

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

ELECTROCHEMICAL BEHAVIOUR OF BIS DIAZENYLS CONTAINING AZULENYL MOIETIES

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Several *meta* and *para* mono and bis (azulen-1-ylazo) or phenylazo substituted phenylene derivatives, **1-4** were electrochemically characterized using DPV and CV methods. All the compounds presented several oxidation and reduction potentials. These values are correlated with HOMO and LUMO energies; a very good fit for oxidations and an acceptable link for reductions were observed. The influence of the arylazo groups on the potentials is discussed in comparison with that of the alkyl groups. Using cyclations in anodic field, films are obtained for the azulenic compounds with the unoccupied 3 position.

INTRODUCTION

The electrochemistry of azulene and its derivatives represents a target for many research groups due to the interesting properties of these compounds and also to their potential technical applications. For example, azulene and its derivatives form either conducting or insulating organic polymers by its electropolymerization or by its electrocopolymerization¹ in the presence of pyrrole, thiophene or styrene. The electrodes covered with such polymer films present valuable modified properties and, therefore, they could be used in analytical purposes.²

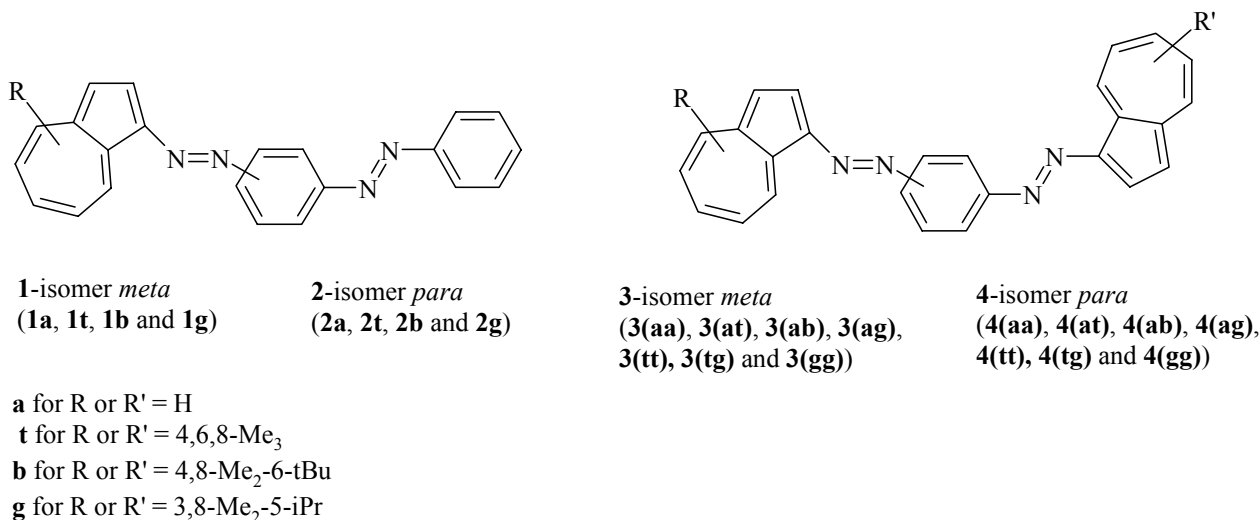
The substitution of different positions in azulene with functional groups³ deeply changes both the electrochemical properties and the stability in either neutral or ionized forms. The aryl-diazenyl is a very interesting substituent as it possesses both donor and acceptor properties and, therefore, it modifies the electronic density of azulene moiety leading to a change in its electrochemical behaviour. In the previous papers

of our group we have investigated the electrochemical properties of diazenyl-azulenes with one azo group, namely, 1-aryloazo-azulenes and 1-heteroaryloazo-azulenes.⁴ The present paper is focused on bis(diazenyls) containing azulenyl moieties.

RESULTS AND DISCUSSION

The investigated bis diazenes **1-4** are depicted in Scheme 1. Formally, these compounds represent phenylene radicals substituted in *meta* or *para* positions with arylazo groups. While at the compounds **1** and **2** one substituent is a 1-azulenylazo moiety and the second is a phenylazo group, at the compounds **3** and **4** these substituents consist in either identical or different 1-azulenylazo moieties. The azulenyls are either unsubstituted – when the compounds are labelled with **a**, or substituted with: 4,6,8-Me₃, 4,8-Me₂-6-*t*-Bu, or 3,8-Me₂-5-*i*-Pr (guiazulenyl), when the compounds are labelled with **t**, **b**, and respectively **g**.

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Scheme 1

The proposed compounds could be also considered as derivatives of already studied phenyl-azo-1-azulene. The introduction of the second azo group extends the system of conjugated π electrons leading to the modification of the redox potentials and absorption wavelengths of the molecules. The effect is higher when the substituent is azulenylazo, as in the compounds **3** and **4**, comparing with phenylazo, as for the compounds **1** and **2**, being more pronounced for *para* isomers. The efficaciousness of azulene moiety is due to its higher π electrons mobility and the substitution in *para* position is favourable to the conjugation between the two substituents.

A) Study of 1-azulen-1-yl-2-[3- or 4-(phenyldiazenyl)phenyl]diazene, compounds **1** and **2**

The compounds **1** and **2** have been studied by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) in millimolar solutions in CH₃CN + 0.1M TBAP. Fig 1 shows an example of the corresponding curves obtained for *meta* derivative **1a**. Several anodic (1a - 5a) and cathodic (1c - 6c) processes have been observed. They are better evidenced by DPV than by CV, where some of them appear overlapped. The peak currents in DPV and CV are proportional with concentration. The CV investigations have been realised at different scan ranges and at sweep rates between 0.2 and 10V/s. Only irreversible electrode processes were observed in CV. The CV data confirm the behaviour in DPV.

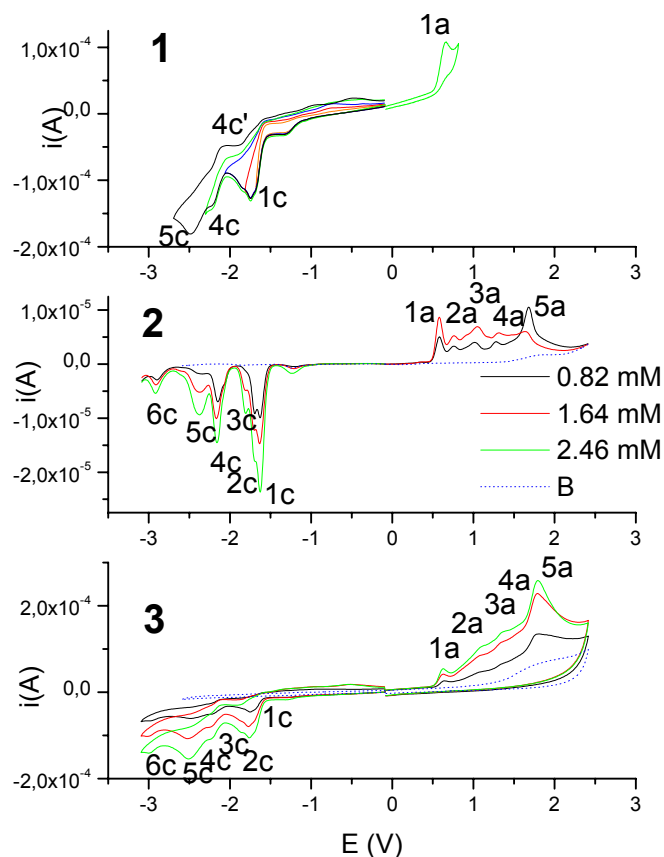
The oxidation and reduction peak potentials were measured from DPV and CV curves in order

to be compared with the values of related compounds. The potentials of the first peaks of reduction (E_{1c}) and oxidation (E_{1a}), corresponding to the formation of the radical cation and radical anion, respectively, are referred in the following as oxidation and reduction potentials of these compounds.

Table 1 shows the potentials values for the oxidation and reduction peaks for the compound **1a** and for the related compounds, **1b**, **1t**, **1g**, obtained by substitution of azulenes with different alkyl groups. These potentials have been taken from the obtained DPV curves, which allow a precise evaluation of the peaks. The peaks which have appeared split have been put in the same box of the table.

The value obtained for the compound **1a** at oxidation is 0.584 V, while at reduction the value is -1.628 V. These values can be compared, for instance, with the values obtained for the corresponding azulene with one azo group, phenylazo-1-azulene, which has the first peaks of oxidation and reduction at the potentials of 0.536 V, and -1.673 V, respectively, as shown in our previous study by DPV. The introduction of a supplementary phenylazo group increases the oxidation potential and decreases the reduction potential in respect with those for phenylazo-1-azulene. These shifts are in agreement with those generated by other electron withdrawing groups in *para* position of the benzene ring. For instance, the chlorine atom shifts the oxidation potential from 0.536 to 0.560 V, while the nitro group to 0.648 V, showing that the phenylazo group has an electron withdrawing character intermediate between the chloro and nitro substituents.

Fig. 1 – CV at 0.1 V/s (1, 3) and DPV (2) curves for meta-(phenylazo)phenylazo-1-azulene (**1a**) at different concentrations (mM) on glassy carbon (3mm in diameter) in 0.1M TBABF₄, CH₃CN.



From Table 1 it can be also seen that the difference between the oxidation potentials (E_{1a}) of the *meta* compounds, **1a**, **1b**, **1t**, **1g** and *para* compounds, **2a**, **2b**, **2t**, **2g** is very small (for instance these values are 0.584 V and 0.581 V for **1a** and **2a**, respectively). The azulene substitution with three methyl groups in the 4,6,8-positions also

decreases the oxidation potentials to 0.448 V for *meta* (**1t**), and 0.475 V for *para* (**2t**) isomers. A switch of the order of the oxidation potentials between the two isomers is observed between **1t** and **2t**. The lowest values for E_{1a} potentials are observed for guaiazulene derivatives, being: 0.341 V (**1g**) and 0.383 V (**2g**), respectively.

Table 1

Oxidation and reduction peak potentials of the compounds **1** and **2** determined from the DPV curves, vs. Fc/Fc⁺ in acetonitrile at a concentration of 1.8 mM

Comp.	-HOMO (eV)	-LUMO (eV)	5c	4c 4'c	3c 3'c	2c	1c	1a	2a 2'a	3a
1a	8.040	1.229	-2.907	-2.370; -2.150	-1.813; -1.703	-1.628		0.584	0.760; 1.049	1.646
1b	7.883	1.112	-2.906	-2.277; -2.334	-1.786	-1.661	-1.455	0.476	0.855; 1.053	1.656
1t	7.863	1.170	-	-2.223; -2.332	-1.758	-1.656		0.448	0.857	1.655
1g	7.750	0.964	-	-2.250; -2.339	-1.830	-1.715	-1.499	0.341	0.792	1.626
2a	8.020	1.340	-	-2.140	-1.846	-1.573	-1.446	0.581	0.770; 0.981	1.719
2b	7.891	1.258	-	-2.250; -2.369	-1.806 -1.930	-1.674	-1.485	0.468;	0.562; 0.809	1.676
2t	7.899	1.282	-	-2.237; -2.337	-1.997	-1.650	-1.470	0.475	0.849	1.685
2g	7.767	1.244	-	-2.340	-2.050	-1.725	-1.486	0.383; 0.532*	0.808	1.693

* possible to appear due to a partial protonation of the product

The variation of the oxidation potentials in correlation with the azulene substituents differs from the literature reports as value, but not as direction. From the observed data for alkylated

azulenes, Kurihara⁵ proposed an equation that anticipates the oxidation potentials of alkylated azulenes depending on the number and position of the alkyl groups in molecules (1):

$$E_{\text{ox}}(\text{Az.subst}) = E_{\text{ox}}(\text{AZ}) - 0,10n_{1,3} + 0,06n_2 - 0,02n_{4,8} - 0,11n_{5,7} - 0,01n_6 \quad (1)$$

In equation (1), n represents the number of alkyl groups on azulene moiety, while the indexes represent the linking positions. The equation indicates that the alkyl groups substituted at the seven-membered ring decrease the oxidation potential of the molecules. This behaviour was observed also for the compounds studied by us, however the decrease of the oxidation potentials was found enhanced. This difference can be explained by electromer effects of azo-substituents

introduced in the azulene molecules, which modify the azulene electron distributions in respect with those present in the unsubstituted azulenes.

The values of the first oxidation potential of the studied compounds **1** and **2** have been correlated with the energies of the HOMO molecular orbitals calculated with MOPAC 6 program-AM1 method.⁶ A good correlation, shown in Fig.2, between the first oxidation peak in DPV ($E_{\text{DPV},1a}$) and HOMO set of values from Table 1 has been found.

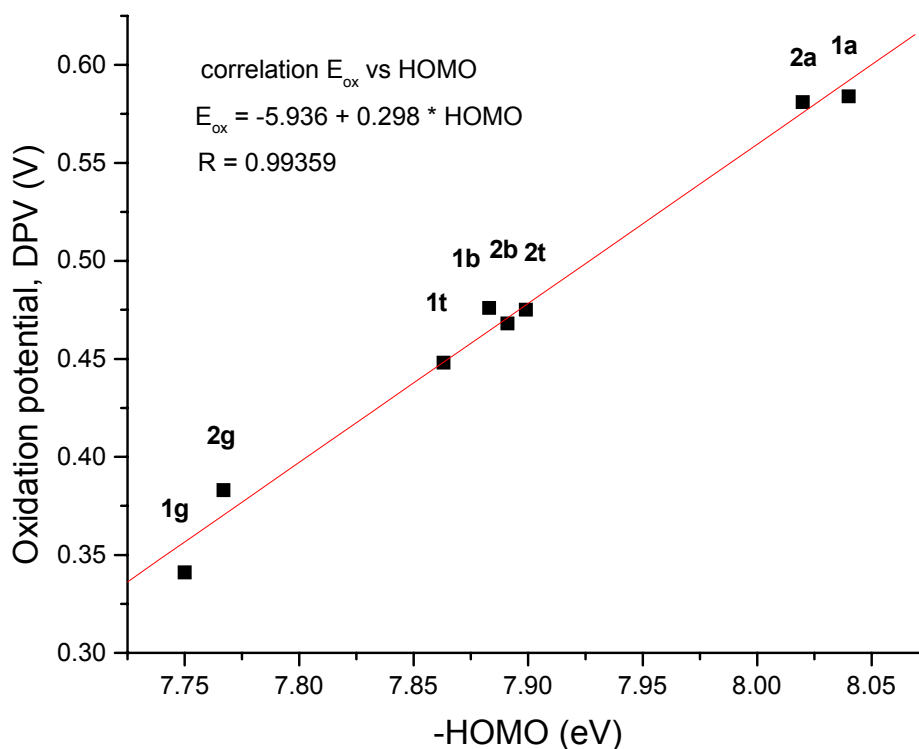


Fig. 2 – Correlation between the oxidation potential (E_{1a} in DPV) and HOMO energies for the compounds **1** and **2**.

The reduction potentials of the compounds **1** and **2** also correlate well with the LUMO energies, Fig. 3-4, but only for each isomer and not for both isomers.

As it can be seen in Table 1, the values for the first reduction potential for bis diazenes are higher in modulo than those observed for phenylazo-1-azulene. For both *meta* and *para* isomers, the guaiazulene derivatives are reduced with more difficulty than phenylazo-1-azulene (which has the first reduction potential at -1.57 V) due to the

enhanced electronic density induced by the alkyl groups. The reduction peaks around -1.5 V were also observed (H_c in Table 1), especially for the *para* isomer. Their presence could be due to a partial protonation of the compounds. It is unclear why these potentials appear only for two of the *meta* isomers.

All the compounds **1** and **2** have more oxidation and reduction peaks than phenylazo-1-azulene. They are shown in Table 1. The upper potentials present the same tendencies as the first ones.

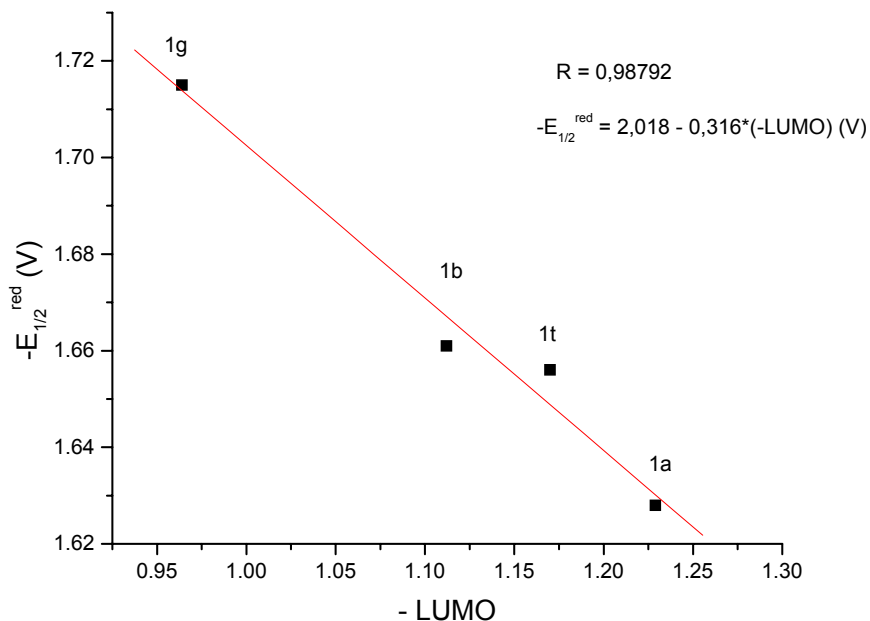
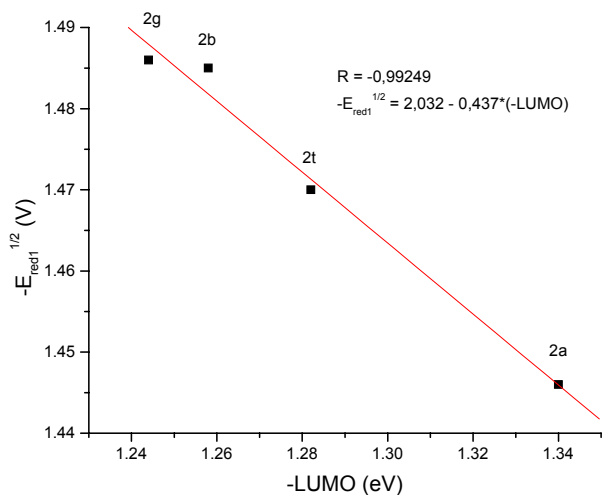


Fig. 3 – Correlation between the reduction potentials and LUMO energies for the peaks E^{red} (2c) in *meta* isomers.



4 – Correlation between the reduction potentials and LUMO energies for the peaks E^{red} (1c) in *para* isomers.

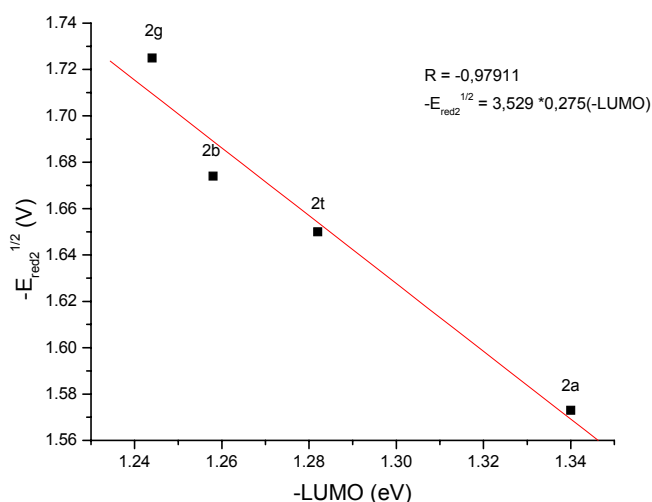


Fig. 4' – Correlation between the reduction potentials and LUMO energies for the peaks E^{red} (2c) in *para* isomers.

B) Study of 1,3- and 1,4-bis (1-azulen-1-yl-2-diazenyl)benzene, compounds **3** and **4**

The electrochemical behaviour of the compounds **3** and **4** has been studied also in 0.1M TBAP in CH_3CN . As a general rule they have lower oxidation potentials and higher reduction potentials than the corresponding mono azulene derivatives. At the same time the differences between the *meta* and *para* isomers are higher than those observed for the mono azulene derivatives.

A decrease in the oxidation potential is expected to occur upon replacement of the phenyl group with the more electron rich azulenyl moiety.

In the case of the *meta* isomer, the gap is 0.13 V for the unsubstituted compound while this difference increases to 0.16 V for the *para* isomer. By substitution with alkyl groups these differences decrease. At the reduction of parent compound, the potential increases with 0.05 V for *meta* and 0.08 V for *para*. The supplementary peaks around -1.5 V, present for both mono and bis azulenic *para* compounds, can be explained by the steric interactions that reduces the conjugation by deviation from the coplanarity between the aromatic rings.

Table 2

Values of the DPV oxidation and reduction potentials of bisazobisazulene derivatives vs. Fc/Fc^+ (**3** and **4**) at a concentration of 1.8 mM. in acetonitrile (V) and HOMO energies (eV)

Comp.	-HOMO (eV)	-LUMO (eV)	4c	3c	2c/2'c	1c	1a/1'a	2a	3a
3(a,a)	7.847	1.286	-2.299	-1.880	-1.673		0.451	1.008	1.472
3(a,t)	7.802	1.295	-2.248	-2.055	-1.772; -1.647		0.418; 0.581	0.955	1.640
3(a,g)	7.751	1.303	-2.293		-1.816; -1.653		0.400; 0.507	0.925	1.565; 1.758
3(t,t)	7.756	1.196	-2.337	-2.218	-1.742		0.418	0.955	
3(t,g)	7.687	1.209	-2.328	-2.196	-1.750		0.389	0.904	1.001
3(g,g)*	7.673	1.172	-2.322	-2.188	-1.772		0.388; 0.581	0.925	1.045
4(a,a)	7.827	1.397	-2.143	-2.040	-1.772	-1.488	0.433	0.762	1.417
4(a,t)	7.647	1.35	-2.383	-2.130	-1.795	-1.525	0.358; 0.493	0.760	1.417
4(a,g)	7.622	1.336	-2.323	-2.130	-1.817	-1.528	0.313	0.687	1.401
4(t,t)	7.624	1.294	-2.308	-	-1.877	-1.543	0.328	0.671	1.371
4(t,g)	7.569	1.290	-2.282		-1.883	-1.546	0.272	0.715	1.393
4(g,g)	7.547	1.288	-2.267	-2.133	-1.880	-1.548	0.226	0.685	1.423

*in dichloroetane

At the substitution of azulenyl moiety with alkyl groups the oxidation potentials of *meta* and *para* bis-(azulenylazo)benzene decrease in the same order as for the mono azulene derivatives, depending on the alkyl number and their position. It has already shown that the easiest oxidizable system is guaiazulene. For the *meta* isomer, the influence of the azulene substitution is more important for the first azulenic moiety and it is negligible for the second one. Therefore, mono guaiazulenyl derivative has a lower oxidation potential with 0.2 V but bis guaiazulenyls ones has almost the same potential with the previous compound. The symmetric substitution with three methyl groups at 4, 6 and 8 decreases the potential

with 0.12 V and the bis substitution preserves the same potentials. At reduction, the alkylation increases the potential needed for reduction.

The influence of substitution is stronger for the *para* isomers. The replacement of the azulenyl group with guaiazulenyl moiety decreases the oxidation potentials with 0.12 V **4(ag)** and bis substitution with more 0.09 V **4(gg)**. The differences are lower for the corresponding 4,6,8-trimethyl derivatives: 0.08 V **4(at)**, respectively 0.03 V **4(tt)**.

The correlation between the oxidation potentials obtained by CV and HOMO energies is good with the R factor of 0.94.

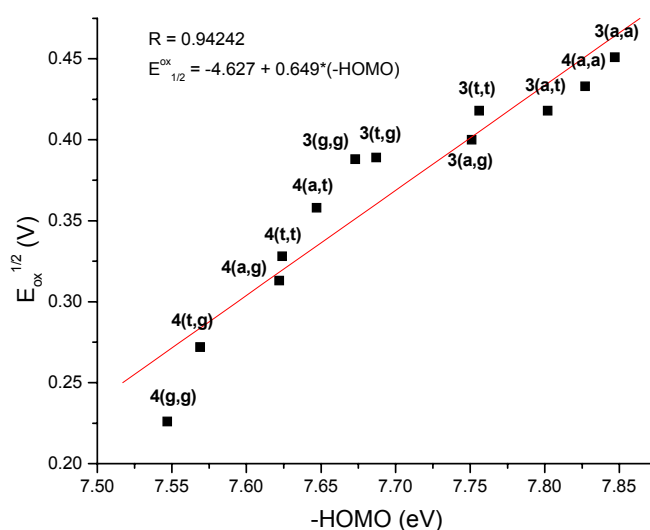


Fig. 5 – The correlation between the oxidation potential and HOMO energies.

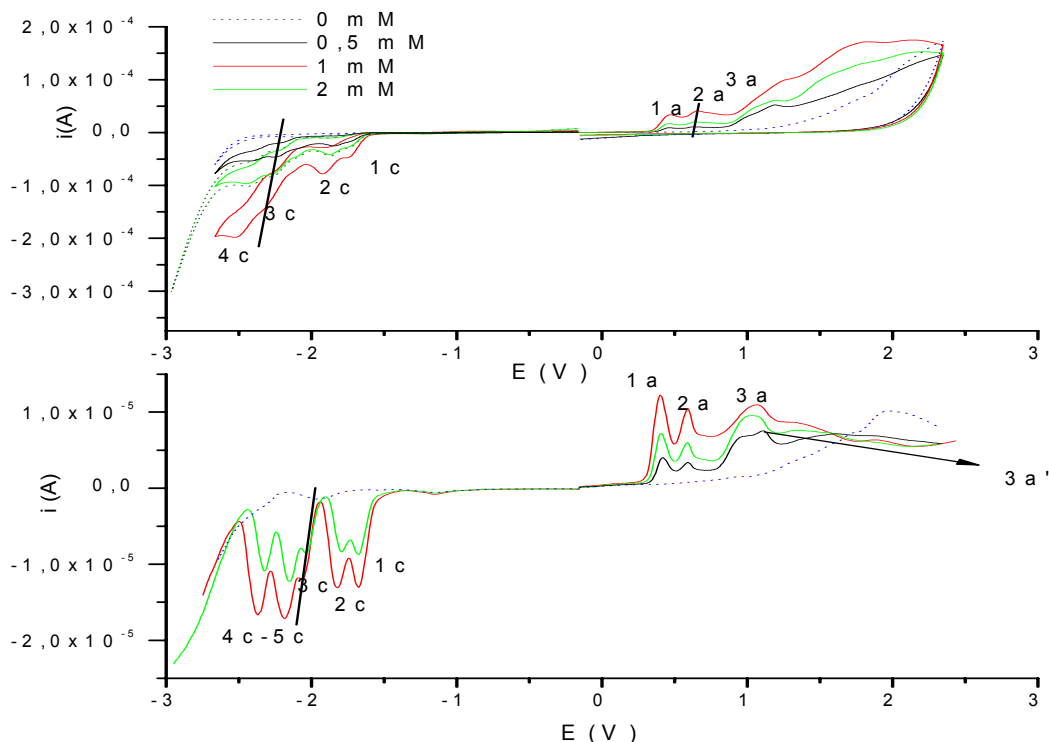


Fig. 6 – DPV and CV curves of compound **3 (a,g)** toward Ag/Ag^+ to diverse concentrations of compound in acetonitrile.

The bis-(azulenylazo)benzenes present also irreversible redox processes. By cycling these compounds in the range of the first anodic process films are obtained on the electrode (Fig. 7). Their

formation has been proved by transfer in ferrocene solutions where its reversible signal was significantly reduced in intensity and shifted in potential.

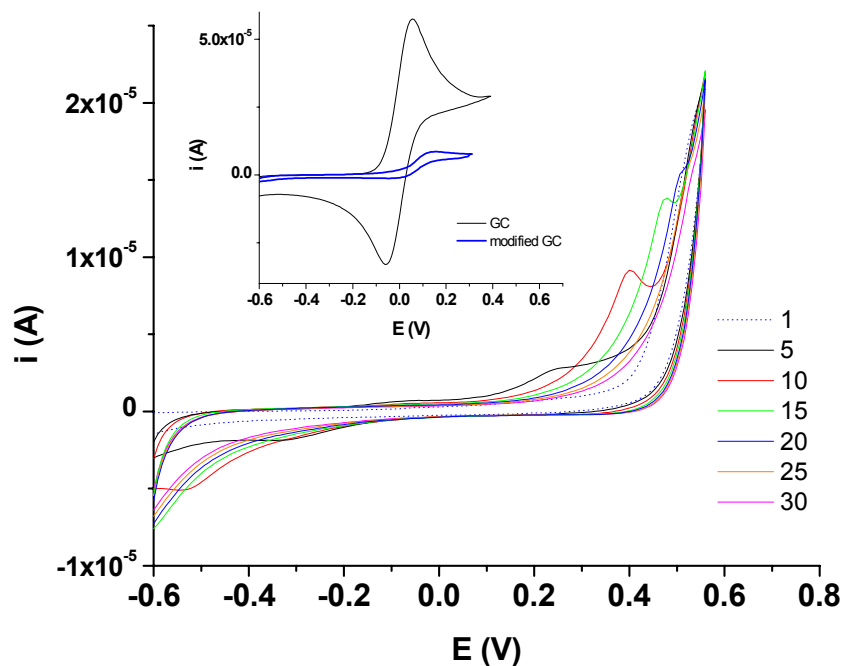


Fig. 7 – Poly **3 (a,t)** film formation in synthesis solution ($[\mathbf{3 (a,t)}] = 2 \text{ mM}$, 0.1 M TBABF_4 , CH_3CHCl_2) on glassy carbon electrode (3 mm in diameter) by scanning in 30 successive cycles (each 5th cycle is shown between 1 and 30). Inset: characterization of the obtained modified electrode in ferrocene (1 mM in 0.1 M TBABF_4 , CH_3CN) transfer solution; 0.1 V/s; CV of the bare (thin line) and modified (thick line) electrode.

However, in the case of compounds substituted in position 3, as for guaiazulene derivatives, *e.g.* **3(g,g)**, is observed a reduction of the first peak intensities only to the first cyclization but then their intensities remain constant, meaning that the process becomes quasi reversible.

Similar effects of the substituents behaviour can be observed in reduction of the 1,3- and 1,4-bis (1-azulen-1-yl-2-diazenyl)benzenes. By replacement of the azulene moiety with guaiazulene for *meta* isomer, the reduction potential increases with 0.14

V and bis replacement makes it higher in absolute value (with 0.04 V). In the case of the tri methylated derivatives, the reduction potential increases only with 0.10 V and then decreases with 0.20 V at bis alkylation. For *para* isomer, a lower reduction potential (around -0.5 V) appears. By alkylation, the potentials also increase but in a lower extent (with 0.02-0.03 V in the measurement errors limits); however the tendency is clear. Even at superior reduction potentials the behaviour is similar, as it can be observed from Fig. 9-10.

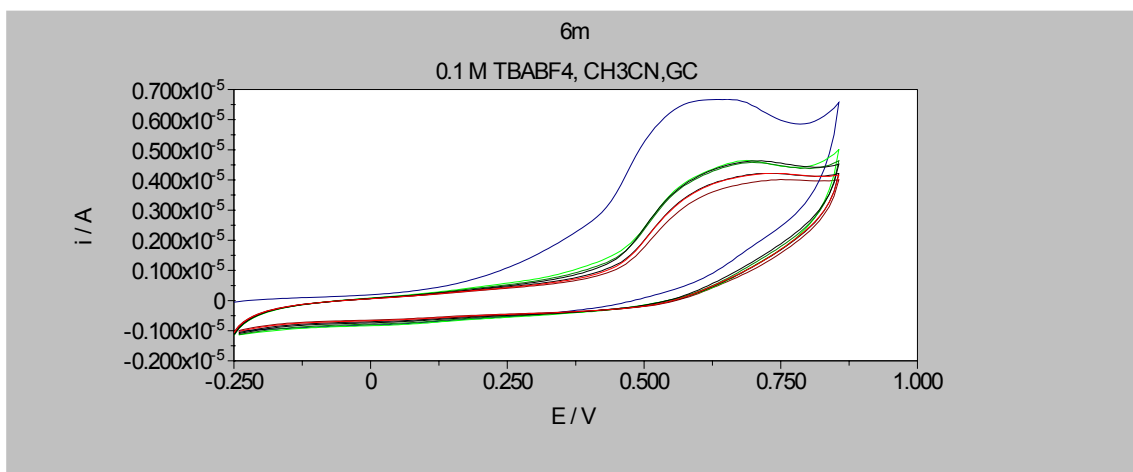


Fig. 8 – The cyclization in anodic field of compound **3(g,g)** at conc ~ 0.25 mM, cyclization of 30 cycles.

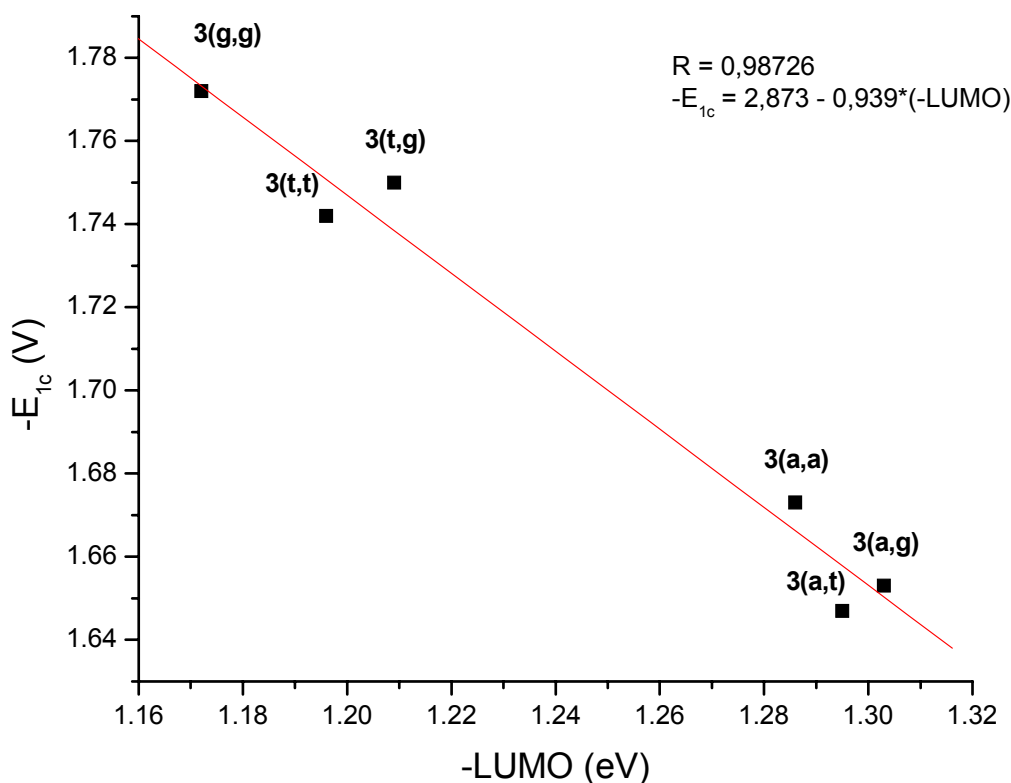


Fig. 9 – Correlation between the reduction potential (E_{1c} in DPV) and LUMO energies for the *meta* isomers **3**.

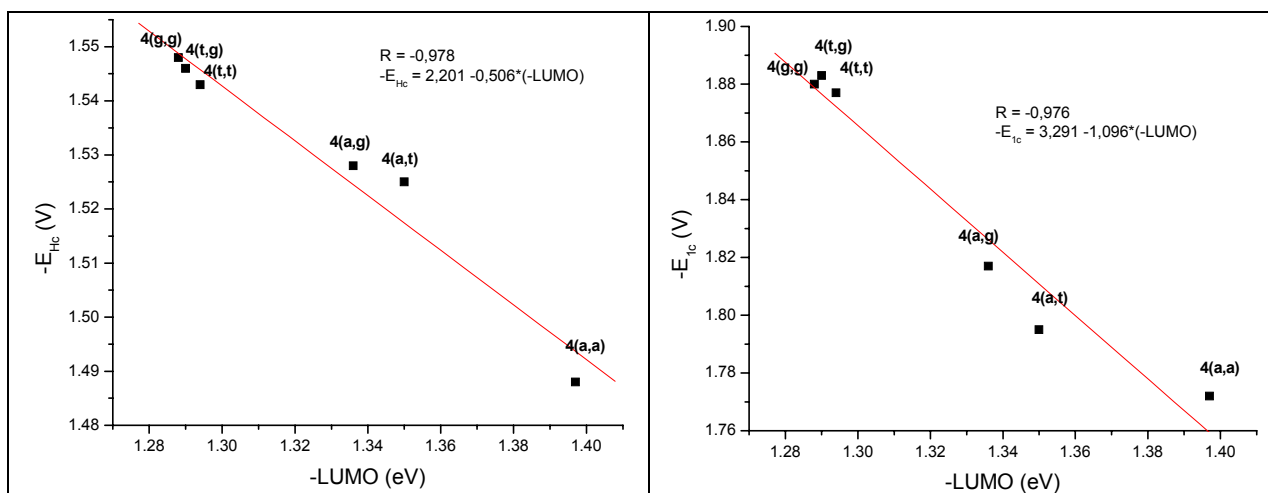


Fig. 10 – Correlation between the first and second reduction potentials (E_{Hc} and E_{1c} in DPV) and LUMO energies for the *para* isomers **4**.

EXPERIMENTAL

Reagents, Instrumentation and Procedure. The investigated compounds have been obtained by specific chemical reactions of azulenes with diazotized 3- or 4-aminoazobenzenes⁷ and (3- or 4-aminophenyl)azoazulenes.⁸ Acetonitrile (Rathburn, HPLC grade), tetra-*n*-butylammonium perchlorate (TBAP) and tetra-*n*-butylammonium fluoroborate (TBABF₄) from Fluka were used as received as solvent and supporting electrolytes, respectively.

DPV electrochemical experiments were performed in a conventional three-electrode cell under argon atmosphere at 20 °C using a PGSTAT 12 AUTOLAB potentiostat. The working electrode was a glassy carbon disk (3mm in diameter) polished with 200 μm diamond paste. The Ag/10 mM AgNO₃ in CH₃CN + 0.1M 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.

CV experiments were performed usually at 0.1 V/s and at different scan rates (0.02 ÷ 50 V/s) when the influence of the scan rate was investigated. DPV curves were recorded at 10 mV/s, with a pulse height of 25 mV and a step time of 0.2 s.

CONCLUSIONS

Several *meta* and *para* mono and bis azulenylazo substituted phenylene derivatives **1-4** were electrochemically characterized. The mono azulenyl compounds present higher oxidation and reduction potentials than are observed at the bis azulenyl derivatives. The redox processes are irreversible. The alkylation of azulenyl moieties reduces the oxidation potential and increases the reduction potentials; however some exceptions are observed. The azulenic compounds with the unoccupied position 3, forms films but those

substituted at position 3 are more stable to oxidation.

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