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Investigation on the correlation between the structure of azulen-1-yl-benzothiazol-2-yl diazenes and their properties. Acidity and electrochemical redox potentials

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ABSTRACT

Acidity and redox potentials of a series of substituted azulen-1-yl-benzothiazol-2-yl diazenes are correlated with several theoretical parameters. From the electronic spectra of the dyes recorded at different pH, the derived pK_a values correlate well with *para* Hammett-constants. The experimental oxidation and reduction potentials, as determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), are in good agreement with the calculated frontier orbital energies, for the studied dyes.

1. Introduction

In the last years growing interest has focused toward organic push–pull materials because many compounds with this property were used in technical applications such as, molecular switches, for NLO, or electrochromic materials, as well as, for the modification of electrode properties. An organic push–pull system consists of two moieties, one electron-donor and, the other, electron-withdrawing group. Between these moieties it is possible to insert a homo- or hetero-atomic bridge such as conjugated double bonds or aromatic moieties. Among the recently used electron-donors, the azulene-1-yl system has attracted attention. We have synthesized a series of chromophores with this moiety: vinylazulenes [1–3] or azoazulenes [4–9] some of which possess good NLO properties [1,3,5]. Among the efficient electron acceptors, thiazol-2-yl or benzothiazol-2-yl moieties have retained our attention and we have already synthesized the azulenyl diazenes **1**–**3** [10] and **4** [11] (Scheme 1), with these acceptors.

The strong donor capacity of azulene and the acceptor property of benzothiazole as well as the large conjugated π electron system must generate the polarization and hyperpolarizability of the push–pull molecules **1**–**4**. The intense solvatochromism observed in the case of several chromophores from these series [12] confirmed our supposition and suggested the possibility to use them as NLO materials. In this perspective we have further investigated their properties namely their acid–base behavior and the determination of oxidation and reduction potentials. The study was also developed in order to find some rules concerning the influence of donor and acceptor substituents on the behaviour of the investigated chromophores. In the following, we report on the result of both these investigations.

2. Results and discussions

2.1. UV–Vis and basicity studies

The electronic structure of the investigated compounds assures an important contribution in the ground state of the molecule of the resonance structure as **1a**(**B**), **1a**(**C**) or **1e**(**B**) with long-range separated charges (Scheme 2) and the positive charge stabilized as tropylium cation. Accordingly, the difference between the energies of frontier orbitals HOMO and LUMO is reduced and as follows, the hyperpolarizability of the compound enhances and the compounds are more solvatochromic. This effect is much more pronounced

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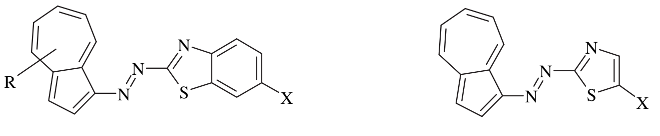
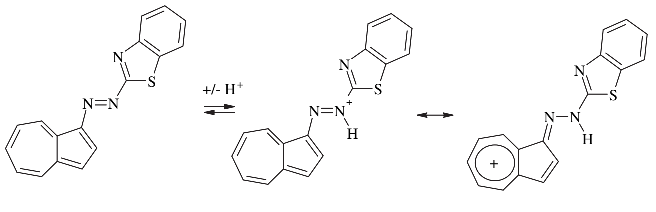


1-3

4 (a)X = H, (b) X = NO_2

1 R = H, (a)X = MeO; (b) X = Me; (c) X = H; (d) X = Cl; (e) X = NO_2
2 X = H, (a)R = 4,6,8-Me_3; (b) R = 3,8-Me_2-5-*i*Pr
3 X = NO_2, (a)R = 4,6,8-Me_3; (b) R = 3,8-Me_2-5-*i*Pr

Scheme 1.



1c

[**1c**]H$^+$ (A)

[**1c**]H$^+$ (B)

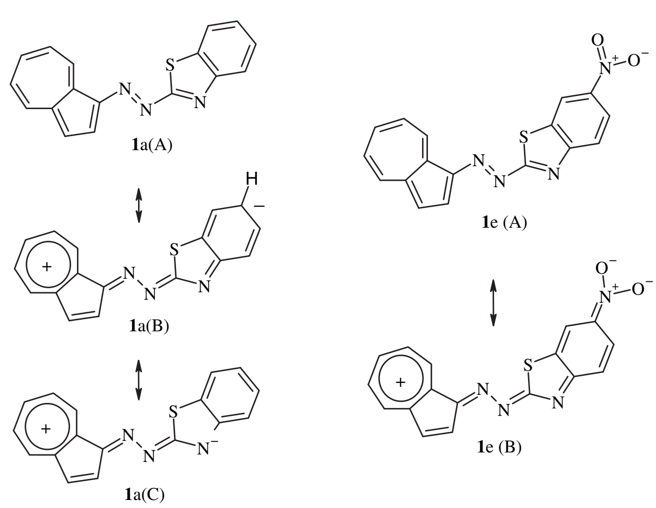
Scheme 3.

when the 6-position of benzothiazole is occupied by an electron acceptor such as the NO_2 group, compound **1e** (Scheme 2). Due to their inductive effect, the alkyl groups substituted on the azulenyl moiety stabilize the tropylium system therefore the electronic structure of the compounds **2** and **3** become more solvent responsive relative to **1**.

The high charge density at nitrogen atoms of the azo group and the stabilization of the positive charge as tropylium cation after protonation, confer acid-basic behavior upon the compounds **1**–**4** (Scheme 3). Therefore, it was interesting to study the correlation between pH of the medium and the electronic spectra in order to obtain the pK_a values of the compounds.

The recorded UV–Vis absorption spectra at various pH values (Table 1) allowed the determination of maxima absorption wavelengths in either neutral medium λ_n [13] or acidic medium, λ_{ac}, as well as, at the isosbestic point, λ_{iso} [14]. It is well known that the pK_a values can be considered equal to the pH at the isosbestic point (Fig. 1 shows two examples for the determination of the isosbestic points). A comparison of the basicity of thiazole diazene **4**a and the corresponding benzannelated derivatives **1** and **2** can lead to some conclusions concerning the influence of annelation.

It is somewhat surprising that, although both electron donating and electron-withdrawing substituents at the 6-position of the benzothiazole ring induce a bathochromic effect, the pK_a values of the conjugated acids correlate linear with *para* Hammett parameters (Fig. 2). Therefore, as shown in Table 1, decreases in the basicity of the compounds **1** can be observed at the increase in the electron-withdrawing ability of the substituent X. For compounds **2**, where alkyl groups are located on the azulenyl moiety of compounds **1**, both a bathochromic effect and a basicity increase are observed in comparison with the unsubstituted analogues.



1a(A)

1e (A)

1a(B)

1e (B)

1a(C)

Scheme 2.

As expected, the benzannelation of thiazole ring in the diazenes **1** induces a bathochromic effect of the main visible band as well as a slightly decreases in the basic character of diazenes as compared with the compounds **4**.

2.2. Electrochemical experiments

The differential pulse voltammetry study for each compound enabled a precise measurement of anodic and cathodic peak potentials and currents. The cyclic voltammetry study, which was performed at different concentrations, scan rates and potential ranges, enabled the establishment of reversible and irreversible electrode processes. Results obtained by CV and DPV were concordant, with respect to peak potentials, and were complementary, yielding specific features for each process. For example, Fig. 3 shows the CV and DPV curves obtained for the compound **2b**. Anodic and cathodic curves are shown in each graph and they have been obtained as described in our previous work [15,16]. The values for recorded oxidation and reduction peak potentials, E_{1a} and E_{1c}, for the compounds **1** and **2**, are summarized in Table 2. These values are compared with the same parameters for benzothiazol-2-yl-(4-dimethylaminophenyl) diazene **5**, azobenzenes **6** and azulene-1-yl-phenyl diazenes **7** depicted in Scheme 4. The recorded values for the compounds **1**–**2** and **5** are accompanied by the calculated ionization potentials and LUMO energies.

According to the electromeric and/or inductive effects of the substituent in the 6-position of benzothiazolyl moiety, the oxidation aptitude of the compounds **1** increases in series **1e**, **1d**, **1c**, **1b** and **1a**. Among the structural features which can participate at the single electron transfer, the azulenyl group is by far the more sensible. The loss of an electron is favored by the stabilizing effect of the tropylium structure generated in the resultant radical cation. Therefore, the azulenyl moiety significantly decreases the oxidation potential of compounds **7**, as compared to the azobenzenes **6** (Table 2); however, it is not as efficient as the 4-dimethylaminophenyl moiety, present in compound **5**. Therefore, it is somewhat surprising that the oxidation potentials correlate well with *para* Hammett-constant, as shown in Fig. 4, despite the distance between the substituents and azulenyl

Table 1
Maxima of the main visible band (in nm) for the compounds **1**, **2** and **4** in ethanol (96%) at neutral and acid pH, as well as, at the isosbestic point.

Compound	X	R	λ_n	λ_{iso}	λ_{ac}	pK_a (=pH_{eq})
1a	MeO	H	508	539	595	1.50
1b	Me	H	500	529	586	1.39
1c	H	H	497	525	577	1.30
1d	Cl	H	503	536	580	0.97
1e[a]	NO_2	H	522	532	567	0.68
			522[b]	540[b]	576[b]	0.40[b]
2a	H	4,6,8-Me_3	503	536	580	1.87
2b	H	3,8-Me_2-5-*i*Pr	530	555	597	1.94
4a	H	–	480	505	558	1.50

[a] Compound **1e** is low soluble in ethanol 96%.
[b] In MeOH (90%) aqueous.