

One-pot electrosynthesis of 2,3-bis(spiro-2-indanyl-1,3-dione)-indeno[1,2-*b*]furan-4-one

Roberto Horcajada,^a Belen Batanero,^a Fructuoso Barba^{a,*} and Avelino Martín^b

^aDepartment of Organic Chemistry, University of Alcalá, 28871 Alcalá de Henares, Madrid, Spain

^bDepartment of Inorganic Chemistry, University of Alcalá, 28871 Alcalá de Henares, Madrid, Spain

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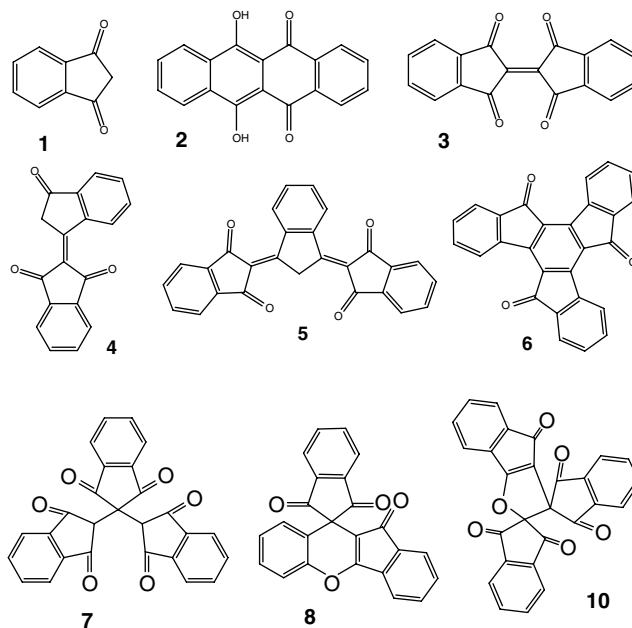
Abstract—The 2,3-bis(spiro-2-indanyl-1,3-dione)-indeno[1,2-*b*]furan-4-one has been synthesized by cathodic reduction of 2,2-dibromo-1,3-indandione in dichloromethane-Bu₄NBF₄. In contrast, tris-indanedione was the main product when acetonitrile was used as a solvent. Sunlight exposition of the dispiro compound afforded the tris-indandione in quantitative yield.

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Since 1,3-indandione (**1**) was synthesized a hundred years ago,¹ chemists have paid a lot of attention to this compound with dyeing properties due to its easy self-condensation, under both acid and basic conditions.² Oxidation of 1,3-indandione afforded a red compound, named by Kaufmann³ as ‘indenigo’ due to its similarity to indigo. This compound turned out later to be 6,11-dihydroxy-5,12-naphthacenedione (**2**). The structure of 2,2'-biindanylidene-1,3,1',3'-tetraone (**3**) was unequivocally determined by X-ray diffraction,⁴ and possesses strong electron acceptor properties, close to those of chloranil. As well, the structure of 1-(indan-1,3-dione-2-ylidene)indan-3-one (**4**) was determined by X-ray diffraction. However, 1,3-[bis(1,3-indandione-2-ylidene)]indane (**5**) and tribenzo[*a,f,k*]trindenone⁷ (**6**) were characterized by NMR.

Derivatives of 1,3-indandione are important intermediates in the synthesis of ninhydrins.⁸ The biologically active tris-indanedione (**7**) was synthesized from ninhydrin⁹ and later its X-ray study was performed.¹⁰ Also, 6- or 7-substituted 2',4-spiro(1',3'-indanedione)-indeno-[3,2-*b*]chromenes (**8**) have been prepared from ninhydrin.¹⁰

On the other hand, Yoshida et al. published a regioselective synthesis of dihydrofurans from 2,2-dibromo-1,3-

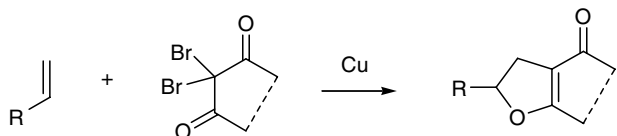


diketones in the presence of olefins with copper powder¹¹ or by electrochemistry,¹² as it is summarized in Schemes 1 and 2, respectively.

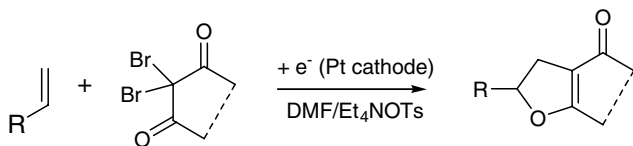
However, the cathodic reduction of 2,2-dibromo-1,3-indandione (**9**) in the presence of an olefin led to the formation of a cyclopropane derivative, rather than a dihydrofuran¹² (see Scheme 3). No explanation was given to this reaction.

Keywords: Cathodic reduction; 2,2-Dibromo-1,3-indandione; Dispiro compound.

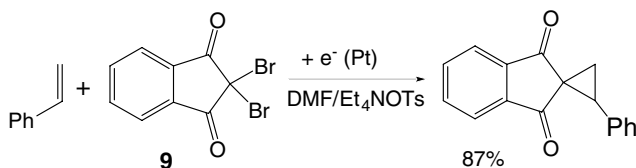
* Corresponding author. Tel.: +34 91 8854617; fax: +34 91 8854686; e-mail: fructuoso.barba@uah.es



Scheme 1.



Scheme 2.



Scheme 3.

In this Letter, we present the achieved results in the electrochemical reduction of 2,2-dibromo-1,3-indandione (**9**) in the absence of olefin. In this case, a new and interesting product, 2,3-bis(spiro-2-indanyl-1,3-dione)-indeno[1,2-*b*]furan-4-one (**10**), with two spiro carbons in the molecule is afforded.

The cyclic voltammetry of **9** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NBF}_4$ (as SSE: solvent-supporting-electrolyte system) on Pt showed an irreversible peak with a reduction potential value of -0.18 V (vs Ag/Ag^+). Furthermore, as it is observed in Figure 1, this compound begins to accept electrons at positive potentials.

Control potential electrolysis ($E = -0.25$ vs SCE) of **9** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NBF}_4$ at platinum mesh cathode did not show any substrate conversion, due to a passivation process. The current measured during the experiment dropped dramatically to zero after a few seconds.

The cyclic voltammetry of **9** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NBF}_4$ (as SSE) on glassy carbon electrode showed an irreversible peak with a reduction potential value of -0.4 V (vs Ag/Ag^+) (see Fig. 2).

Different behavior was observed when dried dichloromethane was used as the solvent. The electrolysis¹³ of **9** at -0.3 V (vs Ag/Ag^+) on a graphite cathode showed an initial current of 200 mA, dropping to residual current (i.e., 20 mA) after the charge corresponding to a 2 F/mol process was consumed. After the work-up, a yellow solid-insoluble in chloroform was obtained in good yield. This compound did not contain any bromine atom, as shown in the MS spectrum, and it had a molecular ion of $M^+ = 432$. The ^1H NMR spectrum in $\text{DMSO}-d_6$, the only suitable solvent for this purpose, did show two multiplets in the aromatic region¹⁴ and one carbonyl group ($\nu = 1761\text{ cm}^{-1}$) was present by FTIR spectroscopy. The compound was crystallized in DMF and an X-ray diffraction study was performed (see Fig. 3) to conclude that the main product of this reaction was the 2,3-bis(spiro-2-indanyl-1,3-dione)-indeno[1,2-*b*]furan-4-one (**10**). Calculated bond lengths and angles support the structural proposal for compound **10** shown in Scheme 4 (see Supplementary data).

The electrochemical formation of **10** can be rationalized through an ionic pathway, as it is indicated in Scheme 4.

However this pathway proposal has two objections: (a) the dibrominated intermediate **h** has experimentally never been detected, and (b) the cathodic reduction peak

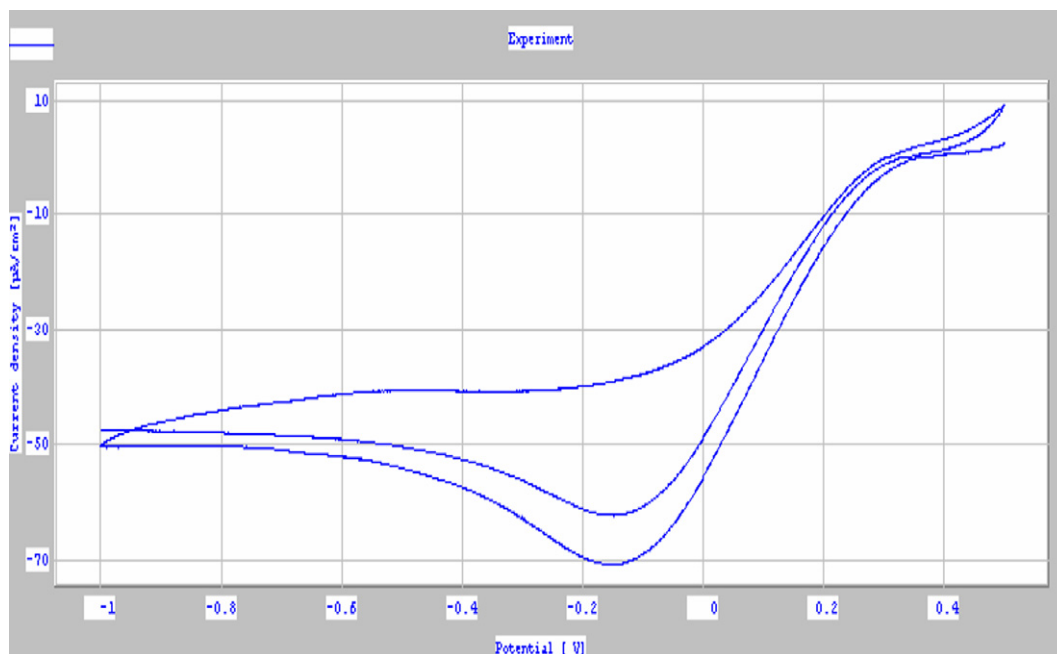


Figure 1. Cyclic voltammetry of 2,2-dibromo-1,3-indandione (**9**) (5 mM) on Pt electrode ($\phi = 0.2\text{ mm}$). $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NBF}_4$ (0.1 M), E versus Ag/Ag^+ .

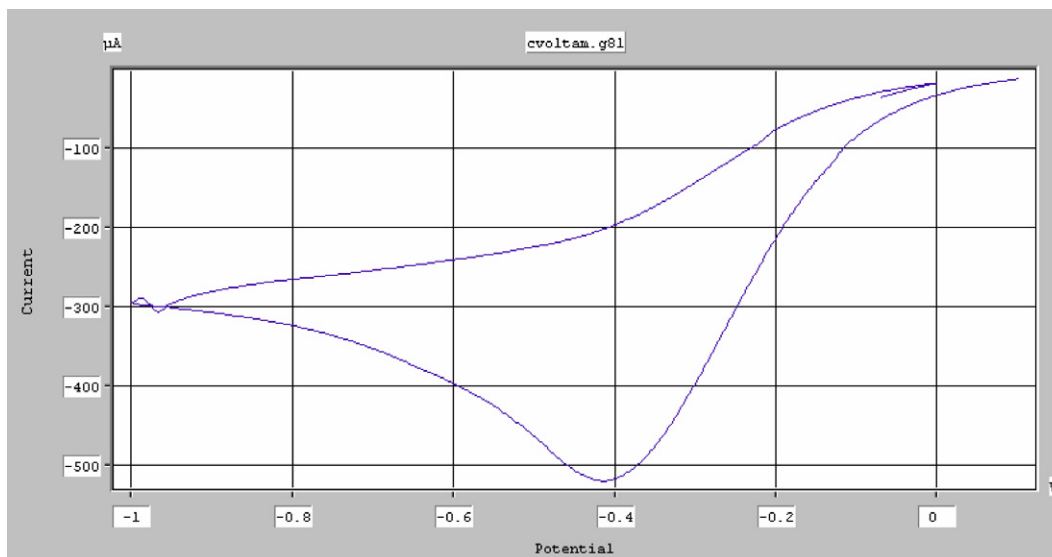


Figure 2. Cyclic voltammetry of 2,2-dibromo-1,3-indandione (**9**) on glassy carbon cathode. $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NBF}_4$ (0.1 M), E versus Ag/Ag^+ .

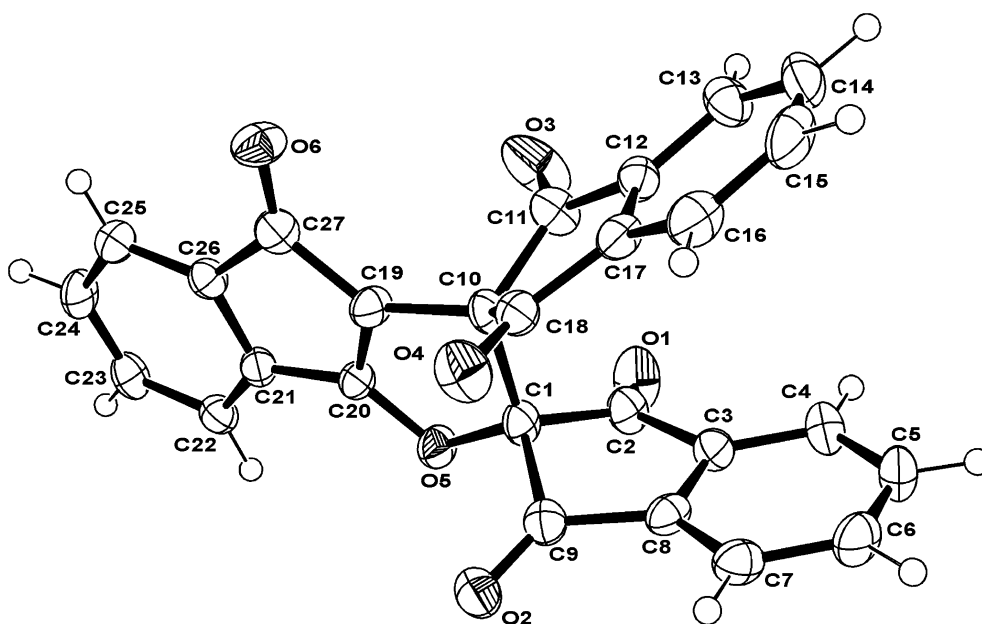


Figure 3. Perspective view of compound **10**. Thermal ellipsoids correspond to 50% probability.

potential of **h**, although close to **9**, should be more negative than it is. To avoid the further electroreduction of **h**, electrolysis of **9** at a constant potential value of -0.2 V (vs Ag/Ag^+) (the voltammogram of **9** shows some reduction current at this potential value) was carried out. Under these conditions compound **10** was again formed, and **h** was not detected.

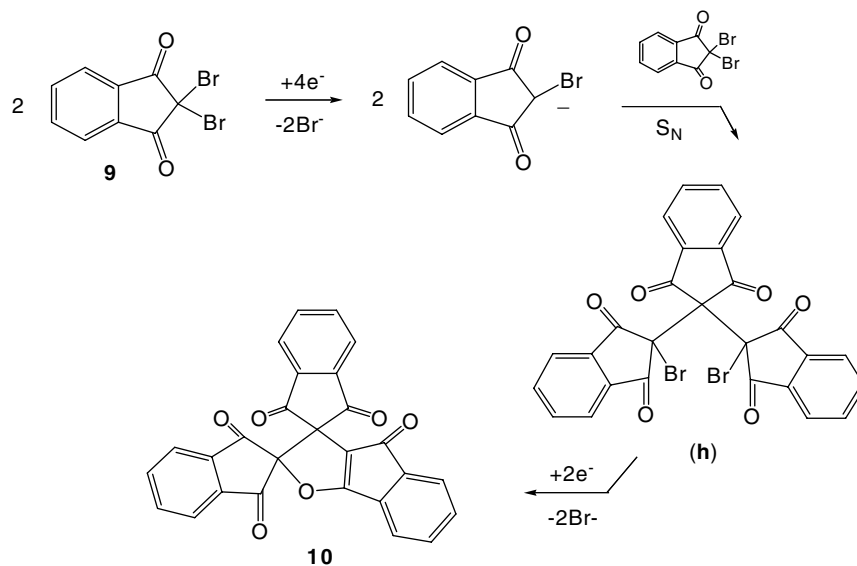
In contrast, the electrolysis of **9** using a graphite cathode and acetonitrile as the solvent allowed the formation of compound **7** according to the MS and NMR spectra.¹⁵

Another mechanism pathway was proposed to explain the formation of **10**. As it is shown in Scheme 5, the implication of a diketocarbene justifies the generation of **7** and **10** (respectively obtained when CH_3CN or

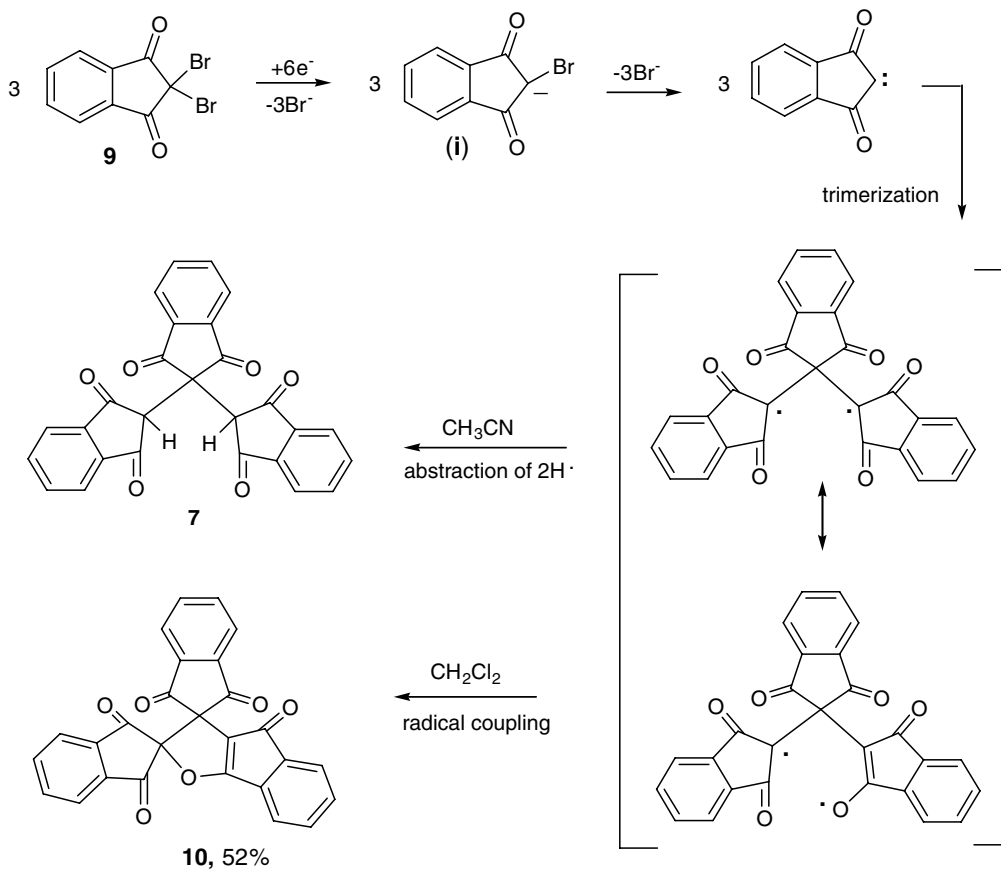
CH_2Cl_2 were employed as the solvent) and it is in agreement with the experimental consumption of charge, corresponding to a $2e^-$ /substrate molecule process.

When acetonitrile is used, radicals are able to abstract H \cdot from the solvent, however with dichloromethane it does not happen. The results obtained in acetonitrile suggest that the bromide evolution from **i** (to get the carbene species) is quicker than the substitution reaction. Besides, electrochemical processes where carbene intermediates are involved have demonstrated that trimerization is favored to dimerization,¹⁶ and in our case no traces of dimer were observed.

The trispirocyclopropane was not formed because both the inherent ring tension and also the hindered effect



Scheme 4.



Scheme 5.

caused by the three indandione groups joined to cyclopropane through spiro carbons. The dihydrofuran formation minimizes the instability.

Finally, it has been observed that **10** in methanol solution can be transformed by sunlight irradiation into **7**, as it was confirmed by MS spectrometry of **10** before and after being exposed to the sunlight.

Crystallography data: Complex **10** crystallized with one molecule of DMF. Data were collected on a Bruker Nonius KappaCCD diffractometer at 200 K, K_{α} (Mo) = 0.71073 Å. The structure was solved, using the WINGX¹⁷ package, by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).¹⁸ X-ray data for $C_{30}H_{19}NO_7$: $0.21 \times 0.16 \times 0.09$ mm³, monoclinic, Cc , $a = 12.487(2)$ Å, $b = 16.180(2)$ Å, $c =$

11.816(1) Å, $\beta = 94.74(1)$, $V = 2379.3(5)$ Å³, $\rho_{\text{calcd}} = 1.411$ Mg/m³. ϕ and ω scans were performed to obtain intensity measurements in the range $6^\circ < 2\theta < 55^\circ$, of the 24395 measured reflections, 2740 were independent; $R_1 = 0.050$ and $wR_2 = 0.098$ (for 1799 reflections with $F > 4\sigma(F)$). Largest difference peak and hole 0.445 and -0.304 e Å⁻³. Hydrogen atoms were geometrically positioned and all non-hydrogen atoms were anisotropically refined.

Acknowledgments

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Supplementary data

Supplementary data (Cif file for compound **10**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.065.

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- Experimental procedure*: The solvents were distilled before use unless state otherwise. Dichloromethane was dried by refluxing over calcium hydride over 2 h and distilled. The electrolyses were carried out using an Amel potentiostat Model 552 with an electronic integrator Amel Model 721. MS spectra (EI, ionizing voltage 70 eV) were determined using a Hewlett–Packard Model 5988A mass-selective detector equipped with a Hewlett–Packard MS Chem Station. IR spectra were obtained, as dispersions in KBr, on a Perkin–Elmer Model 583 spectrophotometer. ¹H NMR (300 MHz) spectra were recorded on a Varian Unity 300 apparatus. The chemical shifts are given in ppm. Melting points were determined on a Reichert Thermovar microhot stage apparatus, and are uncorrected. Cyclic voltammetry were recorded on a VoltaLab PGZ100 using a 0.1 M solution of Bu₄NBF₄ (Fluka)/CH₂Cl₂ as SSE and a Ag/Ag⁺ reference electrode. *Synthesis of 2,2-dibromo-1,3-indandione (9)*: 1,3-Indandione (**1**) (Fluka, 4.37 mg, 30 mmol) was dissolved in glacial acetic acid (Panreac, 50 ml). Bromine (Fluka, 3.2 ml, 62.5 mmol) was dissolved also in acetic acid (20 ml). The bromine solution was added on the 1,3-indandione solution for 30 min with stirring of the mixture. After that time, a pale yellow solid is filtrated and recrystallized with methanol (6.52 mg, 72%). Mp 177–178 °C. ¹H NMR (CDCl₃): $\delta = 7.96$ – 8.02 (2H, m, Ar); 8.0 – 8.1 (2H, m, Ar); [lit. (Kosmrlj, J.; Kocevar, M.; Polancs, S. *Synth. Commun.* **1996**, *26*, 3583): ¹H NMR (CDCl₃): $\delta = 7.9$ – 8.0 (2H, m, Ar); 8.0 – 8.1 (2H, m, Ar)]. MS (EI): m/z (%) = 306 (M⁺+4, 50), 304 (M⁺+2, 100), 302 (M⁺, 49), 226 (21), 224 (20), 197 (30), 195 (29), 169 (56), 167 (57), 104 (21), 76 (25). *Cathodic reduction of 9*: The electrolysis of 2,2-dibromo-1,3-indandione (2 mmol, 0.05 M) was carried out under controlled potential conditions using as a solvent-supporting-electrolyte system Bu₄NBF₄ (0.1 M)/CH₂Cl₂ (40 ml) in a divided cell equipped with a magnetic stirrer containing a piece of glass tubing with a glass frit at one end (anodic compartment). Sodium thiosulfate (2.1 g, 0.14 mmol) was added in the anodic compartment to avoid the evolution of the generated chlorine and bromine. As electrode system, a graphite cathode, platinum anode and Ag/Ag⁺ reference were chosen. The electrolysis was carried at -0.3 V versus Ag/Ag⁺ until the initial current of 200 mA dropped to a residual current of 20 mA. After electrolysis the solvent was evaporated 1/5 under reduced pressure and passed through a filtrating column containing silica gel and eluted with ether to remove the electrolyte. After evaporation of the solvent, chloroform was added. The mixture was introduced in a sonic bath for 2 min and the insoluble yellow solid filtrated. This process was repeated five times and the several filtrated solids were collected to obtain 149 mg (52%) of 2,3-bis(spiro-2-indanyl-1,3-dione)-indeno[1,2-*b*]furan-4-one (**10**), which was crystallized from DMF at low temperature for X-ray crystallography. Mp 248 °C (decomp.), ¹H NMR (DMSO): $\delta = 7.30$ – 7.36 (1H, m, Ar), 7.48 – 7.58 (6H, m, Ar); 7.72 – 7.80 (1H, m, Ar), 7.90 – 8.0 (4H, m, Ar). IR (KBr): $\nu = 1716$, 1603, 1583, 1465, 1405, 1240, 1099, 915, 768. MS (EI): m/z (%) = 434 (M⁺+2, 6), 433 (M⁺+1, 18), 432 (M⁺, 62), 348 (35), 263 (20), 187 (21), 104 (71), 76 (100).
- ¹³C NMR was not possible to record because DMSO decomposes compound **10** in the time scale of the experiment.
- ¹H NMR of **7** (CDCl₃) $\delta = 5.45$ (2H, s, CH), 7.86 – 8.03 (12H, m, Ar). MS of **7** (EI): m/z (%) = 436 (M⁺+2, 1), 435 (M⁺+1, 6), 434 (M⁺, 20), 390 (15), 389 (53), 290 (29), 289 (11), 189 (14), 146 (12), 105 (28), 104 (100), 77 (33), 76 (83).
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