

2D NMR, Solvatochromic Behaviour and DFT Studies of Some Azo-quinoline Derivatives

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In this study, the chemical structures of three azo-quinoline derivatives (S1, S2, and S5) were unequivocally established using comprehensive 2D NMR techniques, including COSY, HSQC, HMBC, and TOCSY. Their solvatochromic behaviour was investigated in seven solvents of varying polarity. Both S1 and S5 showed moderate correlations (R^2) of 0.45 and 0.681 with solvent polarity function and dispersive effects respectively. DFT/TD-DFT calculations at the B3LYP/6-311++G (d, p) level showed S5 as having the smallest gas-phase HOMO-LUMO energy gap (2.71 eV) and the most elongated N=N bond (1.3277 Å), indicating enhanced conjugation. The excellent agreement between the computed and experimental absorption maxima for S2 validated the computational protocol. These structure-property correlations provide a pedestal for designing quinoline-based chemosensors and optoelectronic materials.

Keywords: Azo-quinoline, 2D NMR, solvatochromism, DFT calculations, optical materials

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Quinoline, a heterocyclic aromatic compound characterized by a fused benzene and pyridine ring, has emerged as a privileged scaffold in medicinal chemistry [1]. Functionalization of the quinoline nucleus has led to medicinal candidates reported as antimalaria [2], anticancer [3], anti-inflammatory [4], antimicrobial [5], antioxidant [6], anticonvulsant [7], antituberculosis [8], cardiovascular [9], and anti-COVID [10]. Quinoline derivatives have also been utilized as analytical reagents [11], organic light-emitting diode (OLED) materials [12], and chemosensors [13, 14]. As a planar bicyclic aromatic system, conjugation with the azo group makes it attractive for cation and anion recognition.

Recently, Olaleye and co-workers [15] reported three new azo-quinoline derivatives, S1 (4-[2-(8-hydroxy-5-nitroquinolin-7-yl)diazen-1-yl]benzene-1-sulfonamide), S2 (7-[2-(2-methoxy-4-nitrophenyl)diazen-1-yl]-5-nitroquinolin-8-ol), and S5 (5-[2-(7-hydroxynaphthalen-1-yl)diazen-1-yl]quinolin-8-ol) as sensitive sensing reagents for nickel ions (Figure 1). These compounds were synthesized via diazotization and diazocoupling. While S1 and S2 utilized nitroquinoline, a known anticancer agent, as a coupling component, S1 also used diazonium generated from sulfanilamide, another antimicrobial agent, as a diazonium ion reagent. S5 was synthesized using diazonium from 8-amino-2-naphthol and 8-hydroxyquinoline as the coupling agent. The researchers reported FTIR, ESI-MS, and 1D NMR spectra of these compounds. This study aimed to

establish the chemical structures of these azo dyes unequivocally by reporting 2D NMR experiments, solvatochromic behaviours, and correlating the experimental absorption maxima with solvent parameter data, and carrying out density functional theory (DFT) and time-dependent density functional theory (TD-DFT).

EXPERIMENTAL

Materials and Method

NMR data were acquired on Bruker Avance spectrometers (UK) at 600 and 800 MHz. S1 and S2 were recorded in deuterated dimethylsulfoxide and S5 in deuterated acetone. UV-vis spectral data were obtained using a Nicolet Evolution 300 UV-visible spectrophotometer (Thermo Electron Corporation, USA) at 25 °C with a 1 cm path length. The UV-Vis spectra of S1, S2, and S5 were recorded at concentrations of 0.0268, 0.0272, and 0.0318 mM, respectively.

Compounds S1, S2 and S5 were synthesized as reported by [15]. All calculations were performed using the Gaussian 09 program package (Revision C.01) [16]. Geometry optimizations were carried out for the neutral singlet ground state (S_0) in the gas phase using the B3LYP functional and the 6-311++G (d, p) basis set and self-consistent field (SCF) as convergence criteria. No symmetry constraints were applied.

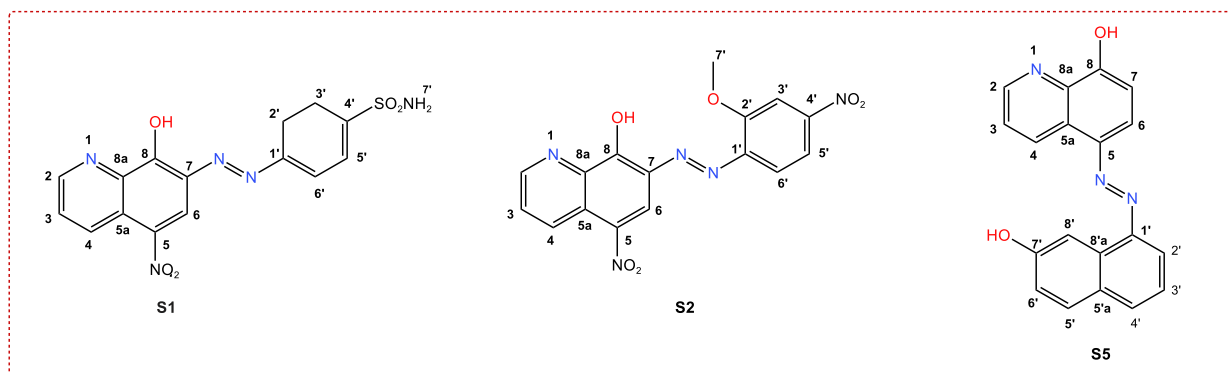


Figure 1. Chemical structures of compounds S1, S2 and S5.

TD-DFT calculations were then performed on the optimized ground-state geometries to obtain the Higher Occupied Molecular Orbital energy (HOMO), Lower Unoccupied Molecular Orbital (LUMO), oscillator strengths, and absorption wavelengths. The same functional and basis set were used, but the number of states was set at 6. Solvent effects were included using the polarizable continuum model (PCM) as implemented in Gaussian 09. The solvents studied were methanol, ethanol, ethyl acetate, dichloromethane, N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile. HOMO and LUMO energies, along with HOMO–LUMO gaps, were calculated from optimized ground-state orbitals in the gas phase, while excitation energies were obtained in solution.

RESULTS AND DISCUSSION

NMR Analysis of S1

Multiplet analysis (Table 1) and ^1H NMR of compound S1 revealed six proton signals [15]. From the integrals, three of the signals were integrated for 1H, δ_{H} 8.12, and $\delta_{\text{N-H}}$ 7.54 for 2H each, and δ_{H} 8.02 – 8.04 by 3H atoms. The δ_{H} 8.12 was from equivalent protons; H-6' and H-2'; and $\delta_{\text{N-H}}$ 7.54 was from sulphonamide protons. The $\delta_{\text{N-H}}$ disappeared when it was exchanged with deuterated water (Figure 2). The ^{13}C NMR spectrum [15] revealed 13 peaks: six methine and seven quaternary carbon signals. The two tall peaks at δ 127.1 and δ 123.1 were sets of equivalent carbons C-6'/C-2' and C-5'/C-3', respectively.

Table 1. Multiplet analysis of compound S1.

H/C position	Chemical shift, δ ppm		Coupling constant, J , Hz	HSQC	HMBC
	$^1\text{H}^*$	^{13}C	$^1\text{H} - ^{13}\text{C}^{**}$		
2	9.37 (1H)	135.93	8.70 (d)	135.93	C3, C4, C8
3	8.04 (1H)	138.91	m	----	C4, C5a
4	9.04 (1H)	147.11	7.20 (d)	147.11	C3, C2, C5
5	-----	126.52	----	----	----
6	8.89 (1H)	117.77	----	117.77	C7, C5a, C8
7	----	134.40	----	----	----
8	-----	162.50	----	----	----
5a	-----	124.84	----	----	----
8a	-----	132.10	----	----	----
1'	-----	153.31	----	----	----
2', 6'	8.12 (2H)	127.07	8.20 (d)	127.07	C3'/C5', C1', C4'
3', 5'	8.03 (2H)	123.07	m	123.07	C2'/C6', C4', C1'
4'	-----	145.53	----	----	----
N-H	7.54 (2H)	-----	s	----	----

*Integral **multiplicity (s, d, and m represent singlet, doublet, and multiplet)

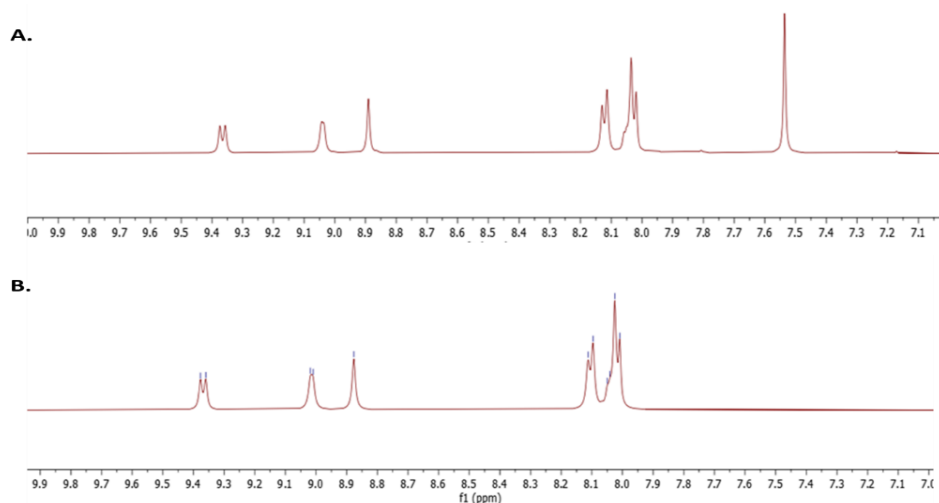


Figure 2. Overlaid ^1H NMR of (A) S1 + DMSO- d_6 (B) S1 + DMSO- d_6 + D_2O indicating exchangeable proton.

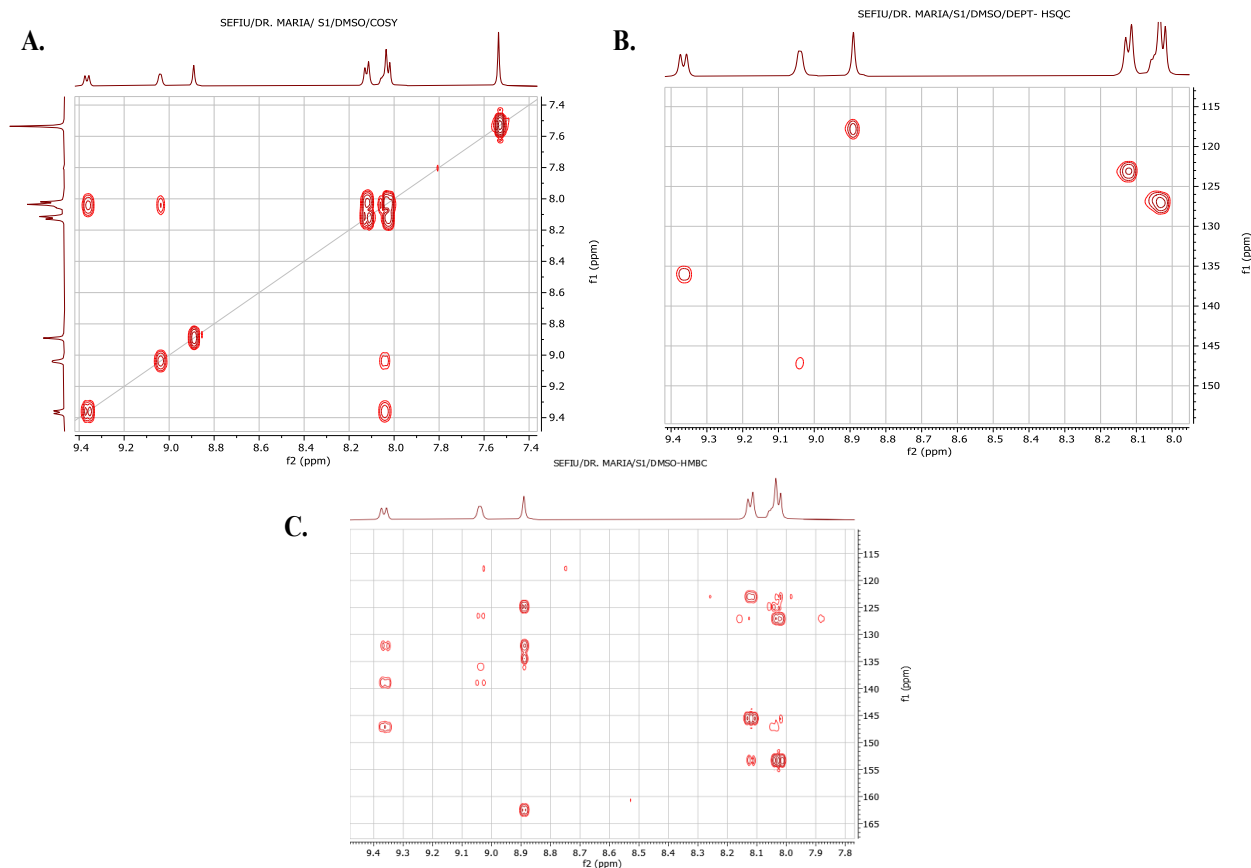


Figure 3. (A). COSY; (B). HSQC; (C). HMBC spectra of compound S1.

The COSY experiment (Figure 3A) showed that the multiplet peak at δ 8.04-8.02 was overlapped by signals of equivalent protons (H-3' and H-5') and H-3. The H-3 signal correlated with H-2 and H-4 and very close were the correlations of H-3', H-6'

and H-2', H-5'. The HSQC-DEPT ($^1J_{\text{CH}}$) (Figure 3B) analysis showed six contours; a broad contour was obvious with the overlapped multiplet signals. The superimposed signals were also evident from HMBC experiment (Figure 3C).

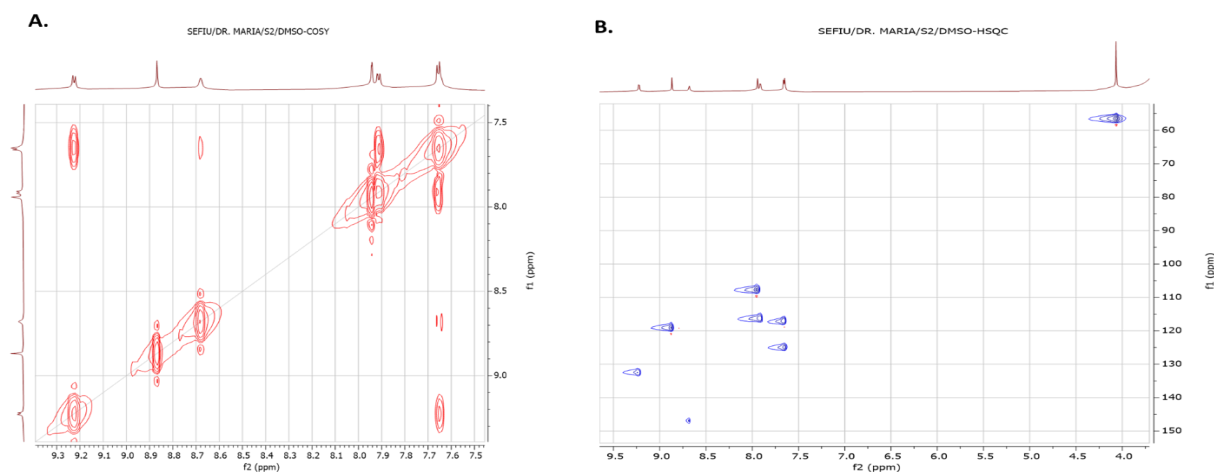


Figure 4. (A). COSY spectra of S2; (B). HSQC spectra of S2.

Table 2. Multiplet analysis of compound S2.

H/C position	Chemical shift δ , ppm		Coupling constant, J , Hz	HSQC	HMBC
	$^1\text{H}^*$	^{13}C			
2	9.23 (1H)	132.67	8.50 (d)	132.67	C3, C4
3	7.72-7.58 (1H)	124.95	m	124.95	C5
4	8.68 (1H)	146.90	4.30, 1.80 (dd)	147.38	----
5	-----	126.52	----	----	----
6	8.87 (1H)	119.24	s	119.24	C5, C8a, C8
7	-----	132.73	----	----	----
8	-----	174.57	----	----	----
5a	-----	146.69	----	----	----
8a	-----	138.14	----	----	----
1'	-----	125.11	----	----	----
2'	-----	155.27	----	----	----
3'	7.94 (1H)	107.91	2.40 (d)	107.91	C2', C4', C5'
4'	-----	147.38	----	----	----
5'	7.91 (1H)	116.44	8.70, 2.40(dd)	116.44	C4', C3'
6'	7.72-7.58 (1H)	117.21	m	117.21	C4', C2', C3'
7'	4.06 (3H)	56.53	s	56.53	C2'

*Integral **multiplicity (s, d, m, and dd represent singlet, doublet, multiplet, and double doublet)

NMR Analysis of S2

Seven proton signals were obvious in the ^1H NMR spectra [15] and signal analysis (Table 2). All signals were aromatic except for $\delta_{\text{H-7'}}$ 4.07, which was aliphatic. The integration of the peaks indicated 1H atom except the aliphatic 3H of methoxyl and multiplet signal δ_{H} 7.72-7.58, which was a result of overlapped peaks. At δ 7.65 of H-3, the COSY experiment (Figure 4A) indicated a correlation

with H-2, δ 9.23. At the same chemical shift of H-3, H-6' correlated with H-5,' thus showing that the overlapped signals were H-3 and H-6'. The HSQC, $^1J_{\text{CH}}$ (Figure 4B), which showed eight correlations, further confirmed the superimposition of peaks $^1J_{\text{CH}}$ at 124.95 (C-3) and 117.21 (C-6') at multiplet peaks δ 7.72-7.58. Notably, $\delta_{\text{H-4}}$ 8.68 was double doublet arising from correlations of ^3J with H-3 and ^4J with H-2. In addition, H-5' δ 7.91 appeared as a double doublet by correlating with H-6' and H-3'. A total of sixteen

carbon signals were present in the ^{13}C NMR and DEPT analysis [15]: seven methine, one methyl, and eight quaternary carbon atoms. The signal at δ 174 ppm, assigned to C-8, indicates tautomerization to the ketonic form in in DMSO- d_6 . From previous studies [17], the carbon atom, which holds a hydroxyl group in the azo form, has a chemical shift of 160 ppm, while the hydrazone carbon resonates at 170-180 ppm. This indicated that S2 existed predominantly as hydrazone in DMSO when ^{13}C NMR was run; however, the δ NH expected in the HNMR of its hydrazone tautomer was absent, which could be due to the rapid shift in equilibrium to the azo form. The molecular structure of compound S2 was established through a detailed analysis of its two-dimensional NMR analysis corroborating the earlier 1D experiment.

NMR Analysis of S5

Multiplet analysis (Table 3) and ^1H NMR [15] of compound S5 in acetone- d_6 illustrated 11 aromatic proton signals δ 7.27 to 9.47, which were all integrated for the 1H atom. In contrast, multiple signals were obtained in the ^1H NMR of S5 run in DMSO- d_6 and pyridine- d_5 [15]. It is worth noting that low-field signals of δ 17.25 and 17.80 were obtained in DMSO

and pyridine, respectively. These deshielded signals were suggestive of NH in the hydrazone tautomeric form of S5 [18]. Thus, S5 exists predominantly as hydrazone tautomers in DMSO and pyridine and azo tautomers in acetone.

The ^{13}C NMR experiments of compound S5 in acetone [15] revealed 19 signals: 11 methine and eight quaternary carbon atoms. Chemical shift at 157.26 ppm was assigned to C-8, which bore a hydroxyl group moiety. On the other hand, in DMSO [15], compound S5 showed $\delta_{\text{C-8}}$ 174.15; the carbon experiment was not run in pyridine. This observation further affirmed the hydrazone predominance of S5 in DMSO, similar to that of S2. The ^1H - ^1H TOCSY-100 experiment (Figure 5A) revealed that H-2 coupled with H-3 ($^3J = 8.50$ Hz) and H-4 ($^4J = 1.60$ Hz); thus, a double doublet peak was observed for H-2. Similarly, H-4 correlated with H-3 ($^3J = 4.10$ Hz) and H-2 ($^4J = 1.60$ Hz). However, H-3 orthocouples H-2 ($^3J = 8.50$ Hz) and H-4 ($^3J = 4.10$ Hz). HSQC (Figure 5B) showed eleven $^1J_{\text{CH}}$ signals, thus confirming the chemical structure of S5. Experiments using HMBC (Figure 5C) revealed $^2J_{\text{CH}}$, $^3J_{\text{CH}}$, and $^4J_{\text{CH}}$ correlations.

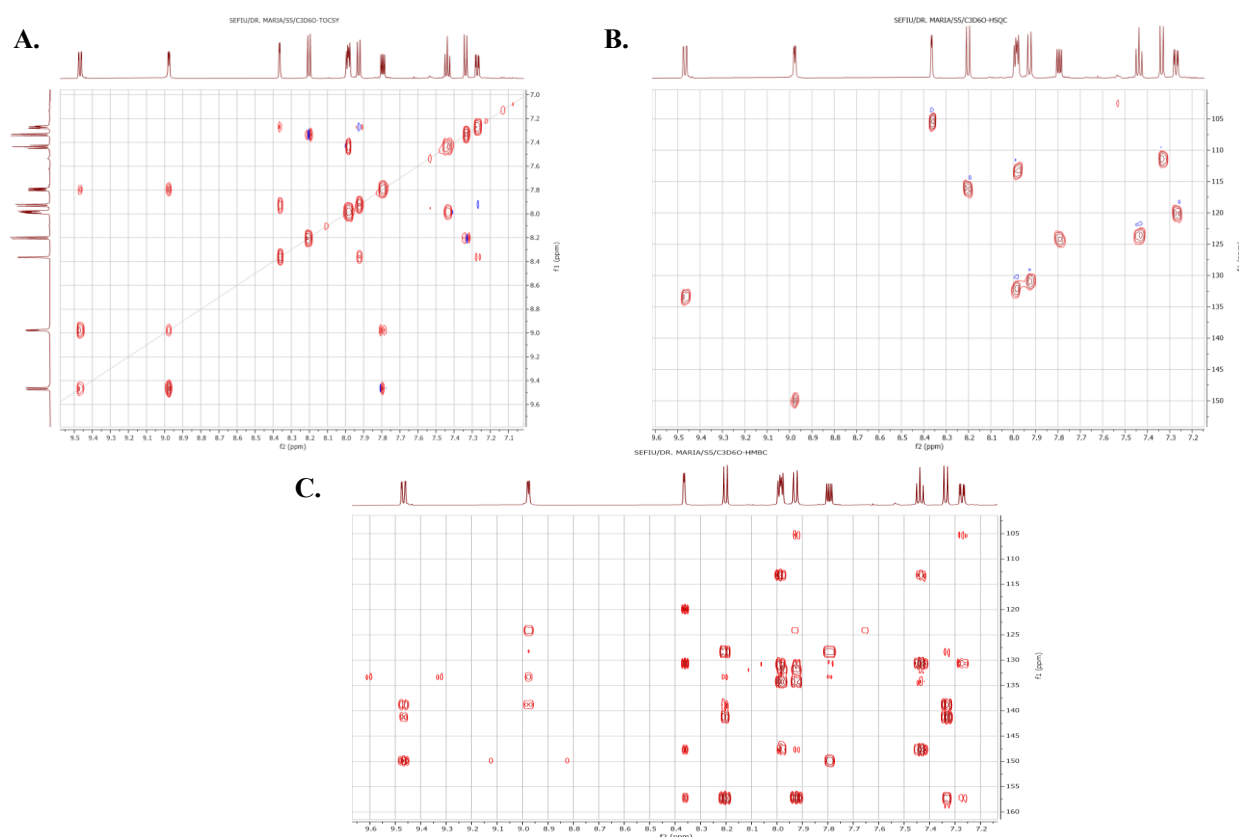


Figure 5. (A). TOCSY; (B). HSQC; (C). HMBC spectra of compound S5.

Table 3. Multiplet analysis of compound S5.

H/C position	Chemical shift, δ ppm		Coupling constant, J , Hz	HSQC	HMBC
	$^1\text{H}^*$	^{13}C	$^1\text{H} - ^1\text{H}^{**}$		
2	9.47 (1H)	133.32	8.50, 1.60 (dd)	133.32	C4
3	7.79 (1H)	124.11	8.50, 4.10 (dd)	124.11	C4, C2, C5
4	8.98 (1H)	149.89	4.10, 1.60 (dd)	149.89	C5a, C2
5	-----	128.34	----	----	----
6	8.20 (1H)	116.04	8.40 (d)	116.04	C5, C8, C8a
7	7.34 (1H)	111.26	8.40 (d)	111.26	C8a, C8, C5a
8	-----	157.26	----	----	----
8a	-----	141.25	----	----	----
5a	-----	138.79	----	----	----
1'	-----	130.77	----	----	----
2'	7.98 (1H)	113.21	3.80 (d)	113.21	C1'
3'	7.44 (1H)	123.41	7.80, 7.80 (t)	123.41	C2', C4', C8a'
4'	7.99 (1H)	131.91	4.20 (d)	131.91	C5a', C2', C5'
5'	7.93 (1H)	130.65	8.90 (d)	130.65	C5a', C7', C8'
6'	7.27 (1H)	119.93	8.80, 2.50 (dd)	119.93	C5', C7', C8'
7'	-----	157.17	----	----	----
8'	8.36 (1H)	105.33	2.40 (d)	105.33	C8a', C7', C6'
8'a	-----	147.67	----	----	----
5'a	-----	134.26	----	----	----

*Integral **multiplicity (d, dd, and t represent doublet, double doublet and triplet)

Solvatochromic Behaviour of Azo-quinolines in Different Solvents

The solvatochromic behaviour of the three azoquinoline derivatives was evaluated by correlating their longest-wavelength absorption maxima (λ_{max}) with a solvent polarity gradient, ranging from low-polarity media, such as ethyl acetate and dichloromethane, to strongly polar protic (methanol, ethanol), and aprotic (acetonitrile, DMF, and DMSO) solvents. This analysis revealed that the spectral shifts are dependent on the chemical structures of the compounds, which determine the interaction between the solvents and the compounds. Representative UV-vis spectra are shown in Figure 6 and wavelengths of maximum absorption are summarized in Tables 6-8.

For compound **S1**, which bears the electron-withdrawing sulfonamide and nitro groups, a bathochromic shift was observed as the solvent polarity increased. In low-polarity ethyl acetate and dichloromethane, λ_{max} remained at 420 nm. Upon moving to ethanol, a shift of +6 nm occurred, but a more substantial red shift became evident upon

transitioning to acetonitrile (+11 nm), DMSO (+15 nm), and DMF (+17 nm). The near-identical absorption in methanol and ethyl acetate suggests that specific hydrogen-bond donation from protic solvents does not significantly affect the electronic structure; rather, the general dipolar nature of the highly polar aprotic media predominantly stabilizes the excited state. The sulfonamide moiety likely facilitates strong dipolar interactions with DMF and DMSO, accounting for the pronounced shifts in these solvents.

In contrast, compound **S2** exhibits a divergent trend. Low-polarity solvents produced absorption maxima of 438 nm in ethyl acetate and 437 nm in dichloromethane. This suggests that ground-state conjugation is well established even in weakly polar media. However, upon introduction of protic solvents, a hypsochromic shift occurs, -8 nm in methanol and further to -12 nm in ethanol. This unusual blue shift indicates that protic solvents may disrupt the intramolecular hydrogen bonding interactions of the methoxy-nitro phenyl ring. Conversely, a red shift occurs when moving to polar aprotic solvents: DMF (+4 nm) and DMSO (+7 nm).

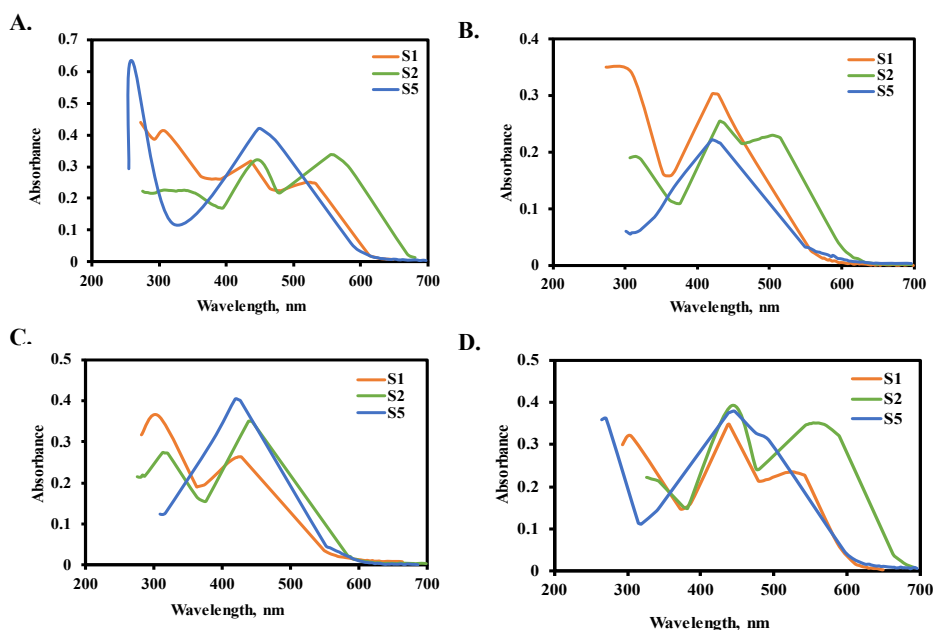


Figure 6. Overlaid UV-vis spectra of S1, S2, and S5 in (A). DMSO; (B). MeOH; (C). EtOAc and (D). DMF.

Compound **S5**, which incorporates an extended naphthol system, displays a unique solvent-specific solvatochromic profile. In low-polarity ethyl acetate and dichloromethane, λ_{max} ranges from 419 to 421 nm, with only slight increases in methanol (420 nm) and ethanol (424 nm). Notably, acetonitrile produces a hypsochromic shift of -3 nm, suggesting that this solvent forces a twisted conformation that disrupts the extended π -conjugation of the naphthol-azo-quinoline framework. Moving to DMF produces a bathochromic shift to 430 nm, while DMSO elicits a large red-shift to +29 nm. This pronounced display in DMSO implies that the naphtholic hydroxyl group engages in strong, specific hydrogen bonding interactions with the highly polar aprotic solvent, which stabilizes a planar, extended chromophore and maximizes π -electron delocalization across the entire molecular skeleton.

Overall, the trends confirm that extended conjugation, electron-donating substituents such as methoxy or hydroxyl, and the ability to form specific solvent-solute hydrogen bonds collectively enhance solvatochromic shift, whereas strong electron-withdrawing groups tend to reduce polarizability and restrict the dynamic range of optical shifts.

Solvent Parameter Correlation Studies

In order to establish the pattern of forces at play that led to the observed spectral patterns by [15] in the various polar protic and aprotic solvents, we correlated function of solvent polarity and function

of dispersive interaction with the maximum absorption peaks of each compound. Solvent parameters data were adapted from [19].

The solvent polarity function measures the interaction between the solute and solvents. This is mathematically denoted as $f(\epsilon, n) = \frac{2n^2+1}{n^2+2} \left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right]$, where ϵ and n are the dielectric constant and refractive index of the solvents respectively.

The variations in the longest absorption maximum with the solvent polarity function are presented in Table 4. All compounds gave positive slopes and the correlation coefficients were in the following order: S1 > S5 > S2. For S1, the correlation was moderate ($R^2=0.450$), suggesting that bulk solvent polarity may contribute to its photophysical behaviour, but this relationship alone does not establish a specific interaction mechanism. The presence of the sulphonamide moiety in S1 could be consistent with greater sensitivity to polar environments, but this interpretation remains tentative.

The dispersive function indicates the intermolecular polarization component of the intermolecular interaction between dyes dispersed in solutions.

The dispersive function $g(n)$ is given by $\frac{3}{2} \left[\frac{n^4-1}{(n^2+2)^2} \right]$, where n represents the refractive index of solvent.

Table 4. Regression equation and correlation coefficients for plot of λ against $f(\epsilon, n)$ and $g(n)$.

Compounds	Regression equation, R^2	
	λ against $f(\epsilon, n)$	λ against $g(n)$
S1	$y = 52.76x + 380.04, 0.450$	$y = 112.37x + 391.31, 0.274$
S2	$y = 139.03x + 328.26, 0.082$	$y = 990.08x + 137.58, 0.557$
S5	$y = 46.44x + 384.09, 0.161$	$y = 260.85x + 342.59, 0.681$

The variations in λ against $g(n)$ are presented in Table 4. The correlation coefficients followed the trend $S5 > S2 > S1$. For S5, the correlation was moderate ($R^2 = 0.681$), indicating a possible sensitivity to dispersive effects, whereas the correlations for the other compounds were weaker. Overall, these results showed qualitative trends rather than strict linear dependencies. The apparent greater dispersive response of S5, which has higher carbon content and fewer polar substituents, may be consistent with this trend, but further experimental or multivariate analysis would be required to confirm it.

Density Functional Theory

Table 5 shows the bond lengths, bond angles, and dihedral angles of the optimized geometries of compounds S1, S2, and S5 in Figure 7A.

The N=N bond is longer in S5 (1.3277 Å) than in S1 (1.2543 Å) and S2 (1.2561 Å), indicating a reduced double-bond character. Similarly, the

C-O(H) bond follows a trend ($S5: 1.3339 \text{ Å} > S1: 1.3279 \text{ Å} > S2: 1.3257 \text{ Å}$), suggesting stronger conjugation with the extended aromatic moiety in S5. Equally, S5 exhibited shortest O-H bond of 0.9615 Å than S1 and S2. This means a stronger phenolic proton bond and reduced propensity to release proton ion [20].

S5 displays the largest bond angle at the quinoline junction ($\text{N37C4C9} = 118.13^\circ$) compared to 114° for S1 and S2. This may be attributable to the steric effect of the naphthyl substituent. The C2C3C8 angles in S1 (127.97°) and S2 (128.03°) against S5 (124.53°) reflect the angular distortion induced by the electron-withdrawing sulphonamide and nitro groups. The dihedral angles indicated that all compounds maintained near-planarity, confirming effective π -conjugation across the azo-bridged systems. S5 shows a minimal twist (1.32°), while S1 and S2 exhibit near-perfect coplanarity. The presence of the naphthol moiety, which introduces steric strain, may be responsible for these observations.

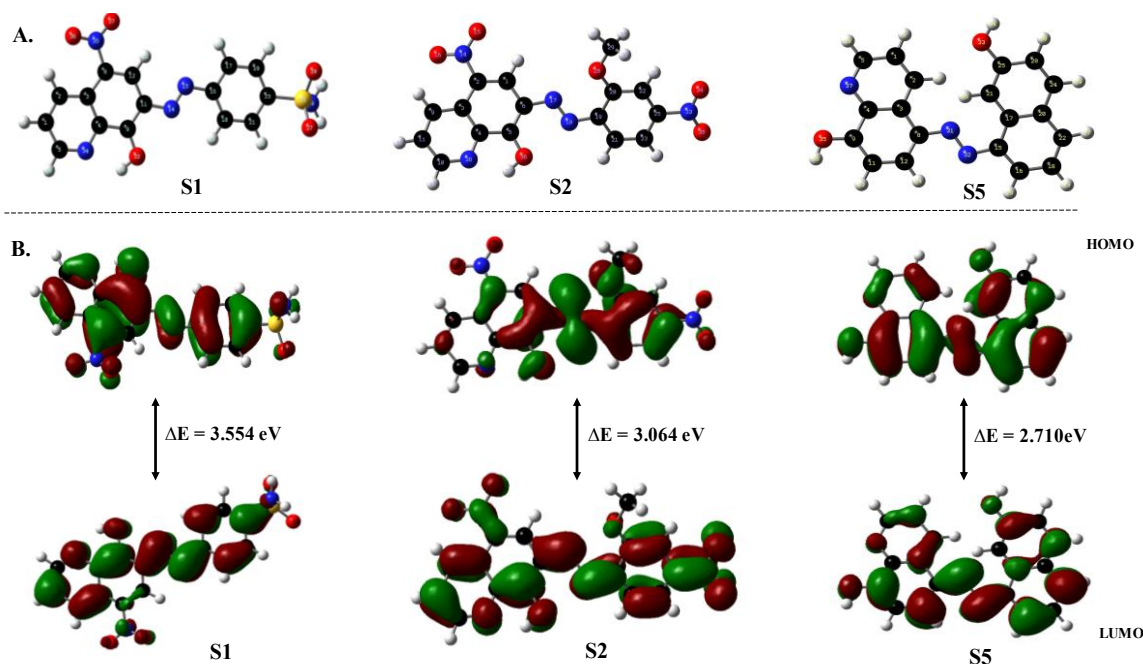


Figure 7. (A). Optimized geometries of S1, S2 and S5; (B). Gas-phase ground HOMO-LUMO energy gaps of S1, S2 and S5.

Table 5. Bond lengths, bond angles and dihedral angles of optimized geometries of compounds S1, S2 and S5.

Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
Compound S1					
N14N15	1.2543	N34C4C9	114.312	N34C4C9O32	-0.6544
O32H33	0.9798	C2C3C8	127.9732	N14C11C12C8	-179.258
C9O32	1.3279				
Compound S2					
N17N18	1.2561	N38C4C5	113.874	N38C5C4O36	0.06556
O36H37	0.9827	C9C3C2	128.0295	N17C6C1C2	-179.643
C5O36	1.3257				
Compound S5					
N31N32	1.3277	N37C4C9	118.1289	N37C4C9O35	0.1397
O35H36	0.9615	C2C3C8	124.532	N31C8C3C2	1.3205
C9O35	1.3339	C21C17C15	124.1097		

The vacuum-phase molecular orbitals and energy gaps is shown in Figure 7B. The HOMO-LUMO gap in S1 is largest (3.55 eV) due to the electron-withdrawing sulphonamide stabilizing the HOMO. S2 and S5 show reduced gaps of 3.06 and 2.71 eV, respectively. The enhanced conjugation and electron-donating substituents such as methoxy in S2 and naphthol in S5, facilitate lower-energy transitions. Planarity across all compounds causes orbital overlap, though S5's slight twist minimally reduces conjugation.

Furthermore, we evaluated the solvatochromic behaviours of the azo-quinoline derivatives across seven solvents by comparing experimental absorption maxima obtained by Olaleye and co-workers [15] with TD-DFT/PCM calculations. Tables 6-8 show the experimental and computational wavelengths, oscillator strength and excitation energy.

The computational wavelengths of S1 range from 402.9 to 410.9 nm, while the experimental values lie between 420 and 437 nm (Table 6). The computational values were 9-30 nm lower than the observed values. The deviation is more pronounced in polar aprotic solvents, such as DMSO and DMF, where the errors are near 30 nm. This pattern indicates that the polarizable continuum model inadequately reflects the specific dipolar and hydrogen-bonding interactions between the sulphonamide group and the polar media. Experimentally, these solvents induced a significant bathochromic shift. This suggests that the excited state is highly stabilized through solute-solvent interactions. The oscillator strength for S1 increases with polarity, highlighting the solvent-induced augmentation of the charge-transfer characteristics.

Table 6. Computational and experimental wavelengths of S1 in different solvents.

Solvents	Experimental λ (nm)	Computational λ (nm)	Oscillator strength	Excitation energy (eV)
Methanol	420	410.9	0.5683	3.5481
Ethylacetate	420	402.9	0.6941	3.5620
Ethanol	426	410.6	0.5975	3.5503
DimethylSulfoxide	435	407.1	0.6953	3.5470
DimethylFormamide	437	407.2	0.7012	3.5475
Dichloromethane	420	406.2	0.6989	3.5563
Acetonitrile	431	406.6	0.6591	3.5459

Table 7. Computational and experimental wavelengths of S2 in different solvents.

Solvents	Experimental λ (nm)	Computational λ (nm)	Oscillator strength	Excitation energy (eV)
Methanol	430	446.6	0.2061	3.0055
Ethylacetate	438	427.1	0.3853	3.0463
Ethanol	426	446	0.2011	3.0107
DimethylSulfoxide	445	439.8	0.1514	3.0382
DimethylFormamide	442	439.9	0.1495	3.0384
Dichloromethane	437	441	0.1159	3.0395
Acetonitrile	436	440.1	0.1510	3.0354

Table 8. Computational and experimental wavelengths of S5 in different solvents.

Solvents	Experimental (nm)	Computational (nm)	Oscillator strength	Excitation energy (eV)
Methanol	420	447.1	0.5338	3.0218
Ethylacetate	419	446.6	0.5640	3.0311
Ethanol	424	447.9	0.5363	3.0210
DimethylSulfoxide	448	448.4	0.5366	3.0205
DimethylFormamide	430	448.7	0.5386	3.0210
Dichloromethane	421	448.6	0.5545	3.0254
Acetonitrile	416	447.0	0.5318	3.0194

Conversely, compound S2, which has methoxy-nitro substitution, shows absolute deviation of 2.1 to 5.2 nm in DMF, dichloromethane, acetonitrile, and DMSO. In polar protic solvents, S2 showed larger deviations in methanol (16.6 nm), and ethanol (20.0 nm). These results support the suitability of the chosen basis set for describing the diazenyl-quinolinol core in solvents where specific short-range interactions are weak, but they do not justify treating S2 as a universal benchmark across all seven solvents. Instead, S2 is a useful benchmark for the computational protocol in solvent environments where bulk dielectric effects dominate and strong hydrogen-bonding or other specific interactions are minimal.

For compound S5 (naphthol derivative), the computed absorption maxima are approximately similar with only 2.1 nm difference across the solvents. However, the experimental wavelengths vary over a 32 nm range (Table 8). This marked difference may be due to solvent-dependent conformational dynamics that are neglected by the implicit model, which assumes a single static geometry. The naphthol framework introduces rotational flexibility and potential intramolecular hydrogen bonds, available for interaction with the surrounding solvents. The computation and experimental values align only in DMSO ($\Delta = 0.4$ nm). This agreement suggests DMSO

uniquely stabilizes a conformation that mirrors the computational geometry, likely by disrupting intramolecular hydrogen bonds to promote a planar, extended chromophore. In contrast, solvents like acetonitrile produced a twisted conformation with a hypsochromic shift.

The oscillator strengths offer corroborative evidence for the differing transition characters. The constant oscillator strength observed for S5 across all solvents implies that the nature of the primary electronic transition ($\pi \rightarrow \pi^*$) remains unchanged, yet the energy is affected by conformational constraints. For S1, the oscillator strength varies with solvent polarity, which may be due to charge-transfer character in more polar media. For S2, the generally lower oscillator strengths indicate a transition that is inherently less allowed, making the photophysical properties less sensitive to external perturbations and hence more reliably predicted by DFT studies.

Energy gap represents energy difference between HOMO and LUMO. S1 exhibits the highest gap of 3.55 eV, attributed to the strong electron-withdrawing sulphonamide and nitro groups that stabilize the HOMO relative to the LUMO. S2 and S5 exhibit lower, comparable gaps of 3.02 eV. The lower ΔE for S2 arises from the electron-donating methoxy

group elevating the HOMO, while the delocalization effects of the extended naphthol π -conjugation in S5 reduced the bandgap.

CONCLUSION

This study unequivocally established the structures of S1, S2, and S5 through 2D NMR spectroscopy, resolving signal overlaps and confirming key structural features. Solvent parameter correlation analysis revealed that S1's absorption is primarily influenced by solvent polarity, while S5's spectral pattern is governed by dispersive interactions. DFT calculations showed that S5 exhibits the smallest HOMO-LUMO gap and greatest N=N bond elongation, indicating reduced double bond character. The solvent-dependent azo-hydrazone tautomerism showed S5 as having potential pH-responsive behaviour. These compounds can find potential future applications as anion chemosensors, OLED materials and pH-responsive probes. In addition, future studies should investigate structure-activity relationships for biological applications, especially anticancer and antimicrobial activities.

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