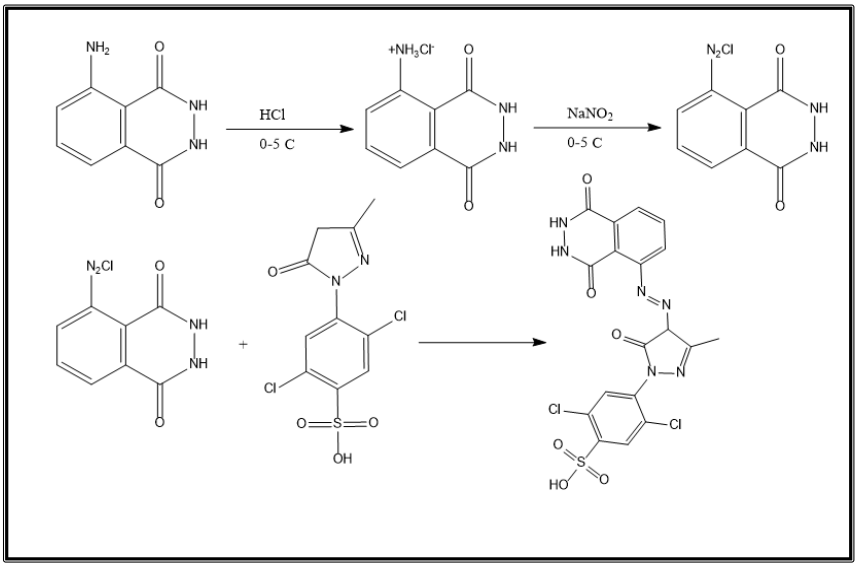
EXPERIMENTAL

Preparation of the reagent (LADCSP)

In an alkaline solution, 1-(2,5-dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone) and diazotate Luminol were combined to create the reagent. by blending 0.5 g of luminol with 3.5 ml of strong hydrochloric acid and solution of sodium nitrite at 0 to 5 C, one can create a diazonium solution. 1-(2,5-dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone) Alkaline solution of 0.5 g was added at (0-5 C0).Overnight was spent letting the mixture stand. The precipitate was removed by filtering, and ethanol was used to crystallize it (16). Schem1



SCHEME 1: preparation of reagent (LADCSP)

Apparatus

Spectrophotometric observations in the UV–visible range were made. Spectrophotometer with a T80 double beam and 1 cm glass cells. The Shimadzu FT.IR 8000 series Test Scan was used to record vibrational spectra. Using an Inolab pH-meter WTW 720 with a glass-saturated calomel combination electrode, pH measurements were taken..

Reagent

Analytical-grade compounds were utilized Luminol, 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone, NaOH, HCl, Na_2CO_3, Ethanol, Methanol, Di methyl sulfoxide (DMSO), N, N-Dimethyl formamide, Acetic acid, Polyvinylpyrrolidone.

luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone) (5 mM)

In 200 ml of deionized water, 0.5122 g of reagent was dissolved.

RESULTS AND DISCUSSION

The electronic structures spectrum of prepared compound

The Uv-VIS absorption spectrum of prepared compound were recorded in deionized water at room temperature.

Azo aromatic compound offer a high intensity ($\pi \rightarrow \pi^*$) peak in the ultraviolet zone, with a low intensity($n \rightarrow \pi^*$) peak in visible [17]

The band of azo compounds more bathochromic shifted compared azo phenyl duo to of expanded resonance order. In group substituted azomethine of prepared compound Luminol azo1-(2,5dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone), may be from possibility to form strong intermolecular hydrogen bonds with a tautomeric shape between azo group and C=N or substituted ortho azomethine.[18]

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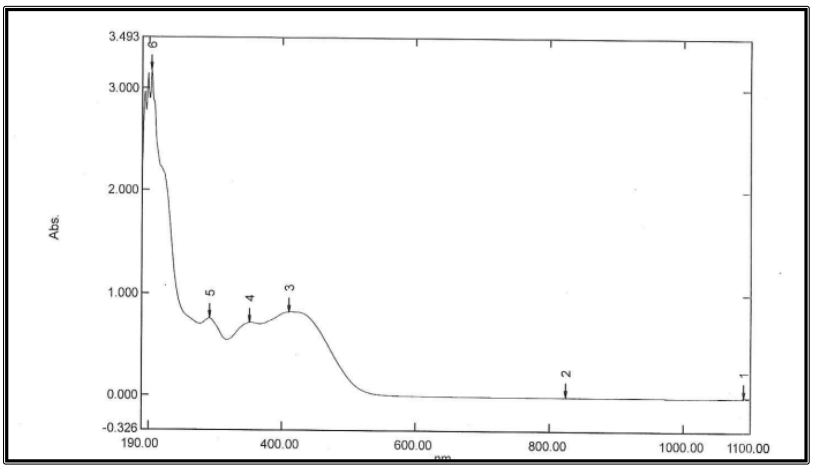

FIGURE 1: The absorption spectrum of the reagent solution (LADCSP).

The band accupied at 204-352 nm conforms to low energy ($\pi \rightarrow \pi^*$) transition including azomethine group and the band at 411 nm can be attributed to an intra molecular change transfer interaction the existence of tautomeric equilibrium.

Reagent FT.IR

Using FT-IR data of LADCSP reagent and its complex are with their probable assignment available in Table 1. When comparing the complex's spectrum with a reagent that aids in the detection of donation sites, significant bands are seen. The broad band of the free ligand's IR spectra at 3419.79 cm^{-1}, which changed to a lower frequency due to O-H stretching vibration, may be explained by this. In complexes, the carbonyl group's stretching frequency, which is 1645.28 (s) cm-1, is changed to a lower frequency range cm-1. The frequency that corresponds to (N=N) at 1521.84.(19) is similar. Fig.4.

TABLE 1: The most important spectral data for reagent

Compound	υ (OH)	υ (C=N)	υ (N=N)	υ (C=O)
LADCSP	3419.79	1666.50	1521.84	1645.28

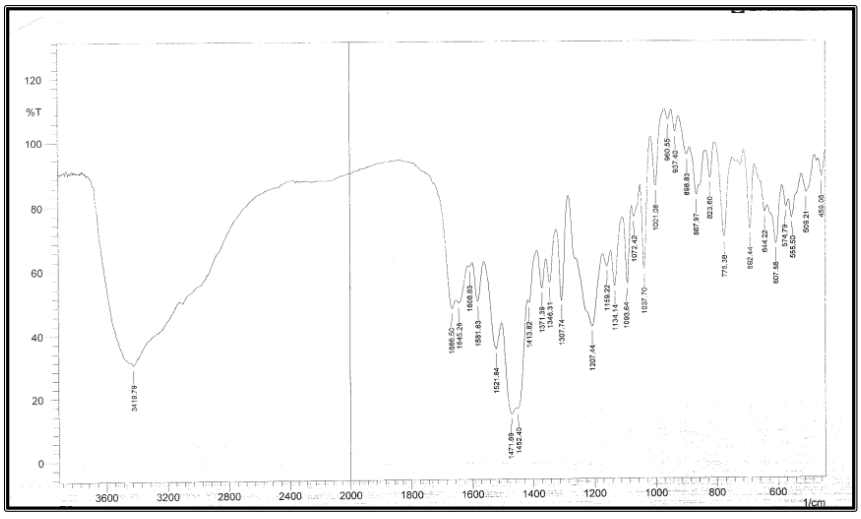

FIG 2: FT-IR spectrum of LADCSP azo reagent

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[1]HNMR Studies(20)

The following signals can be seen in the 1HNMR the created azo compound's spectrum after it was dissolved in di methyl sulfoxide solutions with tetramethyl saline acting as an internal standard. The 1H NMR spectra for (L) reveal a multiplet at (7.84 – 7.58 (m, 9H) ppm (m,H Ar) that is caused by the phenyl group., and -OH alcohol at δ 5.79 (s, 1H), for C-CH3, at δ (1.67) ppm, and NH pyrozole ring at δ11.54(s, 1H).

TABLE 2: The [1]H NMR values of the reagent (LADCSP)

Compound	CH-N=N	C-CH_3	H aromatic	N-H
LADCSP	1.14	1.67	7.84 – 7.58	11.54

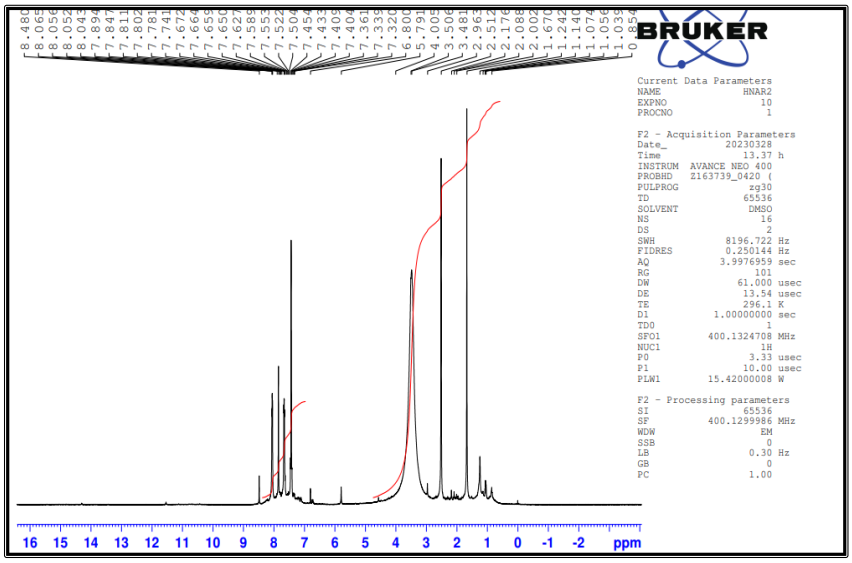

FIG 3: [1]HNMR spectrum of LADCSP azo reagent

Influence of solvent on absorption spectra of prepared azo dye

In order to study of influence of solvent on tautomerism equilibrium and solvent- solute interactions the ultraviolet -visible spectra in different of solvents was studied, The absorption spectra of azo reagent may be effected by the environment medium and that the solvents bring about a variation in the intensity, as a result of the solvent and solute molecules interacting, the location and kind of absorption bands [(21)] .

To estimate the forces of intermolecular between solute molecule and solvent, we study of the UV-Visible spectra for azo reagent in different solvents such as (Ethanol, Methanol, Acetic Acid, Di methyl sulfoxide, Di methyl formamide) at 25C. The result are shown in table 3 , fig 4

TABLE 3: Reagent values in different solvents

Solvent	Wavelength	Molar absorption coefficient
Ethanol	405	3495
Methanol	429	3375
DMF	416	2560
DMSO	469	2864
Ac. Ac	253	6320

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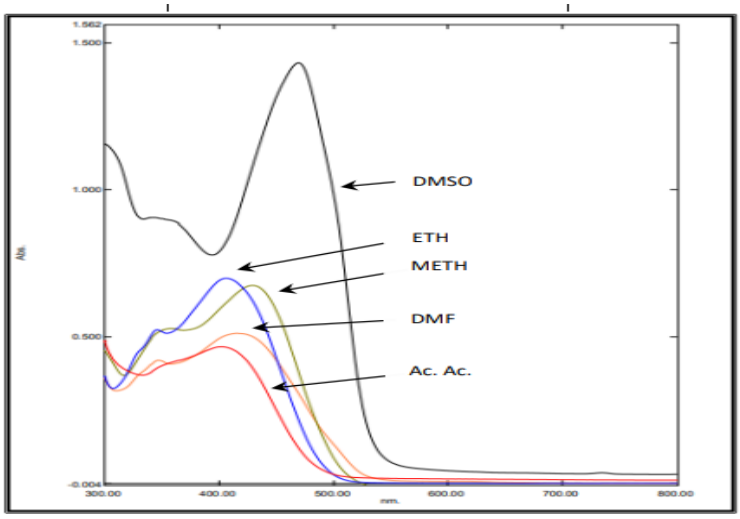

FIG 4: Influence of solvent on absorption spectra of azo dye(LADCSP)

It is explicit that in deionized water luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone) display three bands 291, 352, 411 nm, It was detected that the band at 204,352 nm offers red shift as the solvent's polarity increased. The positive solvatochromism of this dye due to the influence of hydrogen bonding strength in polar solvent and dipole moment charge. [22]

The optical properties of the luminol azo1-(2,5dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone

The optical density, transmittance as well as reflectance spectra was measured at 300-800 nm to the prepared film of Luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone:PVP quartz substrate were described in the fig (5,6,7). From the fig, the absorbance spectrum, the maximum absorption noticed at wave length zone (330-370) nm and become zero at wavelength less than 600 nm the results obtained from absorption edges of the test samples beggars at wavelength zone (480-520) nm according to photon energy (2.8 ev), while the transmittance increase in the average of the sample films more than 70%. The maximum value of the reflectance at region (370-390) nm where as the minimum its in the wavelength zone (330-520) nm[23,24].

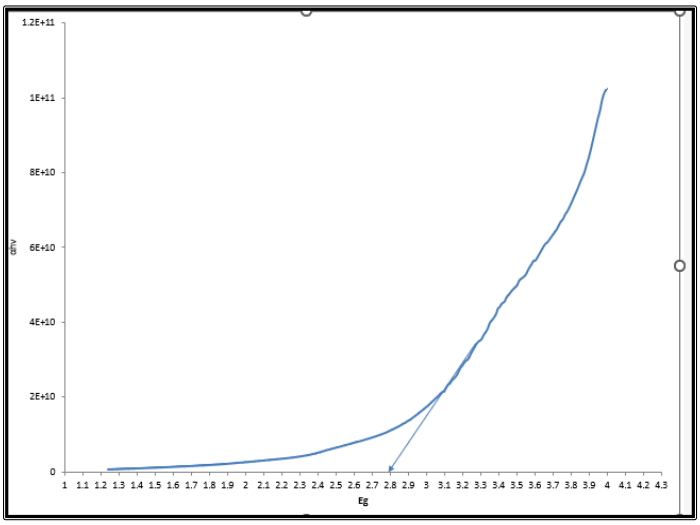

FIG 5: plot of (αhv)$^{0.5}$as a function to photon energy of prepared of luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone :PVP film

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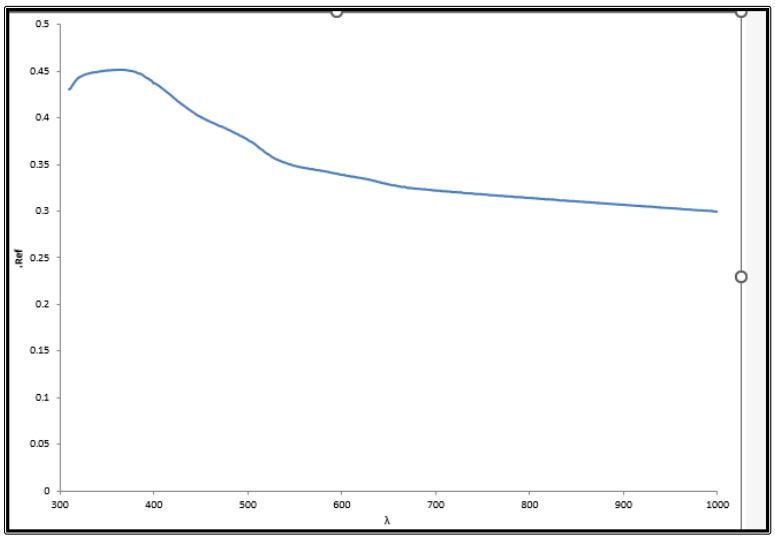

FIG 6: Reflectance spectral versus wavelength of luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone :PVP film

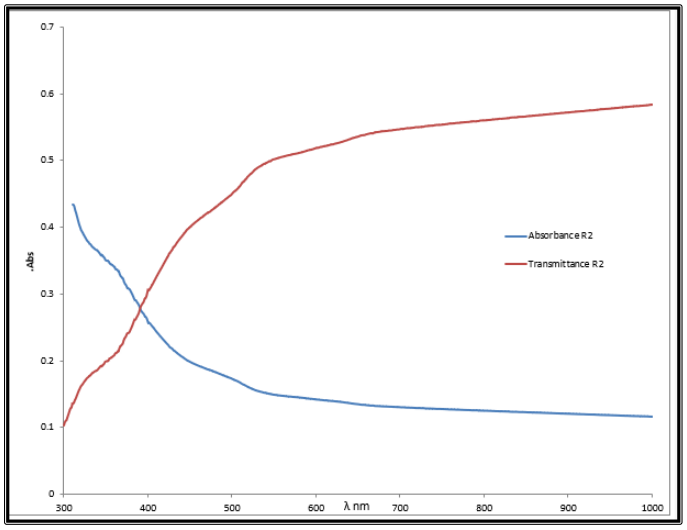

FIG 7: The Uv-VIS absorption spectrum of the luminol azo 1-(2,5dichloro-4-sulfophenyl)-3-methyl-5- pyrazolone :PVP film

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