Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Evidence for a π-dimer
In the electrochemical reduction of 1,3,5-trinitrobenzene:
A reversible N_2-fixation system

Iluminada Gallardo*, Gonzalo Guirado, Jordi Marquet, Neus Vilà

Departament de Química, Universitat Autònoma de Barcelona
E-08193 Bellaterra, Barcelona (Spain)
Fax: (+34)93-581-2920
e-mail: Iluminada.Gallardo@uab.es

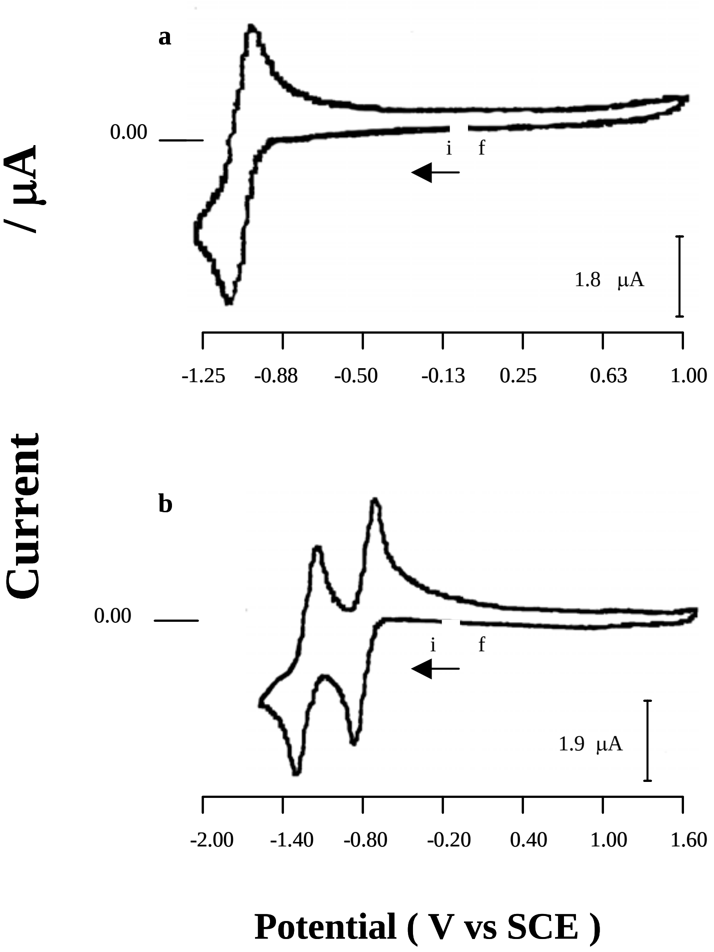

Figure 1. a) CV of nitrobenzene (6.0 mM) in ACN+ 0.1M $n\mathrm{Bu_4NBF_4}$ at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.5 mm diameter). The scan is in the potential range: 0.00/-1.25/1.00/0.00 V

b) CV of 1,3-dinitrobenzene (6.0 mM) in ACN + 0.1M $n\mathrm{Bu_4NBF_4}$ at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.5 mm diameter). The scan is in the potential range: 0.00/-2.00/1.50/0.00 V

Spectro-electrochemistry Experiments

The application of micro structured electrode materials in UV/Vis spectrochemical cells allow us to detect all the intermediates formed during the electrochemical experiments as well as determining the kinetic constant.

Optical transparent thin layer electrochemistry [1-2] (OTTLE): An Optically Transparent Electrode-Lithographic-Galvanic (OTE-LIGA) is used as a working electrode (WE). Figure 2 shows the working electrode named (Optically Transparent Electrode) as well as the electrochemical cell, called OTTLE. The honey-holes of the WE are 20 mm wide, which corresponds to the separation space between them. The OTE-LIGA has an internal diameter of 3 mm, an external diameter of, 5 mm (covered by a Teflon ring) and is 110 mm high. The electrode was made out of gold. The solution enters the cell by capillarity through a Teflon tube, which is perpendicular to the beam of light. Small quartz pieces are located in the optical pathway to the OTE followed by the beam of light. The reference electrode (RE) used is a Ag/AgCl, while a platinum (Pt) wire acted as a counter-electrode (CE). The system was isolated and sealed by Teflon pieces.

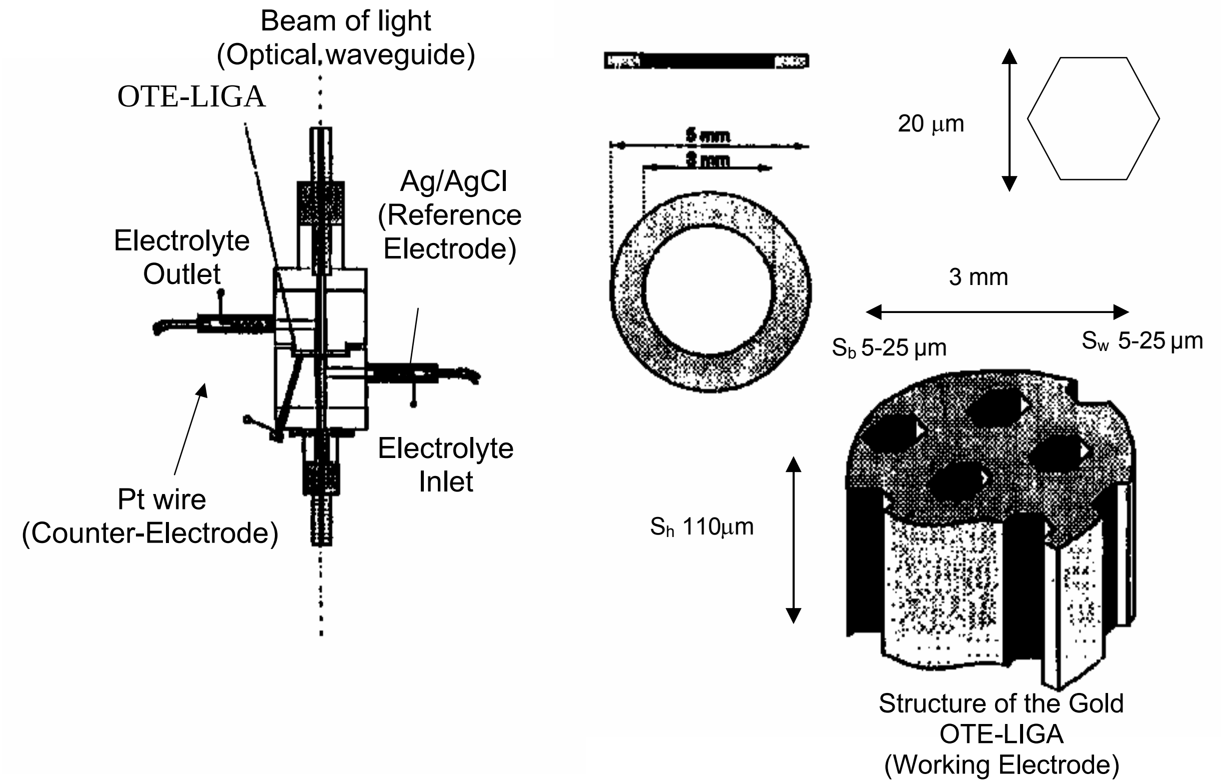

Figure 2. Technical details of the OTTLE system used.

For spectrocyclovoltamogram experiments (figure 1) of **1** (0.5 mM) at scan rate v = 0.1 $V.s^{-1}$; E_{in}= 0.00V and switching potential E_{sw}=-1.00 V in the UV/Vis spectroelectrochemical LIGA cell with a honey combed Au-LIGA structure parameters: S_w (scanner width)=15 μm; S_b (stick width)= 20 μm; S_h (structure height)= 110 μm; d=2.2 mm; A_{LIGA}= 26.7 mm^2; (100%); $A_{honeycomb}$= 20.5 mm^2; (77%); A_{stick}= 6.2 mm^2; A_{disk}=7.6mm^2; (28%). A disk is the topside area of the LIGA-structure including the opening of the honeycombs) and a capillary slit of about 50 μm (between the LIGA structure and the quartz rods).

A diode array spectrometer makes it possible to record of 61 spectra during one cycle of a voltammetric scan at a scan rate of 0.1 V/s within less than 0.2 s. In our case we were able to detect the first two intermediates; the radical anion and the biradical dianionic complex or π-complex. The radical anion of 1,3,5-trinitrobenzene (**1**) appears in the initial spectra, at –0.46 V (absorption wave at 475 nm) and rapidly becomes a biradical dianionic complex or π-complex (**2**) as a result of the dimerization process that we explained earlier (absorption waves at 475 nm and 492 nm) (figure 1d of the manuscript).

A potential step experiment in an OTTLE cell helps measure the measuring of accurate kinetics. So as to benefit the presence of the final product, σ-complex in the mixture (**3**), so we performed electrolysis on a Pt minigrid at –1.00 V. The initial the the biradical dianionic complex or π-complex (**2**) formed on the grid surface at –1.00 V vs Ag/AgCl. The evolution of the compounds present in the mixture was following during the electrolysis process was observed using by a UV/Vis spectrophotometer. A spectrum was registered each 4 seconds. Figure 3 shows the growth of the absorption wave at 518 nm, which corresponds to the appearance of **3**.

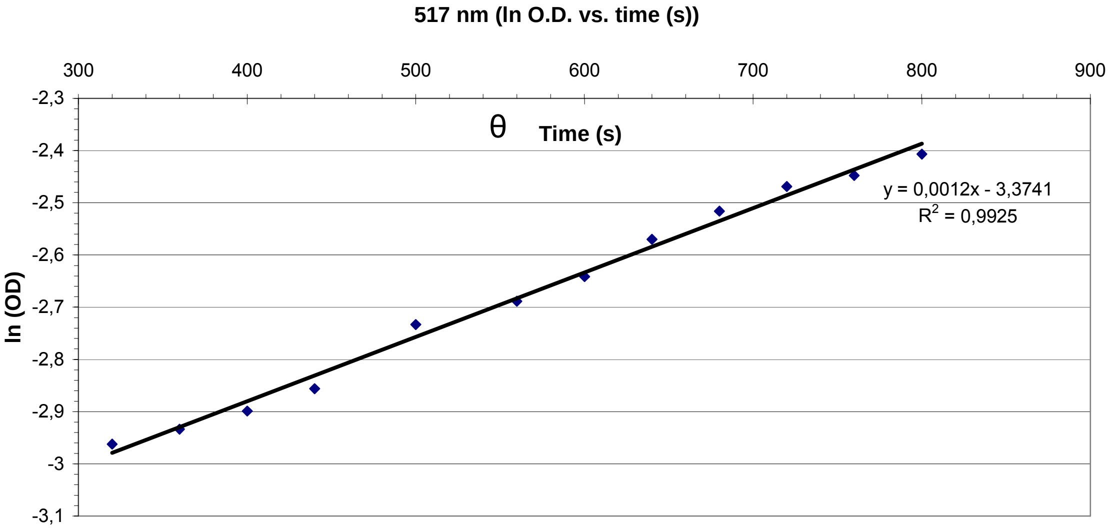

Figure 3. In situ UV-Vis spectra at 517 nm of the isomerisation process **2** to **3**. Curve ln Optical Density *vs.* time during a potential step experiment (E_1= 0.00, E_2 = -1.00, E_3=0.00) of **1** (0.5 mM) in ACN+ 0.1 M nBu$_4$NBF$_4$.

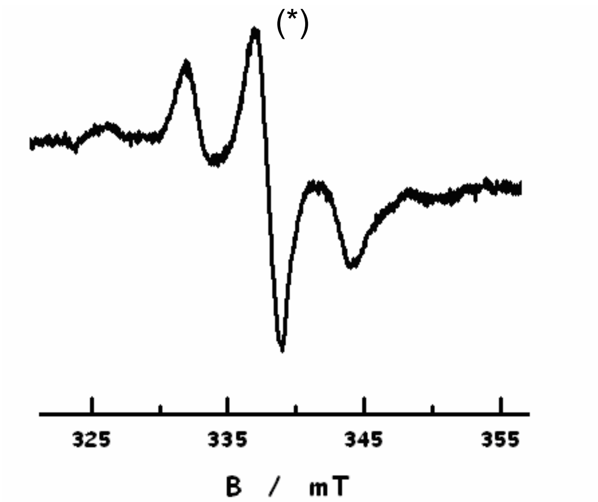

Figure 4. EPR spectrum of a frozen solution of **2** in DMF (X-band, ν=9.36 GHz) in a quartz tube at 77K.

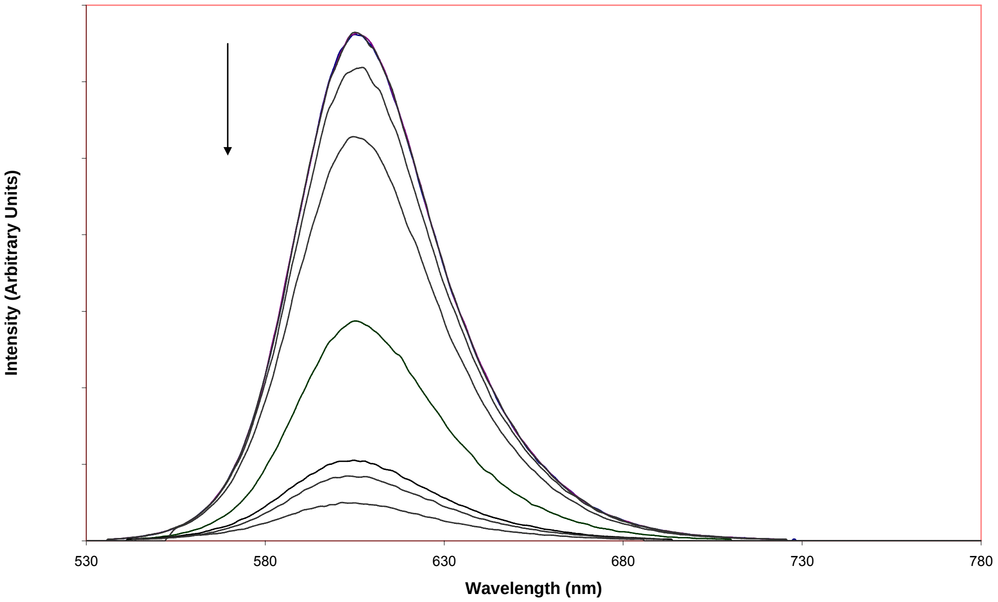

Figure 5. Normalized emission spectra of 3.33 x 10-^{5} M of **2** in ACN ($\lambda_{absorption}$ = 425 nm) where $\lambda_{emission}$ = 606 nm.

Single crystal X-ray diffraction data collection And Structure Determination

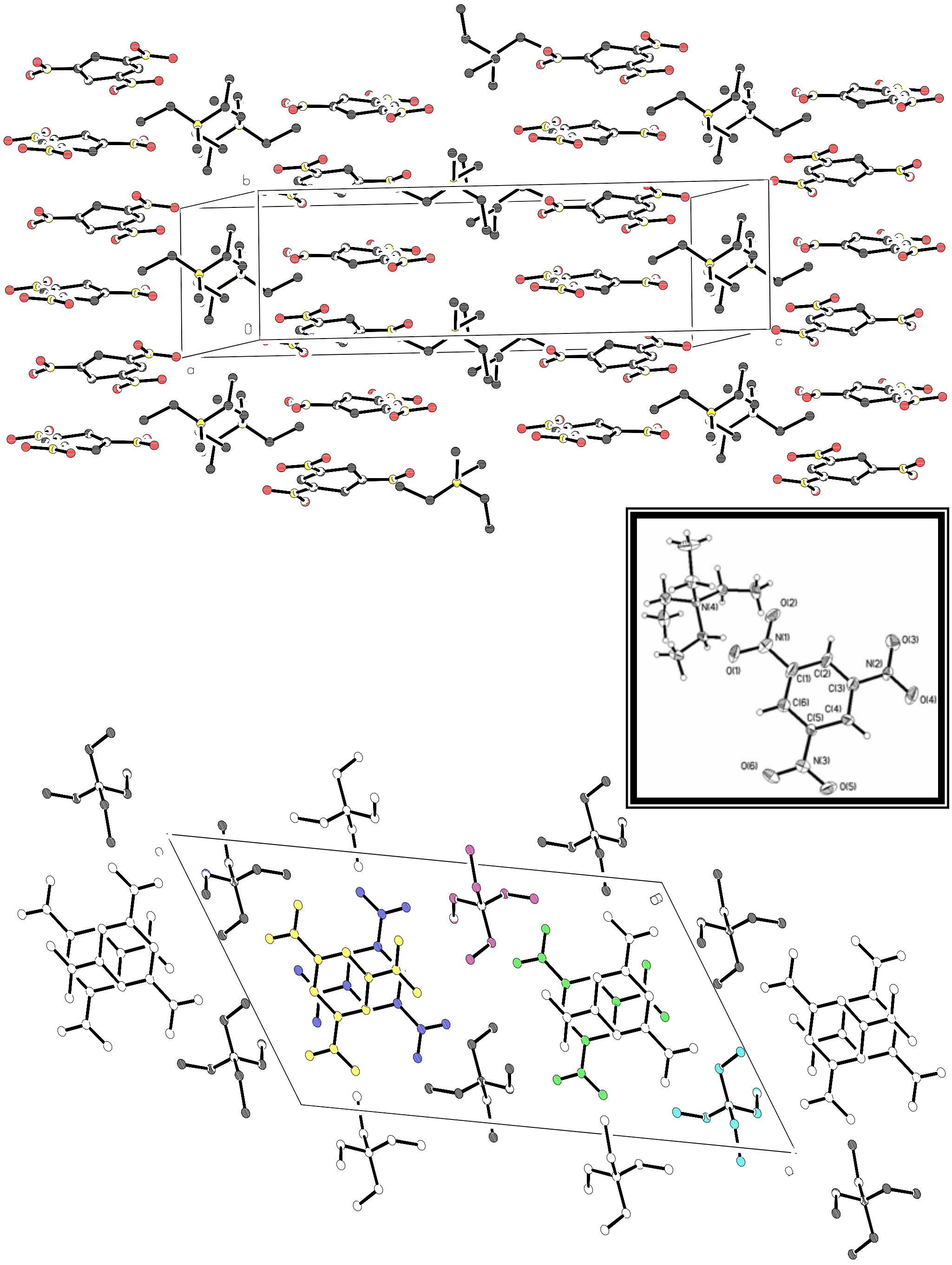

Figure 6. Crystal structure of $(Et_4N)_2$ **2** from two different perspectives. Inset: Selected bond distances of **2** in Å: N1-C1 1.401(15), N2-C3 1.408(14), N3-C5 1.400(14), C1-C2 1.435(18), C5-C4 1.419(17), C3-C4 1.426(17), C1-C6 1.379(16), C3-C2 1.396(18), C5-C6 1.397(15).

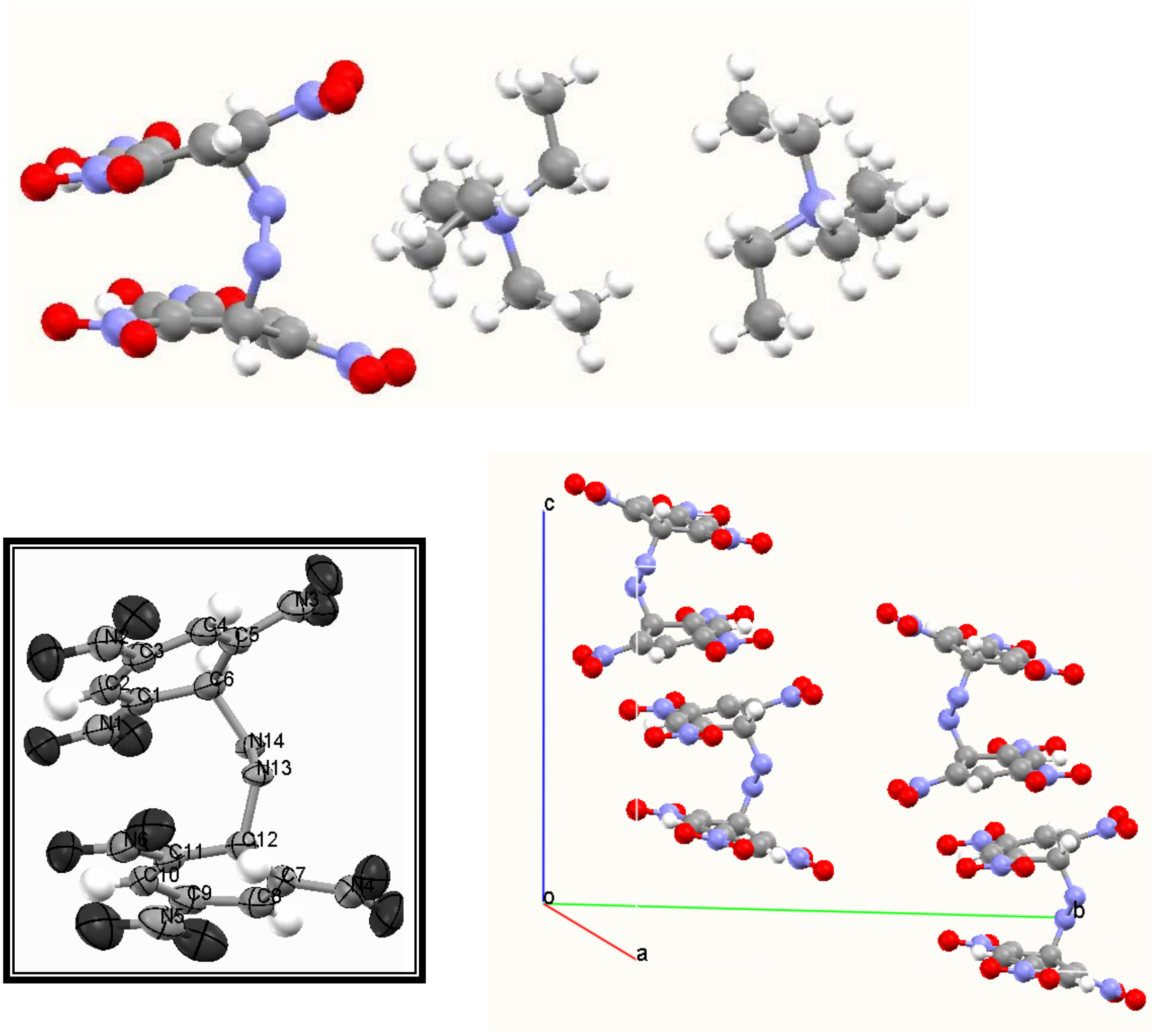

Figure 7. *Top:* crystal structure of $(Et_4N)_2$ **4** (with counterions, Et_4N^+). *Bottom Left:* Selected bond distances of **4** in Å: N4-C7 1.428(6), N6-C11 1.424(6), N5-C9 1.396(7), C12-C7 1.480(7), C7-C8 1.356(7), C8-C9 1.399(7), C9-C10 1.408(7), C10-C11 1.364(7), C11-C12 1.482(7), N14-C6 1.475(6), N13-C12 1.472(6), N13-N14 1.481(5), C12---C6 3.490(10). *Bottom Right:* Packing of $(Et_4N)_2$**4** (counterions are omitted).

---

[1] A. Neudeck, L. Dunsch, *J. Electroanal. Chem.,* **1993**, 370, 17

[2] A. Neudeck, L. Dunsch, *J. Electroanal. Chem.,* **1995**, 386, 13