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Synthesis, structural characterization, antimicrobial activities and theoretical investigations of some 4-(4-aminophenylsulfonyl) phenylimino) methyl)-4-(aryldiazenyl) phenol

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ABSTRACT

The azo-azomethine dyes with a different substitution have been designed from the reaction of 4,4′-diaminodiphenyl sulfone with 2-hydroxy-5-(aryldiazenyl)benzaldehyde. The compounds have been characterized by elemental analysis, Mass, IR, UV–Vis, TGA-DTA and NMR spectroscopy. The solvatochromism behaviors, effects of substitution and pH on the electronic absorption spectra of dyes were evaluated. The in vitro antimicrobial activities were also screened for their potential for antibiotic activities by broth micro dilution method. Also, the optimum molecular geometries, molecular electrostatic potential (MEP), nucleus-independent chemical shift (NICS) and frontier molecular orbitals (FMO), vibrational spectra (IR) and electronic absorption (UV–Vis) spectra of the title compounds have been investigated with the help of DFT and TDDFT methods with 6-311++G(d,p) basis sets and PCM calculations. The results of the calculations show excellent agreement with the experimental value.

1. Introduction

Aromatic azo compounds are very important chemical materials that find various applications in industry as dyes and pigments, inks, paper, textiles, colorimetric indicators, food additives, cosmetics, therapeutic agents and drug deliveries [1–6]. Also, azo-azomethines dyes are known to be involved in a number of antibacterial, antifungal, antitumor and antioxidant activities [7–10]. On the other hands, sulfones were used preferentially as antimicrobial/chemotherapeutic agents to treat infections caused by streptococcus, mycobacteriaceae, and other bacteria [11]. Dapsone (4,4′-diaminodiphenyl sulfone; DDS) is the only remaining sulfone congener used in human therapeutics (in rifampin-based multiple-drug regimens for treating multibacillary and paucibacillary leprosy). Because of its dual mechanism of action—antimicrobial and anti-inflammatory/immunomodulatory effects—dapsone alone or in conjunction with other drugs is used worldwide for preventing and treating pathogen-caused diseases (e.g., leprosy, Pneumocystis jiroveci pneumonia in individuals with HIV infection) or chronic inflammatory diseases, especially in the field of dermatology (e.g., autoimmune bullous eruptions) [12–15]. Currently, 4,4′-diaminodiphenyl sulfone has been widely used in broad areas in chemistry, as a curing agent of epoxy resins, and a monomer for preparing polyimide. Various compounds and polymers (electrochromic behavior) have also been derived from DDS by exploiting the reactivity of its terminal primary amine [16–20]. Furthermore, proton tautomerism plays a significant role in various fields of chemistry and particularly biochemistry [21]. The prototropicenol-imine, keto–enamine equilibrium is the most studied tautomeric process inherent in Schiff bases. Tautomeric Schiff bases can serve as a special type of molecular switches in optical recording technology, molecular electronics, and computing [21–26]. The bistable tautomeric azo-azomethines constitute a two-level system which can be manipulated by solvent, light, heat or electric current. The tautomerism of azo-azomethines received renewed interest due to application of improved experimental and theoretical methods. Most of these studies have been focused on estimation of tautomeric preferences, investigation of the role of substituents on the position of the tautomeric equilibria, solvato-, iono-, thermo- and photochromic effects [27–29]. In line with the search for some factors for the treatment of tautomeric equilibrium, the aims of this study are to apply the experimental and theoretical methods in the case of title compounds in order to: (a) validate the presence of both tautomers in gas phase and compare the experimental facts (b) investigate the solvatochromic behavior and substituent effects of the prepared dyes in various solvents; and (c) investigate the relative antibacterial properties of azo-azomethines dyes.

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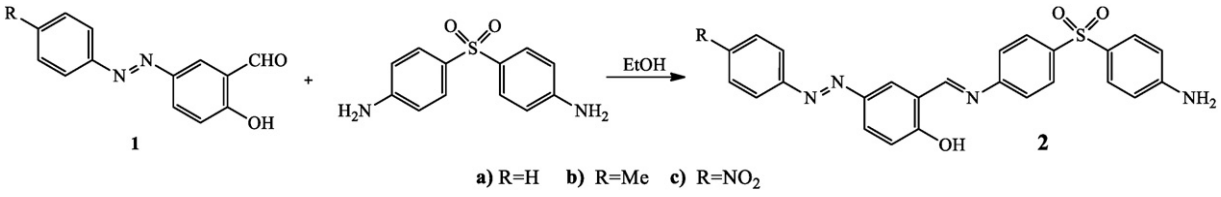


Fig. 1. The synthesis of **2a–c** compounds.

2. Experimental details

2.1. Materials

All chemical reagents were obtained from the Merck and used without further purification. The solvents used in the reactions were of analytically reagent grade and dried using standard procedures, whereas, for UV–Vis experiments spectroscopic grade solvents (>99.9%) were used, without any further purification. 2-hydroxy-5-(aryldiazenyl) benzaldehyde (**1a–c**), 4-phenylazophenol (**3**) and 4-(4-aminophenylsulfonyl) phenylimino) methyl) phenol (**4**) compounds (See supplementary information) have been prepared and purified according to the method reported in the literature [25,26,30–31].

2.2. Measurements

Carbon, hydrogen and nitrogen analyses were performed on an Elementar Vario EL III elemental analyzer. Mass spectra were recorded on a Agilent MS Model 5973. Melting points were measured with Electrothermal 9300 apparatus. IR spectra in the range 4000–400 cm^{-1} were obtained on Shimadzu 8400 S spectrometer with samples investigated as KBr discs. The nature of all synthesized compounds was confirmed by ^{1}H and ^{13}C NMR spectra, in DMSO-d_6 as solvent on a Bruker AV 300 MHz spectrometer. The UV–Vis spectra were recorded with a Shimadzu 1650 spectrophotometer. The pH variation experiments were carried out in a microprocessor pH meter (HANNA 211 pH) at ambient temperature. The pH meter was accurate to ±0.01 pH unit and was calibrated with standard buffer solutions of pH 4.00, 7.00 and 9.00. The pH-meter reading recorded in ethanol–water solution was converted to hydrogen ion concentration as described by Van Uitert and Hass [32]. Thermogravimetric analyses (TGA) were recorded on a Shimadzu TGA-50 H. TGA was carried out in a dynamic nitrogen atmosphere (80 mL min^{-1}) with a heating rate of 10 °C min^{-1}.

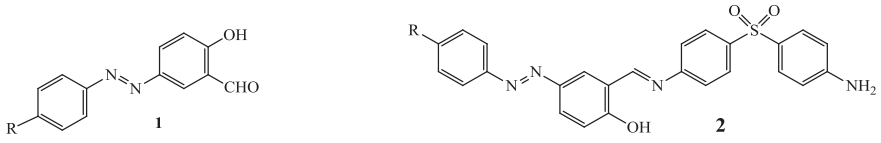
2.3. Biological analyses

The antimicrobial activity of compounds **2a–c** was evaluated against both gram positive and gram negative organisms by broth micro dilution method [33,34] and ciprofloxacin was used as the standard. The used strains were *Bacillus cereus, Staphylococcus aureus, Escherichia coli*, *Proteus mirabilis* and *Pseudomonas aeruginosa*. Also the antifungal activity against the fungus *Candida albicans* was done by agar diffusion method and *Griseofulvin* was used as standard. Broth micro-dilution technique was performed with 96-well round-bottom micro titer plates. Each plate included bacteria without an antimicrobial (positive control), medium only (negative control) and serial two-fold dilutions of each of the three antimicrobials, all in Muller Hinton broth medium (Merck, Germany). Dye-containing wells included final concentrations, ranging from 250 to 3.90625 μg/mL. The final volume of each well was 200 μL. The micro plates were incubated at 37 °C for 24 h. The minimum concentrations which no visible growth was observed were defined as the MIC, and were expressed in μg/mL. Also, the minimum bactericidal concentration (MBC) was determined by monitoring the subculture of the wells showing no growth. The MBC was defined as the lowest concentration of dyes that inhibited 99.9% of the growth in subcultures [34].

3. Results and discussion

The compounds 4-(4-aminophenylsulfonyl) phenylimino) methyl)-4-(Aryldiazenyl) phenol (**2a–c**) were obtained from the condensation reaction of 2-hydroxy-5-(aryldiazenyl) benzaldehyde (**1a–c**) with 4,4′-diaminodiphenylsulfone in Ethanol (Fig. 1). All prepared

Table 1
Summary of the UV–Vis absorption bands for compounds **1a–c** and **2a–c**[b].



	DMSO		DMF		MeOH	
Compound	λ(nm)	Abs.	λ(nm)	Abs.	λ(nm)	Abs.
1a	340	0.21	340	0.21	343	0.18
	441(sh)[a]	0.08	450	0.11		
1b	350	0.2	349	0.23	345	0.19
	441(sh)	0.09	444	0.16		
1c	377	0.26	365	0.21	361	0.19
	526(sh)	0.11	535	0.42	456(sh)	0.05
2a	396	0.23	399(sh)	0.2	360	0.2
	453	0.31	452	0.34	451	0.09
2b	395	0.24	396	0.2	361	0.2
	454	0.34	451	0.25	450	0.09
2c	364(sh)	0.08	419(sh)	0.14	366	0.207
	418(sh)	0.135	539	0.6	471(sh)	0.127
	536	0.592				

[a] sh: shoulder.
[b] Abs: absorbance.