SHORT COMMUNICATIONS

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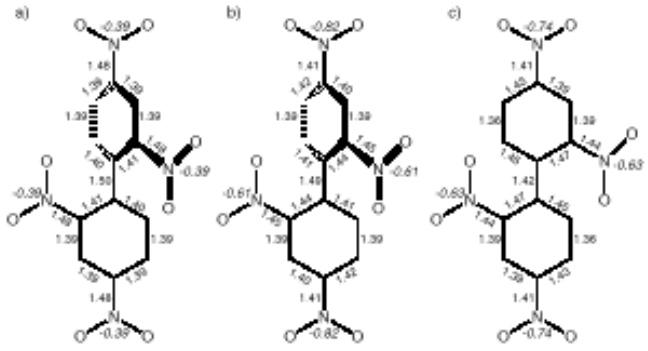
Iluminada Gallardo, Gonzalo Guirado, Jordi Marquet, Miquel Moreno



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Evidence for a Transition Between Singlet and Triplet States in the Electrochemical Reduction of 2,2'-4,4'-tetranitrobiphenyl

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In this paper the electroreduction of 2,2'-4,4'-tetranitrobiphenyl is carefully studied. Details of the synthesis and analysis of its dianion are given. Our results give clear evidence of the presence of two different dianion species close in energy. The one first formed has biradical characteristics such as a clear triplet EPR spectrum that slowly evolves to another, not showing EPR signal. This second species is essentially described as a quinoid form. Density Functional Theory (DFT) calculations support the existence of two states of the dianion, singlet and triplet, rather close in energy (less than 10 kcalmol^{-1}) in gas phase. The quinoid singlet state is the most stable one so that this is the final state of the dianion. However our results show that the dianion is first electrochemically obtained in a thermally triplet (i.e. biradical) state. A rationale for this behaviour is advanced.

KEYWORDS:

Singlet and Triplet States • Electrocemistry • 2,2'-4,4'-tetranitrobiphenile

Introduction

Radical centres, separated by suitable spacers, constitute one of the basic principles in the design of organic molecular ferromagnets.[1] However, the use of extended quinones as electron acceptors for the production of organic conducting materials[2-4] has been increasing. Thus, 2,6-di-*tert*-butylphenoxyl radical systems[5,6] connected by *m*-phenylene units in the 4 positions, have been largely used to synthesise oligo-radicals with triplet, quartet and quintet ground states.[7-10] In some cases, the biradical systems, in which two phenoxyl radicals are coupled by various *p*-arylene spacers quantitatively exist in an equilibrium with extended quinones.[11-13] In this case, the biradical is electrochemically generated (two successive one-electron oxidation of correspondent bisphenol) and characterised by cyclic voltammetry and EPR spectroscopy. The variation of the spacers in the extended quinones influence both the electrochemical behaviour, and the spectroscopic properties of these extended quinones and their biradicals.[14]

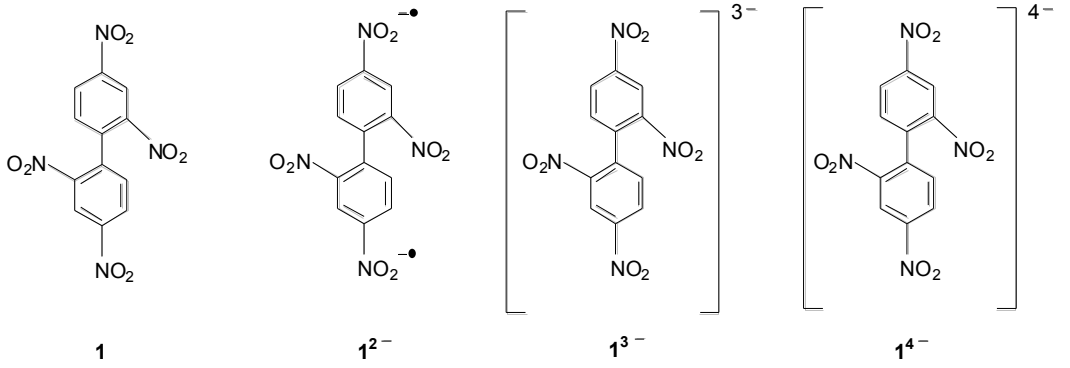
It is well known that, for a given molecular system different electronic states have a very different chemical behaviour. Well

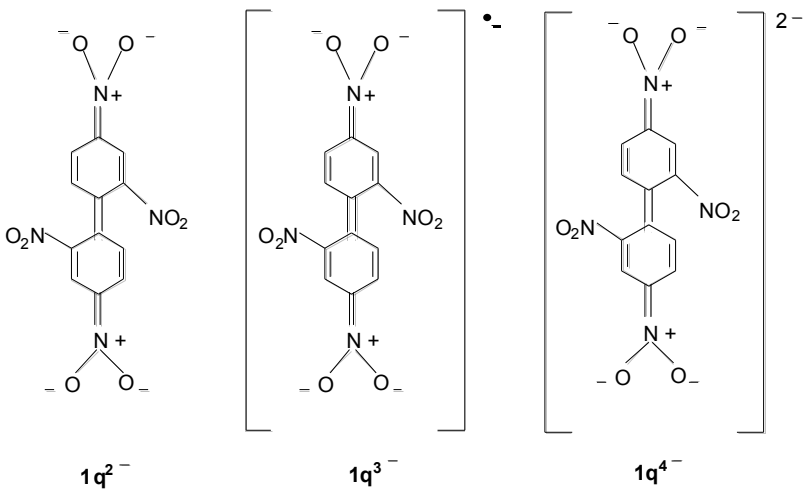
known examples are the singlet and triplet states of oxygen and carbenes.[15,16] An equilibrium between two different electronic states of diphenylcarbene and *p*-extended bisaroxyls has been previously reported.[17] In the case of biradicals, 2,2-dimethyl-2*H*-benzo[*cd*] fluoranthene and 2,2-dimethyl-2*H*-dibenzo[*cd,k*] fluoranthene[18], the singlet-triplet gap has been estimated to be in the range of 0.8 - 2.8 kcalmol^{-1} with a singlet or a triplet ground state depending on the molecule. Given that spin inversion is a forbidden process, the interconversion rate may be rather slow (less than $10^3 s^{-1}$).[19]

Electrochemical reduction of dinitrocompounds in non-aqueous solvents, presents two successive, fast one-electron transfer or one fast simultaneous two-electron transfer,[20] and several authors[21-23] have put forward quinoid structures in the mechanistic scheme for the dianion obtained after two electron transfers. The exact electronic structure (singlet or triplet)) of the dianion electrochemically formed is one question that, to our knowledge, remains unsolved.

In order to clarify this problem, we present here a study devoted to the electroreduction behaviour of 2,2'-4,4'-tetranitrobiphenyl,**1**.

The different compounds detected during electrochemical experiments are summarised in Scheme 1. We present the electrosynthesis of the tetraethylammonium salt of [*trans*-bis(2,4-dinitro-2,5-cyclo hexadien-1-iliden)dianion], **1q^{2-}** from 2,2'-4,4'-tetranitrobiphenyl, **1** . We report the details of the synthesis and analysis of **1q^{2-}** both by classical techniques and MALDI-TOF (Matrix-assisted laser desorption time-of-flight mass spectrometry) and ESI-MS$_n$ (Electrospray ionization mass spectrometry with consecutive fragmentation steps). Previously to **1q^{2-}**, another species is produced **1^{2}**. Our results indicate that whereas **1q^{2-}** is a ground-state singlet corresponding to an extended quinoidal π-system, with no EPR spectrum, **1^{2-}** is a triplet in the ground state similar in structure to **1** and shows an EPR spectrum characteristic of a triplet-state. Density functional calculations give support to this interpretation.





Electrochemical Results

No bibliographical reference has been found about the electrochemical behaviour of 2,2'-4,4'-tetranitrobiphenyl, **1.** Our results (in DMF 0.1M nBu$_4$NBF$_4$) seem to indicate that, such behaviour may be described as being the sum of the electrochemical behaviour shown by 2,2'-dinitrobiphenyl and that of 4,4'-dinitrobiphenyl, in accordance with the literature.[20] Figure 1 shows the cyclic voltammogram where four reduction waves can be observed for **1**. The first wave (at –0.68 V) corresponds to a two successive fast electron transfers with a E^0 (difference of standard potentials) of 60 mV. They may be associated with one-electron successively entering into each one of the aromatic rings. The similarity between the standard potentials shows the relative independence of the two aromatic rings (**1**$^{2-}$, Scheme 1). The second and third waves at –1.48 V and –1.72 V, correspond to fast one-electron transfers (in comparison with the reduction wave of anthracene in the same medium).

By analogy to 2,2'-dinitrobiphenyl, they may be associated with one-electron processes (**1**$^{3-}$ and **1**$^{4-}$, Scheme 1). The fourth wave (E_p=-2.54 V) corresponds to a chemically irreversible multi-electronic transfer (>4) which leads to nitroso oxidation waves (E_p = –0.38 V) in the reverse anodic scan. Additionally, two low-intensity oxidation peaks at +0.45 V and at +0.65 V may be observed, which can be associated to the reduction waves of –2.54 V and –0.68 V, respectively. It must be underlined that, if the potential sweep is initially carried towards positive potentials, no oxidation waves appear.

As the formation of nitroso derivatives is not the goal of our current study, voltammetry characterisation has been carried out within potential ranges: from 0.00 V to –1.80 V; from –1.80 V to +1.40 V and from +1.40 V to 0.00 V (indicated as: 0.00/-1.80/+1.40/0.00 V) which means reaching the third reduction wave (Fig 2 a). In another experiment we have limited the range of the negative potential down to –1.00 V. In this way only the first reduction wave was studied (Fig 2 b).

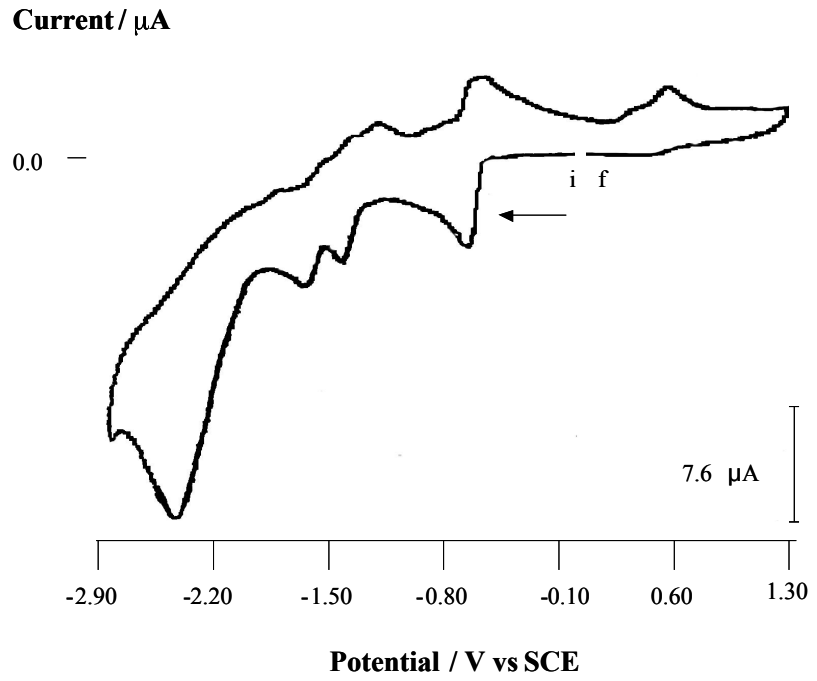


Figure 1. Cyclic Voltammetry of 2,2'-4,4'-tetranitrobiphenyl **1** (6.0 mM) in DMF + 0.1M nBu$_4$NBF$_4$ at 13.0°C. Scan rate:1Vs^{-1}, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/–2.90/ /+1.30/0.00 V.

Our results, in accordance with the voltammetric data, suggest the reduction mechanism outlined in Scheme 2 for **1**. The first of the three reversible waves corresponds to two successive and fast one-electron transfers (with a difference of standard potentials of 60 mV) at $E°$ = -0.68 V. The other two waves correspond to two one-electron transfer at $E°$ = -1.46 and –1.70 V.

The analysis of the shape of the cyclic voltammograms upon change of the scan rate is shown for v>10 Vs^{-1} (Fig 2 c). The oxidation wave at +0.68 V has disappeared. This oxidation wave is associated with the first electron transfer (Fig 2 b). Therefore, the species which oxidises at +0.68 V must come from a chemical reaction. Upon addition of 30µL of water (0.33 mM) this wave disappears.

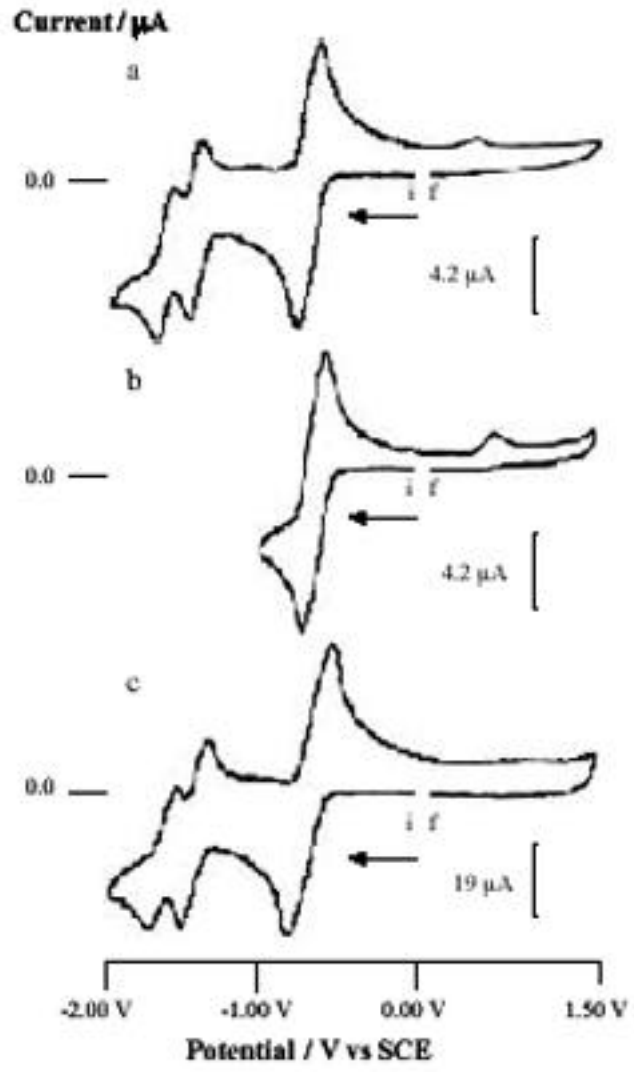
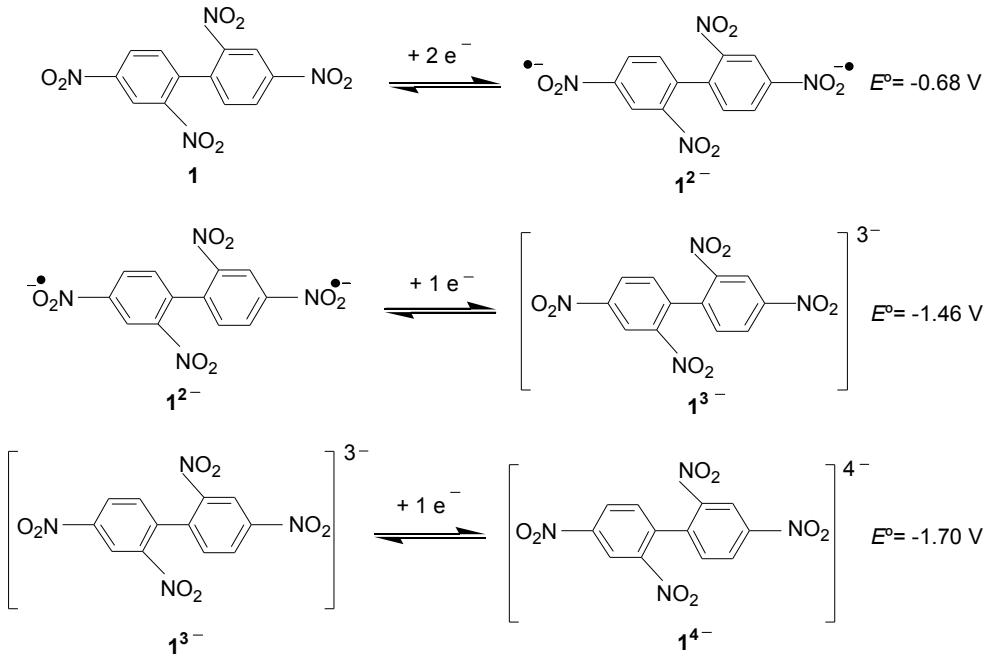


Figure 2. Cyclic Voltammetry of 2,2'-4,4'-tetranitrobiphenyl 1 (6.0 mM) in DMF + 0.1 M nBu_4NBF_4 at 13.0°C, glassy carbon disk electrode (0.05 mm diameter).
a. Scan rate 1 Vs^{-1}, the scan is in the potential range: 0.00/–1.80/+1.40/0.00 V.
b. Scan rate 1 Vs^{-1}, the scan is in the potential range: 0.00/–1.00/+1.40/0.00 V.
c. Scan rate 10 Vs^{-1}, the scan is in the potential range: 0.00/–1.90/+1.40/0.00 V.



Scheme 2

When a solution 10mM of **1** is reduced by a short electrolysis (0.2 F) at –0.71 V, $\mathbf{1}^{2-}$, dianion of **1** is generated. This solution presents an EPR signal under argon atmosphere at room temperature (Figure 3). The EPR spectrum indicates that $\mathbf{1}^{2-}$ is a biradical. The EPR signal disappears upon time. The UV–vis spectrum of this solution (Figure 4 a) is similar to the one reported for **1** (268 nm) with a shoulder at 330 nm.

On the other hand, the exhaustive electrolysis of a solution of **1**, at – 0.71 V, after removing the solvent and the support electrolyte and posterior purification, gives a solid compound. The elementary analysis, UV and ^{1}H-NMR spectra of this compound (which does not show EPR signal) corresponds to what is it expected for structure $\mathbf{1q}^{2-}$ [*trans*-bis(2,4-dinitro-2,5-cyclo hexadien-1-iliden)dianion] (Scheme 1). The tetraethylammonium salt of $\mathbf{1q}^{2-}$ is obtained in 33% yield. Product $\mathbf{1q}^{2-}$ is also identified by mass spectrometry techniques as MALDI-TOF (Matrix-assisted laser desorption time-of-flight mass spectrometry) and ESI-MS_n (Electrospray ionization mass spectrometry with consecutive fragmentation steps) as two additional totally electrolysed solutions of **1** at –0.71 V.

$\mathbf{1q}^{2-}$ is produced after a long electrolysis of a solution 10 mM of **1**, at –0.70 V. The cyclic voltammogram of this solution (Fig 5a) shows the following:

1) The increase of the oxidation peak at +0.68 V by 80% and the decrease by approximately 80% of the first reduction wave (-0.68 V) of **1**.
2) The appearance of new second and third waves at -1.27 V and –1.48 V, corresponding, each one, to a rapid one-electron transfer, and
3) A new residual reduction wave at –0.88 V.

The UV-vis spectrum of this solution (Figure 4 b) presents a new band at 550nm, a value characteristic of σ-complexes[24] and the residual bands at 268 nm and 335nm, attributed to **1** and $\mathbf{1}^{2-}$ respectively.

The cyclic voltammogram of a solution 4.0mM of $\mathbf{1q}^{2-}$ is shown in Figure 5b. Only

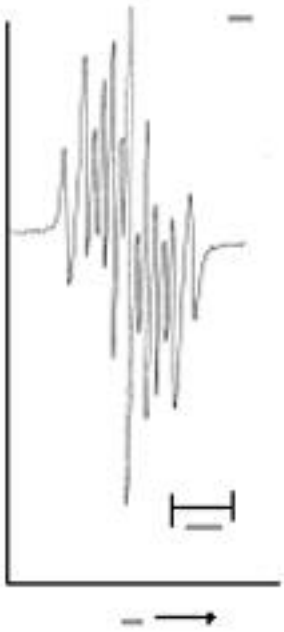


Figure 3. EPR spectrum of **1** $^{2-}$. Product $\mathbf{1}^{2-}$, dianion of **1**, is generated by the short reduction electrolysis (0.2 F) at –0.71 V of a solution 10 mM of **1**.

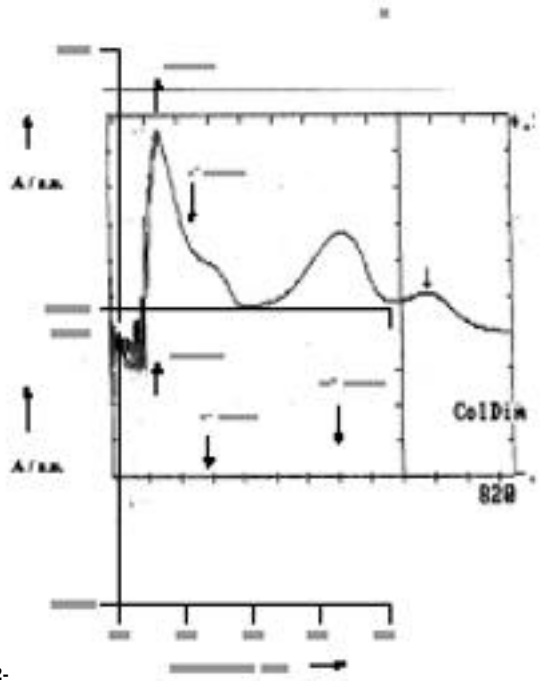


Figure 4. UV-vis spectrum of a solution of **1** after:
a. Short reduction electrolysis (0.2 F) at –0.71 V.
b. Long electrolysis of a solution of **1** at – 0.71

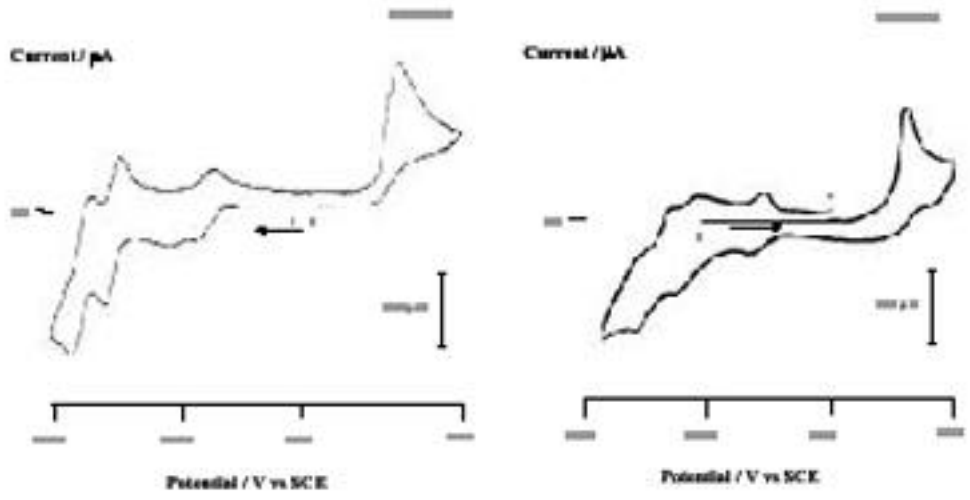
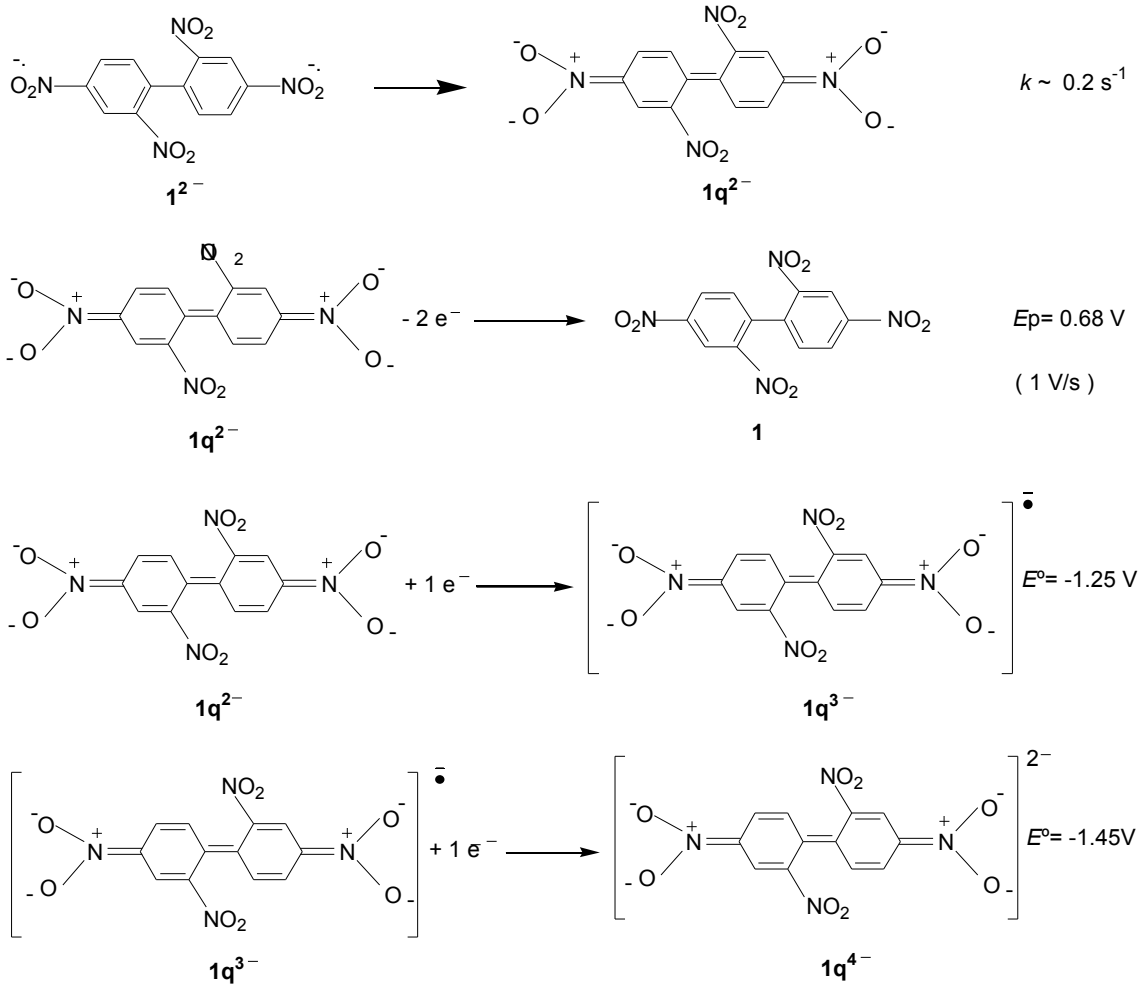


Figure 5. **a.** Cyclic Voltammetry after the reduction of 2,2'-4,4'-tetranitrobiphenyl **1** (6.0 mM) in DMF + 0.1 M nBu_4NBF_4 at 10.0°C at -0.71 V passing 3.5 F, glassy carbon disk electrode (0.05 mm diameter). Scan rate: 1 Vs^{-1}. The scan is in the potential range: 0.00/-1.60/+1.00/0.00 V **b.** Cyclic Voltammetry after the reduction of $\mathbf{1q}^{2-}$ (4.0 mM) in DMF + 0.1 M nBu_4NBF_4 at 10.0°C, glassy carbon disk electrode (0.05 mm diameter). Scan rate: 1Vs^{-1}. The scan is in the potential range: -1.00/1.00/-1.90/0.00 V.

2,2'-4,4'-tetranitrobiphenyl **1** is obtained after the complete oxidation of $\mathbf{1q^{2-}}$.
The exhaustive oxidation electrolysis of the solution at 0.70 V and passing 2 F is shown in Figure 5b. It permits to obtain, after corresponding work up (see Experimental Section), 85% of **1** and 15% of 4,4'-dinitrobiphenyl ($E°$=- 0.88 V). [20]

In short, $\mathbf{1q^{2-}}$ is oxidised, with loss of 2 electrons, to **1** (reduction wave at –0.68 V)[25] and $\mathbf{1q^{2-}}$ is reduced in two successive reversible steps (waves at –1.27 and –1.48 V).Moreover, reduction of $\mathbf{1q^{2-}}$ is not observed in cyclic voltammograms of **1** (Fig 2 a and b), a fact that can be explained by admitting that, within the cyclic voltammetry time-scale, $\mathbf{1q^{2-}}$ is not formed in enough quantity. $\mathbf{1q^{2-}}$ is formed slowly from $\mathbf{1^{2-}}$ and the rate constant of this reaction is ca. 0.2 s^{-1} as calculated by Digisim ®(Scheme 3)

Structure $\mathbf{1q^{2-}}$, which is a dianion of quinoid type, must be chemically different from $\mathbf{1^{2-}}$, a dianion biradical. $\mathbf{1^{2-}}$ is stable with respect to reduction at potentials less negatives than –1.40 V. Nevertheless $\mathbf{1^{2-}}$ partially leads to the formation of $\mathbf{1q^{2-}}$, a stable dianion with charges spread around the whole aromatic ring. $\mathbf{1q^{2-}}$ is stable with respect to reduction at potentials less negative than –1.27V. $\mathbf{1q^{2-}}$ is reduced in two reversible one-electron transfers.



Scheme 3

Theoretical Results

In accordance with the electrochemical results indicating that the two electron transfers have similar standard potentials, the neutral molecule, the S=0 and S=1 dianions have been studied for **1** using the Density Functional Theory (DFT, see Experimental Section). Figure 6 depicts the results of full geometry minimisation and the parameters calculated for the three molecular structures. The reported parameters are the bond distances and the Mulliken charges of the nitro groups (for the sake of clarity the charges of the rest of the molecule are not posted in the Scheme 2).

When comparing the neutral molecule (Fig 6 a) with the S=1 dianion (Fig. 6 b), it is clear that the two additional charges are mostly found in the nitro groups and, among them, the ones in position 4 and 4' show a more prominent increment of negative charge. As a consequence, the C-N distances have diminished, in special those at the -4 and -4' positions that have shortened 0.07Å. The rest of the molecule is not appreciably modified, both structures showing an almost perpendicular arrangement of both aromatic rings. This electronic distribution would correspond to the structure of $\mathbf{1}^{2-}$ (Scheme 1). Conversely, the S=0 dianion has an almost planar structure with the charge more spread (Fig 6 c). Nitro groups still support the greater part of negative charge but a larger amount of it (around 0.8 electrons) is delocalised within the two benzene rings. This electronic distribution would correspond to the structure of $\mathbf{1q}^{2-}$ (Scheme 1).

Compound	E^o_1(V)	E^o_2(V)	E_{pa}(V)	λ_{max}(UV) nm	EPR	4-NO_2 charge	C1-C1' Distance (Å)	Dihedral angle
$\mathbf{1}^{2-}$	-1.46	-1.70	-0.68	330-5	Yes	-0.82	1.49	70.4º
$\mathbf{1q}^{2-}$	-1.25	-1.45	0.68	550	No	-0.74	1.42	25.9º

Table 1. Different parameters for structures $\mathbf{1}^{2-}$ and $\mathbf{1q}^{2-}$.

Two quite relevant geometric parameter showing the different electronic distribution of the two states are the dihedral angle and the C-C bond distance between both phenyl rings. This angle is almost 90° (85.6° to be precise) in the neutral molecule. This angle is slightly smaller in the triplet state (70.4°) but it tends towards a planar configuration (as expected for a quinoid form) in the singlet state that has a dihedral of only 25.9°.

As for the relative stability of the two dianions, the S=0 case is more stable than the S=1 dianion but the difference is rather small: 9.17 $kcalmol^{-1}$.

Discusion

In Table 1, the main spectroscopic, electrochemical, and geometrical parameters of structures $\mathbf{1}^{2-}$ and $\mathbf{1q}^{2-}$ are gathered.

The proposed structures for $\mathbf{1}^{2-}$ and $\mathbf{1q}^{2-}$ can justify their fundamental electrochemical properties. Thus, $\mathbf{1q}^{2-}$ is more easily reduced but its oxidation is more difficult. Indeed, this must be due to the much higher charge delocalisation of the quinoid structure $\mathbf{1q}^{2-}$.

This delocalisation must be also responsible of the observed relative stability of both dianions.

The calculated structures for $\mathbf{1}^{2-}$ and $\mathbf{1q}^{2-}$ and their parameters can also justify their observed dynamic behaviour. As the geometry of the neutral molecule is closer to that of the triplet dianion than to the singlet one, it is to be expected that after the two electrons uptake the dianion will be in its triplet (biradical) state. Intersystem crossing to the singlet state is an electronically forbidden process, and in this case, a structural and conformational barrier must be added to this electronic barrier, since the minimum energy geometry for the singlet state is almost planar and one ring must spin by over 50° with respect to the other to reach the preferred singlet state geometry. Therefore, the dianion is first produced in the triplet state and it slowly evolves towards the quinoid singlet state.

$\mathbf{1q}^{2-}$ is the final product of the reaction. The electron transfer steps lead to $\mathbf{1}^{2-}$ and not to $\mathbf{1q}^{2-}$ as the geometry reorganisation required to obtain the quinoid structure does not occur at the radical anion level (this would imply an ECE-DISP mechanism) but only at the $\mathbf{1}^{2-}$ level. A slow chemical reaction transforms $\mathbf{1}^{2-}$ into $\mathbf{1q}^{2-}$. Our theoretical calculations give a difference in stability of 9.17 $kcalmol^{-1}$ but the calculations refer to the gas phase whereas the experiments were carried out in DMF (a polar, aprotic solvent). In this particular case, a differential stabilisation of the triplet state over the singlet one when passing from the gas phase to solution must be expected, reducing in this way the energetic gap. Hence, our calculations show a significantly higher localisation of the charge in the nitro groups of the triplet state, therefore this state will become more stabilised in solution, thus justifying the observed behaviour.

Conclusions

The analysis of the electrochemical behaviour of 2,2'-4,4'-tetranitrobiphenyl has revealed the presence of two distinct dianions: a biradical species and a quinoid form. Theoretical calculations have shown that for dianions the S=0 and S=1 spin electronic distributions are close enough so that both states may be involved in the electrochemical processes. For the first time, this behaviour has been seen in nitroderivative compounds. Our results also indicate that the S=1 dianion is initially accessed but over time the system evolves towards the S=0 electronic distribution, which is the ground state and has a quinoidlike structure.

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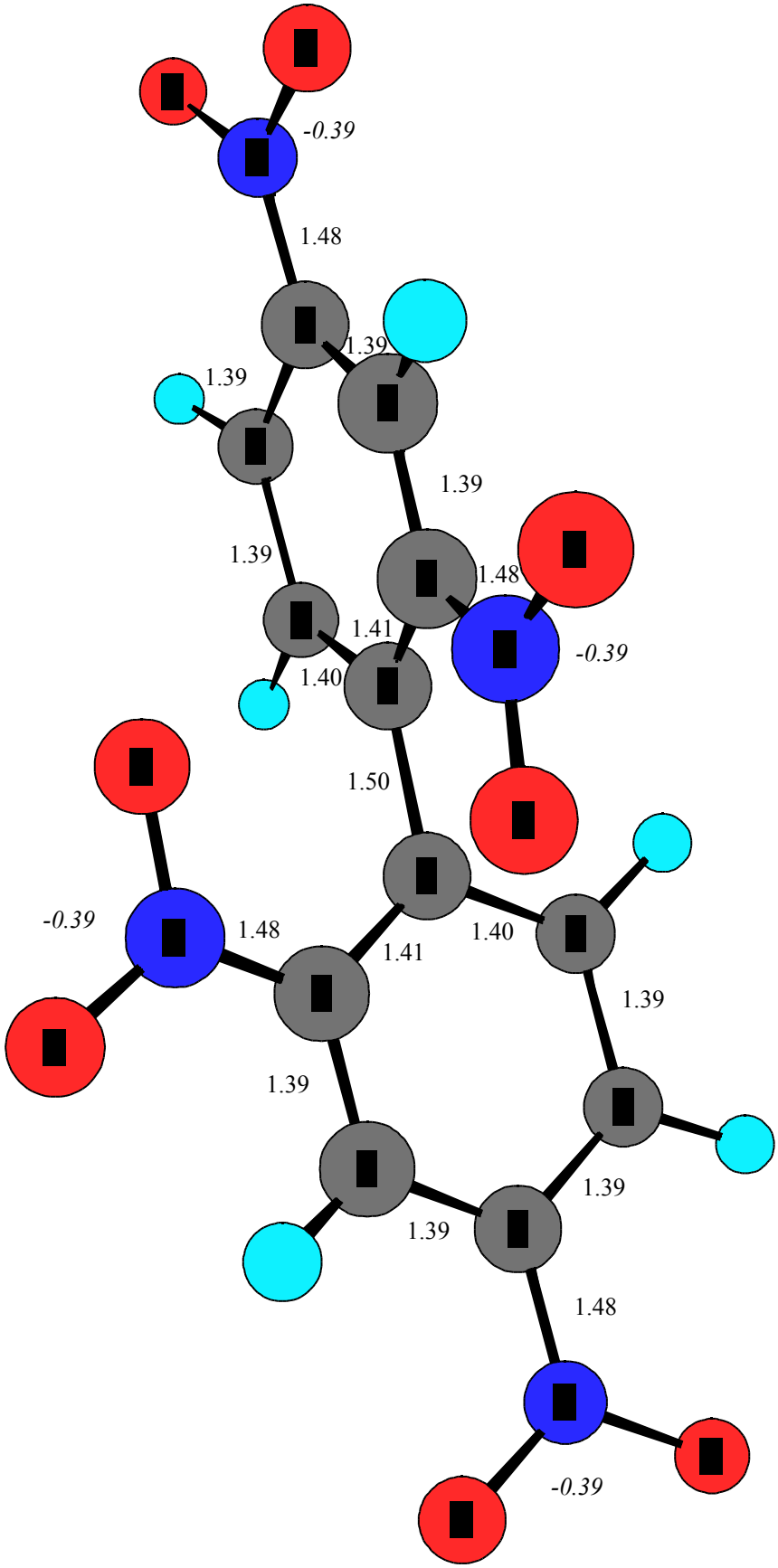

Figure 6. Calculated Molecular Structures for the 2,2'-4,4'-tetranitrobiphenyl **1**
a. Neutral molecule The negative values (in italic) indicate the Mulliken charges on the nitro groups.

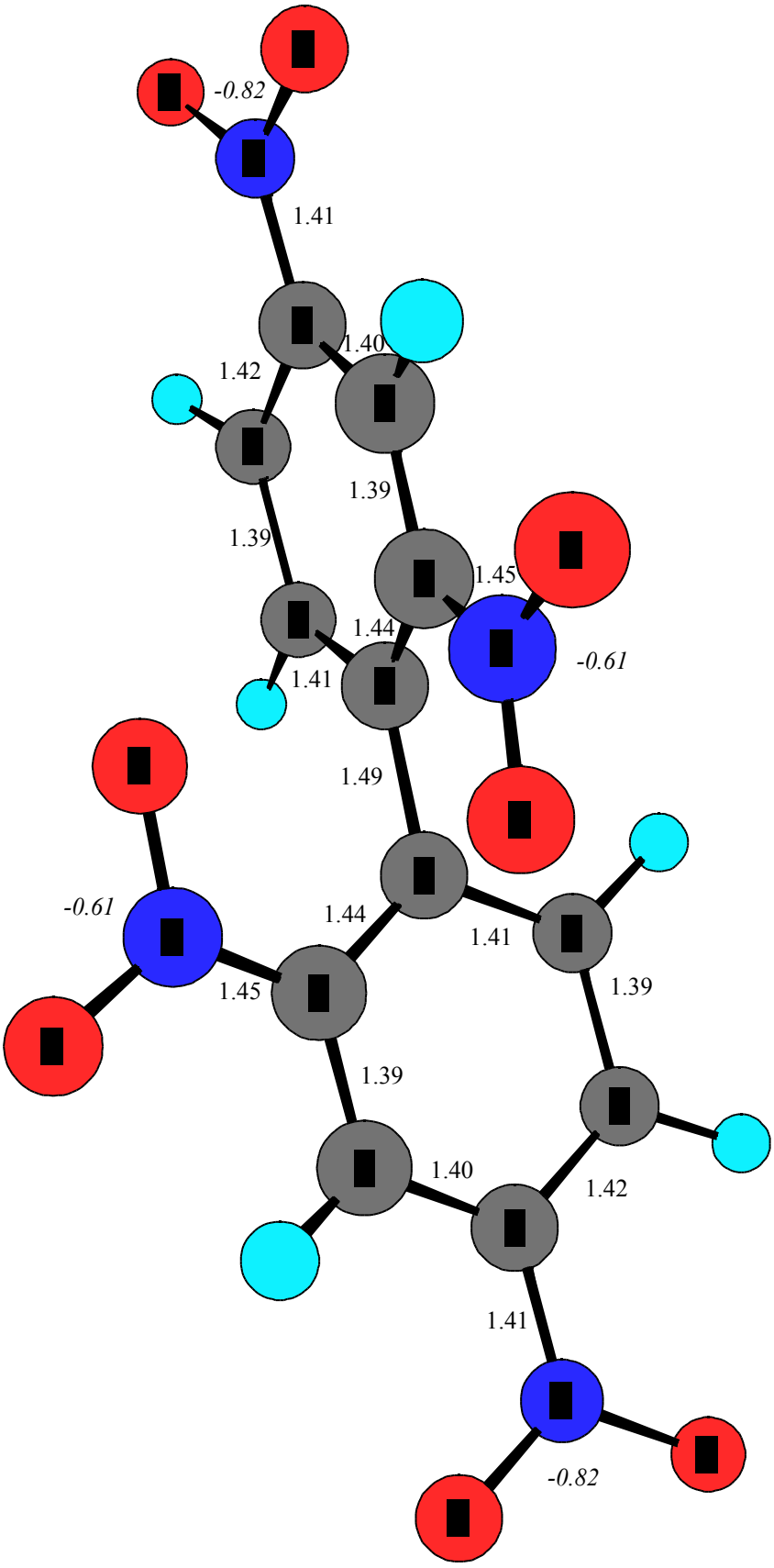

Figure 6. Calculated Molecular Structures for the 2,2'-4,4'-tetranitrobiphenyl **1**
b. S=1 dianion, c. S=0 dianion. The negative values (in italic) indicate the Mulliken charges on the nitro groups.

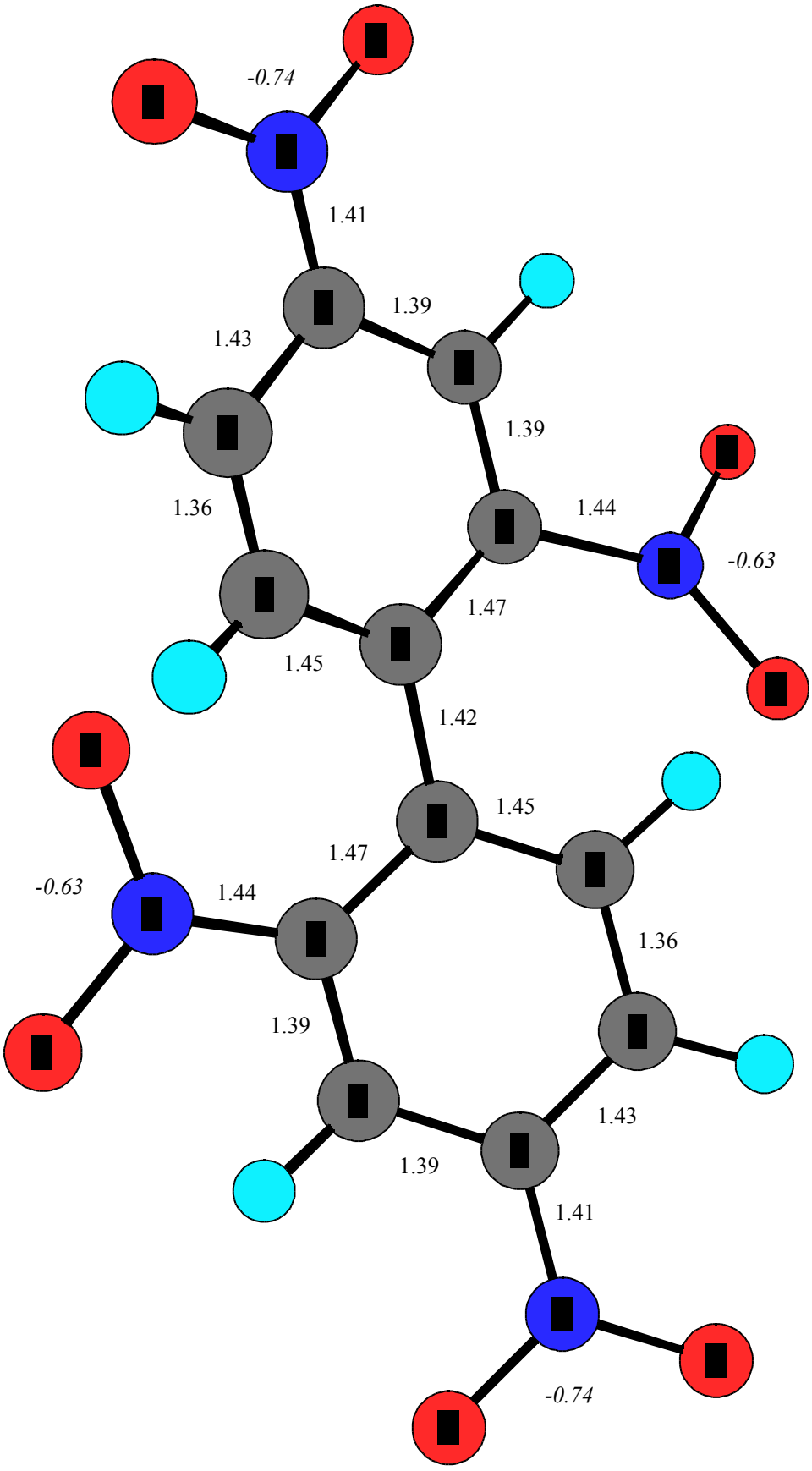

Figure 6. Calculated Molecular Structures for the 2,2'-4,4'-tetranitrobiphenyl **1** c. S=0 dianion. The negative values (in italic) indicate the Mulliken charges on the nitro groups.

Experimental Section

Chemicals:

DMF (SDS pour syntheses peptidiques) and nBu$_4$NBF$_4$, Et$_4$NBF$_4$ (Fluka puriss.) were used as received.

Compound 1 was prepared as in reference.[26] ^{1}H NMR (250 MHz, [D$_3$]CH$_3$CN,25ºC,TMS): δ = 7.78 (d, *J*= 8.45 Hz, 2H), δ = 8.64 (dd, *J*=8.45 and 2.28 Hz, 2H), δ = 8.99 (d, *J*= 2.28 Hz, 2H). E^o = -0.68 V *vs* SCE.

Compound 1q^{2-} was isolated as a tetraethylammonium salt. It was prepared by electrochemical reduction of a solution 50 mM of **1** in acetonitrile (ACN), using 0.1M of Et$_4$NBF$_4$ as supporting electrolyte. After exhaustive, controlled-potential of **1** at –0.71 V, the product formed was precipitated by addition of 50 ml of dry ether, collected by suction under nitrogen atmosphere, washed with ether and dried by passing dry nitrogen there through. The product was kept under nitrogen blanket at 0°C. Yield 33 %. Freshly samples were used in all the cases so as to perform NMR, cyclic voltammetry and UV-Vis experiments.

^{1}H NMR (250 MHz, [D$_3$]CH$_3$CN,25ºC,TMS): δ = 0.93 (t, *J*= 1.66 Hz, 24H), δ = 2.28 (q, *J*= 1.66 Hz, 16H), δ = 6.98 (d, *J*= 9.05 Hz, 2H), δ = 7.25 (dd, *J*=9.05 and 1.50 Hz, 2H), δ = 8.38 (d, *J*= 1.50 Hz, 2H).

Elemental analysis was carried out to recrystallised samples in mixtures ACN/ether under nitrogen atmosphere. Calculated for: C$_{28}$H$_{46}$N$_6$O$_8$.2BF$_3$: C (46.00%), H (6.35%), N (11.50%). Found: C (46.31%), H (6.15%), N (11.16%).
$E°_1$ = -1.25 V, $E°_2$ = -1.45 V and E_p^{ox} (1.0 Vs^{-1}) = 0.68 *vs* SCE.

Reductive Electrolysis of 1 : The electrolysis of 1 at –0.71 V *vs* SCE led to **1q^{2-}** (see synthesis of **1q^{2-})** and in this case the reaction mixture was treated directly.

An exhaustive electrolysis of **1** (20mM) in DMF, which contain nBu$_4$NBF$_4$ 0.1 M as supporting electrolyte at - 0.70 V *vs* SCE was carried out under argon atmosphere. First, a MALDI-TOF experiment and then Electrospray mass spectrometry with consecutive fragmentation steps (ESI-MS$_n$) were used to analyse the electrolysis mixture. It was the first time in our knowledge that these techniques were applied to analyse the final products obtained in an electrolysis.

Mass Spectrometry: Matrix-assisted laser desorption time-of-fight (MALDI-TOF) mass spectrometry has been the first technique used for characterise **1q^{2-}**, the dianionic product present in the mixture. MALDI-TOF has been used because it is a ionisation whose a low internal energy is required to produce ions, then the fragmentation of the analyte could be minimise. MALDI-TOF is predominantly used to molecules that have high molecular weight, in our case the application of this technique seems not to be very attractive. However, quite good results were obtained. The mixture was analysed in two modes.

In positive mode the presence of two signal at *m/z*=242 and 243, which correspond to the tetrabuthylammonium. In negative mode several signals were found at *m/z*=539, this correspond to an adduct formed between a single monoanion of **1q^{2-}** and 3 molecules of BF$_3$, at *m/z*=335 (molecular peak corresponding to a single monoanion of **1q^{2-}**), at *m/z*=274, at *m/z*=250 (the most intense signal) and *m/z*= 234. At first, the last three signals were not possible to determine if the were connected with the ionisation of **1q^{2-}** or not. If they are connected making consecutive MS of each peak, it will be possible to achieve a known *m/z* peak. For instance consecutive fragmentation of **1q^{2-}**, a logical fragment that must be obtained will be the half of the molecule (similar to 1,3-dinitrobenzene peak at *m/z*=168).

Electrospray mass spectrometry with consecutive fragmentation steps (ESI-MS$_n$) was used so as to obtain more information about the peaks at *m/z*=274, at *m/z*=250 intense and *m/z*= 234, found in MALDI-TOF spectra. The solution was diluted 1:1000 in CH$_2$Cl$_2$ and a infusion of 3μLmin^{-1} of this mixture was done in order to carry out this analysis.

The mixture was analysed in two-ion mode. In positive anion mode the countercation must be detected. The

tetrabuthylammonium cation was detected at *m/z*= 242 as the most intense signal. In negative mode, several signals were detected, one of them correspond to the tetrafluoroborate anion (*m/z*=87), the counteranion present in our supporting electrolyte.

The tetranitrodiphenyl component is detected as singly charged ion at *m/z*=392. In the MS/MS and MS^3 spectra you can find fragmentation due to losses of phenyl, nitro, and CH_2 groups. In addition, MS^n data of the most intense signal at *m/z*=274 is connecting with Malditof data.

Notice that all the tetranitroquinoide compound is detected as single ion at several *m/z*. In the MS/MS and MS^3 spectra the fragmentations due to losses of phenyl, NO_2 (-46), NO(-30), O(-16).

Oxidative Electrolysis of $1q^{2-}$: An exhaustive oxidative potential controlled electrolysis (2F) of a solution 10 mM of **$1q^{2-}$** at 0.85 V *vs* SCE was performed using a carbon graphite electrode. After that, the reaction mixture was extracted with water/toluene. The organic layer was dried with Na_2SO_4 and evaporated affording a residue that was analysed by Gas Chromatography. The analysis showed the presence of compound **1** (85%), and to 4,4'-dinitrobiphenile (15%). The products were analysed by Gas Chromatography, ^{1}H NMR and cyclic voltammetry and identified by comparison of their spectroscopic behaviour with the reported in the literature in each case, and with pure samples.

4,4'-dinitrobiphenile (15%): ^{1}H NMR (250 MHz,[D_3] CH_3CN, 25ºC, TMS): δ = 7.80 (d, *J*= 9.03 Hz, 4H), δ = 8.27 (dd, *J*=9.03, 4H)

Mass Spectrometry: Matrix-assisted laser desoprtion time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex in Modus Reflection. Laser source 330nm, voltage 19.00 kV no matrix were used.

Electrospray ionisation mass spectrometry with consecutive fragmentation steps (ESI-MS_n) were recorder on a Esquire 3000 Bruker.

UV-Spectroscopy: UV spectra were measured using a Diode Array Hewlett-Packard (8452A) spectrometer connected with a HP Vectra computer.

Cromathography: Gas Chromatography was performed using a Hewlett-Packard 5890 serie II Plus Chromatograph linked with a Hewlett-Packard 3396 serie II integrator. The column used was a HP-5(cross-linked 5% Ph-Me silicone) 30 m x 0.32 mm x 0.25 µm.

NMR: ^{1}H RMN spectra were recorded on a Bruker AC250 spectrometer (250 MHz) at room temperature.

EPR spectra were recorded at room temperature on a Varian E-12 spectrometer with a 100kHz field modulation, operating at 9.5 GHz microwave frequency. The modulation amplitude values range between 0.1 and 0.001 G, the microwave power level was 10 mW, the time constant was 0.3 s and the scan range was 40.0 G. The sample was maintained in an inert atmosphere.

Electrochemical Instruments and Procedures: The instrumentation and electrochemical procedures were the same as previously described.[27]

Theoretical Calculations:
Electronic calculations have been performed using he Gaussian 98 series of programs.[28] The Density Functional Theory (DFT) has been used with the three-parameter hybrid functional of Becke and the Lee-Yang-Parr correlation functional best known as B3LYP functional.[29] The basis set used was the split-valence 6-31G(d) with a set of d-polarization functions added for heavy (non-hydrogen) atoms.[30] In all the cases full geometry minimization has been carried out by means of the standard Schlegel gradient algorithm using redundant internal coordinates.[31]

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4.4. Conclusiones

4.4. Conclusiones Generales (parte II)

1. Respecto al comportamiento electroquímico del TNB:

    a. Se ha determinado minuciosamente el comportamiento electroquímico del TNB, tanto en reducción como oxidación.

    b. Se ha aislado y caracterizado por primera vez a través de técnicas electroquímicas (VC y electrólisis), EPR , AE, UV-vis, ^{1}H RMN, ^{13}C RMN un intermedio biradicalario previo a la formación del complejo de Meisenheimer (σ^{H}-diaducto dianiónico).

    c. Se ha obtenido la primera estructura cristalina de un dímero intermedio por cristalización del biradical bis(1,3,5-trinitrobenceno) dianión en atmósfera de nitrógeno. Demostrándose de forma inequívoca tanto la no existencia de enlace C-C, como la presencia de 2 molecúlas de TNB y 2 moléculas de tetraetilamonio en el monocristal. Gracias a la inserción de la molécula de nitrógeno la estabilización del biradical en una red cristalina perfectamente ordenada fue posible.

2. Respecto al comportamiento halodinitrobencenos:

    a. Se han determinados las constantes de velocidad de rotura C-X de los aniones radicales del 1-Br-2,4-DNB y 1-Cl-2,4-DNB.

    b. Se ha determinado que el radical anión del 1-F-2,4-DNB tiene asociada una reacción de dimerización, a diferencia de los anteriores, cuya valor constante de velocidad ha sido determinado.

    c. Se ha demostrado , tal y como se hizo previamente en la literatura para compuestos relacionados, que la energía de disociación de enlace D_{RX} es el factor que gobierna la reactividad de los diferentes radicales aniones estudiados.

    d. Se ha visto que el cambio de reactividad por parte del anión radical del 1-F-2,4-DNB permite la obtención del 2,2'-4,4'-tetranitrobifenilo como

consecuencia de la oxidación electroquímica del complejo σ dianiónico formado por dimeriación de 2 aniones radicales. En este caso particular esta reacción constituye un precedente en lo que pudiera ser rutas alternativas a la reacción de Ullman para sintetizar dímeros simétricos.

3. Respecto al comportamiento electroquímico del 2,2'-4,4'-tetranitrobifenilo:

   a. Se ha puesto de manifiesto por primera vez en compuestos nitroaromáticos la presencia de dos tipos de dianiones, triplete (S=1, paramagnético) y singlete (S=0, diamagnético), comportamiento ya descrito en la literatura para compuestos aromáticos de tipo quinónico.

   b. Los resultados experimentales obtenidos por VC, EPR y cálculos DFT aportan evidencias experimentales de la formación inicial de un compuesto dianiónico biradicalario (S=1, onda bielectrónica reversible), que posteriormente evoluciona hacia el dianión (S=0, forma quinónica) que es el más estable.

   c. Por primera vez se han obtenido evidencias experimentales de la existencia de estructuras quinónicas como entidades químicas más allá de su corriente utilización como forma resonante más estable de los derivados nitroaromáticos dianiónicos.

   d. Se han aplicado con éxito y por primera vez nuevas técnicas de análisis como son MALDI-TOF y ESI-MS_n para el análisis de forma directa de la mezcla de reacción después de realizar de las electrólisis.

A partir de ahora se podrá catalogar el comportamiento electroquímico de cualquier tipo de nitroderivado al variar su velocidad de barrido de potencial (*v*) incluyéndolo en uno de los 4 grupos según sea la reactividad asociada a sus radicales aniones o biradicales (esquema 45).

Así:

Grupo I

El compuesto posee una onda de reducción reversible a un electrón a cualquier velocidad de barrido de potencial (*v*).

Grupo II

El compuesto posee dos ondas de reducción reversibles mono- o una bielectrónica a cualquier velocidad de barrido de potencial (*v*) y, además, **aparecen nuevas ondas en un barrido posterior de oxidación no asignables a derivados nitrosos.**

Grupo III

El compuesto posee una onda de reducción parcialmente reversible a más de un electrón a bajas velocidades de barrido de potencial (*v*), pasando a una onda de reducción monoelectrónica reversible a altas velocidades de barrido de potencial (*v*).

Grupo IV

El compuesto posee una onda de reducción monoelectrónica irreversible a bajas velocidades de barrido de potencial (*v*), pasando a una onda de reducción monoelectrónica reversible a altas velocidades de barrido de potencial (*v*).

En esta parte del estudio se han descrito tres nuevos mecanismos para compuestos nitroaromáticos: grupos 2,3 y 4.