

Study on 5-(azulen-1-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones by electrochemical methods

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Abstract Electrochemical study of several 5-(azulen-1-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones was performed by cyclic and differential pulse voltammetry to evaluate the influence of donor and acceptor substituents on their electrochemical behavior. The number and characteristics of the redox processes for each compound were established. The electrochemical parameters have been correlated with ionization potentials and lowest unoccupied molecular orbital energies evaluated through computational methods for the azulene moiety grafted with different functional groups.

Keywords Azulene-methylene-malonate · Cyclic voltammetry · Differential pulse voltammetry · Computations

Introduction

Azulenenes are organic compounds with a special structure, having a five-membered cyclic moiety that is electron rich

and a seven-membered cyclic moiety that is electron poor. This structure enables the influence of the substituent nature and position on the electrochemical properties (number and potentials of redox waves) to be observed. The azulene moiety is a better electron donor than acceptor, possessing special redox chemistry, and it can be involved in both oxidation and reduction reactions. Moreover, the azulenes are molecules with unique properties, as well as potentially enhanced nonlinear optical coefficients [1] and electrochromic behavior [2]. Via electrochemistry, azulene derivatives could generate polymers that have similar properties to the reported azulene polymers, which have high electrical conductivity [3]. This makes them attractive as active cathode materials for rechargeable batteries [4]. Some electrochemical studies have been done on the preparation of polyazulene films [5–7], or on metal complexes of azulene derivatives [8, 9].

Vinylazulenes are interesting compounds as they have special properties due to the weak reactivity of the double bond, enabling selective halogenation, reduction or hydrolysis. In spite of the low stability of 1-vinylazulene [10], some stable compounds belonging to this class were prepared by substituting the β -vinyl position with aryls or electron-withdrawing groups such as COOH, COOR or CN [11]. 1-Styrylazulenes were prepared by several groups, and their physical and chemical properties were investigated. These compounds could be prepared by (a) Wittig reaction [12], (b) condensation between the azulenic Schiff base and an arylacetic acid, a reaction that affords only *trans*-isomers [13], and (c) direct condensation of Meldrum's acid with 1-azulenecarbaldehyde derivatives to generate stabilized 1-vinylazulenes [14].

This paper is devoted to an electrochemical study of new vinylazulenes under the structure of six azulene-methylene-malonates [15]. The present study is part of a

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large investigation of azulene derivatives through electrochemical means by our group [16–18].

Results and discussion

The investigated compounds have the general formula shown in Fig. 1. They are all derivatives of 5-(azulen-1-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**1**). In the other compounds **2–6**, the azulene moiety of the parent compound **1** is substituted in the seven-membered ring with electron-donating alkyl groups as 4,6,8-trimethyl (**2**), in both rings as 3,8-dimethyl-5-isopropyl (**3**), or in the five-membered ring at position 3 with carboxyl (**4**), bromide (**5**) or carboxymethyl (**6**).

For each compound, two complementary methods have been used for the electrochemical investigation: differential pulse voltammetry (DPV) and cyclic voltammetry (CV). Both CV and DPV studies have been done in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in millimolar solutions of 5-(azulen-1-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones. The DPV study for each compound enabled the measurement of anodic and cathodic peak potentials and currents. The CV study, which was performed at different concentrations (0.4–2 mM), scan rates, and potential ranges, enabled the establishment of the reversible or irreversible character of the processes.

CV and DPV studies

Figure 2 shows characteristic DPV and CV curves obtained for the azulene derivative **3**. Both anodic and cathodic curves are shown in the graphs.

In the DPV curve of **3** (Fig. 2, DPV), one anodic peak at +0.561 V (1a) and five reduction processes in the cathodic region at –1.425 V (1c), –1.827 V (2c), –2.37 V (3c), –2.476 V (4c), and –2.852 V (5c) can be observed.

Cyclic voltammograms for compound **3**, at different scan ranges, are shown in Fig. 2 (CV). In the anodic scans one oxidation process, 1a, is revealed, which presents an irreversible peak (this irreversible behavior persists at the scan rate of 1 V/s). In the cathodic scans, only four

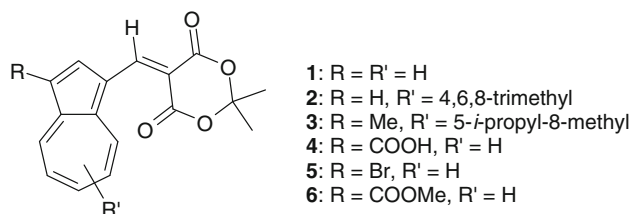


Fig. 1 Formula of the investigated compounds

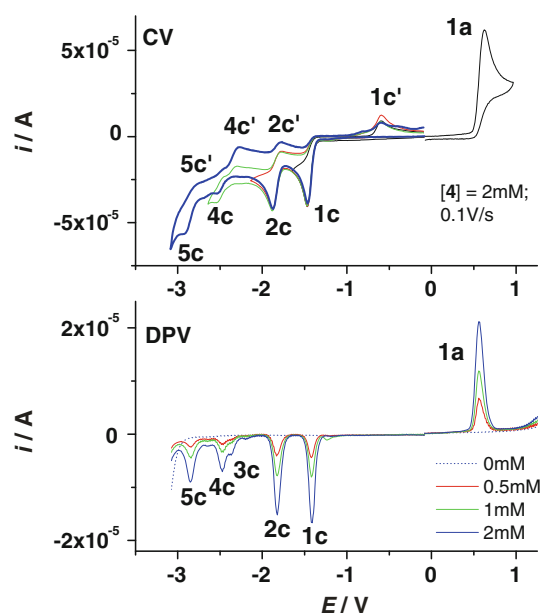


Fig. 2 DPV and CV (0.1 V/s) curves for **3** at different concentrations (mM) on glassy carbon electrode (3 mm diameter) in 0.1 M TBAP, CH₃CN

reduction peaks are evidenced. In the potential domain of the first cathodic peak (1c) an irreversible process occurs. It has, in the reverse scan, a corresponding oxidation process, evidenced by the peak 1c'. The current value for 1c' is smaller than for 1c, which indicates an EC process in the direct scan (1c' is shifted versus 1c by about 1 V). The second cathodic peak (2c) has, in the reverse scan, a corresponding anodic counterpeak (2c') at –1.8 V. This indicates that 2c exhibits some reversibility. The reduction peak 3c cannot be observed in the CV scans, overlapping with the peak 4c. The peaks 4c and 5c correspond to quasireversible processes as shown by the existence of small counterpeaks in the reverse scans (4c' and 5c', respectively).

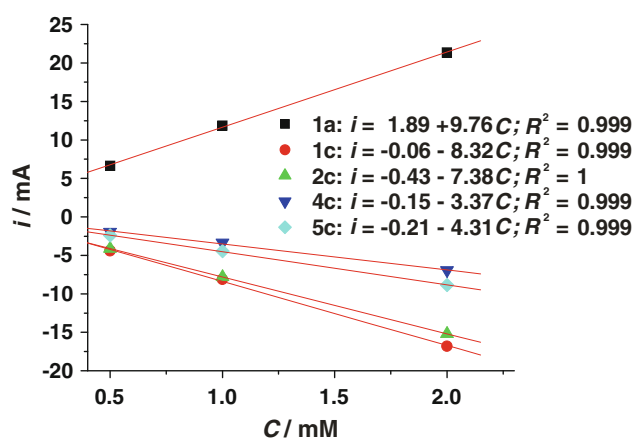
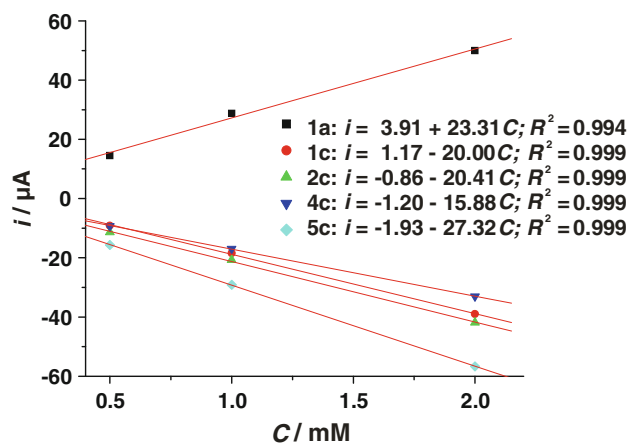
The DPV and CV peak potentials, as well as their character (reversible, quasireversible or irreversible), for the other compounds are given in Table 1.

Figures 3 and 4 present the dependences of the peak currents on concentration for compound **3**, as obtained from DPV and CV experiments, respectively. Linear dependences of the DPV and CV peak currents on concentration were also obtained for the other compounds (Table 2). These linear dependences could be used in analytical determinations of **1–6** by these electrochemical methods.

The reversibility of the first anodic and cathodic processes has been evaluated from the CV curves obtained at different scan rates. Linear dependences of the peak currents on the square root of the scan rate have been obtained for compound **3** (Fig. 5, inset). They have slopes of +145,

Table 1 CV and DPV peak potentials for compounds **1–6** (1 mM in 0.1 M TBAP, CH₃CN) and estimation of reversibility from CV (i = irreversible peak, q = quasireversible peak, r = reversible peak)

Cpd.	R	R'	$-E(\text{HOMO})$ (eV)	$-E(\text{LUMO})$ (eV)	Method	Peak potential (V)					
						1a	1c	2c	3c	4c	5c
1	H	H	8.439	1.785	CV	0.863 i	-1.42 i	-2.33 r	-	-	-
					DPV	0.803	-1.37	-2.20	-	-	-
2	H	4,6,8-Me ₃	8.253	1.577	CV	0.714 i	-1.503 q	-2.172 q	-2.452 q	-2.616 q	-
					DPV	0.67	-1.442	-2.124	-2.385	-2.552	-
3	CH ₃	8-Me-5- <i>i</i> -Pr	8.119	1.56	CV	0.686 i	-1.465 i	-1.872 q	-	-2.529 q	-2.915 q
					DPV	0.561	-1.425	-1.827	-2.370	-2.476	-2.852
4	COOH	H	8.92	2.186	CV	1.2 i	-1.28 i	-1.473 q	-	-	-
					DPV	1.146	-1.245	-1.432	-	-	-
5	Br	H	8.532	1.93	CV	0.938 i	-1.26i	-2.05 q	-	-	-
					DPV	0.88	-1.22	-2.025	-2.322	-	-
6	COOM	H	8.731	1.965	CV	1.097 i	-1.318 i	-2.036 q	-2.421 q	-	-
					DPV	1.024	-1.262	-1.981	-2.263	-2.348	-

**Fig. 3** Influence of concentration of azulene derivative **3** (*C*) on the DPV currents (*i*) on glassy carbon (3 mm diameter) in 0.1 M TBAP, CH₃CN**Fig. 4** Influence of concentration of **3** (*C*) on the CV (0.1 V/s) peak currents (*i*) on glassy carbon (3 mm diameter) in 0.1 M TBAP, CH₃CN (total currents presented)

-98 , and $+40 \mu\text{A} (\text{V/s})^{-1/2} (\text{mM})^{-1}$ for 1a, 1c, and 1c', respectively. In the range of the investigated scan rates, both 1a and 1c peaks are irreversible (i).

The results obtained by DPV and CV methods for all compounds **1–6** are summarized in Tables 1, 2, and 3.

Table 1 presents the peak potentials in CV and DPV experiments (invariant with concentration) and also the characteristics of the redox behavior of each process.

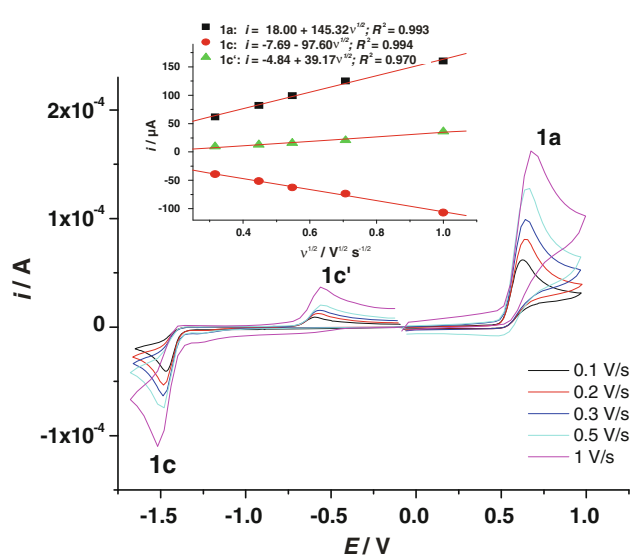
The equations of the DPV and CV peak current dependences on the substrate concentration are given in Table 2. For the anodic peak 1a, it can be seen that the dependences have positive slopes of about $15 \mu\text{A}/\text{mM}$ in DPV, and slopes of about $47 \mu\text{A}/\text{mM}$ in CV. From an analytical point of view it seems that the CV method gives a more sensitive response with a bigger slope. However, the DPV method allows the recording of much lower concentrations than CV. For the cathodic peaks 1c and 2c, the variation with concentration of the DPV peak currents presents smaller negative slopes (in absolute value) than those for the anodic peak 1a. This could be explained by the difference in the scan rates of the two methods. In DPV the scanning is slower, leading to greater consumption of the intermediate (anion radical) in parasitic reactions (with protons from residual water).

Table 3 presents the peak current dependences on the square root of the scan rate for the first anodic and cathodic peaks 1a and 1c from CV experiments. Mean slopes of about 183 and $-133 \mu\text{A} (\text{V/s})^{-1/2} (\text{mM})^{-1}$ are obtained for 1a and 1c, respectively, reflecting that the cathodic intermediate formed in the first reduction step 1c is more reactive than the anodic intermediate formed in the first oxidation step 1a.

The results for the investigated 5-(azulene-1-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones obtained by CV

Table 2 Equations of the DPV and CV (0.1 V/s) peak currents (μA) dependences on the substrate concentration (mM) for compounds **1–6** (in 0.1 M TBAP, CH_3CN)

Cpd.	Method	Peak				
		1a	1c	2c	3c	4c
1	CV	$i = 12.18 + 75.22C$ $R^2 = 0.999$	$i = -2.83 - 45.16C$ $R^2 = 0.999$	$i = -8.26 - 30.19C$ $R^2 = 0.996$		
	DPV	$i = 9.07 + 18.38C$ $R^2 = 0.992$	$i = -3.43 - 16.41C$ $R^2 = 0.990$	$i = -1.98 - 9.93C$ $R^2 = 0.981$		
2	CV	$i = 3.04 + 21.07C$ $R^2 = 0.999$	$i = -1.22 - 16.83C$ $R^2 = 0.999$	$i = -1.43 - 12.21C$ $R^2 = 0.992$	$i = -2.40 - 18.16C$ $R^2 = 0.997$	$i = -2.77 - 19.55C$ $R^2 = 0.997$
	DPV	$i = 1.42 + 9.39C$ $R^2 = 0.999$	$i = 0.50 - 9.53C$ $R^2 = 0.999$	$i = -0.18 - 1.17C$ $R^2 = 0.996$	$i = 1.11 - 8.16C$ $R^2 = 0.981$	
3	CV	$i = 3.905 + 23.31C$ $R^2 = 0.994$	$i = 1.17 - 20.0C$ $R^2 = 0.999$	$i = -0.855 - 20.41C$ $R^2 = 0.999$	$i = -1.2 - 15.88C$ $R^2 = 0.999$	$i = -1.925 - 27.32C$ $R^2 = 0.999$
	DPV	$i = 1.89 + 9.76C$ $R^2 = 0.999$	$i = -0.061 - 8.32C$ $R^2 = 0.999$	$i = -0.43 - 7.38C$ $R^2 = 1$	$i = -0.15 - 3.37C$ $R^2 = 0.999$	$i = -0.205 - 4.31C$ $R^2 = 0.999$
4	CV	$i = 5.16 + 52.5C$ $R^2 = 0.981$	$i = -0.87 - 9.41C$ $R^2 = 0.964$	$i = 1.53 - 17.95C$ $R^2 = 0.970$		
	DPV	$i = 3.15 + 12.89C$ $R^2 = 0.987$	$i = 0.42 - 5.16C$ $R^2 = 0.978$	$i = 1.59 - 7.90C$ $R^2 = 0.959$		
5	CV	$i = -0.48 + 39.98C$ $R^2 = 0.999$	$i = -0.66 - 29.11C$ $R^2 = 0.986$	$i = -1.53 - 14.51C$ $R^2 = 0.985$		
	DPV	$i = 1.04 + 15.68C$ $R^2 = 0.995$	$i = 0.78 - 14.10C$ $R^2 = 0.995$	$i = -0.05 - 2.86C$ $R^2 = 0.999$	$i = -0.68 - 4.89C$ $R^2 = 0.978$	
6	CV	$i = -15.73 + 69.07C$ $R^2 = 0.991$	$i = 15.21 - 58.74C$ $R^2 = 0.995$	$i = 5.91 - 29.49C$ $R^2 = 0.993$	$i = 10.11 - 45.9C$ $R^2 = 0.992$	
	DPV	$i = -2.31 + 24.34C$ $R^2 = 0.999$	$i = 2.61 - 21.41C$ $R^2 = 0.999$	$i = 1.87 - 8.15C$ $R^2 = 0.994$	$i = 2.72 - 10.04C$ $R^2 = 0.995$	$i = 2.08 - 10.09C$ $R^2 = 0.998$

**Fig. 5** Influence of the scan rate (v) on the CV currents on glassy carbon (3 mm diameter) for **3** (2 mM) in 0.1 M TBAP, CH_3CN . Inset: dependences of the peak currents on the square root of the scan rate

and DPV were concordant with respect to peak potentials, and were complementary, yielding specific features for each process.

Comparison between substrates

In the CV and DPV curves of the investigated azulene derivatives, the first oxidation peak can be attributed to formation of the radical cation from the azulene moiety, because the azulene is by far the most susceptible to oxidation. The highest electron density on azulene was found to be at positions 3, 5, and 7 [16]. Therefore, after ionization, the positive charge was probably delocalized mainly on the azulene moiety. The assumption is also based on the irreversibility of the first oxidation peak, which is specific to most of the azulene derivatives [16]. This irreversibility may be associated with the high reactivity of 1,3-positions on the azulene nucleus.

The potential values from Table 1 for the first oxidation peak (1a) vary according to the electronic effects of the substituents: $E_{1a}(\mathbf{3}) < E_{1a}(\mathbf{2}) < E_{1a}(\mathbf{1}) < E_{1a}(\mathbf{5}) <$

Table 3 Equations of the dependence of 1a and 1c CV peak currents (μA) on the square root of the scan rate (V/s) for the investigated compounds

Compound/ peak	1a	1c
1 (2 mM)	$i = 43.75 + 369.89v^{1/2};$ $R^2 = 0.999$	$i = -1.91 - 282.40v^{1/2};$ $R^2 = 0.998$
2 (1.4 mM)	$i = -0.54 + 34.97v^{1/2};$ $R^2 = 0.997$	$i = -4.97 - 66.46v^{1/2};$ $R^2 = 0.991$
3 (2 mM)	$i = 18.00 + 145.32v^{1/2};$ $R^2 = 0.993$	$i = -7.69 - 97.60v^{1/2};$ $R^2 = 0.994$
4 (1.1 mM)	$i = 12.09 + 163.32v^{1/2};$ $R^2 = 0.998$	$i = -3.10 - 29.19v^{1/2};$ $R^2 = 0.961$
5 (1.2 mM)	$i = 9.33 + 128.72v^{1/2};$ $R^2 = 0.992$	$i = -6.22 - 101.52v^{1/2};$ $R^2 = 0.989$
6 (2 mM)	$i = 51.09 + 254.13v^{1/2};$ $R^2 = 0.99$	$i = -46.39 - 217.89v^{1/2};$ $R^2 = 0.986$

$E_{1a}(\mathbf{6}) < E_{1a}(\mathbf{4})$. These differences are mainly due to the electronic influences of the substituents on the azulene electron density. Thus, the three methyl groups, with their electron-donating capacity, increase the electron density on azulene, and therefore, the oxidation potential of compound **2** is lower than that of the parent compound **1**. In case of the guaiazulene moiety (compound **3**), the position and nature of the substituents reduce the molecular symmetry and thus perturb even more the already low aromaticity of azulene and diminish the oxidation potential. On the contrary, the electron-attracting substituent bromine (in compound **5**) slightly increases the oxidation potential. The presence of both inductive and electromeric effects of COOR groups makes compounds **4** and **6** the least prone to oxidation.

The potential difference of compounds **2** and **3** versus **1** may also be explained by the steric effects of the methyl group grafted on the seven-membered ring, which reduces the conjugation between the azulene and diketone moieties.

In conclusion, when explaining the oxidation potential values, two effects should be taken into consideration: the electronic effects, resulting from the donating or attracting substituents, and the steric effects of the methyl substituent grafted on the seven-membered ring (compounds **2** and **3**).

For the reduction potentials, the substituent influences become more complex, and therefore, the first reduction potential is more difficult to correlate with the substituent. However, a distinction between the obtained potential values for peak 1c could be seen, if we compare compounds **1–3** (with electron-donating substituents) with **4–6** (with electron-withdrawing substituents). This behavior could be explained by the difference between their electronic effects.

In Scheme 1 the electronic processes for compounds **4** and **6** are described. The positive charge of the radical cation is more likely situated on the azulene moiety, which is stabilized as a tropylic structure. On the contrary, on reduction the negative charge is located mainly on the oxygen atoms, which are the most electronegative. The positive polarization of the azulene moiety in these compounds favors the reduction and draws back the oxidation process.

All of the studied compounds present a double bond (at position 1) connected to the 2,2-dimethyl-1,3-dioxane-4,6-dione and different substituents in position 3. At this double bond, the first reduction process of those compounds is the most prone to occur. A detailed comparison between their DPV curves is given in Fig. 6 [the peaks are denoted in their order of appearance in oxidation (1a) or reduction (1c, 2c) scans].

When examining the DPV curves for **2** and **3** (Fig. 6), it could be seen that the process 1c appears in the DPV of **3** at less negative potential (-1.425 V) than in **2** (-1.442 V). This is an unexpected behavior, because **3** contains 8-Me and 5-*i*-Pr groups which have more donating effect than 4,6,8-trimethyl (in **2**) and should appear at more negative potential than peak 1c from **2**. A possible explanation for the easier reduction of **3** with respect to **2** is the more reduced symmetry of the substituted azulene moiety in **3**. It seems that the first reduction process of compound **3** appears as two signals (at -1.425 and -1.827 V), as the integration of both cathodic peaks (1c and 2c) from the DPV of **3** gives the same area as for the first anodic peak (1a).

From Fig. 6 it can be seen that the first reduction process of compound **4** appears as two signals (-1.245 and -1.432 V). This fact could be the result of partial ionization of the carboxyl group, compound **4** acting as a mixture of unionized and ionized forms. In compound **4** (unionized form) the effect of the carboxyl group, which decreases the electron density on the conjugated system, activates the electrochemical reduction, making the double bond reduced at a less negative potential (-1.245 V) than the parent compound **1** (-1.37 V). In the ionized form of **4** the negative carboxylate group increases the electron density on the conjugated system in comparison with that of unionized **4**, making the double bond reduced at a more negative potential (-1.432 V) than the unionized **4** (-1.245 V). Support for this hypothesis could be the integration of both cathodic peaks (1c and 2c) from the DPV of **4**, which gives the same area as for its first anodic peak (1a). A similar integration in the case of compound **6**, which cannot exist in ionized form, leads to the same area for the cathodic peak (1c) and for the first anodic peak (1a). These aspects should be further investigated by other relevant methods like rotating disk electrode, gas chromatography-mass spectrometry (GC-MS). These works are in progress. At the same time, the potential of the first oxidation process of **4** is

Scheme 1

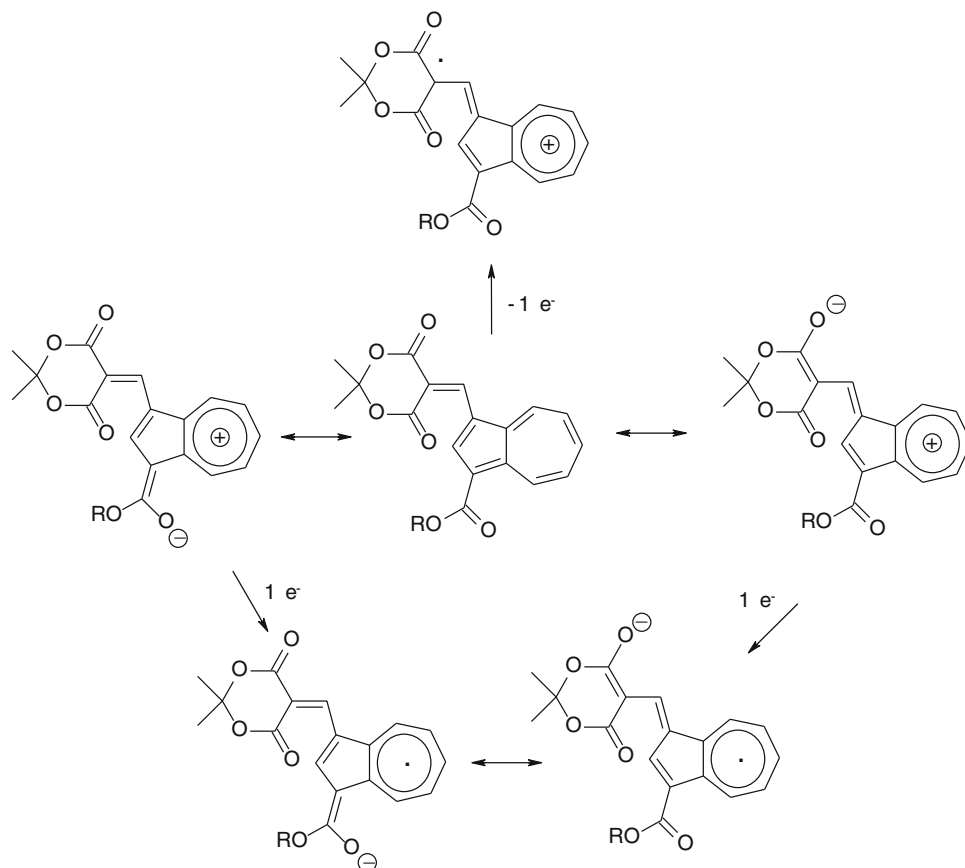
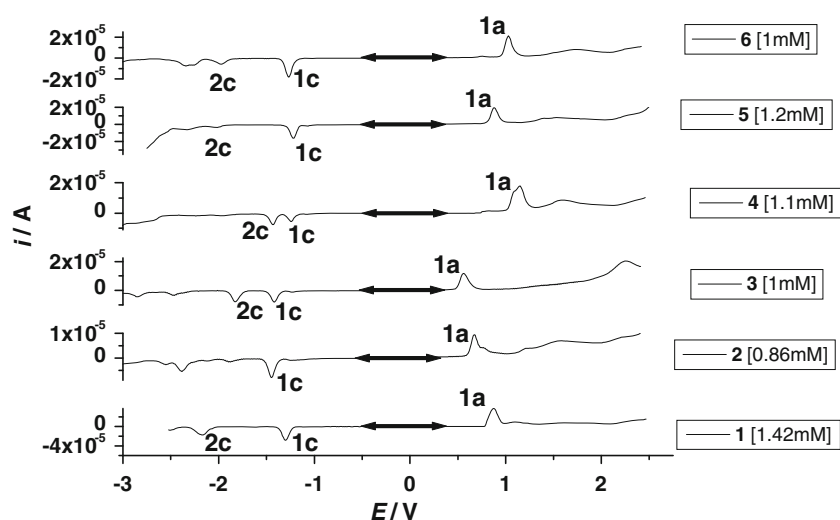


Fig. 6 Anodic and cathodic DPV curves for the investigated compounds (~ 1 mM) in 0.1 M TBAP, CH_3CN on glassy carbon (3 mm diameter)



less affected by this partial ionization, due to the lesser influence of the carboxylic group ionization on the π azulene electrons involved in this process, and the result is only a broadening of the signal for 1a.

For **5**, the first reduction process occurs at less negative potential in this series of compounds. This is due to the fact that bromine atoms are very labile in this position

(1-bromoazulene is an unstable compound in polar solvents). Therefore, Br is easily removed from **5** by reduction (at -1.22 V) with the generation of a bromide ion and azulene radical.

Table 1 shows an important variation of the oxidation peak potentials with respect to the nature of substituents R and R'. The oxidation potentials varied in CV or DPV

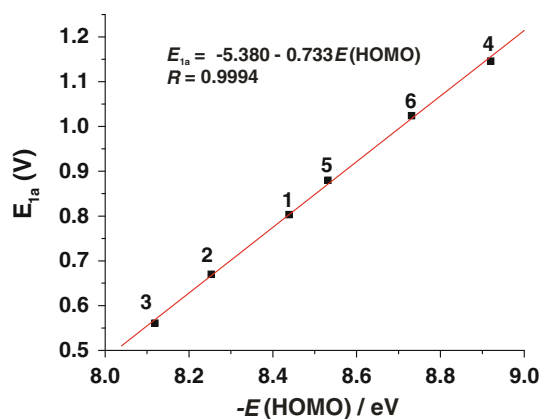


Fig. 7 Correlation between the experimental oxidation potentials E_{1a} (from DPV, at 1 mM on glassy carbon in 0.1 M TBAP, CH_3CN) and $E(\text{HOMO})$ using the AM1 method

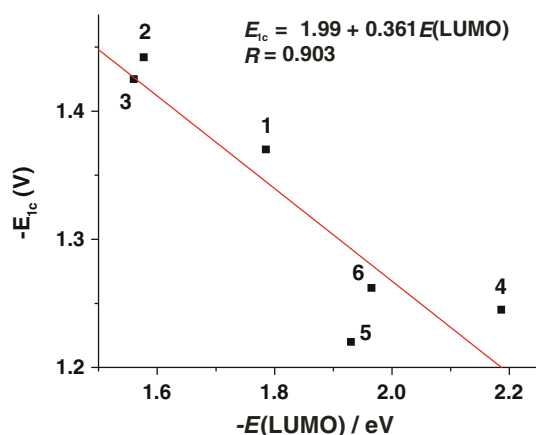


Fig. 8 Correlation between the experimental reduction potentials E_{1c} (from DPV, at 1 mM on glassy carbon in 0.1 M TBAP, CH_3CN) and $E(\text{LUMO})$ using the AM1 method

curves according to the electronegativity of their substituents. Figure 7 shows a very good correlation between the experimental oxidation potentials and the highest occupied molecular orbital (HOMO) energies/ionization potentials computed using the MOPAC program (AM1 method).

On the contrary, the correlation of the first reduction potential with lowest unoccupied molecular orbital (LUMO) energies was weaker (Fig. 8). This could be explained by the fact that the reduction mechanism could be more complicated due to the interference of substituent reduction in the case of halogen and carboxyl derivatives. For more precise evaluation, density functional theory (DFT) calculations have to be performed in order to improve the correlation.

Film formation

Formation of a polyazulene film has been attempted by successive scans in the domain of the first anodic (1a) or

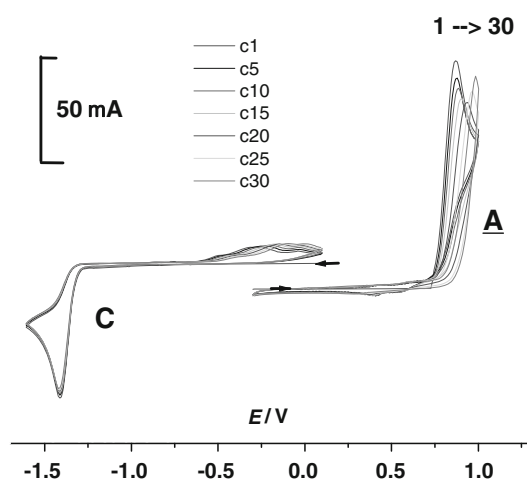


Fig. 9 Successive anodic (A) and cathodic (C) cyclic voltammograms for **1** on glassy carbon in 0.1 M TBAP, CH_3CN at 0.1 V/s

first cathodic (1c) processes in millimolar solutions of each compound in CH_3CN + 0.1 M TBAP. Successive anodic and cathodic curves for compound **1**, as an example, are given in Fig. 9. In successive anodic scans the oxidation peak is shifted progressively to positive values, indicating electrode coverage with oxidation products. In repeated cathodic scans the successive curves are practically unchanged. No growth of a conductive polymeric film on the electrode surface was observed.

Conclusions

This work explored the electrochemical properties of some 5-(azulene-1-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones and established rules concerning the influence of donor and withdrawing substituents on their electrochemical behavior. Two electrochemical methods were used for this purpose: DPV and CV. DPV enabled precise determination of oxidation and reduction process potentials. The peak potentials were found to be constant when the concentration was varied, leading to unique fingerprints for each compound. The proportionality of peak current to substrate concentration proved to be a useful test of the analytic value for the DPV method. CV allowed the features of each electrode process to be established. For all the investigated compounds, the oxidations were totally irreversible, while some reductions were quasireversible or reversible.

Although the azulene moiety is by far the most sensitive to oxidation, important peak potential variations were observed with respect to the nature of the azulene substituent at position 3. Very good correlations between the experimental oxidation potentials and MOPAC computed ionization potentials were found. The studied compounds

present a double bond at position 1 and different substituents at position 3. At this double bond, the first reduction process is the most prone to occur. Detailed comparison between their DPV curves shows that both electronic effect of the substituents and steric effect influence the reduction potential.

Experimental

Reagents, instrumentation, and methods

Acetonitrile [Rathburn, high-performance liquid chromatography (HPLC) grade] and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolytes. The investigated compounds were obtained by specific chemical reactions [18]. Structure and physical characteristics were confirmed by elemental and spectral [^1H nuclear magnetic resonance (NMR), ^{13}C NMR, GC–MS] analyses. CV and DPV experiments were conducted 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 (3 mm diameter from CH Instruments) polished with 0.1 μm diamond paste. The Ag/10 mM AgNO_3 in CH_3CN + 0.1 M TBAP system was used as reference electrode. All potentials were referred to the potential of ferrocene/ferricinium (Fc/Fc^+), which was 0.07 V with our experimental conditions. CV experiments were usually performed at 0.1 V/s, and with different scan rates (0.1–1 V/s), for investigation of scan rate influence. DPV curves were recorded at 10 mV/s with pulse height of 25 mV and step time of 0.2 s.

Computational methods

Calculations were performed with the MOPAC package and AM1 approach [19].

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