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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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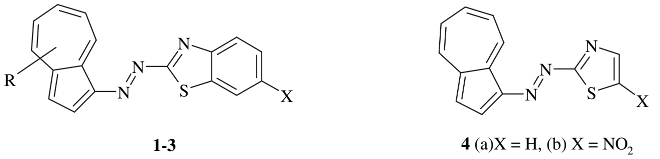


1-3 **4** (a)X = H, (b) X = NO$_2$

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

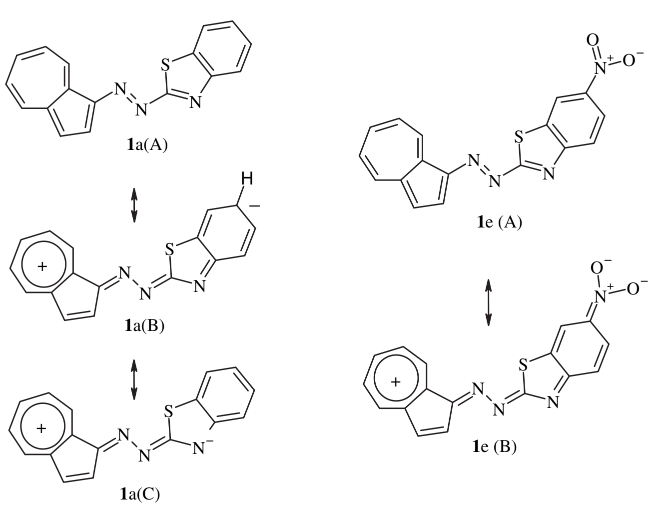
Scheme 1.

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**.

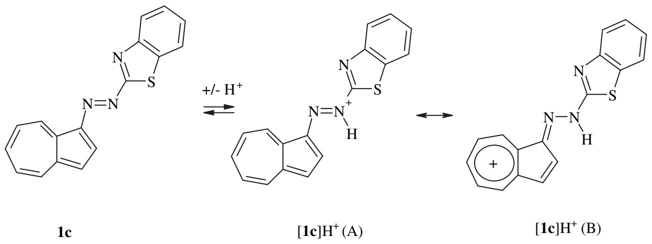
The high charge density at nitrogen atoms of the azo group and the stabilization of the positive charge as tropylium cation after protonation, confer acid-basic behavior upon the compounds **1**–**4** (Scheme 3). Therefore, it was interesting to study the correlation between pH of the medium and the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



Scheme 2.



Scheme 3.

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.

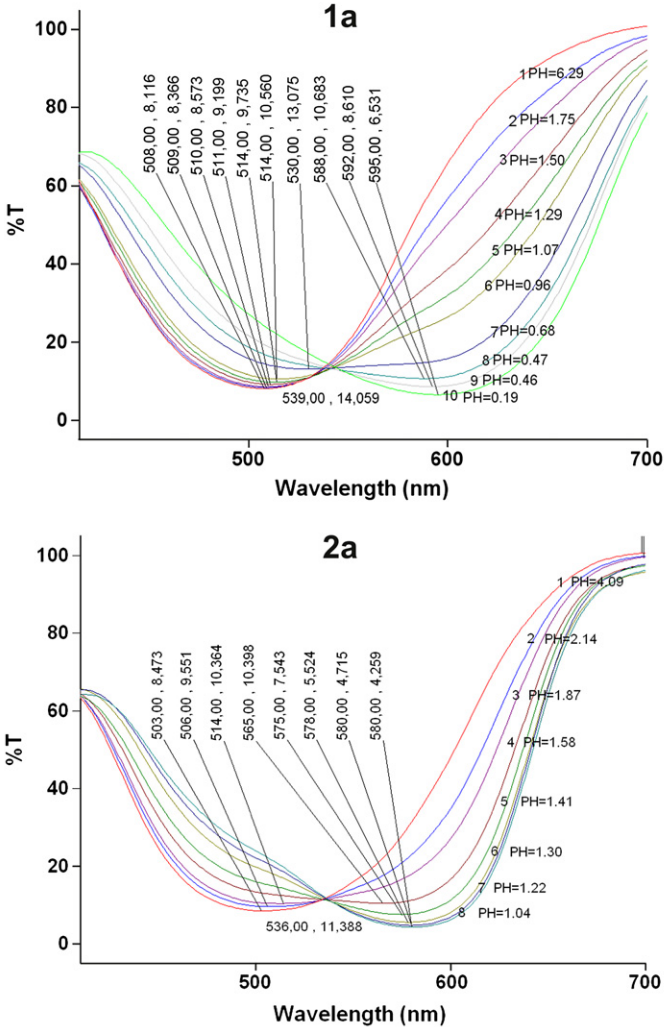


Fig. 1. Determination of the isosbestic points for the compounds **1a** and **2a**.

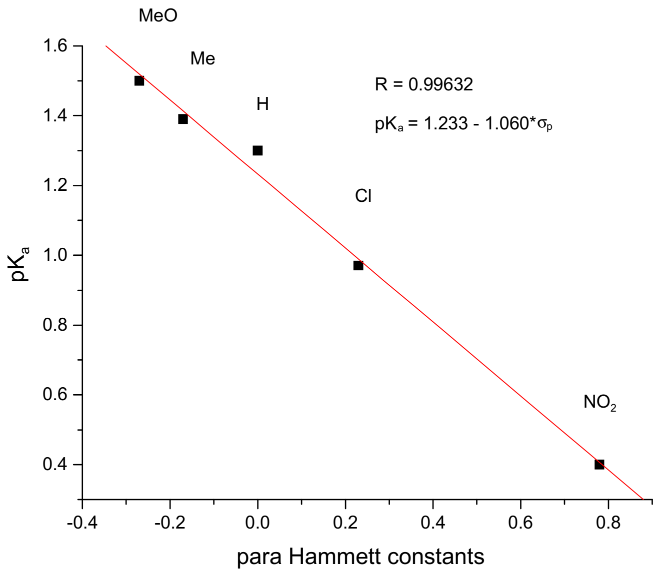


Fig. 2. Correlation of pK_a determined for conjugated acids of the compounds **1** with *para* Hammett-constants.

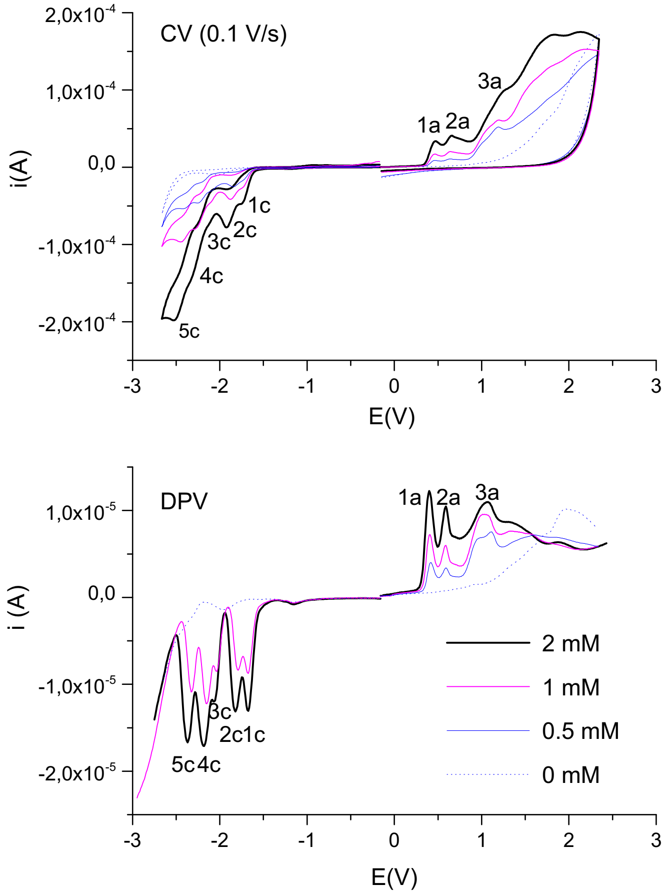


Fig. 3. DPV and CV (0.1 V/s) curves on glassy carbon (2 mm in diameter) for **2b** at different concentrations in 0.1 M TBAP, CH_3CN.

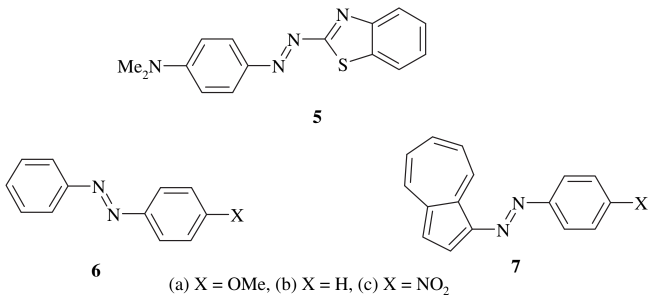
moiety. The increase in the oxidation potential of the compounds is in good agreement with the calculated ionization potentials (Table 2).

Among the compounds **1** and **2**, lower oxidation potentials, E_{1a} are registered for the compounds **2**, where the alkyl substituents on the azulenyl moiety enhance the electron transfer ability toward electrode. The replacement of phenyl in **7**b with benzothiazol-2-yl in **1**c increases the oxidation potential in spite of the observed slight bathochromic shift. It must be noted the higher oxidation potential of diazene **2**a as compared to **2**b, is explained by the lower symmetry for the latter compound. This loss in symmetry disturbs the azulene polarization needed for preserving its aromatic character.

Table 2

Values for recorded oxidation and reduction peak potentials, E_{1a} and E_{1c} (obtained by DPV), and calculated ionization potentials, I_p ($-[I_p]$ = [HOMO]) and LUMO for several diazenes.

Compound	E_{1a}	E_{1c}	I_p	LUMO energy
1a	0.632	−1.302	8.10	−1.47
1b	0.656	−1.286	8.13	−1.49
1c	0.673	−1.276	8.15	−1.52
1d	0.724	−1.210	8.24	−1.60
1e	0.823	−0.940	8.42	−1.92
2a	0.606	−1.308	8.03	−1.45
2b	0.532	−1.318	7.29	−1.44
5	0.427	−1.952	8.23	−1.01
6a	1.127	−1.854	–	–
6b	1.320	−1.733	–	–
6c	1.517	−1.228	–	–
7a	0.475	−1.650	–	–
7b	0.620	−1.673	–	–
7c	0.648	−1.250	–	–



5

6

7

(a) X = OMe, (b) X = H, (c) X = NO$_2$

Scheme 4.

The recorded values for reduction potentials prove that the substituent in the 6-position of benzothiazolyl moiety has a higher influence on reduction than on the oxidation potentials. It is possible that the azo bond with the contribution of benzothiazole system is more implied in the electron receiving than azulenyl moiety. Obviously, the compound **1e**, with a 6-NO$_2$ group can be most easily reduced, while the hardest reduction is noted for **1a**, with MeO at the 6-position. At the same time, the alkylated azulenes, having higher electron density, are hardly reduced. Based on the present information, a correlation between the LUMO-s energies and the reduction potentials, as well as, the Hammett correlation seem to be uncertain.

3. Experimental

3.1. Reagents

Acetonitrile (Rathburn, HPLC grade), tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium fluoroborate (TBABF$_4$) from Fluka were used as received like solvent and supporting electrolytes, respectively. The investigated compounds, **1** and **2**, have been obtained by specific chemical reactions of azulenes with diazotized unsubstituted and 6-substituted 2-benzothiazolamines [10].

3.2. Determination of the isosbestic points and pK_a values

The electronic spectra were recorded on Varian Cary 100 spectrophotometer. The diazenes were dissolved in aqueous ethanol (96% EtOH) or methanol (90% MeOH) to get 3×10^{-5} M solutions, then aqueous 0.1 N hydrochloric acid solution was added with a syringe and the pH values were measured. The amount of water present in aqueous alcoholic solutions assured a good reproducibility of the pH measurements. The dilution brought by aqueous hydrochloric acid introduction was negligible. The electrodes were regenerated after each measurement by introducing them into the etalon pH-solutions for pH 1, 4 and 10, otherwise the pH values become not reproducible due to the alcohol diffusion into the measurement electrode.

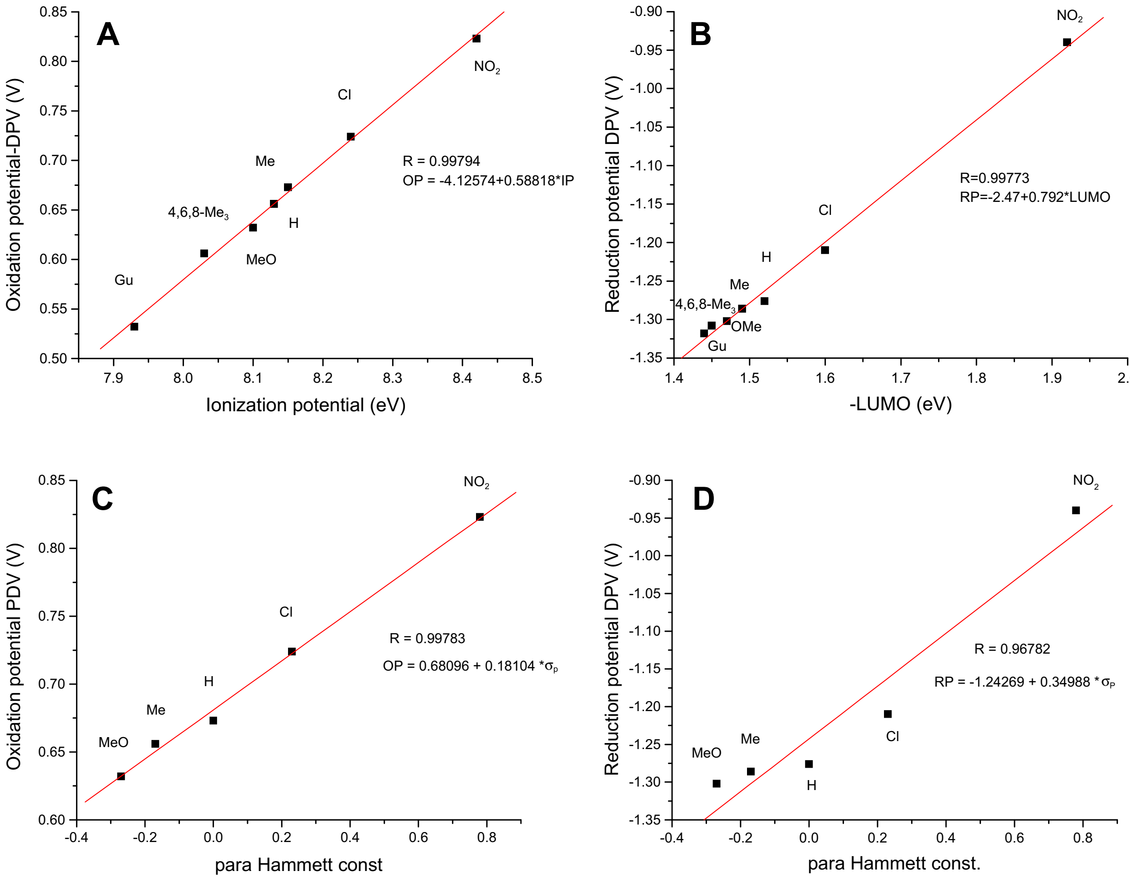


Fig. 4. The correlation between frontier orbital energies and the experimental oxidation (A) and reduction (B) peak potentials (obtained by DPV) and between these potentials and Hammett-constants (C, D).

3.3. Electrochemical experiments

Electrochemical experiments were performed by cyclic voltammetry, as well as differential pulse voltammetry in a conventional three-electrode cell under argon atmosphere at 20 °C using a PGSTAT 12 AUTOLAB potentiostat. The CV was conducted usually at 0.1 V/s, or at different scan rates (0.02–50 V/s), for investigation of scan rate influence. DPV curves were recorded at 10 mV/s with a pulse height of 25 mV and a step time of 0.2 s. The working electrode was a glassy carbon disk (2 mm in diameter) polished with 200 μm diamond paste before each experiment. The Ag/10 mM $AgNO_3$ in $CH_3CN + 0.1$ M TBAP system was used as reference electrode. All the potentials were referred to the potential of ferrocene/ferricinium (Fc/Fc^+) couple, which in our experimental conditions was 0.07 V.

3.4. Computational methods

Calculations were performed with a MOPAC program using AM1 method [17].

4. Conclusions

The investigated correlation between the structure of compounds **1**, **2** and **3** and their electronic spectra, recorded at different pH, allowed the determination of the pK_a values, which correlate well with *para* Hammett-constants. The basicity of these compounds increases both when the azulene is substituted with alkyl groups and when benzothiazole possesses electron donating groups and, of course, decreases in the case of benzothiazole substitution with electron-withdrawing groups.

The redox properties of the dyes **1** and **2** are studied and are compared with those for **5**, **6** and **7**. In the latter substances, the azo group was substituted by benzothiazol-2-yl and 4-dimethylaminophenyl, by phenyl and 4-substituted phenyl or by azulene-1-yl and 4-substituted phenyl, respectively. Although the azulenyl system is by far the most oxidizable moiety of the compounds **1**, **2**, **3** and **7**, the nature of the substituents on azulene or benzothiazolyl group also deeply influence the oxidation and reduction potentials of these compounds. The oxidations are more influenced by the presence of electron-releasing groups at azulene, while the reductions are more sensitive to benzothiazolyl substitution. At the same time, the oxidation and reduction potentials are in good agreement with the calculated values for the energies of the frontier orbitals.

Acknowledgments

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