A comprehensive examination of the reactivity and interaction behaviour of the synthetic dye E124

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ABSTRACT

Dyes have long been utilized extensively in industries as well as in everyday life. In order to clarify the function of hydrogen bonding and the polarity of the environment in the ground and excited states, the photophysical behaviour of E124 dye in isotropic and anisotropic solvent environments was examined in this research. The Kamlet-Taft solvent polarity scale was employed for a more thorough examination of the environmental impacts. The findings demonstrated that hydrogen bonding is crucial for promoting the tautomerization of the azo-hydrazone form and enhancing its structural stability. The estimated dipole moment shows that it significantly increases in more polar circumstances and that the excited state of this sulfonated dye exhibits efficient internal charge transfer and effective charge separation.

Lastly, the relative stability of the azo and hydrazone tautomers in various settings was evaluated for the first time using the "intrinsic polarity index" scale, which offers a mathematical framework for describing their stability and reactivity.

Keywords: *E124, Dipole moment, Interaction, Polarity, Intrinsic Polarity Descriptor (IPD).*

1. *INTRODUCTION*

Since ancient times, dyes have been employed in wall painting, fabric dyeing, and other crafts [1-3]. These substances are found naturally in both plants and animals. The development of synthetic dyes marked a major breakthrough in dye chemistry due to human desire for a wider range of hues and higher colour stability [4,5]. Nowadays, dyes are widely used in many scientific disciplines, industry, and the arts. As a result, it has been crucial to evaluate and select different dye types for usage in diverse scientific fields [6,7].

Due to its many applications in textile dyeing [8], sensor technology [9], biomedical imaging, photodynamic treatment (PDT) [10,11], and optical materials [10,12], azo dyes have attracted a lot of attention recently. Their spectral and photophysical activities are strongly influenced by the features of their environment. Depending on their chemical structure, solvent molecules and intermolecular interactions like hydrogen bonding can have a substantial impact on the absorption, emission, and tautomeric activity of azo dyes [13, 14].

This work investigates E124, a member of the azo dye family with strong emission and absorption in the visible region of the electromagnetic spectrum, across a range of polarity-varying solvent environments. The way solute molecules interact with solvents is influenced by both general factors, such as dielectric properties, and particular effects, such as hydrogen bonding. To evaluate these solvent-induced changes, researchers commonly use polarity scales and solvatochromic parameters [15]. Because a single polarity parameter is usually insufficient to reflect the intricacy and depth of molecular interactions, multi-parameter scales are employed. A popular approach based on linear free-energy connections is the Kamlet–Abboud–Taft (KAT) [16] formalism:

$$v = v_0 + a\alpha + b\beta + s\pi^* \qquad (1)$$

In this model, the dimensionless variables π^*, β, and α define the solvent's dipolarity and polarizability [17], hydrogen bond acceptor (HBA) strength [18], and hydrogen bond donor (HBD) strength [19]. The number Δv_o represents the baseline shift of the reference solvent, and multiple linear regression analysis

produces the coefficients a, b, and s. These coefficients clarify how different solvent parameters impact the spectrum behaviour of solute moleculesIn order to enhance the understanding of material interactions, Zakerhamidi et al. developed a quantitative model based on intrinsic variables that includes an intrinsic polarity descriptor (IPD) [16] to assess the adaptability of a dye molecule in response to its environment.
This study carefully examines the solvatochromic properties of the synthetic azo dye E124 in a variety of solvent conditions, including isotropic and anisotropic media. The sample's dipole moments are also ascertained using the solvatochromic technique. Changes in a selected sample's dipole moment and spectral properties in solvents with different polarities can offer vital information about its function in a range of optical phenomena. Furthermore, the stability of the azo and hydrazone tautomers in different solvents was assessed using the Intrinsic Polarity Descriptor (IPD) scale, which provides an objective way to understand their environmental persistence and reactivity.

2. *EXPRIMENTAL SECTION*

2.1 Materials

Merck supplied the azo family colourant E124 (Fig. 1), which was utilized without further purification. The spectroscopic solvent polarity characteristics of the isotropic solvents employed in this study, all of which were of Merck's highest analytical quality, are summarized in Table 1 [20]. Furthermore, Table 2 displays the average dielectric constants and solvent polarity characteristics for six nematic liquid crystal mixtures chosen as anisotropic solvents (obtained from Merck Ltd.) [21–23]. In order to methodically examine solvent-dependent effects on the photophysical behaviour of the dyes under study, these experiments were carried out at 25°C over a range of dielectric constant values.

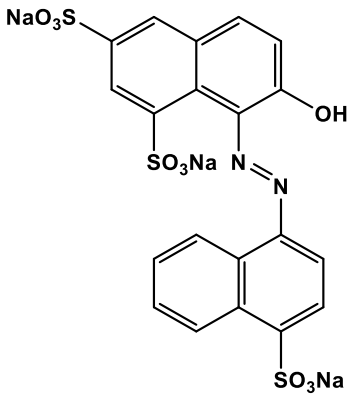


Fig. 1. *Chemical structure of E124*

Table 1. *Polarity parameters, and polarity functions of employed solvents.*

Solvent	ε	n	α	β	π*
Cyclohexane	*2.02*	*1.42*	*0.00*	*0.00*	*0.00*
1,4–Dioxane	*2.22*	*1.42*	*0.00*	*0.37*	*0.49*
Chlorobenzene	*5.62*	*1.52*	*0.00*	*0.06*	*0.65*
1–Decanol	*8.00*	*1.43*	*0.70*	*0.85*	*0.45*
1-Heptanol	*11.30*	*1.42*	*0.64*	*0.96*	*0.39*
Methylamine	*12.65*	*1.35*	*0.64*	*0.78*	*0.98*
Dimethylamine	*5.30*	*1.34*	*0.66*	*0.80*	*0.95*
1–Hexanol	*13.00*	*1.41*	*0.67*	*0.94*	*0.40*
1-Butanol	*17.40*	*1.39*	*0.84*	*0.84*	*0.47*
2–Propanol	*19.90*	*1.37*	*0.76*	*0.84*	*0.48*
Ethanol	*24.30*	*1.36*	*0.86*	*0.75*	*0.54*
Methanol	*33.70*	*1.32*	*0.98*	*0.66*	*0.60*
Ethylene glycol	*37.00*	*1.43*	*0.90*	*0.52*	*0.92*
DMF	*39.25*	*1.43*	*0.00*	*0.69*	*0.88*
DMSO	*47.24*	*1.47*	*0.00*	*0.76*	*1.00*
Water	*78.40*	*1.33*	*1.17*	*0.47*	*1.09*

Table 2. *Spectroscopic polarity parameters, physical properties and polarity functions of employed LCs*.

Solvent	ε	n	T_C/℃	α	β	π*
ML-0643	*5.60*	*1.52*	*80.00*	*0.26*	*0.54*	*0.55*
MLC-6292	*6.20*	*1.50*	*120.0*	*0.33*	*0.55*	*0.56*
MAT-160968	*12.00*	*1.57*	*72.70*	*0.49*	*0.49*	*0.46*
MLC-2082	*20.60*	*1.56*	*89.90*	*0.36*	*0.58*	*0.62*
MLC-2053	*22.10*	*1.59*	*86.00*	*0.29*	*0.58*	*0.62*
MLC-2144	*23.70*	*1.59*	*113.0*	*0.35*	*0.68*	*0.81*

2.2 Absorption and emission spectroscopy

A double-beam Shimadzu UV-2450 UV-Visible spectrophotometer was used to capture absorption spectra between 300 and 800 nm in wavelength. For spectroscopic observations in solution, standard quartz cuvettes measuring (5 × 1 × 1 cm) were utilized, whereas quartz cells measuring (5 × 1 × 0.2 cm) were utilized for investigations in the liquid crystal medium. A JASCO FP-750 spectrofluorometer was used to quantify fluorescence at a concentration of 5 × 10⁻5 mol/L.

2.3 Estimation of the dipole moment

In this study, the behaviour of a polarizable dipole moment is modelled using second-order perturbation theory in quantum mechanics. The total and difference of the absorption and emission band maxima in different surrounding media are explained by the resulting equations, which are expressed in cm⁻¹. Solvatochromic spectral shift analysis, a popular technique that evaluates how solvent polarity influences spectral transitions, may be used to calculate the dipole moment:

$$\tilde{\nu}_a - \tilde{\nu}_f = m_1 f(\varepsilon, n) + const. \quad (1)$$

$$\tilde{\nu}_a + \tilde{\nu}_f = -m_2 [f(\varepsilon, n) + 2g(n)] + const. \quad (2)$$

The parameters m_1 and m_2 for the sum and difference of wave numbers may be obtained from the slopes of linear plots. These parameters exhibit a linear connection with solvent polarity functions f(ε, n) and g(n), which consider the dielectric constant (ε) and refractive index (n) of the surrounding medium.

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (3)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (4)$$

The solute's ground and excited state dipole moments are represented by the symbols μ_g and μ_e, respectively. The symbols h and c stand for the Planck constant and the speed of light in a vacuum, respectively. An alternate expression for the radii of Onsager cavities (a) and the solvent polarity functions f (ε, n) and g(n) is as follows:

$$f(\varepsilon, n) = \frac{\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}}{\left(1 - \frac{2\alpha}{a^3}\frac{\varepsilon - 1}{2\varepsilon + 1}\right)\left(1 - \frac{2\alpha}{a^3}\frac{n^2 - 1}{2n^2 + 1}\right)^2} \quad (5)$$

$$g(n) = \frac{\frac{n^2 - 1}{2n^2 + 1}\left(1 - \frac{\alpha}{a^3}\frac{n^2 - 1}{2n^2 + 1}\right)}{\left(1 - \frac{2\alpha}{a^3}\frac{n^2 - 1}{2n^2 + 1}\right)} \quad (6)$$

The dielectric permittivity, refractive index, solute spherical cavity radius, and average polarizability are denoted by ε, n, a, and α in these correlations, respectively. Bakhshiev discovered the following connections, and the requirements for the solute's isotropic polarizability are typically satisfied:

$$f_{BK}(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \quad (7)$$

$$g_{BK}(n) = \frac{3}{2}\left[\frac{n^4 - 1}{(n^2 + 2)^2}\right] \quad (8)$$

The dipole moments of the ground and excited states, when expressed in parallel form, can be written as follows:

$$\mu_g = \left|\frac{m_2 - m_1}{2}\right|\left[\frac{hca^3}{2m_1}\right]^{1/2} \quad (9)$$

$$\mu_e = \left|\frac{m_2 + m_1}{2}\right| \left[\frac{hca^3}{2m_1}\right]^{1/2} \qquad (10)$$

2.4 *Intrinsic Polarity Descriptor (IPD)*

In a chemical system, the difference in dipole moment (μ_e - μ_g) between the ground and excited states indicates how strongly a molecule is connected to its surroundings. However, in many physical processes, the effect of these changes on the system's energy is frequently proportional to the square of the change. In an electric field, the dipole interaction energy is given by:

$$E.dipole \propto (\mu_e - \mu_g)^2 \qquad (12)$$

The sensitivity of a dye molecule to its environment, particularly with respect to solvent polarity and hydrogen bonding interactions, is measured using a metric known as the Intrinsic Polarity Descriptor (IPD). First, it is defined as:

$$IPD = (\mu_e - \mu_g)^2 / Vm(\pi^* + HBD + HBA) \qquad (13)$$

The symbols μ_e and μg represent the dipole moments in the excited and ground states, respectively. The π^* solvent polarity parameter indicates the solvent's ability to stabilize the excited state. HBD (Hydrogen Bond Donor) and HBA (Hydrogen Bond Acceptor) quantify the solvent's ability to give and accept hydrogen bonds, respectively.

The IPD was initially developed to explain how hydrogen bonding interactions and solvent polarity impact the dipole transition in dye molecules. Normalization is required to allow for universal comparisons across various dye molecules and solvent conditions since IPD is composed of physical units. The following natural physical constants have been chosen for normalization:

$$IPD^* = IPD / \varepsilon_0 h \Delta v \text{ Stokes shift} \qquad (14)$$

h: Planck's constant, which characterizes scaling in quantum mechanics; ε0: The permittivity of empty space, which alters the dipole interaction with the surroundings; Δv: The difference in frequency between absorption and fluorescence (Stokes shift), which includes the energetic effects of solvent interactions. This form allows a direct comparison of molecule polarity changes under various chemical circumstances since all units are eliminated. Additionally, IPD is highly helpful for fluorescence-based research since it takes into account both solvent effects and energy relaxation processes. Lastly, regardless of the experimental circumstances, the IPD* formulation expresses the universal intrinsic feature of the dye molecule. It uses the Stokes shift and fundamental physical constants to scale the dye molecule's normalized sensitivity to its solvent environment. Regardless of the absolute levels of dipole moments or solvent properties, this metric shows how solvent interactions affect the dye's electronic structure.*

3. RESULTS AND DISCUSSION

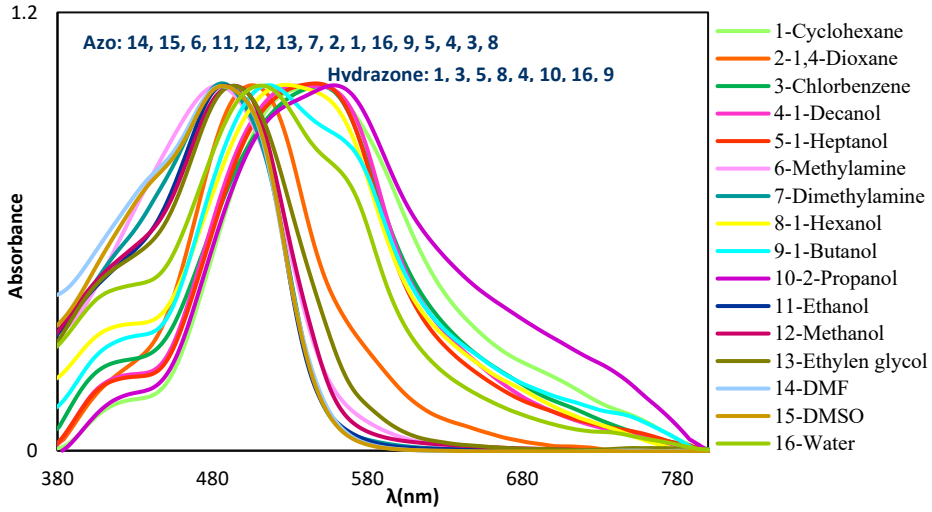
3.1 The media effects on the absorption and emission spectra behaviors

Absorption and fluorescence spectroscopy were used to study the photophysical behaviour of E124 in both isotropic and anisotropic liquid-crystal (LC) environments. Measurements were made at room temperature in solvents with varying polarity and hydrogen-bonding capacities; Tables 5 and 6 summarize the absorption and

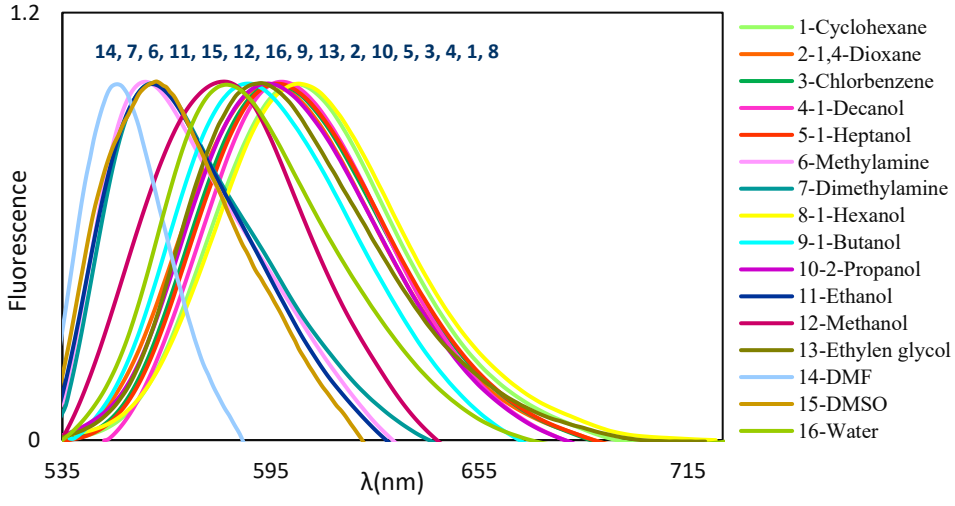
fluorescence maxima, showing how the surrounding medium affects the spectral properties; Figures 2 show the normalized absorption and fluorescence spectra of E124 in particular solvents. Complicated spectral behaviour is produced via azo–hydrazone tautomerism, which is made possible by the hydroxyl and azo functional groups in E124. Gaussian fitting spectral deconvolution was used to precisely identify each tautomer's absorption maxima. Azo and hydrazone forms were regularly found in isotropic solvents.

The presence of the two tautomeric forms results in wide bands with a main peak and a shoulder in the absorption spectra. The hydrazone form often shows a sharper and more powerful absorption peak in protic solvents, whereas the azo form shows up as a weaker shoulder at shorter wavelengths. On the other hand, the hydrazone peak diminishes or vanishes in aprotic solvents with significant hydrogen-bond-accepting capacity, such DMF and DMSO, leaving the azo form as the predominant characteristic. A bathochromic shift of 28 nm for the azo form and 18 nm for the hydrazone form is seen in Table 3.

The existence and sensitivity of both tautomers are verified by fluorescence spectra. Emission bands that represent the relative populations of each type are produced by excitation at respective absorption maxima. The normalized fluorescence spectra of the azo and hydrazone forms are shown in Figures 2. Table 3indicates that the bathochromic changes in fluorescence are 52 nm for the azo form and 24 nm for the hydrazone form, confirming the solvent-dependent sensitivity of the excited-state behaviour.



(a)



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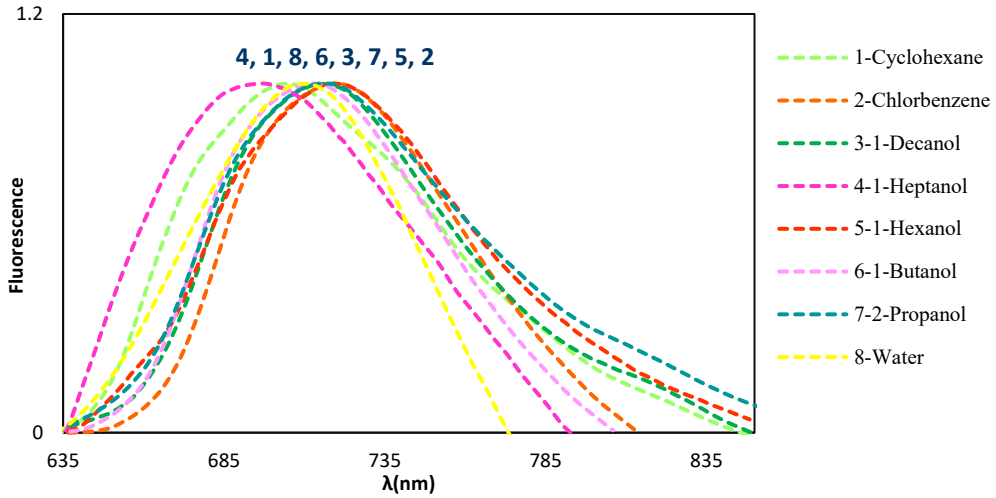


(c)

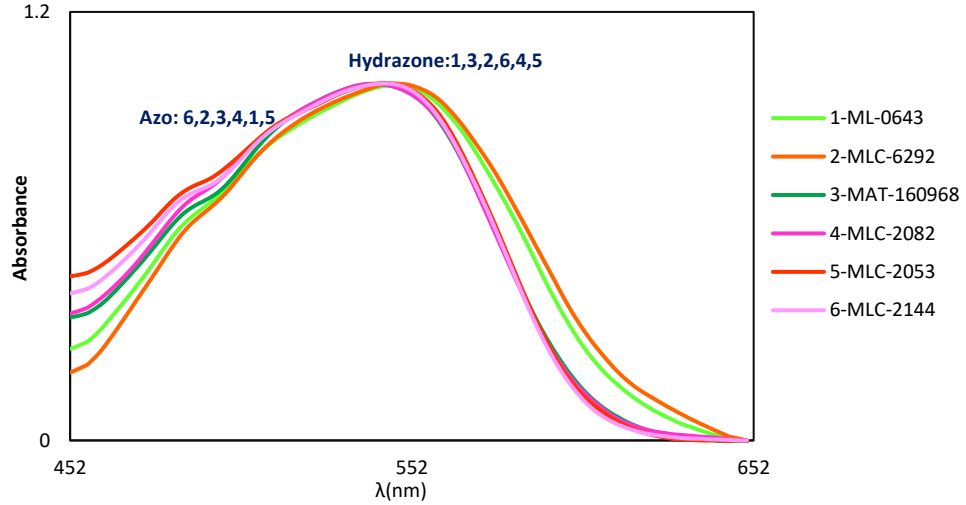
Fig. 2. *Normalized spectra of E124 in selected solvents with different polarities: (a) absorption spectra (b) azo form fluorescence spectra (c) Hydrazone form fluorescence spectra.*

Table 3. *Absorption and fluorescence spectral data of E124 in various organic solvents.*

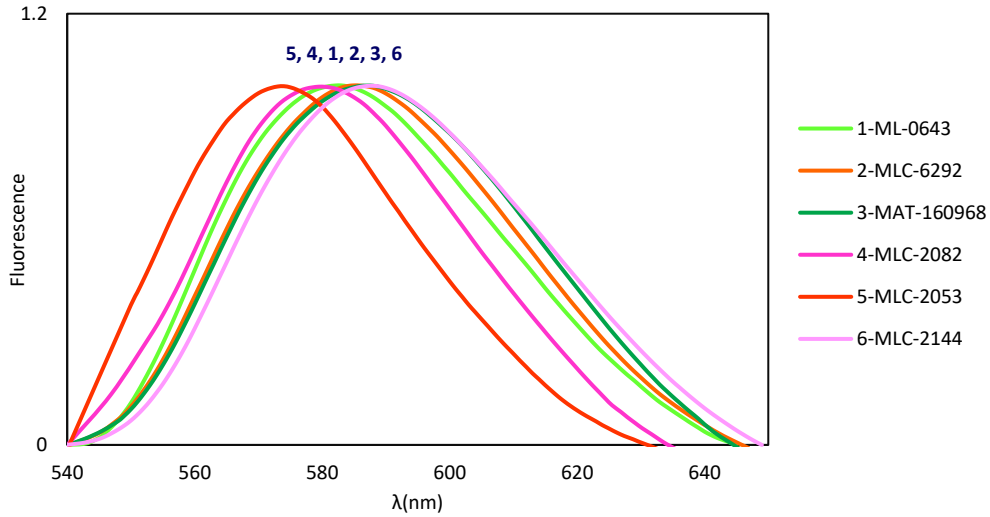
Solvent	λ_{1max} (Abs)*(nm)*	λ_{1max} (Fluo)*(nm)*	λ_{2max} (Abs)*(nm)*	λ_{2max} (Fluo)*(nm)*
Cyclohexane	*504*	*602*	*553*	*704*
1,4–Dioxane	*503*	*594*	-	-
Chlorobenzene	*513*	*596*	*555*	*720*
1–Decanol	*510*	*597*	*564*	*716*
1-Heptanol	*509*	*595*	*560*	*696*
Methylamine	*490*	*558*	-	-
Dimethylamine	*497*	*557*	-	-
1–Hexanol	*514*	*602*	*563*	*719*
1-Butanol	*508*	*587*	*571*	*712*
2–Propanol	*508*	*594*	*567*	*716*
Ethanol	*491*	*560*	-	-
Methanol	*494*	*581*	-	-
Ethylene glycol	*496*	*592*	-	-
DMF	*486*	*550*	-	-
DMSO	*487*	*561*	-	-
Water	*507*	*581*	*570*	*711*

Both tautomers contribute to the absorption spectra of E124 in anisotropic LC settings, although the hydrazone form is often more prominent. The hydrazone form is stabilized by the LC phase's directional ordering, but the azo form manifests as a weaker shoulder. Bathochromic changes in the absorption and fluorescence spectra show how the anisotropic media affects E124's photophysical characteristics. The spectral maxima in different LC hosts are summarized in Table 4, where the hydrazone form shifts by 18 nm and the azo form exhibits a bathochromic shift in fluorescence of about 12 nm. The normalized fluorescence and absorption

spectra in LC media are shown in Figure 2. Interestingly, neither the absorption nor the fluorescence maxima in isotropic and anisotropic media displayed a straightforward monotonic shift with increasing solvent polarity. Rather, irregular bathochromic and hypsochromic changes were seen, indicating that both general polarity effects and particular solute–solvent interactions, including hydrogen bonding, govern the photophysical characteristics of E110. When combined, these variables make it difficult to establish a strong association between polarity parameters and spectrum locations, demonstrating that solvent polarity is insufficient to explain the observed spectral patterns. As a result, it is crucial to research how materials interact.



(a)



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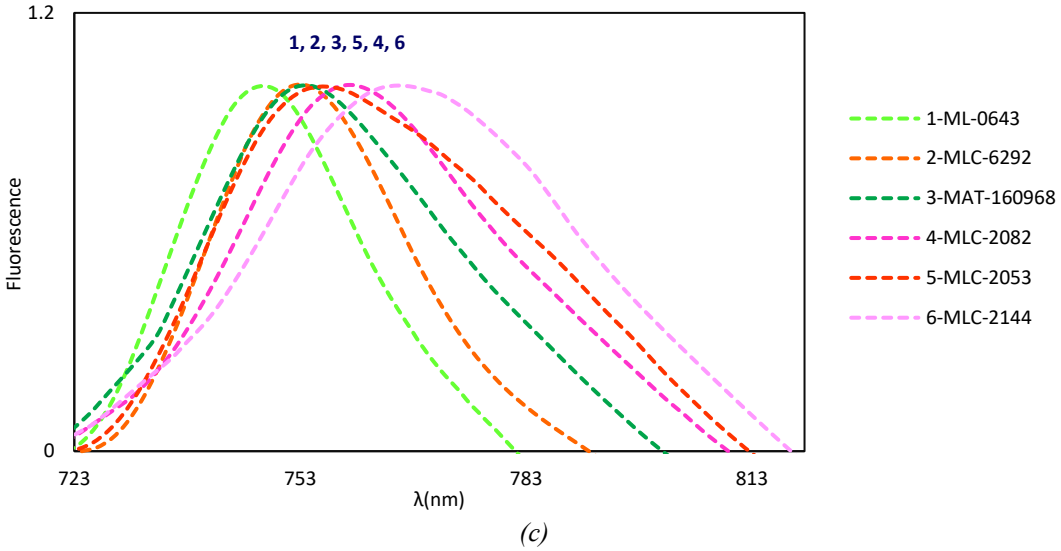


(c)

Fig. 3. *Normalized spectra of E124 in selected LCs with different polarities: (a) absorption spectra (b) azo form fluorescence spectra (c) Hydrazone form fluorescence spectra.*

Table 4. *Absorption and fluorescence spectral data of E124 in various lcs.*

LCs	λ_{1max} *(Abs)(nm)*	λ_{1max} *(Fluo)(nm)*	λ_{2max} *(Abs)(nm)*	λ_{2max} *(Fluo)(nm)*
ML-0643	*510*	*582*	*547*	*748*
MLC-6292	*512*	*585*	*548*	*752*
MAT-160968	*515*	*587*	*543*	*753*
MLC-2082	*511*	*580*	*546*	*759*
MLC-2053	*512*	*575*	*545*	*756*
MLC-2144	*517*	*587*	*548*	*766*

3.2 Correlation with multi-parameter solvent polarity scale

The contributions of solvents on the spectrum characteristics of E124 were evaluated using multi-parameter solvent polarity scales in accordance with the Kamlet–Abboud–Taft (KAT) model. A suitable selection of solvents was selected to get the most dependable correlations based on statistical indicators (R2 values and F-test significance) and visual examination of the data after all solvents were first included in the multi-parameter study.

The findings of several linear regression analyses of absorption, fluorescence, and Stokes shift data using the multi-parameter polarity scales are summarized in Tables 5 and 6. These studies yielded appropriate correlations for the chosen solvents. For easy comparison with the information shown in Figures 4 and 5, the results were converted into percentage contributions of the different solvent polarity parameters.

Table 5. *Regression fits to Kamlet–Abboud–Taft solvatochromic parameters for absorbance, fluorescence and Stokes' shift for dyes in organic solvents.*

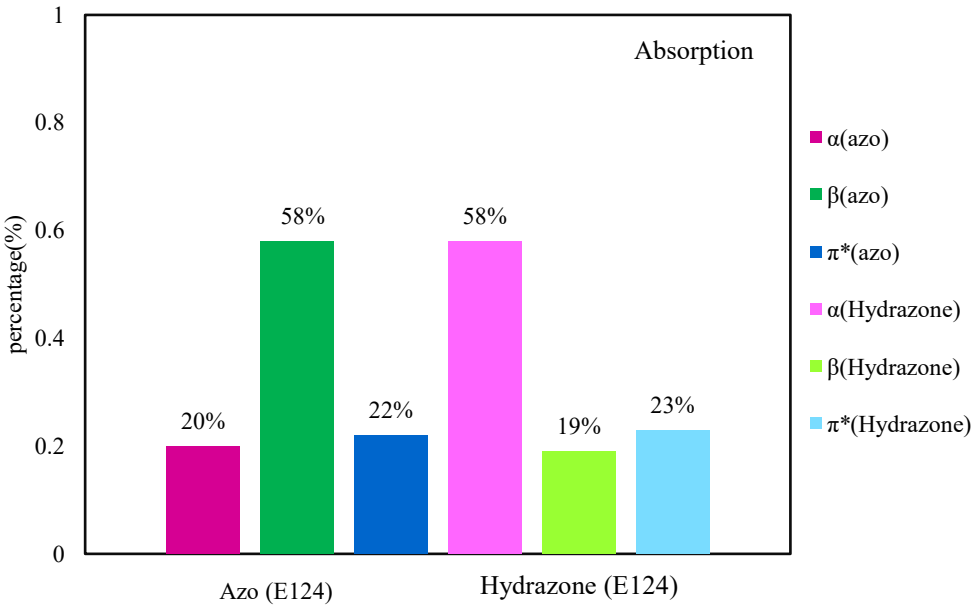
Dye	υ_0	*a*	*b*	*s*	R^2
Azo					
Abs	*24.132 (±1.408)*	*-1.164 (±0.254)*	*-3.371 (±1.168)*	*-1.278 (±0.626)*	*0.91*
Flu	*22.063 (±2.121)*	*-1.397 (±0.303)*	*-4.127(±1.690)*	*-1.142 (±0.965)*	*0.96*
St	*5.069 (±1.465)*	*0.536 (±0.446)*	*-2.563 (±1.301)*	*-1.028 (±0.812)*	*0.86*
Hydrazo					
Abs	*18.083 (±0.034)*	*-1.419 (±0.472)*	*0.462 (±0.148)*	*0.552 (±0.915)*	*0.99*
Flu	*14.211 (±0.088)*	*-10.950 (±3.271)*	*3.330 (±0.998)*	*10.170 (±3.004)*	*0.92*
St	*3.873 (±0.158)*	*-0.460 (±0.640)*	*-0.108 (±0.543)*	*0.349 (±0.341)*	*0.82*

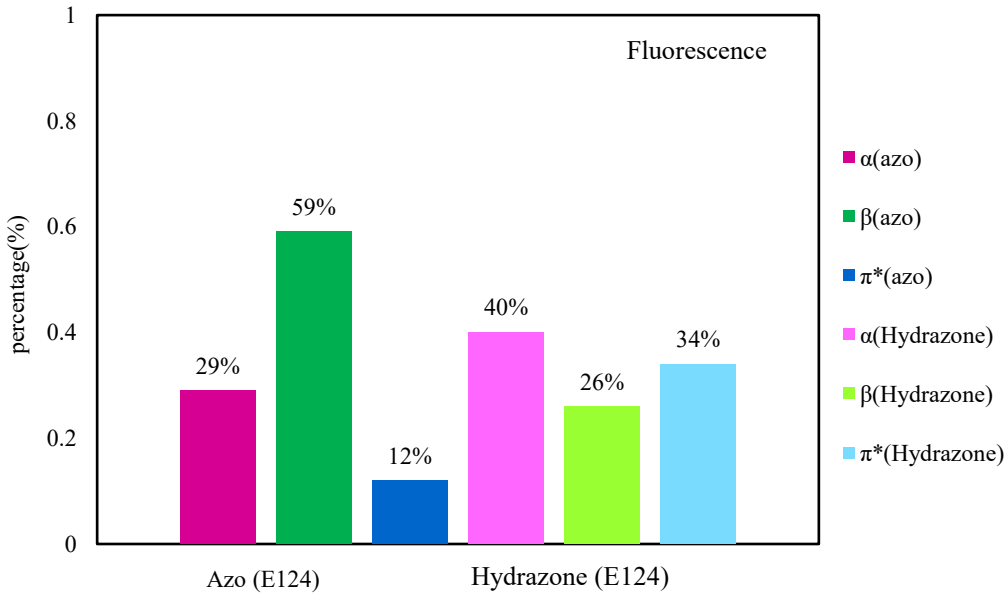
Table 6. *Regression fits to Kamlet–Abboud–Taft solvatochromic parameters for absorbance, fluorescence and Stokes' shift for dyes in Lcs.*

Dye	υ_0	*a*	*b*	*s*	R^2
Azo					
Abs	*20.62 (±4.144)*	*-0.623 (±0.483)*	*-4.193 (±1.771)*	*2.526(±0.998)*	*0.81*
Flu	*2.004 (±0.783)*	*-0.343 (±0.605)*	*80.223 (±3.172)*	*-43.690 (±1.714)*	*0.91*
St	*6.476 (±2.347)*	*-1.131 (±0.284)*	*-13.710 (±0.985)*	*6.881 (±5.028)*	*0.91*
Hydrazo					
Abs	*15.341 (±4.384)*	*0.439 (±0.338)*	*12.413 (±1.774)*	*-7.024(±0.959)*	*0.86*
Flu	*12.420 (±5.206)*	*-0.300 (±0.737)*	*5.659 (±1.973)*	*-3.853 (±1.042)*	*0.94*
St	*4.048 (±0.454)*	*1.319(±0.351)*	*34.138(±1.841)*	*-17.821(±9.948)*	*0.94*

The surrounding medium's polarity and hydrogen-bonding properties obviously affect E124's spectral behaviour. The azo tautomer of E124 is greatly influenced by the hydrogen-bond accepting ability (β) and dipolarity/polarizability (π) of common solvents. The dye structure's hydrogen-bonding and polar functional groups are consistent with the ground state's destabilization, as shown by the negative signs of the Kamlet–Abboud–Taft coefficients for the absorption process, and the excited state's stabilization through particular solvation, as verified by the negative coefficients found for the fluorescence wavenumbers. The hydrazo tautomer's absorption, fluorescence, and Stokes shift are primarily influenced by the hydrogen-bond donor ability (α) and the dipolarity/polarizability of the medium. The associated Stokes shift coefficients show that while greater dipolarity/polarizability promotes solvent reorientation around the dye, an increase in hydrogen-bond donor ability results in decreased reorientation.*

The polarity-dependent behaviour of E124 in liquid-crystal environments differs from that observed in conventional solvents; the effective solvation parameters are the hydrogen-bond accepting ability and the dipolarity/polarizability of the LC medium, with the hydrogen-bond donor ability playing a minor role. Since hydrogen bonding in LC phases is directional, the medium does not significantly aid conversion between the azo and hydrazo forms in the excited state. Therefore, thermodynamic stability rather than interaction-driven stabilization mostly determines the dominant tautomeric form of E124 in the LC environment, and the probability of ESIPT happening is minimal.


Absorption
percentage(%)
1
0.8
0.6
0.4
0.2
0
20%
58%
22%
58%
19%
23%
Azo (E124)
Hydrazone (E124)
α(azo)
β(azo)
π*(azo)
α(Hydrazone)
β(Hydrazone)
π*(Hydrazone)


Fluorescence
percentage(%)
1
0.8
0.6
0.4
0.2
0
29%
59%
12%
40%
26%
34%
Azo (E124)
Hydrazone (E124)
α(azo)
β(azo)
π*(azo)
α(Hydrazone)
β(Hydrazone)
π*(Hydrazone)

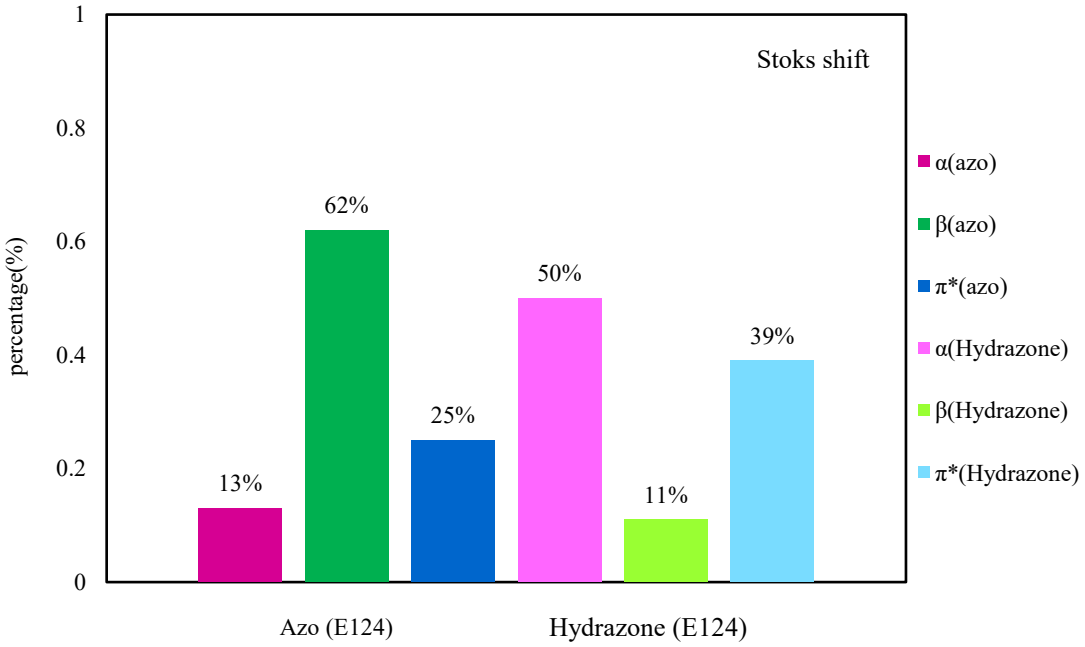
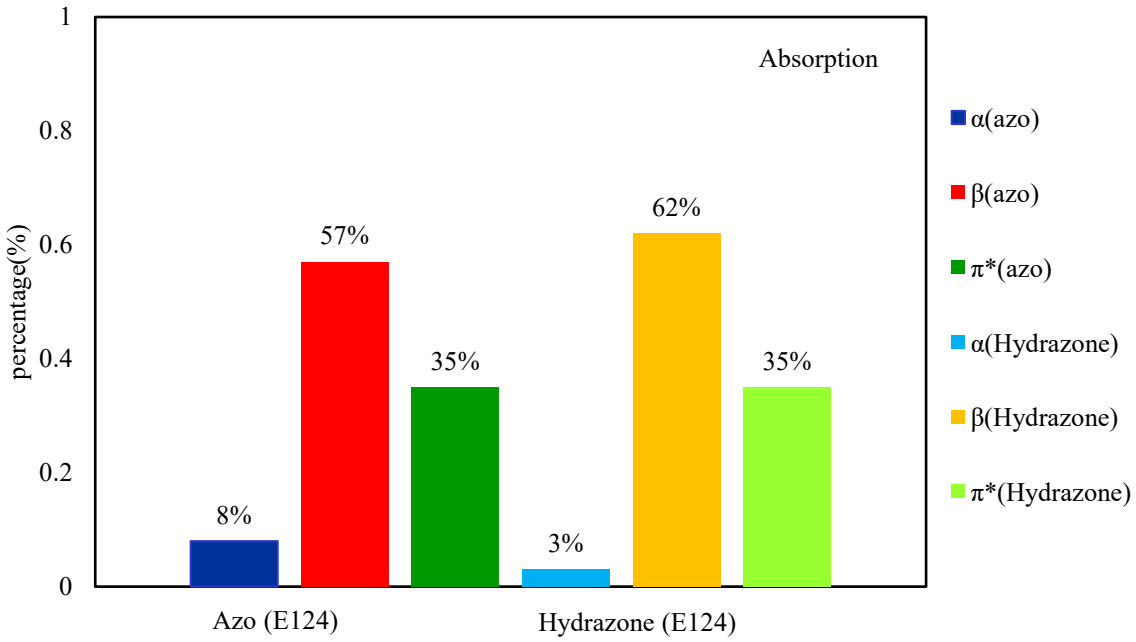


Fig. 4. *Percentage contribution of Kamlet–Abboud–Taft solvatochromic parameters for Absorption, Fluorescence and Stokes' shift of E124 in selected solvents.*



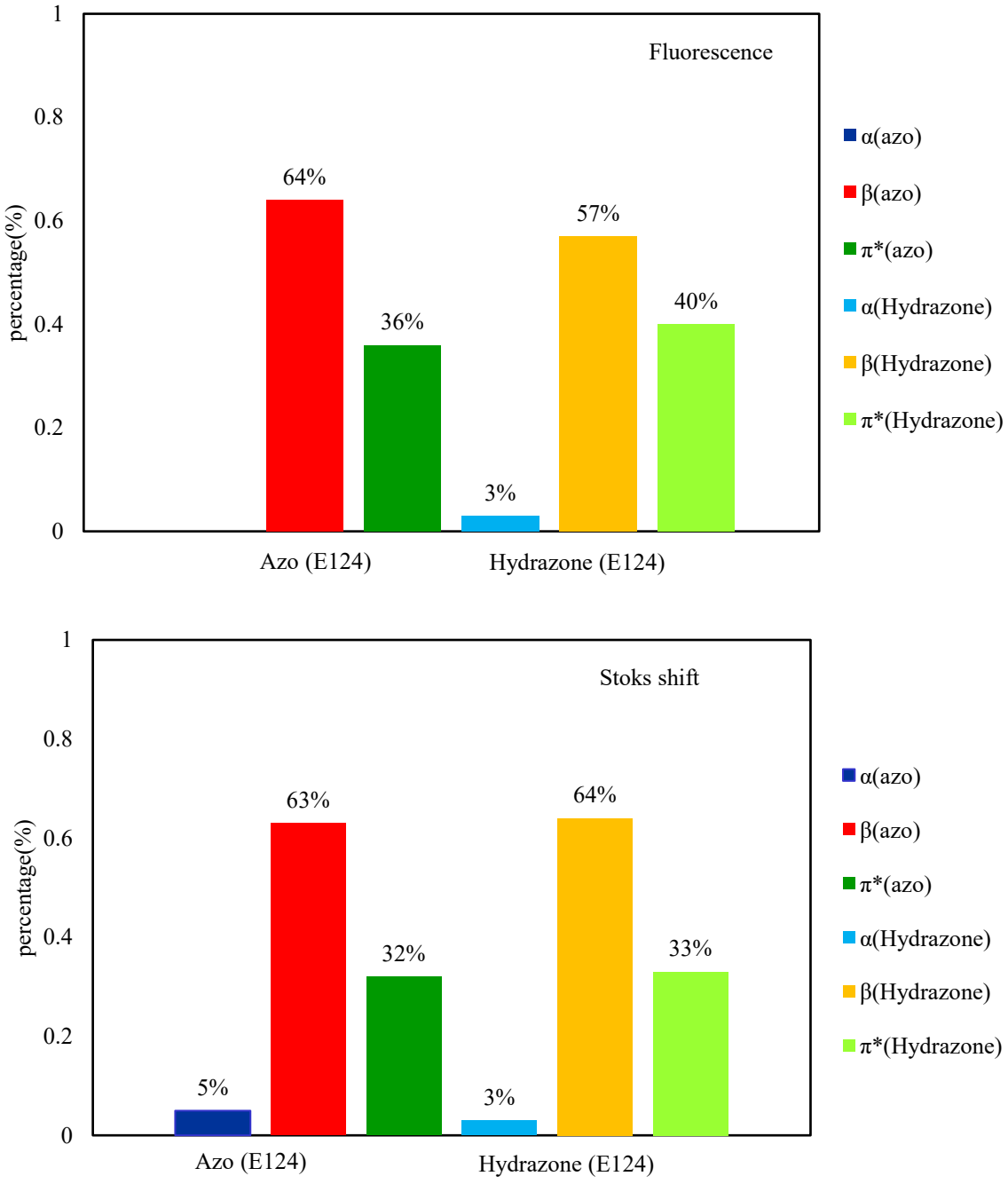


Fig. 5. *Percentage contribution of Kamlet–Abboud–Taft solvatochromic parameters for Absorption, Fluorescence and Stokes' shift of E124 in selected Lcs.*

3.3 Estimation of ground and excited state dipole moments

The ground- and excited-state dipole moments of E124 in its azo and hydrazone forms were estimated using solvent polarity functions, f(ε,n) and f(ε,n)+2g(n), and linear correlations of the spectrum shifts (va−vf) and (va+vf) with these functions. Table 7 presents the findings.

Table 7. *Dipole moments, cavity radius and correlation factor (R^2) for E124*

Dye	*Radius(Å)*	μ_g*(D)*	μ_e*(D)*	R^2
Bakhshiev(solvent)				
E124(Azo)	*6.10*	*1.64*	*6.15*	*0.87*
E124(Hydrazo)	*6.31*	*2.26*	*5.15*	*0.80*
Bakhshiev(Lcs)				
E124(Azo)	*6.10*	*1.74*	*4.65*	*0.91*
E124(Hydrazo)	*6.31*	*0.99*	*3.64*	*0.97*

The excited-state dipole moment of the azo form (μe = 6.15 D) in isotropic liquids is much larger than that of the ground state (μg = 1.64 D), indicating considerable intramolecular charge redistribution following photoexcitation in isotropic solvents. This phenomenon is explained by excited-state intramolecular proton transfer (ESIPT), which results in a highly polarized excited-state structure when an electron density shift from oxygen to nitrogen occurs simultaneously with proton transfer from the hydroxyl group to the azo nitrogen. However, the hydrazone form exhibits an ICT-dominated excited-state behaviour (μe = 5.15 D) and a bigger ground-state dipole (μg = 2.26 D) because ESIPT is less beneficial in this tautomer. This pattern demonstrates that the azo form is more vulnerable to excited-state charge redistribution, whereas the hydrazone form has a greater intrinsic ground-state polarity. The resonance structure of E124 in solvent solutions is seen in Figure 6.

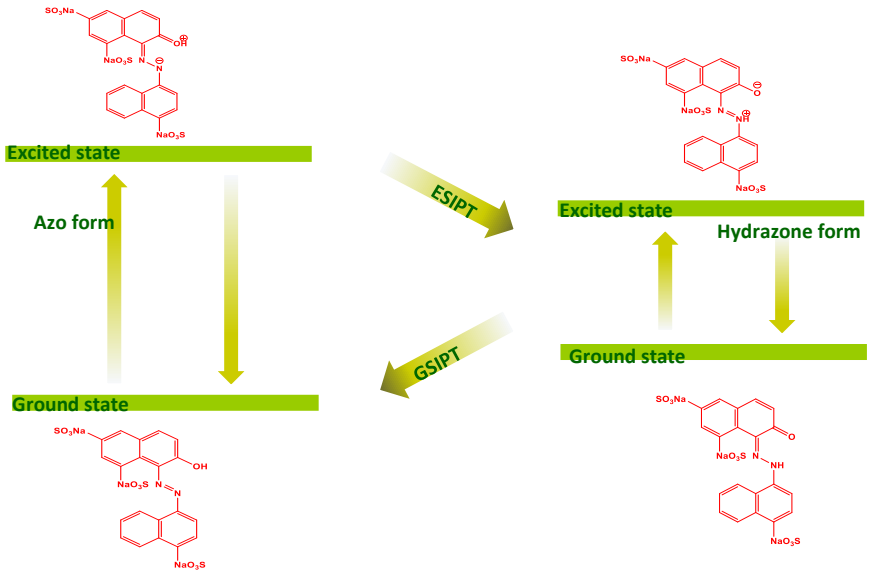


Fig. 6. *Resonance structure of E124 in solvent media.*

In anisotropic environments such as LC media, the excited-state dipole of the azo form considerably decreases (μe = 4.65 D) due to structural constraints imposed by the ordered and directed LC matrix. Similarly, the excited-state dipole of the hydrazone form is reduced (μe = 3.64 D), and the ground-state dipoles are also changed: the hydrazone form decreases (μg = 0.99 D), while the azo form somewhat increases (μg = 1.74 D). These restrictions on the molecular motions required to complete ESIPT or ICT processes lead to lower excited-state polarity and changed ground-state dipoles. Furthermore, by reducing the possibility of ground-state proton transfer (GSIPT) between the azo and hydrazone tautomers, the LC environment increases the stability of the hydrazone form in the ground state. These findings demonstrate that the photophysical behaviour of E124 is significantly influenced by intramolecular interactions such as ESIPT and ICT, which are further controlled by solvent polarity and the degree of molecular ordering in LC media. While the azo form is mostly dependent on excited-state charge redistribution, the hydrazone form shows greater ground-state polarity. By restricting chemical rearrangements and proton transfer, the LC matrix stabilizes certain tautomers and influences both ground-state and excited-state dipole moments.

3.4 Intrinsic polarity descriptor (IPD)

The polarity responsiveness of E124 in its azo and hydrazone tautomeric forms may be quantified using the intrinsic polarity descriptor (IPD) and its normalized form (IPD). These factors provide a logical explanation of how solvent polarity and medium anisotropy regulate the photophysical behaviour of this dye. They include molecular volume, dielectric and refractive characteristics of the surroundings, and the change in dipole moment upon excitation. Tables 8-9 provide a summary of the computed IPD* values for E124 in isotropic solvents and liquid-crystal (LC) media.*
The azo form of E124 has modest IPD values in isotropic environment in most solvents (0.35–1.50), but it increases significantly in polar hydrogen-bonding environments like DMSO (0.88), DMF (0.89), water (1.47), and methanol (1.00). A partial excited-state intramolecular charge-transfer (ICT) character inside the azo tautomer is consistent with these data, which show a significant shift in dipole moment upon excitation. The obtained IPD* values show that E124 in its azo form is nevertheless somewhat sensitive to the polarity and hydrogen-bond donating capacity of the medium, despite the rise in polarity being less noticeable than in more highly ESIPT-active azo dyes. On the other hand, in isotropic solvents, the hydrazone tautomer of E124 consistently exhibits low IPD* values (0.08–0.39). This behaviour, which reflects increased ground-state stiffness and decreased charge-redistribution capacity, unmistakably shows a small dipole-moment shift following activation. This tautomer's inhibition of ESIPT leads to improved structural stability and a reduced interaction with the solvent polarity field. Consequently, the hydrazone form is more persistent yet less sensitive to the environment; this characteristic is usually associated with azo dyes' greater biological stability and cytotoxic potential.*

Table 8. IPD parameter of azo dye in isotropic solvents.*

Solvent	IPD* *Azo*	IPD* *Hydrazo*
Cyclohexane	*0*	-
1,4–Dioxane	*0.38*	-
Chlorobenzene	*0.35*	*0.08*
1–Decanol	*0.95*	*0.26*
1-Heptanol	*0.95*	*0.28*
Methylamine	*1.30*	-
1–Hexanol	*1.50*	-
1-Butanol	*0.95*	*0.26*
2–Propanol	*1.10*	*0.31*
Acetone	*0.99*	*0.28*
Ethanol	*1.16*	-
Methanol	*1.00*	-

Ethylene glycol	*0.97*	-
DMF	*0.89*	-
DMSO	*0.88*	-
Water	*1.47*	*0.39*

Table 9. *IPD* parameter of azo dye in Lcs.*

LCs	IPD*	IPD*
	Azo	*Hydrazo*
ML-0643	*0.31*	*0.11*
MLC-6292	*0.33*	*0.12*
MAT-160968	*0.34*	*0.11*
MLC-2082	*0.37*	*0.12*
MLC-2053	*0.39*	*0.12*
MLC-2144	*0.45*	*0.14*

E124 maintains the same basic trend seen in isotropic liquids in anisotropic LC environments. Despite the structural limitations imposed by the ordered LC matrix, the azo tautomer exhibits moderate IPD values (0.31–0.45), suggesting that observable excited-state polarity enhancement still takes place. The LC environment limits molecular rearrangements, partially reducing both ICT and ESIPT-related charge redistribution, as seen by the lower IPD* when compared to isotropic solvents.*

The hydrazone form, on the other hand, sustains extremely low IPD values (0.11–0.14) in all LC hosts, supporting its distinctive ground-state stability and little polarity shift following activation. A stiff, less polarizable electronic structure that is unable to effectively adjust to external ordering is indicated by a low IPD*. Since the tautomer is less reactive yet accumulates more easily in biological settings, this tendency is consistent with the common fact that hydrazone-enriched systems show greater persistence and higher cytotoxicity. A distinct tautomer-dependent polarity response is seen in E124. The hydrazone form is more stable and just slightly sensitive (very low IPD*), while the azo form exhibits more polarity sensitivity and environmental reactivity (higher IPD*). These findings show how solvent polarity and medium anisotropy control the overall behaviour of the two tautomers and emphasize their basic photophysical differences.*

CONCLUSION

E124 also experiences azo–hydrazone tautomerism due to the existence of proton-donating and proton-accepting sites, resulting in two different photophysical behaviours. In comparison to the azo form, the hydrazone tautomer continuously absorbs and emits at longer wavelengths due to its greater conjugation and intrinsic higher polarity. Dipole-moment analysis for both tautomers reveals a definite rise in polarity from the ground state to the excited state, although the degree of this shift varies significantly between them. The hydrazone form displays a more moderate rise, consistent with its weaker ICT nature and stronger ground-state stability, whereas the azo form displays a more prominent excited-state dipole augmentation, indicating partial ESIPT-assisted charge redistribution. The functional groups that control polarity also vary between the tautomers: the NH moiety controls the polarity pattern in the hydrazone form, whereas the phenolic OH group drives resonance and charge displacement in the azo form. The degree of dipole rearrangement upon stimulation and solvatochromism are controlled by these structural variations. Accordingly, the IPD parameter shows that in isotropic liquids, the hydrazone form of E124 retains low polarity responsiveness and good intrinsic stability, whereas the azo tautomer shows increased environmental reactivity and stronger polarity sensitivity. Although the azo form is still the more polarizable species, space constraints in liquid-crystal media inhibit chemical rearrangement, resulting in lower IPD* values for both tautomers.*

Overall, the azo form of E124 exhibits higher excited-state reactivity and increased susceptibility to medium effects, whereas the hydrazone form is intrinsically more stable and greatly less affected by solvent polarity. Complementary cell-based research might shed more light on the possible harmful consequences of hydrazone-dominated systems in photothermal or bio-related applications, as high stability and low responsiveness may be associated with enhanced biological persistence.

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