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Synthesis, characterization, and DFT studies of a novel azo dye derived from racemic or optically active binaphthol

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1. Introduction

Azo dyes are compounds that contain azo groups linked to methine or aromatic sp²-hybridized C-atoms. The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling occurs at low temperature in the presence of nucleophilic coupling components. The reactivity of a nucleophilic substrate increases with increase in phenolates and amines.¹ 1,1'-Binaphthalene-2,2'-diol (BINOL) is one of the best-known representatives of axially chiral C2-symmetric molecules; BINOL and its derivatives are among the most widely used ligands for a variety of asymmetric reactions. Interconvertible conformational isomers resulting from a rotation around their δ -bond are known as 'atropisomers'. BINOL and its derivatives have been extensively used to provide a chiral environment in asymmetric synthesis,² chiral ligands,³ and in polymer synthesis.⁴ Application of 1,1'-binaphthalene-2,2'-diol (BINOL) and its derivatives in asymmetric catalysis has been broadly studied.⁵ Enantiomerically pure BINOL is easily obtainable by resolution of the low-cost racemate and is one of the most used chiral auxiliaries for asymmetric synthesis.⁶ New insoluble chiral catalysts were prepared from non-cross-linked copolymers with

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ABSTRACT

We present a new azo reactive dye from racemic or optically active BINOL. This dye was characterized by UV–vis, FTIR, mass, ¹H NMR, and ¹³C NMR spectroscopic techniques and elemental analysis. The structure and spectrometry of this azo dye have been investigated theoretically by performing HF and DFT levels of theory using the standard 6-31G* basis set. The optimized geometries and calculated vibrational frequencies are evaluated via comparison with experimental values. The vibrational spectral data obtained from solid phase FTIR spectra are assigned based on the results of the theoretical calculations. The theoretical electronic absorption spectra have been calculated using CIS, TD-DFT, and ZINDO methods. In addition, a good agreement between calculated and experimental NMR data is observed.

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(*R*)-BINOL pendant groups by Ikegami et al.⁷ Asymmetric synthesis of macrocyclic BINOL dimers was reported by Harada et al., Cram et al., and Diederich et al.⁸ Recent fields of applications of BINOL derivatives are the synthesis of HIV-protease inhibitors^{9,10} and chiral stationary phases.¹¹

Only a few theoretical works dealing with BINOL were found in the literature. Based on DFT calculations, Sahnoun et al. reported the mechanism of the isomerization of 1,1'-bi-2-naphthol (BINOL)¹² and Havlas et al. presented the racemization barriers of BINOL.¹³

As part of our ongoing research program into the synthesis and theoretical studies of azo dyes,¹⁴⁻¹⁸ we report the synthesis of a new azo reactive dye by the reaction of *p*-diazonium benzene sulfonyl azide with racemic or optically active BINOL as coupling component in the presence of a base. These interesting compounds have both the character of BINOL as an auxiliary and as an asymmetric ligand for complexation. In addition, these compounds are reactive and can be used in other reactions.

2. Result and discussion

2.1. Computational details

The molecular structures of 6-[4-(azidosulfonyl)phenyl]-1-diazenyl-1,1'-binaphthalen-2,2'-diol in the ground state have been already optimized by the Hartree–Fock (HF) method, Becke 3–Lee–



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Scheme 1. Chemical structure of compound 1.

 Table 1

 Specific rotations of the new BINOL dve derivatives

Мр	Specific rotation ^a
213-215	_
199–201	+54.7
194–196	-55.1
	Mp 213-215 199-201 194-196

^a $[\alpha]_{D}^{25}$ (c 0.5, acetone).

Yang–Parr (B3LYP) functionals,^{20,21} and by combining the results of the GaussView program²² with symmetry. Vibrational frequency calculations were made with a high degree of accuracy as well. There is always some ambiguity in defining internal coordination. However, the defined coordinates form a complete set and match quite well with the motions observed using the GaussView program. Finally, the calculated vibrational frequencies of normal modes, the visible absorption maxima, NMR, and thermodynamic properties were also calculated with these methods. These calculations were performed at HF and DFT (B3LYP functionals) levels using the Gaussian 03W program package.²³

 Table 2

 Selected bond distances (Å), bond angles (°) and dihedral angles (°) of 1

Parameters	HF/6-31G*	B3LYP/6-31G*	Parameters	HF/6-31G*	B3LYP/6-31G*
Bond lengths (Å)				
S-C14	1.7639	1.7834	C6-C7	1.4221	1.4268
C14-C15	1.3853	1.3969	C7-C8	1.3534	1.3690
C15-C16	1.3824	1.3906	C8-C10	1.4292	1.4304
C16-C11	1.3875	1.4031	C5-C9	1.4164	1.4129
C11-C12	1.3919	1.4067	C2-0	1.3485	1.3626
C12-C13	1.3799	1.3881	C1-C1′	1.4976	1.4949
C13-C14	1.3894	1.4006	C2'-0	1.3522	1.3681
C11-N	1.4209	1.4175	N=N	1.2213	1.2654
C6-N	1.4113	1.4046	S–N	1.6859	1.7769
C6–C5	1.3594	1.3854			
Bond angles (°)					
C10-C1-C1'	121.5	121.6	0-C2'-C1'	118.8	118.0
C2-C1-C1'	119.8	119.6	C1'-C9'-C8'	122.2	122.2
C9'-C1'-C1	121.3	121.4	C4'-C10'-C5'	121.3	121.6
C2'-C1'-C1	119.7	119.5	C1-C10-C8	122.1	122.0
C7-C6-N	124.1	124.7	C4-C9-C5	121.3	121.6
C12-C11-N	124.3	124.7	C13-C14-S	119.5	119.1
C16-C11-N	115.3	115.3	C15-C14-S	119.1	119.0
0-C2-C3	119.8	120.6			
Dihedral angles	(°)				
C10-C1-C1'-C2'	-91.5	-91.0	C13-C14-S-N	-99.1	-98.5
C2-C1-C1'-C9'	-91.7	-91.1	0-C2-C1-C1'	0.8	0.6
C11-N=N-C6	179.9	179.7	0-C2'-C1'-C1	0.7	0.7
C14-S-N=N	98.1	104.6			
C15-C14-S-N	80.7	81.3			



Figure 1. The structure of compound 1, optimization has been performed by the B3LYP/6-31G* method.

Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree–Fock level, adopting the standard 6-31G* basis set. This geometry was then re-optimized at B3LYP level, using the same basis set for better description. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all the stationary points as minima. The vibrationally averaged nuclear positions of this compound were used then for the harmonic vibrational frequency calculations resulting in an IR frequency together with the intensities. The vibrational frequencies for these species were calculated using these methods and then scaled by 0.8991 and 0.9663 for HF/6-31G* and B3LYP/6-31G*.²⁴ CIS, ZNIDO, and the time-dependent density functional theory (TD-DFT) calculations of electronic absorption spectra were also performed on the optimized structure.

In order to obtain further Supplementary data for the postulated structure, we calculated the ¹H and ¹³C NMR chemical shifts for this structure by DFT GIAO²⁵ model at B3LYP/6-311+G(2d,p) level²⁶ on the structure of the optimized compound by the B3LYP/6-31G* method.

2.2. Molecular structure of azo dyes

The general route for the synthesis of compound **1** is shown in Scheme 1 (Table 1). The optimized structural parameters of this



Figure 2. The experimental FTIR spectra of the compound 1.



Figure 3. Predicted spectra of compound 1 at B3LYP/HF/6-31G* level.

compound calculated by ab initio and DFT/B3LYP levels with the 6-31G* basis set are listed in Table 2 and the optimized configuration is shown in Figure 1. Since the crystal structure of this compound is not available, the optimized structure can only be compared with the other similar systems for which the configurations have been optimized. For example, the optimized bond lengths of C–C in the naphthyl ring fall in the range 1.3690–1.4304 Å for the HF/6-31G* method and 1.3534–1.4222 Å for the B3LYP/6-31G* method, which are in good agreement with a similar molecular structure, 1.385– 1.439 Å.¹² Moreover, the optimized bond lengths of C–C in the phenyl ring fall in the range 1.3799–1.3894 Å for the HF/6-31G* and 1.3881–1.4068 Å for the B3LYP/6-31G* method, which are in good agreement with the molecular structure of a phenyl ring with an arensulfonyl group (1.385–1.400 Å).²⁷

The HF optimized C₁₁–N and C₆–N bond lengths are 1.4209 Å and 1.4113 Å and for the B3LYP/6-31G* are 1.4176 Å and 1.4046 Å, respectively. For C_{ring}–S bond, the optimized lengths are 1.7640 Å for the HF/6-31G* method and 1.7835 Å for the B3LYP/6-31G* method (see Table 2). Based on the above comparison, although there are some differences between our values and the literature data, the optimized structural parameters can reproduce the literature ones, and they are the bases for further discussion. With respect to the dihedral angle between the two naphthyl planes, it has been previously reported that there are two minima: one about 90° and another is near 60° (see Ref. 13 and references therein). Interestingly, DFT and HF calculations only showed that the C10C1C1′C2′ dihedral angles are -91.0° and -91.6°, respectively.



Figure 4. Comparison of corrected frequencies in $\rm cm^{-1}$ normalized IR intensities at HF/6-31G* level of compound 1.



Figure 5. Comparison of corrected frequencies (cm⁻¹) normalized IR intensities at B3LYP/6-31C⁺ level of compound.

2.3. Assignments of vibrational frequencies

Vibrational spectroscopy is used extensively in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, reaction kinetics, etc. Assignment of complex systems can be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamental modes. The observed experimental FTIR spectra and the theoretically predicted IR spectra are shown in Figures 2–5. The resulting vibrational wave numbers for the optimized geometry and the proposed assignments are given in Table 3. The vibrational spectral data obtained from the solid phase FTIR spectra are assigned based on the results of the normal coordinate calculations. The observed and the calculated spectra are found to be in good agreement with each other. Based on the comparison between the calculated and experimental results, assignments of fundamental modes were carried out. The assignment of the experimental frequencies is based on the observed band frequencies

Table 3				
Comparison of the observed	l and calculated	vibrational	spectra of	compound

	HF (I)	B3LYP (I)	Exp	Assignment
1	3666(31.3254)	3755(59.2998)	3411	ν(OH)
2	3662(41.0163)	3751(110.21)	3396	ν(OH)
4	3154(81.322)	3236(0.4601)	3098	ν(CH)
5	3138(49.4995)	3206(39.0718)	3061	ν(CH)
6	2164(225.519)	2137(223.739)	2126	N ₃
7	1777(64.2301)	1647(37.842)	1582	Vring
8	1694(228.188)	1565(44.5621)	1532	Vring
9	1618(100.655)	1523(7.1679)	1507	v(N=N)
10	1573(300.476)	1482(30.4452)	1451	Vring
11	1440(671.019)	1383(77.7509)	1379	$v_{sym.}(N_3)$
12	1397(57.8738)	1331(98.7896)	1339	$v_{asym.}(SO_2)$
13	1319(44.0809)	1314(72.4877)	1253	v(CN)
14	1164(45.8744)	1201(4.6582)	1226	$\pi(CH)$
15	1159(45.736)	1195(39.0304)	1185	δ(OH)
16	1076(26.3607)	1085(55.5398)	1168	$\pi(CS)+\pi(CN)$
17	982(25.2746)	1002(0.3048)	1143	$v_{sym}(SO_2) + v(CN)$
18	952(24.44)	975(30.2545)	987	$\pi(SN) + \pi(CH)$
20	903(330.226)	921(9.7702)	893	$\pi(CH) + \pi(CN)$
21	856(144.542)	874(26.8148)	835	δ _{ring}
22	809(19.466)	807(22.6099)	787	δ _{ring}
23	768(36.7133)	777(3.27)	757	δ _{ring}
24	695(300.959)	709(98.206)	685	π(OH)
25	651(166.765)	669(107.557)	634	$\pi(CS)+\pi(CN)$
26	607(73.9234)	623(19.3551)	588	δ _{ring}
27	506(53.2987)	514(17.2638)	504	δ(SO ₂)
28	403(17.3051)	423(5.6278)	417	$\pi_{ring+}\omega(SO_2)$

v, stretching; δ , in-plane bending; π , out-of-plane bending; ω , wagging. Subscript: asym., asymmetric; sym., symmetric.

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Table 5



Figure 6. Graphic correlation between the experimental and the theoretical frequencies obtained by B3LYP/6-31G* method and HF/6-31G* method.

in the infrared spectra of this species confirmed by establishing one to one correlation between observed and theoretically calculated frequencies.

The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. Two factors may be responsible for the discrepancies between the experimental and computed spectra of azo dyes. The first is caused by the environmental conditions and the second one arises from the fact that the experimental value is an anharmonic frequency while the calculated value is a harmonic frequency.²⁸ Assignment of all the vibrational bands has been carried out on the basis of the DFT calculations. A linearity between the experimental and calculated wave numbers (i.e., for the whole spectral range considered) can be estimated by plotting the calculated versus experimental wave numbers (Fig. 6). The values of the correlation coefficients indicate good linearity between the calculated and experimental wave numbers (correlation coefficients of 0.899, 0.999).

The naphthyl ring modes predominantly involve C-C bonds and the vibrational frequency is associated with the C-C stretching modes of the carbon skeleton. The C-C stretching modes, known as semi-circle stretching, predicted at $1510-1660 \text{ cm}^{-1}$ are in excellent agreement with the experimental observation of the FTIR value at 1508–1582 cm⁻¹. The ring breathing mode at 755 cm⁻¹ coincides satisfactorily with a very weak band at 757 cm^{-1,29} The OH group vibrations are likely to be most sensitive to the environment so they show pronounced shifts in the spectra of the hydrogen-bonded species. The absorption of nonhydrogen bonded or free hydroxyl groups appears strongly in the 3550–3700 cm⁻¹ region. In general, the OH in-plane bending vibration in phenol lies in the 1150–1270 cm⁻¹ region and is not much affected due to hydrogen bonding. The FTIR frequency band at 1143–1253 cm⁻¹ is attributed to this vibration. The OH out-ofplane deformation vibration in phenol is located in the 517-710 cm⁻¹ region for the associated OH.³⁰ The FTIR frequency band at 685 cm⁻¹ is correlated to this vibration. In both inter-molecular and intra-molecular associations, the frequency is at a higher

Carbon	HF	B3LYP	Exp
C11	168.8	152.3	159.2
C2	167.1	149.5	155.1
C2′	167.2	149.7	155.1
C6	159.5	143.9	149.9
C14	151.5	138.0	143.7
C10	142.6	128.1	133.5
C9′	142.3	128.8	133.4
C5′	140.7	127.1	131.7
C10′	140.0	126.4	130.7
C9	140.6	126.1	130.2
C4	137.6	123.4	128.9
C4′	136.9	123.1	128.9
C13	137.6	123.0	128.5
C15	138.0	123.5	128.5
C5′	136.6	122.1	127.4
C7′	134.1	121.6	127.0
C8′	135.2	121.7	126.1
C8′	134.8	120.3	125.8
C12	133.4	119.9	124.6
C16	132.4	119.9	124.6
C6′	131.3	117.7	123.9
C1	133.8	118.1	122.7
C1′	133.6	118.0	122.7
C3	128.3	113.6	119.5
C3′	128.1	113.5	119.5
C7	125.6	110.0	116.2

Experimental and calculated ¹³C NMR chemical shifts (ppm) of compound **1**

 Table 6

 Experimental and calculated ¹³C NMR chemical shifts (ppm) of compound 1

Poroton	HF	B3LYP	Exp
Нон	8.23	8.86	9.19
Н _{он}	8.48	8.87	9.19
H5	9.11	7.99	8.14
H7	7.89	7.89	8.08
H8	6.84	7.83	7.97
Hphenyl	6.45	7.63	7.74
Hphenyl	8.02	7.31	7.74
Hphenyl	8.15	7.43	7.86
Hphenyl	8.64	7.93	7.86
H5′	7.70	7.49	7.68
H4	7.87	7.36	7.57
H4′	8.23	7.42	7.57
H8′	6.63	7.32	7.48
H7′	7.04	7.23	7.31
H6′	7.14	7.03	7.19
H3	6.58	6.99	7.03
H3′	8.26	7.54	7.03

value than in a free OH. The frequency increases with hydrogen bond strength because of the larger amount of energy required to twist the out-of-plane O–H bond.³¹

The aromatic structure of compound **1** shows the presence of C–H stretching vibrations in the $2900-3200 \text{ cm}^{-1}$ region, which is characteristic for the fast identification of the C–H

Table 4	
Experimental and theoretical electronic absorption spe	ectra values

Ехр	Calculated/ λ_{cal} (nm)	Calculated/ λ_{cal} (nm)						
	CIS		TD		ZNIDO			
	Wave length (nm)	Oscillator strength	Wave length (nm)	Oscillator strength	Wave length (nm)	Oscillator strength		
489, 316, 226	428.86	0.0001	440.41	0.0001	387.89	1.0217		
	325.13	0.0015	357.23	0.0004	342.76	0.2862		
	197.62	0.2013	242	0.2909	317.73	0.0384		



Figure 7. Plot of the calculated versus the experimental ¹H NMR chemical shifts (ppm) of compound 1.

stretching vibrations. The vibrations in this region (2900–3200 cm⁻¹) are in agreement with the experimental assignment of 3061–3098 cm^{-1,32,33} The C–H in-plane bending vibrations assigned in the 1050–1290 cm⁻¹ region are usually weak. The absorption of C–H out-of-plane bending is predicted at 1085 cm⁻¹ by the B3LYP/6-31G*, while HF calculations give them at 1076 cm⁻¹.

The calculations also show that the π (CH) vibrations are not pure, and contain significant contributions of other modes (v(SN) and π (CN)). The stretching v(C–N) vibrations could be observed for the studied compound over a broad energy range, depending on the π -bonding nature of the C–N bond. The S–N stretching vibration exhibits a moderate band at 987 cm⁻¹. The band observed at this region is not pure v(SN) vibration, but contains a significant contribution of π (CH) mode. The bands corresponding to the N₃ stretching vibrations belonging to the SO₂N₃ and azo group are expected to appear near 2126 cm⁻¹ and 1507 cm⁻¹, respectively, in the IR spectrum of this azo dye.

The observed bands at 1339 cm⁻¹ and 1143 cm⁻¹ were assigned to the v(SO₂) asym. and v(SO₂) sym. modes, respectively. The band at 504 cm⁻¹ was assigned to the SO₂ scissors and SO₂ wagging vibrations, and has partly overlapped in this region. Calculations show that ω (SO₂) vibration contains a considerable contribution with the π ring.³⁴ The major band (at 634 cm⁻¹) relates to the S–C stretching.



Figure 8. Plot of the calculated versus the experimental 13 C NMR chemical shifts (ppm) of compound 1.

2.4. UV-vis spectra

The properties of azobenzenes, or in other words the -N=N-group, have been mostly investigated by UV/vis spectroscopy and various theoretical and experimental results have been reported.³⁵ Absorption maxima (λ_{max}) of compound **1** were calculated by the CIS, ZNIDO, and TD methods. The observed and calculated visible absorption maxima of **1** in this study are given in Table 4. Calculations of molecular orbital geometry show that the visible absorption maxima of this kind of azo dye correspond to the electron transition from HOMO to LUMO. The λ_{max} is a function of the electron of the naphthyl, phenyl ring, and azo group (transition of π - π * type).

Comparing the TD-B3LYP results, we have performed CIS calculations on optimized structures, which lead to similar results. As shown in Table 4, the energy and oscillator strength calculated by CIS coincide reasonably with TD-DFT results as well as the experimental values. However, ZNIDO correctly predicts much larger oscillator strength.

2.5. NMR spectra

Experimental and theoretical values for ¹H, ¹³C NMR, and the calculated structural parameters of compound **1** are given in Tables 5 and 6 (in Supplementary data the ¹H and ¹³C NMR spectra have been provided). The theoretical ¹H and ¹³C NMR chemical shifts of **1** have been compared with the experimental data. According to these results, the calculated chemical shifts and coupling constants are in line with the experimental findings. In order to compare the experimental chemical shifts, correlation graphics based on the calculations have been presented in Figures 7 and 8. The carbon and proton chemical shifts' correlation values are found to be 0.9913 and 0.9919 for HF and B3LYP with the 6-31G* basis set, respectively.

As shown in Figure 1, compound **1** has 26 different carbon atoms, which is consistent with the structure based on molecular symmetry. Chemical shifts were reported in parts per million relative to TMS for ¹H and ¹³C NMR spectra. Spectra were obtained at a base frequency of 125.76 MHz for ¹³C and 500.13 MHz for ¹H nuclei. Relative chemical shifts were then estimated by using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference. Calculated ¹H and ¹³C isotropic chemical shielding for TMS at the HF/6-31G* and B3LYP/6-311+G(2d,p) levels in methanol were 32.60 ppm, 199.98 ppm, 31.88 ppm, and 182.46 ppm. The experimental values for ¹H and ¹³C isotropic chemical shifts for TMS were 30.84 ppm and 188.1 ppm, respectively.³⁶

The calculated NMR spectra of the other possible isomers of the molecule are presented in Supplementary data section. Comparison between the calculated data for compound **1** and those obtained reveals that the coupling has occurred at position 6 (see Supplementary data).

2.6. Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions: heat capacity $(C_{p,m}^{o})$, entropy (Sm^{o}) , and enthalpy (H_{m}^{o}) were obtained and listed in Table 7. Several calculated thermodynamic parameters are presented in Table 8. Scale factors have been recommended³⁷ for an accurate prediction in determining the zero-point vibration energies and the entropy. The total energies and the change in the total entropy at room temperature at different methods are also presented.

Table 7				
Thermodynamic properties at	different temperatures at	HF/6-31C* and	B3I VP/6-31C* le	vel

Т	Method	E _{tot} (kcal/mol)	H _{tot} (kcal/mol)	S _{tot} (cal/mol K)	C _v (cal/mol K)	G _{tot} (kcal/mol)
298	HF	-1963.4926	260.601	182.546	110.64	206.175
	B3LYP	-1973.6822	261.691	204.187	115.839	200.813

Table 8

Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal/mol K), and dipole moment (*D*) for compound **1**

Parameters	HF/6-31G*	B3LYP/6-31G*
Total energy	-1963.4926	-1973.6822
Zero-point energy	242.87998	242.43205
Rotational constant	0.25464	0.25464
	0.03000	0.03000
	0.02888	0.02888
Entropy		
Total	182.546	204.187
Translational	44.486	44.486
Rotational	38.519	38.519
Vibrational	99.540	121.182
Dipole moment	8.4250	9.7728

3. Conclusions

6-[4-(Azidosulfonyl)phenyl]-1-diazenyl-1,1'-binaphthalen-2,2'diol has been synthesized and characterized by elemental analysis, IR, UV–vis, ¹H NMR, ¹³C NMR spectroscopy, and mass spectrometry. The calculated vibrational frequencies and the experimental IR spectra complement each other. The predicted electronic absorption spectra have some blue shifts compared with the experimental data. Molecular orbital coefficient analysis suggests that the electronic spectra are assigned to the $\pi \rightarrow \pi^*$ electronic transitions. The experimental and the theoretical investigations of this compound have been performed successfully by using NMR and quantum chemical calculations. The computation analysis of this compound by HF and B3LYP methods is in excellent agreement with all the experimental findings.

4. Experimental section

4.1. General

4-Acetamidobenzenesulfonyl chloride and (*R*)- or (*S*)-BINOL were purchased from Merck and were used without further purification. Racemic BINOL was synthesized by the method reported by Toda et al.¹⁹ IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer using KBr discs. NMR spectra recorded on a Bruker 500 ultrasheild spectrometer NMR and DMSO- d_6 was used as solvent. Mass spectra were determined on a Uk Fisons Trio 1000 spectrometer using electron impact at 70 ev. UV spectra were recorded on a JASCO V-570 UV/Vis/NIR spectrophotometer. Elemental analysis was determined using a LECO instrument. Specific rotations were recorded on a Gallenkamp apparatus and are not corrected. Analytical TLC was performed on Silica Gel F₂₅₄ plates (Merck). Merck silica gel 60 (40–63 μ m, 230–400 ASTM) was used for column chromatography.

4.2. Typical procedure for diazotization and diazocoupling reaction

4.2.1. 4-Acetamidobenzenesulfonyl azide

4-Acetamidobenzenesulfonyl chloride (48.6 g, 208 mmol) was dissolved in acetone (500 ml) and the solution was cooled to

temperature of 0 °C over a period of 60 min. A chilled aqueous solution of sodium azide (20 g, 312 mmol, 200 ml) was added dropwise and the resultant solution allowed to stir for a further 60 min at that temperature. The solution was then poured into an ice/water slurry (1.5 L) and the white precipitate was collected by filtration, washed with ice-cold water, and dried under vacuum. 4-Acetamidobenzenesulfonyl azide could be used in the next step directly and recrystallized from a solution of acetone and water giving white crystals (37.5 g, 75%); mp 108–110 °C (Ref. 38, 113–114 °C); $\delta_{\rm H}$ (500 MHz, DMSO- d_6): $\delta_{\rm 8.4}$ (s, 1H, NH), 7.82 (d, 4H, J 8.3, phenyl), 2.23 (s, 3H, *Me*); $\delta_{\rm C}$ (500 MHz, DMSO- d_6): 169.5, 144.1, 132.3, 128.9, 119.6, 24.7; $\nu_{\rm max}$ (KBr): 2125, 1674, 1160 cm⁻¹; m/z: (EI-MS) 240 M⁺.

4.2.2. 4-Aminobenzenesulfonyl azide

4-Acetamidobenzenesulfonyl azide (12 g, 50 mmol) and concentrated HCl (12 M, 45 ml) were heated under reflux for 35 min, then cooled to approximately 0–5 °C. The solution was neutralized with saturated sodium bicarbonate solution and solid sodium bicarbonate until a pH of approximately 6. The light brown mixture was extracted with diethyl ether, washed, dried (MgSO₄), and then filtered. Evaporation of the diethyl ether solution provided a brown solid, which could be recrystallized from a small portion of diethyl ether (7.6 g, 70%); mp 34–36 °C (Ref. 39, 35–39 °C). [Found: C, 36.48; H, 3.14; N, 28.32. C₆H₆N₄O₂S requires: C, 36.36; H, 3.05; N, 28.27%.] $\delta_{\rm H}$ (500 MHz, DMSO- d_6): 7.7 (d, 2H, *J* 8 Hz, phenyl), 6.7 (d, 2H, *J* 8 Hz, phenyl), 4.36 (br, 2H, $-NH_2$); $\delta_{\rm C}$ (500 MHz, DMSO- d_6): 152.5, 129.8, 125.1, 116; $\nu_{\rm max}$ (KBr): 3475, 2128, 1175 cm⁻¹; *m/z*: (EIMS) 198 M⁺.

4.2.3. 6-[4-(Azidosulfonyl)phenyl]-1-diazenyl}-1,1'-binaphthalen-2,2'-diol

4-Acetamidobenzenesulfonyl azide (2.4 g, 10 mmol) and concentrated HCl (12 M, 9 ml) were heated at reflux for 35 min, and the resulting solution then cooled in an ice/salt bath to 0 °C. The solution was diazotized with a solution of sodium nitrite (0.76 g, 10 mmol) in water (20 ml), with the temperature maintained below 5 °C, and then stirred for a further 30 min. The solution was then neutralized with saturated sodium bicarbonate solution. The reaction mixture was stirred while maintaining a temperature of 0-5 °C. To this cooled mixture of p-diazonium benzene sulfonyl azide (2.4 g, 10 mmol), 1,1'-binaphthalene-2,2'-diol (4.95 g, 10 mmol) was added slowly. After stirring for an additional 30 min by keeping temperature below 0 °C, the mixture was further neutralized with a saturated sodium carbonate solution (pH=7) and then was maintained stirring until precipitation was deemed to be complete (3-4 h). The precipitate was filtered and recrystallized from toluene. The product was obtained as red-orange crystals. Yield: 45%; mp 199-201 °C. [Found: C, 62.88; H, 3.38; N, 14.05; C₂₆H₁₇N₅O₄S requires: C, 63.02; H, 3.46; N, 14.13%.] $\delta_{\rm H}$ (500 MHz, DMSO- d_6): 9.1 (br, 2H, -OH), 8.1 (1H, s, H5), 8 (1H, d, J 8.3 Hz, H7), 7.9 (1H, d, J 8.39 Hz, H8), 7.7 (4H, d, 4H, J 8.9 Hz, phenyl), 7.68 (1H, d, J 8.5 Hz, H5'), 7.57 (2H, d, J 8.7 Hz, H4, 4'), 7.48 (1H, d, J 8.54 Hz, H8'), 7.31 (1H, t, H7'), 7.19 (1H, t, H6'), 7.03 (2H, d, J 8.7 Hz, H3, 3'); δ_C (500 MHz, DMSO-*d*₆): 116.2 (C7), 119.5 (C3, 3'), 122.7 (C1, 1'), 123.9 (C6'), 124.6 (C12, 16), 125.8 (C8') 126.1 (C8), 127 (C7'), 127.4 (C5'), 128.5 (C13, 15), 128.9 (C4, 4'), 130.2 (C9), 130.7(C10'),131.7(C5),133.4(C9'),133.5(C10),143.7(C14),149.9(C6), 155.1(C2, 2'), 159.2 (C11); v_{max} (KBr): 3311, 3306, 2126, 1582, 1570, 1507, 1379, 1339, 1192, 1168, 1143 cm⁻¹; λ_{max} (DCM) 226, 316, 489 nm; *m*/*z*: (EIMS) 495 M⁺.

Optically active azo dyes were synthesized under the optimized reaction conditions, from optically active BINOL and specific rotations are recorded in Table 1.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.104.

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