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

Abbas Teimouri [a], Alireza Najafi Chermahini [b,*], Mohammad Emami [c]

[a] Payame Noor University (PNU), Isfahan, PO Box 81395-671, Iran
[b] Department of Chemistry, Yasouj University, Yasouj, Iran
[c] Department of Chemistry, Shahid Beheshti University, Tehran, Iran

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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, ^{1}H NMR, and ^{13}C 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.

1. Introduction

Azo dyes are compounds that contain azo groups linked to methine or aromatic sp^2-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 C_2-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 (*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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* Corresponding author. Tel./fax: +98 7412223048.
E-mail address: najafi@mail.yu.ac.ir (A.N. Chermahini).

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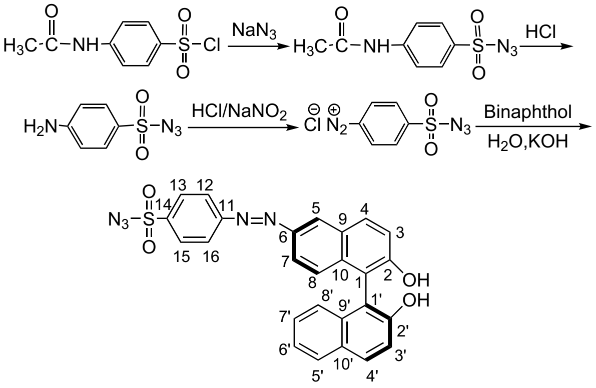

Scheme 1. Chemical structure of compound **1**.

Table 1
Specific rotations of the new BINOL dye derivatives

Compound	Mp	Specific rotation[a]
R,S	213–215	—
R	199–201	+54.7
S	194–196	−55.1

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

Yang–Parr (B3LYP) functionals,[20,21] and by combining the results of the GaussView program[22] 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–O	1.3485	1.3626
C12–C13	1.3799	1.3881	C1–C1′	1.4976	1.4949
C13–C14	1.3894	1.4006	C2′–O	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	O–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
O–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	O–C2–C1–C1′	0.8	0.6
C11–N═N–C6	179.9	179.7	O–C2′–C1′–C1	0.7	0.7
C14–S–N═N	98.1	104.6			
C15–C14–S–N	80.7	81.3			

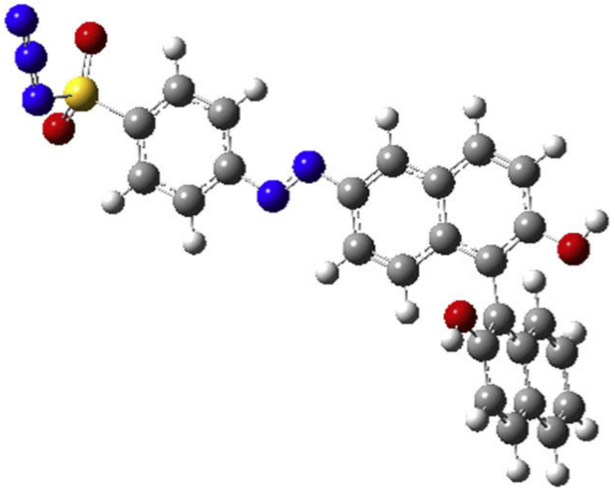

Figure 1. The structure of compound **1**, optimization has been performed by the B3LYP/6-31G* method.

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 ^{13}C NMR chemical shifts for this structure by DFT GIAO[25] model at B3LYP/6-311+G(2d,p) level[26] 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

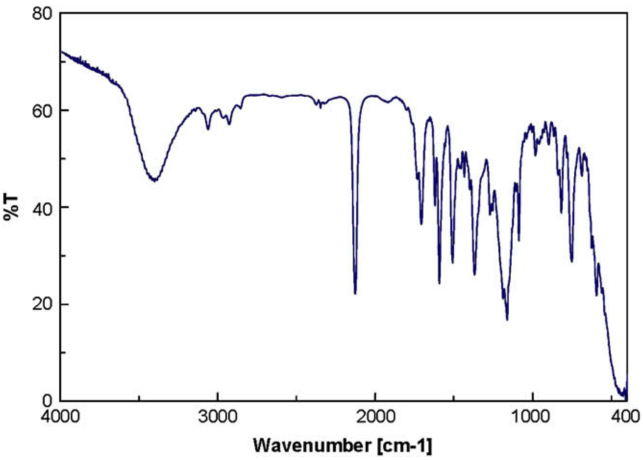

Figure 2. The experimental FTIR spectra of the compound **1**.