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The First Spiroconjugated TTF- and TCNQ-Type Molecules: A New Class of Electroactive Systems?

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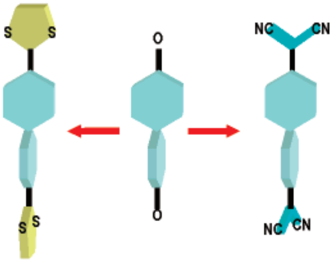
ABSTRACT



Spiroconjugated TTF-type electron donors (13a–c) and TCNQ-type electron acceptors (10, 11) have been prepared from spiroquinone 9. Cyclic voltammetry reveals a relatively weak accepting ability for 10 and 11, and a strong electron-donor character for 13a–c. Whereas the spiroconjugation introduces a destabilization of the LUMO for compounds 9–11, the opposite is observed for compound 13, thus justifying the redox potential values.

The rational design of new organic materials exhibiting nonconventional optoelectronic properties is based on the synthesis of molecules with appropriate geometrical and electronic structures.[1] In this context, most of the electron donors (tetrathiafulvalene, TTF, and its derivatives such as BEDT-TTF)[2] and electron acceptors (tetracyano-*p*-quinodimethane, TCNQ, and quinones)[3] reported in the literature are mainly concerned with conjugated planar molecules. These planar electroactive systems play an outstanding role in the field of organic conductors forming charge transfer (CT) complexes and salts with conducting and superconducting properties.[4] The CT complex TTF-TCNQ is considered the pioneer compound that paved the way for the field of molecular organic conducting materials.[5]

Typically, these electroactive derivatives give rise to quasi one-dimensional CT complexes when they form segregated stacks. Substitution of sulfur by selenium or tellurium atoms on the TTF skeleton,[6] the presence of chalcogen atoms on the periphery of the TTF molecule,[7] and the existence of

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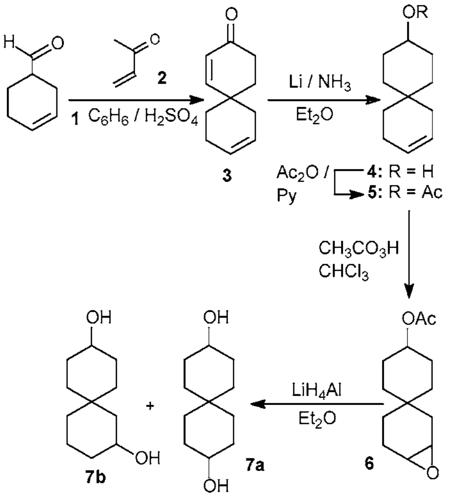
hydrogen bonds[8] have been used to increase the dimensionality of the donor partner. On the acceptor side, substitution on the central ring as well as coordination of the nitrogen atoms of the cyano groups to metal atoms have afforded the formation of multidimensional networks.[3,9]

Another interesting and much less studied approach to increase dimensionality is based on the spiroconjugative effect.[10] Although the interest of spirocompounds has focused on aspects such as conformational transmission, helical structure, or photochromism,[11] there are only a few examples in the literature in which spiroconjugation has been used to prepare electroactive molecules.[12] In this paper we describe the first examples of spiroconjugated analogues of TCNQ (**10**) and DCNQI (**11**) acceptors, as well as analogues of TTF (**13a−c**) (Scheme 3). The multistep synthetic procedure and the spectroscopic and electrochemical characterization are now reported.

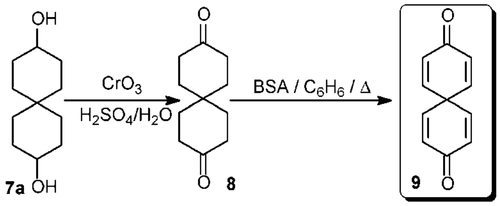
The preparation of spiro[5,5]undecatetraenedione (**9**) was carried out by following an improved version of the procedure reported by Farges et al.[13] A full characterization of the intermediate compounds, which were not totally characterized in the prior work, is also provided (see Supporting Information). Creation of the spirane system takes place in the first synthetic step by Michael addition of 1,2,5,6-tetrahydrobenzaldehyde (**1**) to methylvinyl ketone (**2**) and subsequent intramolecular aldol reaction to yield **3**. Birch reduction of ketone **3** yielded alcohol **4**, whose acetylation followed by treatment with peracetic acid gave rise to epoxide **6**. Reduction of **6** with $LiAlH_4$ led to a mixture of alcohols (**7a** and **7b**), which were separated by several careful chromatographies. Diol **7a** was submitted to oxidation by treatment with Jones' reagent to afford spirodione **8** (Schemes 1 and 2).

Scheme 1



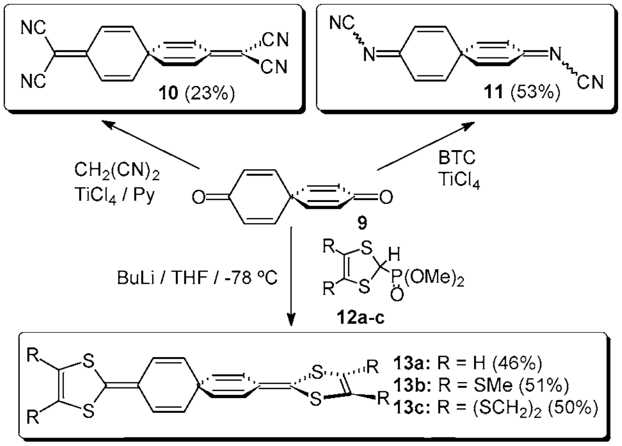
Oxidation of spiro[5,5]undecan-3,9-dione (**8**) to **9** was a hard task. We first used the conditions followed by Farges et al.,[13] who claimed to obtain **9** in 34% yield by treatment with dichlorodicyano-*p*-benzoquinone (DDQ). In our hands, reaction of **8** under the same reaction conditions or modifying the solvent, temperature, and reaction time was unsuccessful. Attempts to obtain **9** using different oxidants such as Br_2/py, NBS/AIBN, and SeO_2 were fruitless. Finally, compound **9** was prepared in 21% yield by oxidation with an excess of benzeneseleninic anhydride (BSA) by refluxing for 4 days (Scheme 2).

Scheme 2



The synthesis of the target spiro-donor and acceptor molecules is depicted in Scheme 3. The spiroanalogue of TCNQ (**10**) was prepared from **9** by reaction with Lehnert's reagent (malononitrile, $TiCl_4$, pyridine).[14] It is interesting to note that this reaction proceeds cleanly without competitive nucleophilic attack of the anion of malononitrile to the conjugated olefinic carbons.

Scheme 3



The spiro DCNQI analogue **11** was synthesized from **9** by following Hünig's procedure,[15] by reaction with bis(trimetrylsilyl)carbodiimide (BTC) and $TiCl_4$ (Scheme 3). In contrast to compound **10**, the ^1H NMR spectrum of **11**

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presents a broad doublet at δ 6.46−6.43 corresponding to the four hydrogens adjacent to the spiro carbon. Now, the four hydrogens close to the cyanoimino groups are not equivalent and appear as two broad doublets at 7.24−7.20 and 6.79−6.55 ppm due to the presence in solution of both *syn* and *anti* isomers. This *syn/anti* isomerism is well-documented in DCNQ and is due to the flipping of the cyano groups attached to nitrogen atoms.[16]

The TTF-type spiro compounds **13a**−**c** were synthesized by Wittig−Horner reaction of the carbanion generated in situ from phosphonate esters (**12a**−**c**),[17] in the presence of *n*-BuLi at −78 °C, with dione **9** (Scheme 3). The analytical and spectroscopic data clearly support the proposed structures (see Supporting Information).

The redox properties of the novel spiro derivatives were determined by cyclic voltammetry (CV) measurements recorded at room temperature. The data obtained are collected in Table 1 together with the redox potentials measured for **9** and for the parent compounds TTF, TCNQ, and DCNQI. The quinone-type spiro compound **9** shows only one irreversible reduction wave at −1.94 V. This value is higher than that measured for *p*-benzoquinone (−0.60 V), suggesting a weak electronic interaction between the two cyclohexenone rings. Spirocompounds **10** and **11** show a stronger electron-acceptor character as a result of the presence of the dicyanomethylene and cyanoimino groups, respectively, which significantly shift the reduction potentials toward less negative values (see Table 1 and Figure 1).

Table 1. Redox Potentials of the Novel Spiro Donor and Acceptor Molecules[a]

compound[b]	$E^1_{\mathrm{red\ (pc)}}$	$E^2_{\mathrm{red\ (pc)}}$	$E^1_{\mathrm{ox\ (pa)}}$	$E^2_{\mathrm{ox\ (pa)}}$
9	−2.07 (−1.94)[c]			
10	−0.89 (−1.09)[c]	−1.28 (−1.47)[c]		
11	−1.03	−1.50		
TCNQ	0.22	−0.35		
DCNQI	0.21	−0.41		
13a			0.55	1.03
13b			0.66	1.09
13c			0.60	0.98
TTF[d]			0.44	0.77

[a] Experimental conditions: GCE as working electrode, $NBu_4^+ClO_4^-$ (0.1 M) as supporting electrolyte. [b] V vs SCE, CH_2Cl_2, 200 mV/s. [c] V vs Ag/Ag^+, CH_2Cl_2, 100 mV/s. [d] Anodic peaks

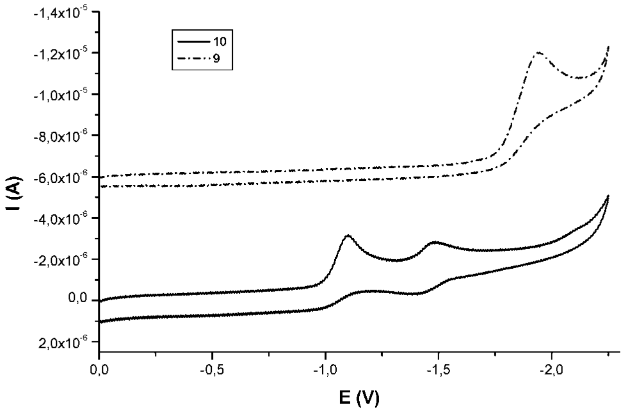

Figure 1. CVs for compounds **9** and **10** measured in CH_2Cl_2 at room temperature (V vs Ag/Ag^+; 100 mV/s).

It is well-established that TCNQ and DCNQI present a similar electrochemical behavior showing two one-electron, reversible reduction waves to the corresponding radical anion and dianion species.[3] The spiro analogues **10** and **11** exhibit a first irreversible reduction wave followed by a second reversible wave (Table 1 and Figure 1). The reduction potentials are cathodically shifted by about 1 V with respect to the values measured for the parent TCNQ and DCNQI and are in the range of those shown by some quinone acceptors such as 9,10-anthraquinone derivatives ($E^1_{\mathrm{red}} \approx -0.9$ V vs SCE).[18]

The novel spiro donor molecules **13a**−**c** show oxidation potentials slightly more positive than those of the parent TTF and quite similar to the well-known BEDT-TTF ($E^1_{\mathrm{ox}} \approx 0.6$ V vs SCE),[2] thus exhibiting a strong electron-donor character. However, the CV measurements are accompanied by an immediate darkness of the solution, which apparently indicates an extensive decomposition process due to the electrochemical instability of the oxidized species. This finding is in agreement with the irreversible character observed for the first oxidation wave in **13a**−**c**.

Compounds **13a**−**c** show a similar behavior. In the first scan, they exhibit an irreversible oxidation wave (~0.6 V), which should be reasonably attributed to the generation of the radical cation. This wave could also correspond to the formation of a diradical dication, in which the two orthogonal dithiole moieties were simultaneously oxidized to a radical cation in a manner similar to that found for some π-extended TTF derivatives.[19] In the following scans, a progressive lowering of the first oxidation wave is observed and a second oxidation wave appeared at more positive potentials.

The above electrochemical behavior suggests an ECE (electrochemical-chemical-electrochemical) process as has

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been previously reported for other dithiafulvene derivatives.[20] The mechanism of dimerization of 1,4-dithiafulvenes into TTF vinylogues has been well established by Hapiot et al.[21] and later skillfully used by other authors to obtain TTF-based dimeric or polymeric species.[22] These electrochemical coupling processes are associated to a high electronic density of unpair electrons at the vinyl carbon in the radical cation, as it could occur in compounds **13a**−**c**.

The electronic structures of compounds **9**, **10**, and **13a** were theoretically investigated at the B3LYP/aug-cc-pVDZ level.[23] The LUMO orbital is doubly degenerate for the electron acceptors **9** and **10** (see Figure 2). The energies calculated for this orbital (**9**, −2.53 eV; **10**, −3.78 eV) are higher than those obtained for *p*-benzoquinone (−3.92 eV) and TCNQ (−5.12 eV). Spiroconjugation therefore introduces a destabilization of the LUMO of 1.3−1.4 eV that justifies the large cathodic shift recorded for the reduction potentials of **9** and **10** (see Table 1). For the electron donors **13**, the effect of spiroconjugation on the HOMO orbital is completely different. The HOMO of **13a** is calculated at −4.97 eV, slightly more stable than the HOMO of TTF (−4.83 eV) and close to the HOMO of BEDT-TTF (−4.98 eV). These values explain the fact that **13a**−**c** exhibit electron-donor strengths slightly weaker than that of TTF and similar to BEDT-TTF.

Figure 2. Electron density contours showing the degenerate nature of the LUMO of compound **9** (D_{2d} symmetry).

Upon reduction of **9** and **10**, the first electron enters in one of the degenerate LUMO orbitals, giving rise to a dissymmetric C_{2v} radical anion, in which the charge and the unpaired electron are located over one of the π-subsystems while the other remains mostly neutral. For **10**, the charges accumulated by each subsystem are −0.85 and −0.15 e, respectively. This result agrees with the localization of the spin density on one dienone moiety evidenced for **9**$^-$ from ESR measurements.[24] The entrance of the second electron occurs on the second LUMO orbital, and calculations indicate that the **10**$^{2-}$ dianion consists of two orthogonal radical anion subsystems bearing identical charges and spin densities. Oxidation of **13a** takes place in a similar way. The first electron is removed from one of the degenerate HOMOs, forming a localized radical cation, and the extraction of the second electron leads to two identical radical cation subsystems.

In summary, the first examples of spiroconjugated TTF-type electron donors (**13a**−**c**) and TCNQ- and DCNQI-type electron acceptors (**10**, **11**) have been synthesized from spirodione **9**. The electrochemical study reveals a relatively weak electron acceptor character in **10** and **11** and a strong donor ability of **13a**−**c**, similar to BEDT-TTF. However, in contrast to the parent TTF, the novel donors **13a**−**c** are electrochemically unstable, leading upon oxidation to unknown electrochemically active species. Work is currently in progress to determine the degree of electronic interaction through the spiro connectivity in the novel electroactive systems, as well as their potential application as building blocks in molecular materials science.

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Supporting Information Available: Experimental details and spectroscopic characterization of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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