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Research Article

The Effect of Substituent on Photophysical Properties of Some 4-(2-Substitutedhydrazinyl)Benzenesulfonamides Derivatives

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ABSTRACT

In this study, the effect of substituent on the photo-physical properties of some sulfonamide derivatives; 4-(2-substitutedhydrazinyl)benzenesulfonamides in which aryl part was changed as phenyl (**S1**), 4-methylphenyl (**S2**), 4-chlorophenyl (**S3**), 4-fluorophenyl (**S4**), 4-bromophenyl (**S5**), 4-methoxyphenyl (**S6**), 4-nitrophenyl (**S7**), 2-thienly (**S8**) and 2-furyl (**S9**) were examined in DMSO: H_2O (1:1 v/v) solution by using UV-Vis absorption, steady-state and time-resolved fluorescence spectroscopy techniques. It was determined that the sulfonamide derivatives studied exhibited fluorescence property at the blue-green region without exception. Their fluorescence properties were varied by changing the aryl part. The photophysical parameters of the sulfonamide derivatives were calculated in DMSO: H_2O (1:1 v/v) solution from the spectroscopic data. Consequently, these molecules having biological activity were spectroscopically characterized, and the effect of substituent on their photo-physical properties was examined.

Keywords: Substituent effect; absorption; fluorescence; photo-physical parameters.

Bazı 4-(2-Substiehidrazin)Benzen Sülfonamit Türevlerinin Fotofiziksel Özellikleri Üzerine Sübtitüent Etkisi

ÖZET

Bu çalışmada aril grubu, fenil (S1), 4-metilfenil (S2), 4-klorofenil (S3), 4-florofenil (S4), 4-bromofenil (S5), 4-metoksifenil (S6), 4-nitrofenil (S7), 2-thienly (S8) ve 2-furil (S9) olarak değiştirilen bazı 4-(2-substiehidrazin)benzen sülfonamit türevlerinin DMSO: H_2O (1:1 v/v) çözeltisi içindeki fotofiziksel özellikleri üzerine sübtitüent etkisi UV-gör. absorpsiyon, durgun-hal ve zamana-bağlı floresans spektroskopisi teknikleri kullanılarak incelenmiştir. Çalışılan sülfonamid türevlerinin tamamının mavi-yeşil bölgede floresans özellik gösterdikleri belirlenmiştir. Bileşiklerin floresans özelliklerinin, aril grubunun değişmesiyle değiştiği gözlenmiştir. Spektroskopik veriler yardımıyla sülfonamit türevlerinin DMSO: H_2O (1:1 v/v) çözeltisi içindeki fotofiziksel parametreleri de hesaplanmıştır. Sonuç olarak, biyolojik aktiviteye sahip olan bu moleküller spektroskopik olarak karakterize edilmiş ve bunların fotofiziksel özelliklerine süstitüent etkisi incelenmiştir.

Anahtar Kelimeler: Süstitüent etkisi; absorpsiyon; floresans; fotofiziksel parametreler.

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1. Introduction

Sulfonamides are known as powerful carbonic anhydrase (CA) inhibitors (Hu et al., 2015). However, sulfonamide derivatives have wide range of biological activities such as antibacterial, antidiabetic, anti-inflammatory and antitumor activities (Khazalpour & Nematollahi, 2015; Reddy et al., 2015; Zani & Vicini, 1998; Zhang, Lin, Liu, & Lin, 2015). They are used widely in the medicinal chemistry because of these significant pharmacological properties. Additionally, these compounds are also involved in spectroscopic studies (Gökoğlu & Yılmaz, 2014; Hu, et al., 2015; Özturk, Förstel, Ergun, Alp, & Rettig, 2008; Suganya & Kabilan, 2004; Yu, Liu, Guo, & Yang, 2013). Recently, an investigation of the changes in the photo-physical properties of sulfonamide derivatives depending on the attached substituent group has consisted an important study area (Zakerhamidi, Ahmadi-Kandjani, Moghadam, Ortyl, & Kucharski, 2011, 2012). In this regard, the changes on the absorption and emission maxima and quantum yields of the compounds can be occurred by the effect of substituents or solvents (Fu & Wang, 2008; Karcı, Demirçalı, Şener, & Tilki, 2006; Raposo, Sousa, Fonseca, & Kirsch, 2005; Yazdanbakhsh & Mohammadi, 2009; Zollinger, 2003). The absorption (or fluorescence) maximum shifted to longer wavelength is called as red or bathochromic shift, while their shifting towards shorten wavelength is called as blue or hypsochromic shift (Zollinger, 2003). Consequently, the fluorescence properties of these type organic compounds can be successfully modified with attaching appropriate substituents.

In the present study, it was reported the effect of substituent on the photo-physical properties of some sulfonamide derivatives having the chemical structure of 4-(2-substitutedhydrazinyl)benzenesulfonamides. Ketones used for the synthesis of S1-S9 were changed as acetophenone derivatives in S1-S7 having electron donating or attracting substituent at 4-position of phenyl ring or 2-acethylthiophene in S8 or 2-acethylfuran in S9 to observe how the differences in substituent on phenyl ring direct the photo-physical properties of the compounds studied or how the differences in aryl moiety (such as phenyl, 2-thienyl, 2-furyl) direct the same properties. The absorption and fluorescence properties of the compounds were spectroscopically characterized as well as their photo-physical parameters.

2. Materials and Methods

2.1. Chemicals

Methanol (MeOH, Sigma), dimethyl sulfoxide (DMSO, Sigma), quinine sulfate (Fluka) and H_2SO_4 (Sigma) were purchased and used without further purification. The stock solution of all compounds was prepared in MeOH. A certain amount of fresh probe samples in DMSO: H_2O (1:1 v/v) solution was prepared from this stock solution by diluting process. For all measurements, the concentrations of the compounds were 1.0x10^{-5} M. All the experiments were performed at room temperature.

2.2. Equipment

The UV-Vis absorption and fluorescence spectra of the samples were recorded with Perkin Elmer Lambda 35 UV/VIS spectrophotometer and Shimadzu RF-5301PC spectrofluorophotometer, respectively. The fluorescence and absorption measurements were taken for all sulfonamide derivatives at room temperature. For the steady-state fluorescence measurements, all samples were excited at the wavelength of 330 nm and the fluorescence intensity were recorded between 340 nm and 600 nm. The fluorescence lifetime measurements were carried out with a LaserStrobe model TM3 spectrofluorophotometer from Photon Technology International (PTI). The excitation source combined a pulsed nitrogen laser/tunable dye laser. The samples were excited at the wavelength of 366 nm. The fluorescence decays were collected over 200 channels using a nonlinear time scale with the time increment increasing according to arithmetic progression. The fluorescence decays were analyzed with the lifetime distribution analysis software from the instrument supplying company. The quality of fits was assessed by χ^2 values (Bozkurt, Acar, Onganer, & Meral, 2014).

The fluorescence quantum yields of the samples were calculated through the Parker-Rees equation:

$$\emptyset_s = \emptyset_r \left({}^{D_s}/_{D_r}\right)\left({}^{n_s^2}/_{n_r^2}\right)\left[\left({}^{1-10^{-ODr}}/_{1-10^{-ODs}}\right)\right] \qquad (1)$$

where D is the integrated area under the corrected fluorescence spectrum, n is the refractive index of the solution, and O_D is the optical density at the excitation wavelength (λ_{ex}= 330 nm). The subscripts s and r refer to the sample and reference solutions, respectively. Quinine sulfate in 0.5 M H_2SO_4 solution was used as a reference solution. The fluorescence quantum yield of quinine sulfate was 0.54 in 0.5 M H_2SO_4 solution (Tan, Bozkurt, Kishali, & Kara, 2014).

The radiative (k_r) and non-radiative (k_{nr}) deactivation rate constants were calculated by using the following equations (Valeur, 2001).

$$k_r = \frac{\Phi_f}{\tau_f} \qquad (2)$$

$$\frac{1}{\tau_f} = k_r + k_{nr} \qquad (3)$$

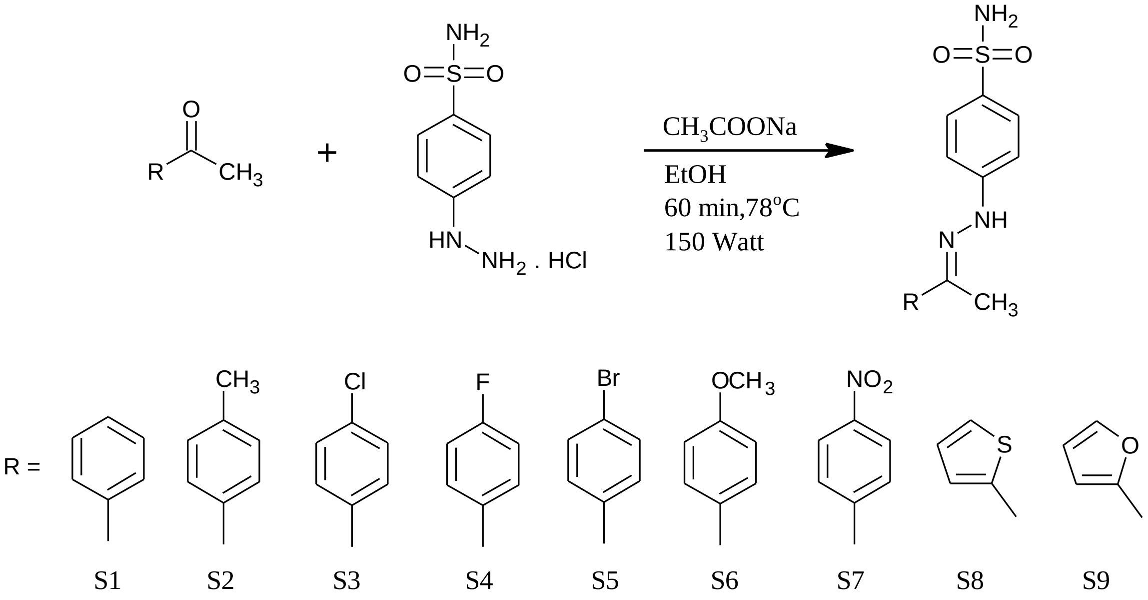
The molar absorptivity coefficients of the samples were calculated using by Lambert-Beer equation:

$$A = \varepsilon\,(\lambda) bC \qquad (4)$$

where A is the absorbance, b is the path length (1 cm^2), λ is the monochromatic wavelength, and ε(λ) is the molar absorption coefficient (Tran et al., 2010).

3. Results and Discussion

The compounds studied were successfully synthesized according to the literature procedure and their chemical structures and biologically activities were confirmed. The 4-(2-substituted hydrazinyl) benzenesulfonamide derivatives (S1–S9) were evaluated for their hCA I and II isoenzymes and were found to be sufficiently active (Gul et al., 2016). The general synthesis of the compounds and their chemical structures are summarized in Scheme 1.



Scheme 1. Synthesis method and chemical structures of the compounds S1-S9

The optical properties of the sulfonamide derivatives in DMSO: H_2O (1:1 v/v) solution were investigated. Normalized UV/vis absorption spectra of all sulfonamide derivatives were given in Figure 1. As seen from Figure 1, the sulfonamide derivatives exhibited absorption band at blue-green region. The existence of electron-donating and electron-attracting substituents in the benzene ring caused bathochromic shifts on the band wavelength absorption maximum as compared to that of the unsubstituted dye S1. Moreover, it was observed that S7 has two absorption bands at 293 and 404 nm (Figure 1 and Table 1). This situation may be related to the n→π* and π→π* transitions as a result of the strong electron-withdrawing power of the $-NO_2$ group (Valeur, 2001).

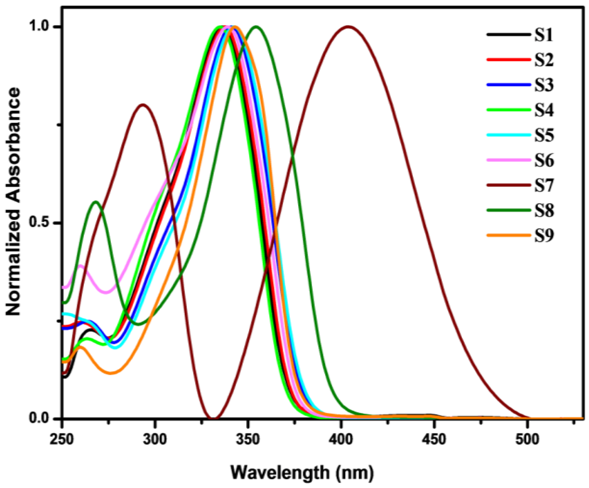


Figure 1. Absorption spectra of sulfonamide derivatives in DMSO: H_2O (1:1 v/v) solution

The fluorescence properties of organic molecules are significant for their practical applications such as cell imaging. In this regard, the determination of the fluorescence properties of the sulfonamide derivatives is necessary.

Table 1. The absorption, fluorescence maxima and molar absorptivity coefficient of sulfonamides derivatives in DMSO: H_2O (1:1 v/v) (λ_{ex}= 330 nm)

Compound	λ_{abs} (nm)	ε ($x10^5/M^{-1}cm^{-1}$)	λ_{ems} (nm)
S1	336	1.15	433
S2	337	2.64	386
S3	341	2.45	393
S4	335	2.66	387
S5	342	2.52	395
S6	339	1.86	389
S7	293/404	0.82	464
S8	354	2.18	422
S9	343	1.62	389

The fluorescence measurements of the compounds were recorded at excitation wavelength of 330 nm. It was determined that sulfonamide derivatives displayed the fluorescence property at different wavelengths by varying the substituents on phenyl ring or aryl ring (Figure 2). A hypsochromic shift was observed at the fluorescence wavelength depending on the substituents available on phenyl ring with the compounds S1-S6 (Figure 3) except for S7 that has nitro substituent on phenyl ring. The hypsochromic shifts were also observed with the compounds S8 and S9, in which aryl part was 2-thienyl and 2-furyl. Both electron-donating and electron-withdrawing substituents on phenyl ring in compounds S2-S6 caused blue-shift in the fluorescence maxima of the compounds compared to that of S1 which has at 4-position hydrogen i.e. nonsubstituted derivative (Table 1). S8 and S9 compounds were also affected in a similar way leading to the blue shift of the fluorescence wavelength of the compounds. The red shift observed with the compound S7 which has nitro substituent on phenyl ring instead of blue shift observed with the other compound S1-S6, S8 and S9 is explained with internal conversion processes in S7. This situation may be related to the considerable charge-transfer of the excited state (Valeur, 2001).

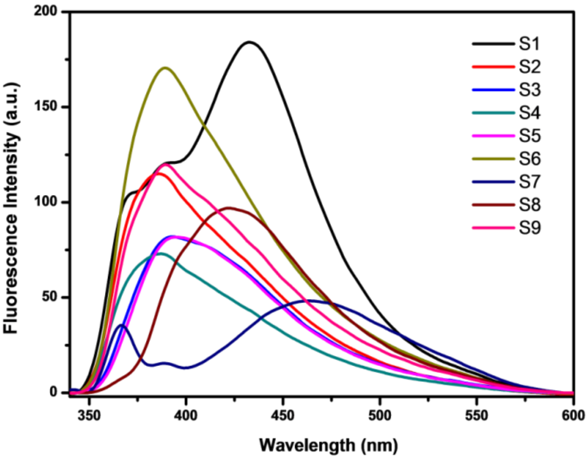


Figure 2. Fluorescence spectra of sulfonamide derivatives in DMSO: H_2O (1:1 v/v) solution (λ_{ex}= 330 nm)

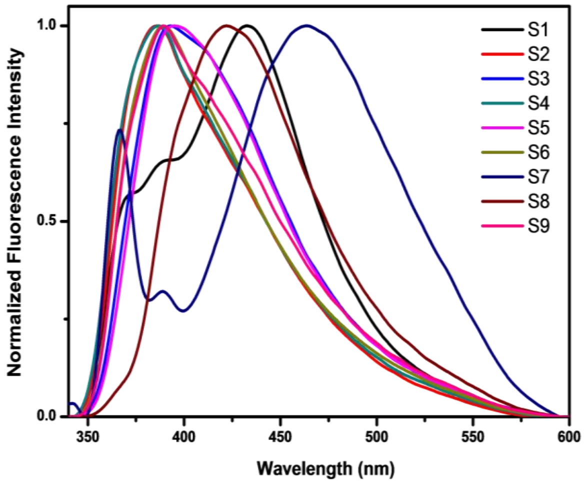


Figure 3. Normalized fluorescence spectra of sulfonamide derivatives in DMSO: H_2O (1:1 v/v) solution (λ_{ex}= 330 nm)

In this study, the fluorescence quantum yields, radiative and non-radiative rate constants of the sulfonamide derivatives were calculated and their fluorescence lifetime values were also determined (Figure 4 and Table 2). As seen from Table 2, the photo-physical parameters of compounds varied depending on the substituents on phenyl ring and difference in aryl.

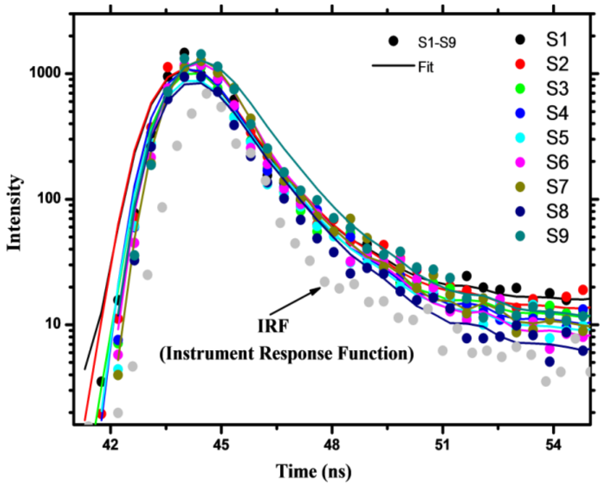


Figure 4. Fluorescence decays of sulfonamide derivatives (λ_{ex}= 366 nm)

Table 2. The photo-physical parameters of sulfonamide derivatives in DMSO: H_2O (1:1 v/v)

Compound	Φ_f	τ (ns)	$k_r x10^{-9}$ (s^{-1})	$k_{nr} x10^{-9}$ (s^{-1})
S1	0.05	0.581	0.079	1.642
S2	0.02	0.582	0.039	1.679
S3	0.02	0.606	0.029	1.621
S4	0.01	0.489	0.030	2.015
S5	0.02	0.663	0.026	1.483
S6	0.08	0.614	0.056	1.573
S7	0.04	0.360	0.110	2.668
S8	0.02	0.760	0.028	1.287
S9	0.03	0.626	0.042	1.556

It was determined that these sulfonamide derivatives had low the fluorescence quantum yields. The great k_{nr} values of each compound suggested that non-radiative deactivation process were more favorable for the compounds studied (Lakowicz, 2006).

4. Conclusion

In the present study, the effect of substituent on the photo-physical properties of some sulfonamide derivatives were first time investigated in DMSO: H_2O (1:1 v/v) solution. For this aim, the sulfonamide derivatives having phenyl or substituted phenyl ring or aromatic rings such as 2-thienyl or 2-furyl in its chemical structure were used. The absorption and fluorescence measurements these sulfonamide derivatives were recorded to determine their photo-physical properties. It was shown that these derivatives have fluorescence property at the blue-green region and the substituent of these compounds changed their fluorescence properties. According to the spectroscopic results, the photo-physical parameters of the compounds were determined. Consequently, the sulfonamide derivatives having biological activity were characterized with the spectroscopic measurement and the photo-physical parameters. It is expected that the presented results will make important scientific contribution into the field containing optoelectronics, chemical sensing and biophysical applications.

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