Understanding Electrochromic Processes initiated by Dithienylcyclopentene Cation Radicals

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SUPPORTING INFORMATION

Contents

Determination of the order of the chemical reaction linked to the electron transfer

Compound 2o

A) Solution 1.341 mM of **2o** in ACN, Ep *vs.* log *v*

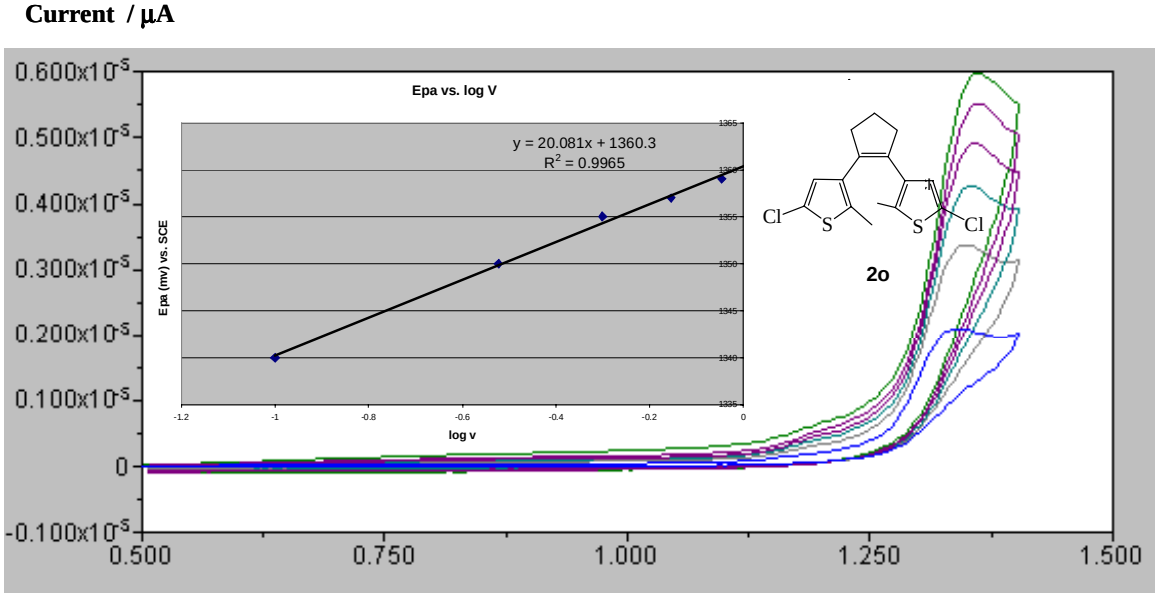

Figure 1. Cyclic voltammetry CV of **6o** (1.35mM) in ACN–0.1 M *n*-Bu_4NPF_6 at different scan rates : 0.1, 0.3, 0.5, 0.7, and 1 $V.s^{-1}$. Working electrode : Glassy carbon electrode (0.5 mm diameter). Inset : Linear dependence for Epa value with log v.

B) Solution 0.708 mM of **1o** in ACN

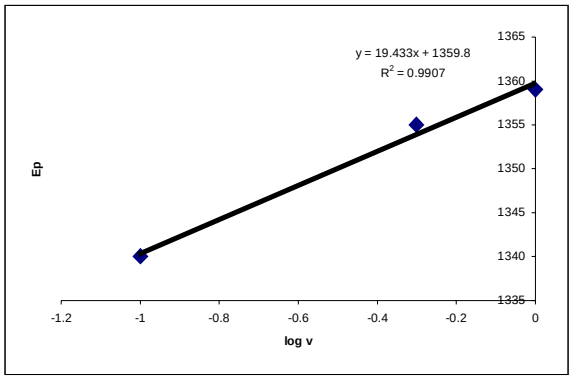

Figure 2. Linear depencence for Epa value with log v.

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C) Solution 2.820 mM of **1o** in ACN, Ep *vs.* log *v*

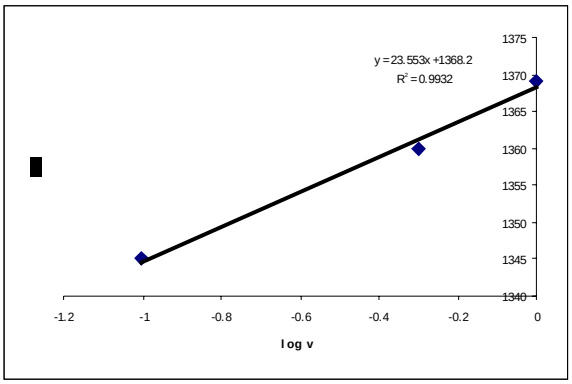


Figure 3. Linear depencence for Epa value with log *v*.

Concentration Dependence Study Ep *vs*. log c

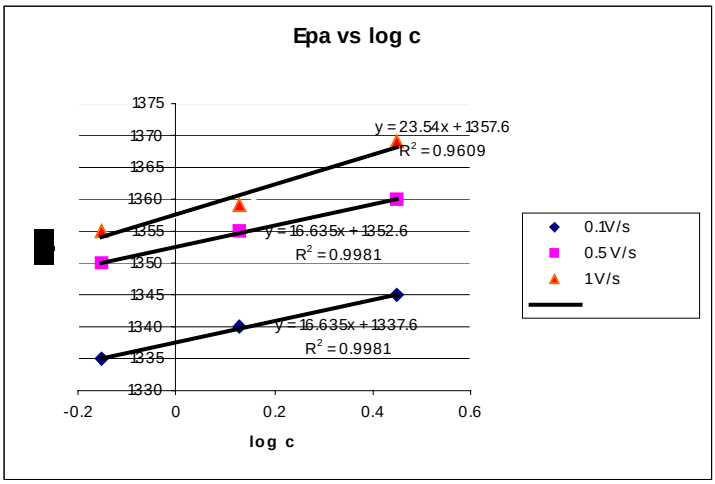


Figure 4. Linear depencence for Epa value with log c at different scan rates.

In ACN, 0.1M *n*-Bu_4NPF_6 (room temperature) at low scan rates, one chemically irreversible oxidation wave appears at 1.35 V. The shape of the voltammograms (peak width) suggests a fast electron transfer with kinetic control by chemical reaction. In the 0.5-5 mM range, the peak potential is concentration-dependent (19 mV by unit log concentration) and the variation of peak potential with the scan rate is 20 mV by unit log scan rate. We can therefore conclude that the initially produced cation-radical reacts following a second order reaction pathway.[1]

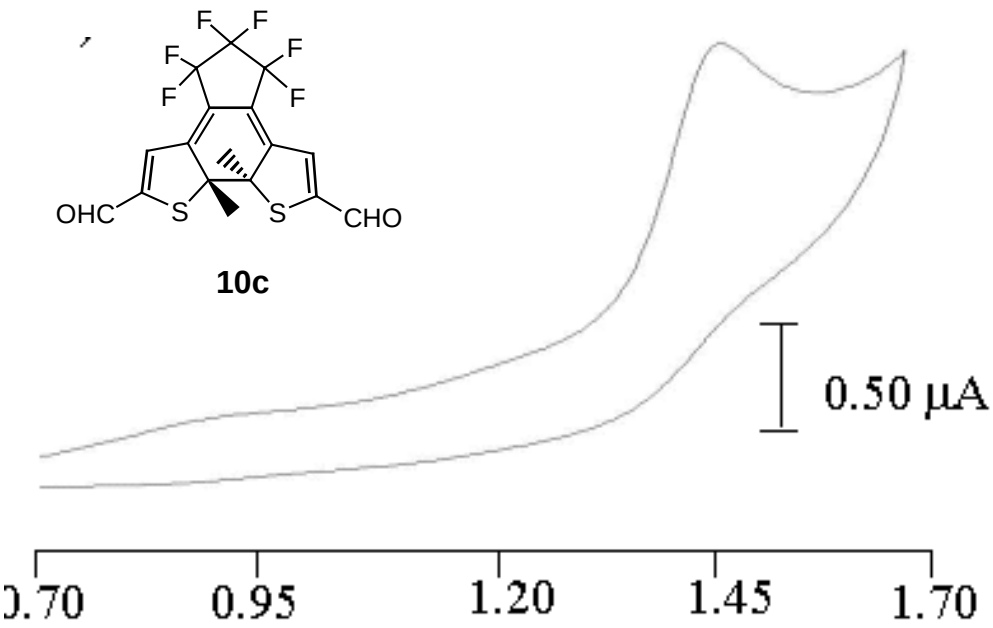


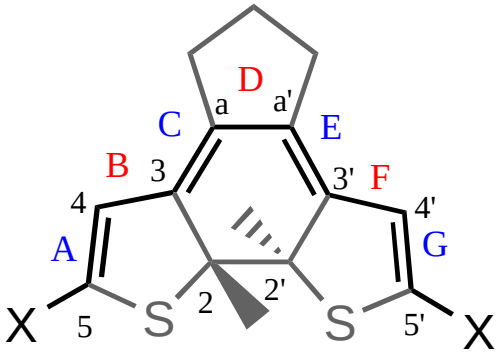
Figure 5 . CV of a solution of **10c** (0.80 mM) in in ACN–0.1 M n-Bu_4NPF_6 at 1.00 $V.s^{-1}$. Working electrode: glassy carbon electrode (0.5 mm diameter).

A one electron irreversible wave (*Ep*a= 1.42 V vs. SCE at 0.1 V.s-1) was found for compound **10c** in all the scan range investigated. The peak width analysis (*ΔEp* = 75 mV), and the shape of the voltagramm reveled that we are under pure kinetic conditions. A linear dependence between Epa and log *v* was found (slope = 33 mV). The α_{app} calculated value is 0.69. All this data is in agreement with an EC stepwise mechanism, as it was found for other ring-closed isomers. Controlled-potential electrolysis at 1.8 V *vs. SCE* was performed. The colored solution was discharged; analysis of the electrolysis sample by thin layer chromatography TLC, CV revealed the presence of the open isomer **10o**.

Table 1

Selected distances (Å) of **2c, 6c** and **11c** cation-radicals optimized at the B3LYP/DZVp level

	2c (X=Cl)	**2c**$^{+\cdot}$ (X=Cl)	**6c** (X=S)	**6c**$^{+\cdot}$ (X=S)	**11c** (X=C)	**11c**$^{+\cdot}$ (X=C)
X-C5	1.809	1.779	1.831	1.795	1.480	1.504
C5-C4	1.378	1.404	1.390	1.418	1.394	1.409
C4-C3	1.464	1.432	1.460	1.427	1.449	1.428
C3-Ca	1.385	1.421	1.387	1.426	1.393	1.421
Ca-Ca’	1.481	1.441	1.479	1.440	1.471	1.438
Ca’-C3’	1.385	1.420	1.387	1.425	1.393	1.421
C3’-C4’	1.464	1.432	1.465	1.424	1.450	1.428
C4’-C5’	1.379	1.404	1.391	1.417	1.394	1.408
C5’-X’	1.808	1.779	1.832	1.795	1.481	1.503
$BLA_{5\text{-}5'}$	0.087	0.023	0.079	0.009	0.064	0.016



$$BLA_{5\text{-}5'} = \frac{A + C + E + F}{4} + \frac{B + D + E}{3}$$

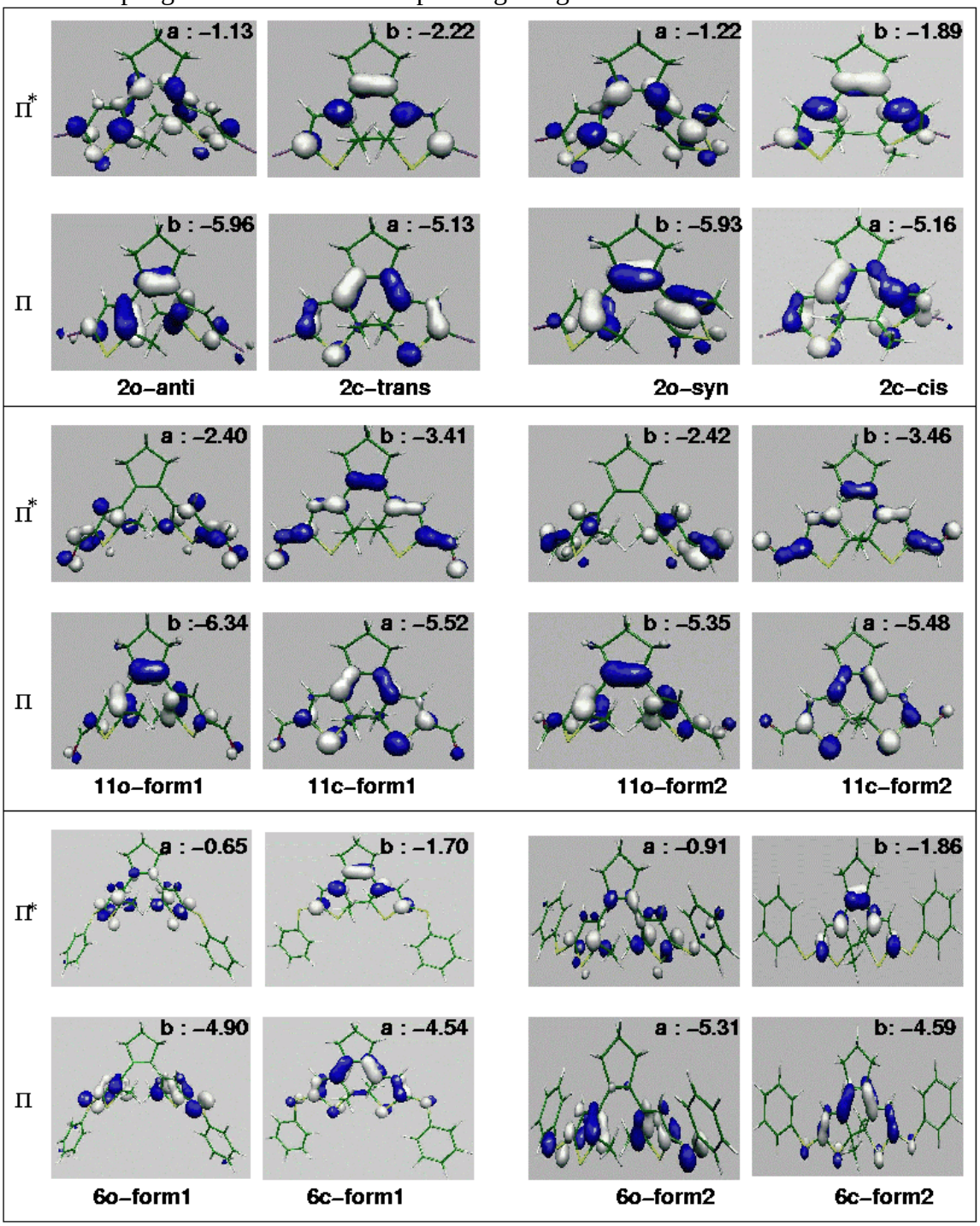
Table 2

Selected distances (Å) of **2, 6** and **11** neutral and cation-radicals optimized at the B3LYP/DZVp level

	2o	**$2o^{+\cdot}$**	**Δd_N-d_{RC}**	**6o**	**$6o^{+\cdot}$**	**Δd_N-d_{RC}**	**11o**	**$11o^{+\cdot}$**	**Δd_N-d_{RC}**
C2-C3	1.404	1.401	+0.003	1.399	1.423	+0.024	1.411	1.442	+0.031
C3-Ca	1.494	1.496	-0.001	1.498	1.484	-0.014	1.495	1.465	-0.030
Ca-Ca’	1.376	1.377	-0.001	1.380	1.385	+0.005	1.377	1.418	+0.041
Ca’-C3’	1.494	1.496	-0.003	1.498	1.484	-0.014	1.495	1.465	-0.031
C3’-C2’	1.406	1.401	+0.004	1.399	1.423	+0.024	1.411	1.442	+0.041
C2-C2’	3.606	3.787	+0.181	3.616	3.333	-0.283	3.669	3.311	-0.358
	2c	**$2c^{+\cdot}$**	**Δd_N-d_{RC}**	**6c**	**$6c^{+\cdot}$**	**Δd_N-d_{RC}**	**11c**	**$11c^{+\cdot}$**	**Δd_N-d_{RC}**
C2-C3	1.562	1.555	-0.007	1.561	1.554	-0.007	1.560	1.555	-0.005
C3-Ca	1.385	1.421	+0.036	1.387	1.426	+0.039	1.393	1.421	+0.028
Ca-Ca’	1.481	1.441	-0.040	1.479	1.440	-0.040	1.471	1.438	-0.033
Ca’-C3’	1.385	1.421	+0.035	1.387	1.426	+0.039	1.393	1.421	+0.028
C3’-C2’	1.562	1.555	-0.007	1.561	1.554	-0.007	1.560	1.555	-0.005
C2-C2’	1.557	1.564	+0.007	1.556	1.554	+0.002	1.557	1.577	+0.020

Table 3

HOMO (π) and LUMO (π∗) frontier molecular orbitals (FMO) plots for the neutral ground state of dithienylcyclopentene derivatives **2, 6 and 11.** The energy (in eV) and the symmetry (according to the C_2 ponctual group, except for the **2o-syn and 2c-cis** compound which are of C_s molecular symmetry) label associated to each FMO are shown at up-right corner of the corresponding image.



References:

[1] L. Nadjo, J.-M. Savéant, *J. Electroanal. Chem.*, 1973, **48**, 113; C. P. Andrieux and J.-M. Savéant, Electrochemical Reactions, in *Investigation of Rates and Mechanism of Reactions, Techniques of Chemistry*, (Ed: C. F. Bernasconi) Wiley, New York, **1986**, vol. 6, ch. 2.1, p. 305.