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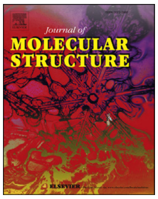

TTF derivative of 2,5-aromatic disubstituted pyrrole, synthesis and electronic study

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ABSTRACT

TTF derivative of substituted pyrrole was obtained by means electrochemical synthesis, the resultant colored mix was characterized by Mass spectrometry, NMR and EPR studies, its intrinsic electronic behavior was measured by a four point probe method, besides theoretical calculations were carried out on the possible structures of the resultant molecular adduct. All the results show that there is a net transfer of an electron between both organic moieties in solution giving place to a semiconductor species.

1. Introduction

The study of electronic materials has been growing and opening new important areas [1–3], the study of this kind of compounds takes account mainly on the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels and the orbital interactions. These last interactions are fundamental for the communication between two different pair of molecules that can show interesting electronic interchanges [4].

The combination of TTF (tetrathiafulvalene) (Fig. 1) with several organic molecules showing electron donor-acceptor and charge transfer complexing abilities has given place to several interesting chemical mixes with important semiconducting behavior [3–7].

TTF molecule is known since 1970 [8–10] and one of the groups interested in its synthesis was the one to find the very important redox behavior of this substance [10]. The authors [10] suggest for the first time that the molecule can reach an aromatic situation on the consecutive lack of two electrons (Fig. 2), therefore, this ion can interact with an electron acceptor counterpart in such a way that the HOMO of TTF and the LUMO of the other species give place to an electronic flux making a redox complex with semiconductor behavior. One of the most studied pairs is that in which TTF interacts with TCNQ [11] which has demonstrated a very good organic semiconductor behavior; however, this is only one example of a large quantity of combinations with interesting electronic characteristics [12].

In other context, the synthesis, characterization and study of the semiconductor behavior of 2,5-aromatic disubstituted pyrrole derivatives have been an interest of our research group [13]. These studies have yielded interesting results in which the importance of the substituent of the aromatic ring joint to the nitrogen atom of the pyrrole unit have been established as a promotion agent of semiconductor behavior.

The goal of this work is to show the nature of the redox complex arising from the interaction among pyrrole derivative and TTF in order to get semiconductor species. The method of electrochemical synthesis, the characterization by several spectroscopic techniques and the study of conductivity are included. A theoretical study of the interaction between TTF and one of the derivatives (the one with the $-NO_2$ substituent) is also shown, the results show a very interesting pathway of electronic promotion and give a chance

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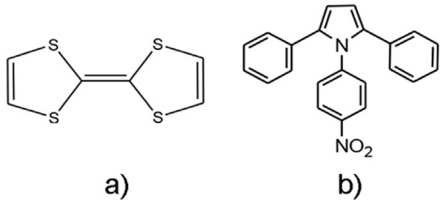


Fig. 1. Molecular structures of TTF (a) and 1-(4-nitrophenyl)-2,5-diphenyl-pyrrole (b) studied in this work.

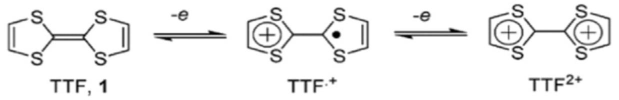


Fig. 2. TTF redox transformation.

for other kind of studies which have started in our group and will be reported in short time.

2. Experimental part

2.1. Synthesis

The synthesis and characterization of 1, 4-diphenylbuta-1, 3-diyne (compound 1); 1-(p-nitro-phenyl)-2, 5-triphenylpyrrole (compound 2) and 1-(p-carboxy-phenyl)-2,5-triphenylpyrrole (compound 3) have been recently described [13,14].

2.2. Electrochemical synthesis

Voltammetric analysis of fresh solutions of substrates, TTF and 1-(4-nitrophenyl)-2,5-diphenylpyrrole, in order to determined the electrochemical oxidation properties prior to bulk electrolysis, was carried out.

Pure acetonitrile, AN, (AR grade) dried over molecular sieves was used as solvent. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP, reagent grade), dried at 90 °C overnight before use. As working electrode a platinum disk microelectrode of about 0.031 cm^2 was used. A silver wire immersed in a solution of 0.01 mol/L in $AgNO_3$ was used as quasi-reference electrode. The silver reference potential according to couple ferrocene/ferricinium was 0.4V. A great surface Au foil is used as auxiliary electrode. Constant potential bulk electrolysis was performed in a 50 mL electrolytic cell using a great surface platinum plaque of about 20 cm^2 with constant stirring using a fresh solution containing 1 mM of compounds 1-(4-nitrophenyl)-2,5-diphenylpyrrole and TTF in presence of TBAP 1 mM as well.

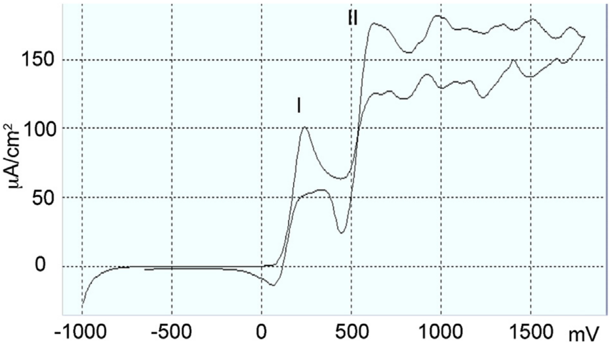


Fig. 5. Voltammetric behavior of compound **4** (TTF), (1 mM), $v = 10$ mV/s, at platinum disk in 0.1 M TBAP in acetonitrile. I: TTF $- 1e^- \rightarrow$ TTF^+; II: $TTF^+ - 1e^- \rightarrow TTF^{2+}$.

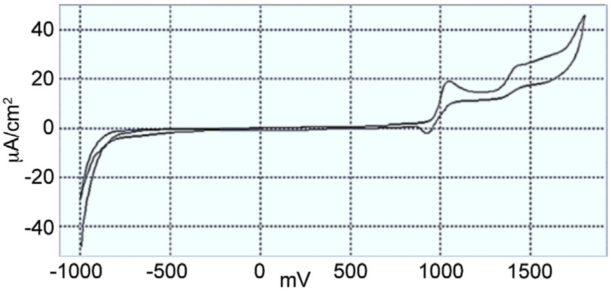


Fig. 6. Voltammetric behavior of compound **2**, (1 mM), $v = 10$ mV/s, at platinum disk in 0.1 M TBAP in acetonitrile.

The cells were maintained in a pure nitrogen atmosphere at all times. Voltammograms and chronoamperometric bulk electrosynthesis were obtained with a DEI-digital electrochemical analyzer (Radiometer-Tacussel).

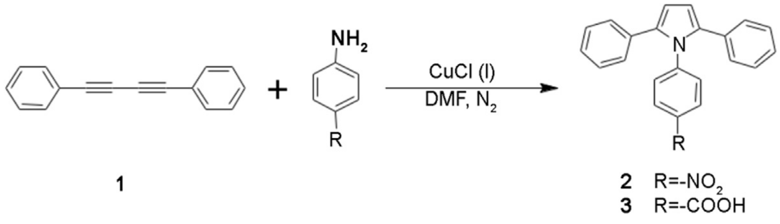


Fig. 3. Chemical reaction of diphenylacetylene with different amines used to obtain the pyrrole derivatives.

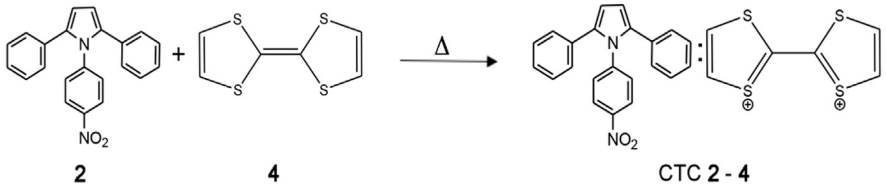


Fig. 4. Proposed reaction of formation of CTC **2**–**4**.

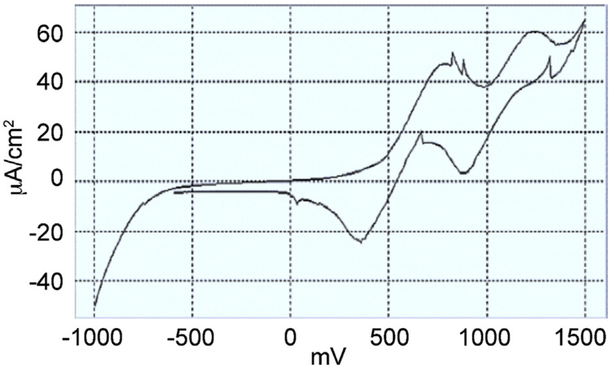


Fig. 7. Voltammetric behavior of compounds **2** and **4** (TTF), (1 mM each), $v = 10$ mV/s, at platinum disk in 1 mM M TBAP in acetonitrile, *before bulk electrolysis.*

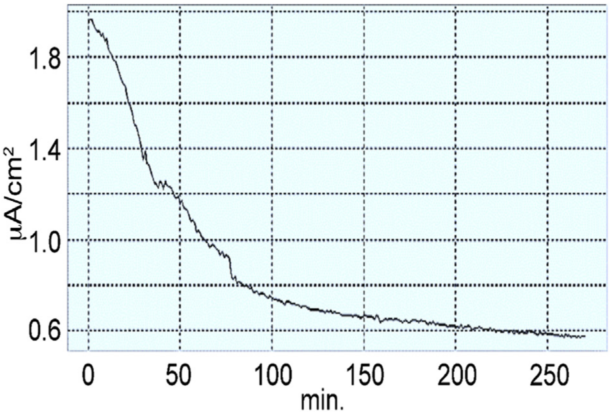


Fig. 8. Chronoamperometric plot during bulk electrolysis of compounds **4** (TTF) and **2**, 1 mM each, at platinum plate in 1 mM M TBAP in acetonitrile. The color solution changes from orange to deep red.

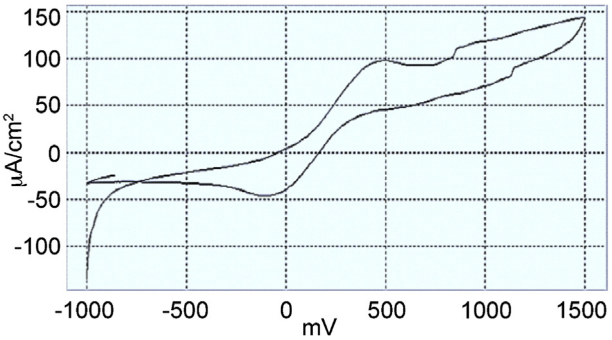


Fig. 9. Voltammetric behavior of compounds **2** and TTF (**4**) (1 mM each), $v = 10$ mV/s, at platinum disk in 1 mM M TBAP in acetonitrile, *after 250 min bulk electrolysis.*

2.3. Computational details

All calculations were carried out using a pure DFT method for energy evaluations, and it was applied Becke's gradient corrections [15] for exchange and Perdew-Wang's for correlation [16]. This scheme gives place to the B3PW91 method which forms part of the Gaussian09 code [17]. All calculations were performed using the 6-31G** basis set. Frequency calculations were carried out at the same level of theory to confirm that the optimized structures were at a minimum of the potential surfaces.

3. Results

3.1. Synthesis

The diacetylenic molecule 1,4-diphenylbuta-1,3-diyne (**1**) (see Fig. 3) was prepared following the Glaser method taking into account the modification of Hay [18,19] which considers the oxidative coupling of terminal alkynes with cooper salts as catalysts and a bidentate ligand, TMEDA, in the present particular case.

As shown in Fig. 3, 1-(p-nitro-phenyl)-2,5-triphenylpyrrole (**2**) and 1-(p-carboxy-phenyl)-2,5-triphenylpyrrole (**3**) were synthesized by the reaction of diphenyldiacetylene with different aromatic amines employing copper chloride (I) as catalyst, the synthesis and characterization of these compounds have been recently described [13,14]. These compounds were obtained by a modification of a reported procedure [20].

3.2. Electrochemical synthesis

The proposed electrochemical reaction is shown in Fig. 4.

The idea is to reach the two oxidative potentials of compound **4** (TTF) in order to share both resultant electrons with molecule **2**. It is known the large capability of compound **4** to form free radicals [8], this characteristic made it a very popular generator of stable conductor systems [3,12]. On other context, compound **2** can have acceptable reduction potentials [13], therefore, the combination of both species is promising to get interesting electronic interactions.

Therefore, the idea is to prepare a transfer charge complex between compounds **2** and **4**, in a first step, a voltamperometric study of both compounds was carried out in order to determinate the nature and potentials for each participant in the reaction, after the compounds were mixed and the electrosynthesis was carried out by means the chronoamperometric technics. The cyclic voltamperograms of **4** and **2** compounds are shown in Figs. 5 and 6, respectively; the potential scan was from −1000 to 1800 mV vs an Ag/AgCl electrode and the solvent was anhydride acetonitrile.

Fig. 5 shows the voltammetric behavior, at 10 mV/s, of compound **4**, TTF (1 mM), on platinum in 0.1 M TBAP in AN. From this figure it is observed that TTF presents two oxidation peaks and two corresponding reduction peaks in the reverse scan, with a relative quotient (Ip^c/Ip^a) ≅ 1. The latter behavior suggests two mono-electronic quasi-reversible oxidation processes according to:

$$\text{I/}\quad \text{TTF} - 1e^- \rightarrow \text{TTF}^+ \quad Ep_I^a = 0.258\ \text{V}$$

$$\text{II/}\quad \text{TTF}^+ - 1e^- \rightarrow \text{TTF}^{2+} \quad Ep_{II}^a = 0.629\ \text{V}$$

A ($Ep^a - E_p^c$) = 0.173 V for both oxidation–reduction processes shows that the cation TTF$^+$ electrogenerated is stable enough in solution as well as the second cation observed, TTF^{2+}.

Fig. 6 shows the voltammetric behavior, at 10 mV/s, of compound **2**, 1 mM, on platinum in 0.1 M TBAP in AN. From this figure it is observed that compound **2** presents one oxidation peak, $Ep^a = 1.04$ V, and a corresponding reduction peak, $Ep^c = 0.90$ V, with a relative quotient (Ip^c/Ip^a) ≅ 1. The latter behavior suggests a mono-electronic quasi-reversible redox that shows that the reduced form of compound **2** is stable in the oxidation range of TTF.

Fig. 7 shows the voltammetric behavior, at 10 mV/s, of the mixture of compound **4** (TTF), and compound **2**, both 1 mM, on platinum in 1 mM TBAP in AN prior to bulk electrolysis. From this figure it is observed that the voltammetric profile is strongly modified since de first oxidation peak of TTF, Ep_I^a, is displaced from 0.258 mV to 0.786 V as well as for the second oxidation peak, Ep_{II}^a, is displaced from 0.629 V to 1.24 V. The corresponding reduction peaks are also modified since ($Ep^a - E_p^c$) = 0.173 V is increased to A

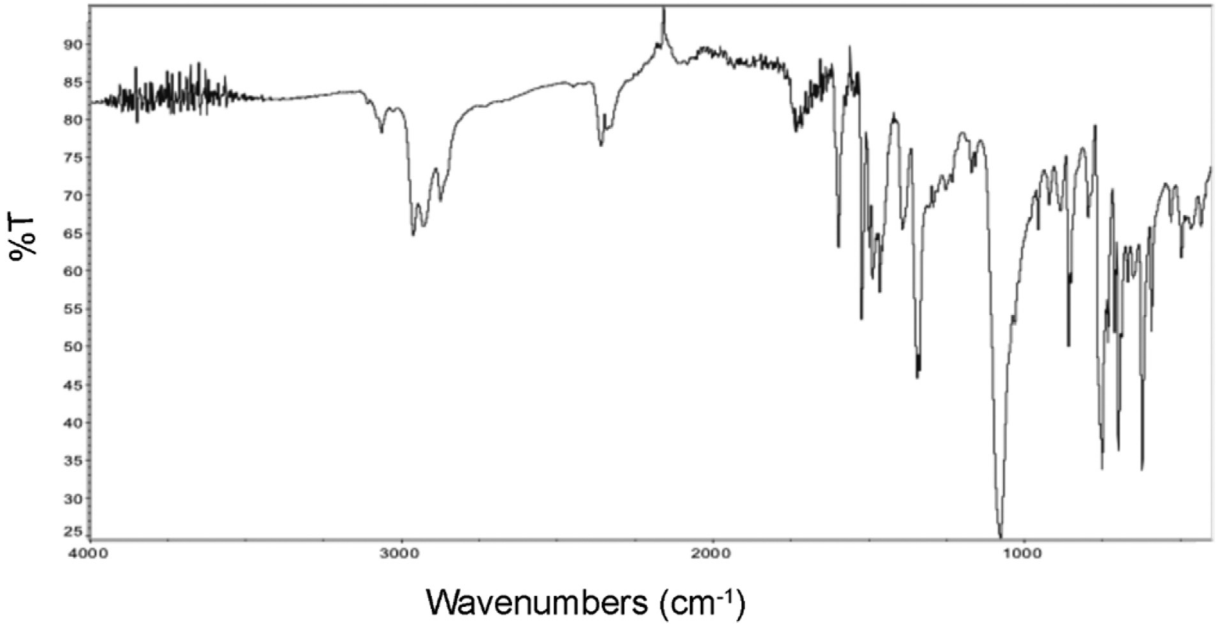


Fig. 10. Infrared spectrum of CTC **2**–**4**.

$(Ep^a - E_p^c) = 0.400$ V. The latter behavior strongly suggests chemical interactions between substrate **2** and TTF (**4**) previous to bulk electrolysis.

The latter solution is submitted to bulk electrolysis on a great platinum plate with strong stirring. Electrolysis current is measured with respect to time imposition of = 1.00 V with respect to the silver quasi-reference electrode. Electrolysis is stopped after 250 min of potential imposition. The orange color of the initial mixture of compounds **2** and TTF (**4**) changes to deep red at the end of the bulk electrolysis procedure.

Fig. 8 shows the typical chronoamperometric plot during the bulk electrolysis. The latter plot shows that exhaustive electrolysis was achieved.

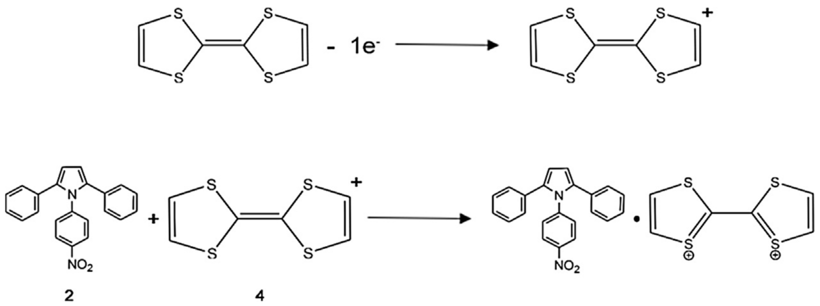
Fig. 9 shows the voltammetric behavior, at 10 mV/s, of the mixture of TTF (**4**) and compound **2**, both 1 mM, on platinum in 1 mM TBAP in AN after 250 min of bulk electrolysis. From this figure it is observed that the voltammetric profile is strongly modified since only de first oxidation peak of TTF is observed. The $(Ep^a\text{-} E_p^c) = 0.173$ V of the original electrochemical oxidation of TTF is strongly increased until $(Ep^a\text{-} E_p^c) = 0.554$ V.

Since the first oxidation of TTF is the electrochemical process that leads the whole mechanistic reaction between compound **2** and TTF (**4**), a electrochemical mechanism of the type E_rC_r is proposed where TTF^+ is stabilized by the presence of compound **2** according to scheme:

3.3. Spectroscopic analysis

The IR spectrum of charge transfer complex of compounds **2** and **4** (TTF) is shown in Fig. 10. Unfortunately, the counterion found in the environment (tetrabutylammonium perchlorate (TBAP)) is present and its bands appear also in the analysis, however, the corresponding IR spectrum of this substance (TBAP) (see Fig. 11) can be subtracted from the total and the important peaks at 2980, 2950, 1370 cm^{-1} coming from the complex can be appreciated. The ^1H NMR of CTC **2**–**4** (see Figs. 12 and 13) shows the corresponding peaks for compound **2**, but there are no evidence of the protons of the compound **4**, this feature arises from the dicationic nature of the TTF^{++} which makes so strong the magnetic moment of the ion, however, the signal of compound **4** appears in the ^{13}C spectrum together with the corresponding signal of the compound **2** (see Figs. 14 and 15).

The EPR spectrum is shown in Fig. 16, whereas the hyperfine structure of the same is shown in Fig. 17. This analysis gives better evidences of the formation of the charge transfer complex because is very clear the presence of the free radical with a g value of 2.0068, but even the hyperfine analysis shows the presence of the other electron and the interaction of it with the one localized on the charge transfer complex, the couples constant is 0.145 mT and the corresponding g is 2.00882. The free electron of the complex is localized on the aromatic ring which supports the $-NO_2$ functional



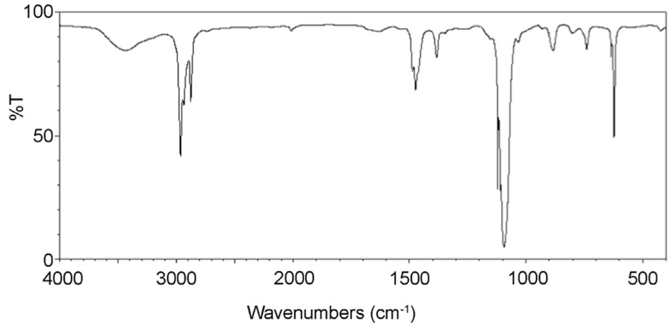


Fig. 11. Infrared spectrum of tetrabuthylammonium perchlorate (TBAP).

group of the pyrrolic counterpart because the number of lines is obtained by means:

$$\eta = 2\,nl + 1$$

where n is the number of neighbors with no cero spin and l is the magnitude of an individual spin, substituting n = 4 (i.e. the four hydrogens of the mentioned aromatic ring) and l = 1/2, the result corresponds with the five lines in the hyperfine spectrum, these results match with the corresponding theoretical simulation which localize the LUMO on the same region of compound **2** and can reproduce a very similar spectra. With the respect of the theoretical simulation mentioned above, the results of this were compared with the experimental spectrum as well as a simulation obtained from the spectrophotometer software in which the experimental data were supplied, the result of these comparisons is shown in Table 1.

This analysis is the better evidence of the formation of the charge transfer complex. However, the electronic spectra and other theoretical calculation were carried out in order to assure the nature of the resultant complex and the transfer of the electron involved in this complex itself. This analysis is shown below in the next section.

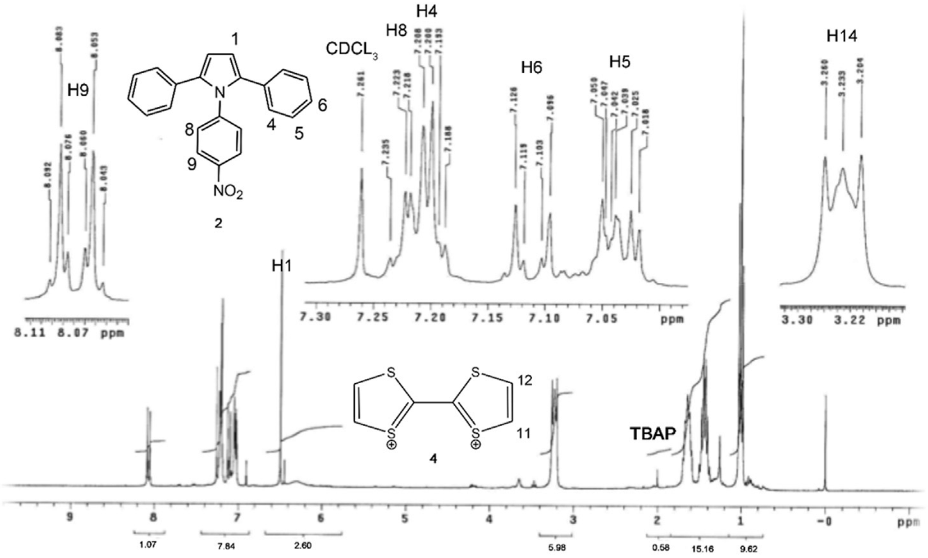


Fig. 12. ^{1}H NMR spectrum of CTC **2**–**4**.

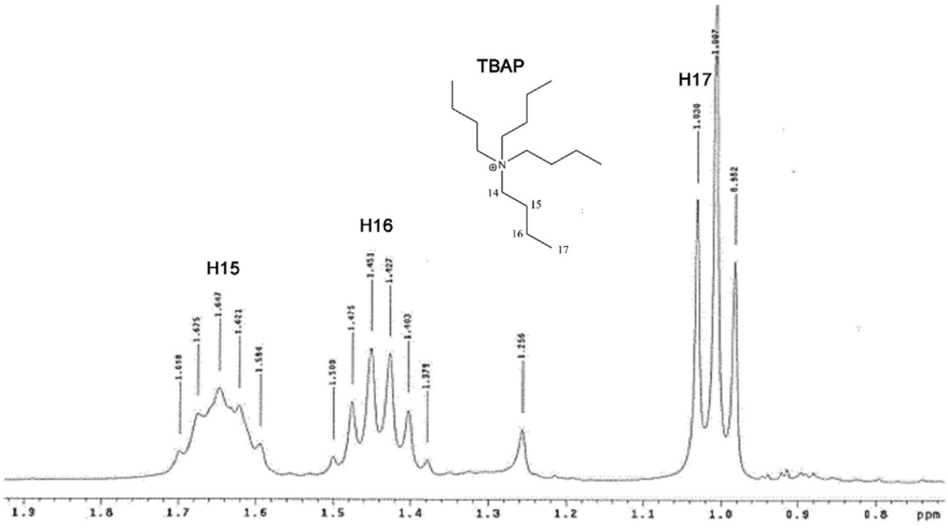


Fig. 13. Expansion of ^{1}H NMR spectrum of CTC **2**–**4** from Fig. 12.

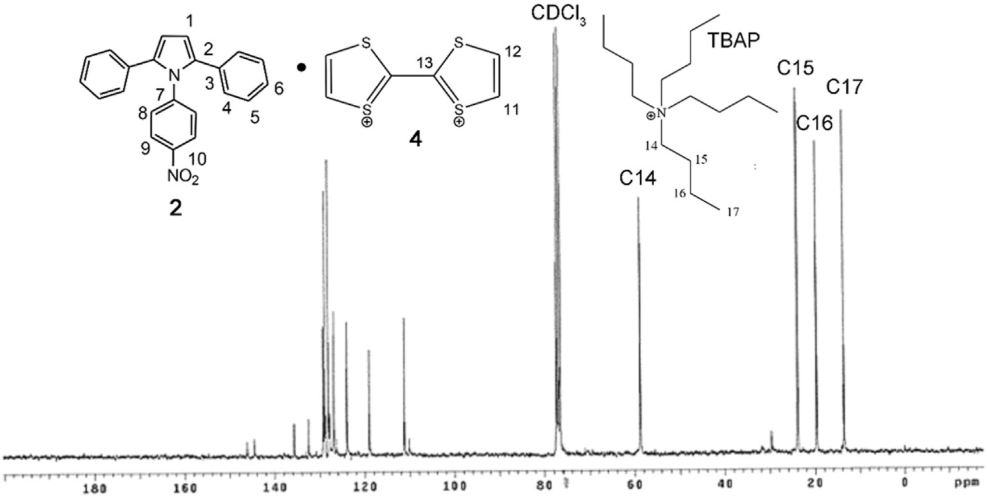


Fig. 14. ^{13}C NMR spectrum of CTC **2**–**4**.

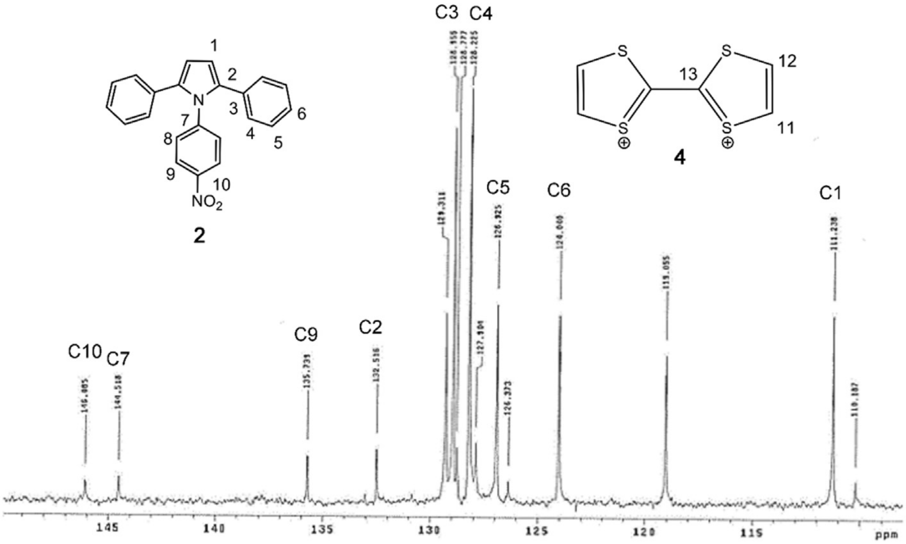


Fig. 15. Expansion of ^{13}C NMR spectrum of CTC **2**–**4**.

3.4. Electronic spectroscopy, conductivity and theoretical calculations

The UV–Visible spectra of the compounds was achieved, it is shown in Fig. 18. The important point is that the main absorption band is localized at 294 nm (4.21 eV), this value is compared with those obtained by means the theoretical calculations which corresponds to the energy gap between HOMO and LUMO which yields 3.89 eV, the matching is very good even considering that the spectrum was captured in chloroform solution and it is considered

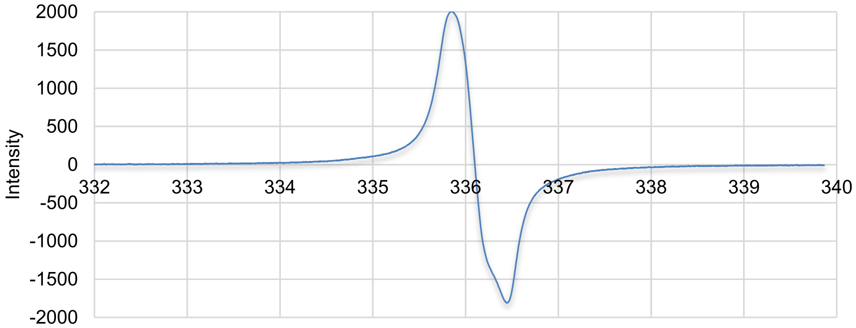


Fig. 16. EPR spectrum of **2**–**4**.

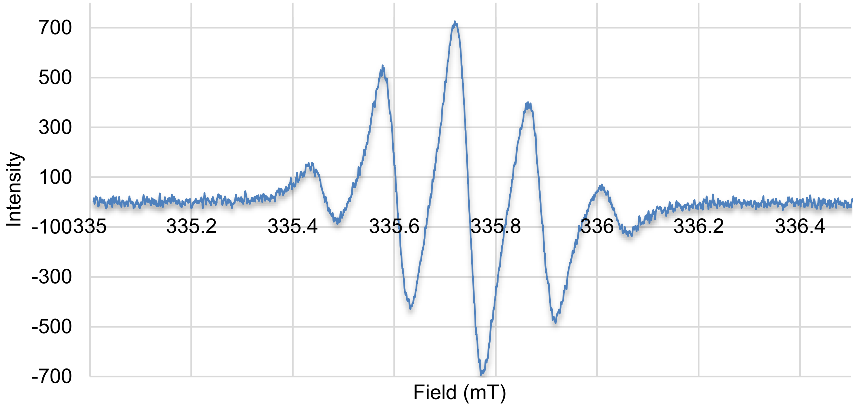


Fig. 17. Hyperfine structure of CTC **2**–**4**.

Table 1
Comparison of parameters experimental EPR analysis and theoretical and experimental simulations.

Parameters measured/simulated	Experimental	Theoretical simulation	Experimental simulation
Number of equivalent atoms	4	4	4
Spín	0.5	0.5	0.5
Factor g	2.00882	2.0088	2.0088
Coupling constant (mT)	0.145	0.150	0.142
Peak broad (mT)	0.089	0.09	0.09
Central signal (mT)	335.747	335.75	335.748

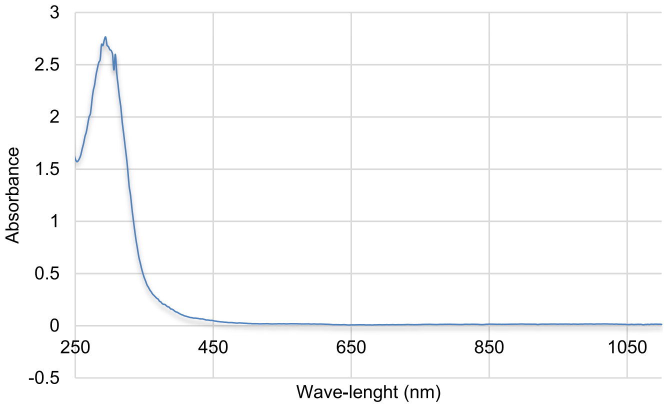


Fig. 18. UV–Visible spectrum of CTC **2**–**4**.

that the calculated molecule is placed in vacuum.

Table 2 shows the eigenvalues of the frontier molecular orbitals of both studied derivatives of pyrrole, in both cases the values correspond to the classification of semiconductors, in fact, the present study contains conductivity measurements which will be discussed below. In the same table is registered the corresponding band gap value of the charge transfer complex, the value is 4.6 eV, but this result even being classified as an insulator should be handled with care because it is a salt susceptible to narrow its gap in solution or by means a dopant agent. The interaction of both moieties of the complex was also simulated, Fig. 19 show it, the schemes b) and c) show the shape of the HOMO and LUMO respectively making emphasis on the strong division of the molecular orbitals on each part of the complex, i.e. the HOMO distributed on all the surface and the LUMO focused on the pyrrole derivative moiety.

Table 3 shows the conductivity of both pyrrole derivatives **2** and **3**, the measurements were carried out by means the four point probe.

4. Conclusions

In this work, the synthesis and characterization of organic compounds containing 2,5-disubstituted pyrroles were carried out. These compounds were the 1-(4-nitrophenyl)-2,5-diphenylpyrrole and 1-(4-carboxyphenyl)-2,5-diphenylpyrrole. There are previous reports of their synthesis by our group.

We also conducted the synthesis and characterization of CTC formed by 1-(4-nitrophenyl)-2,5-diphenylpyrrole and tetrathiafulvalene (TTF) (which has no previous reports in literature) by electrochemical method. The results of the characterization of the CTC synthesized show that the compounds involved share an electron from the TTF that migrates to the structure of 1-(4-nitrophenyl)-2,5-diphenylpyrrole.

It was also carried out the calculation of the difference in HOMO-LUMO energy levels (band gap) of compounds 1-(4-nitrophenyl)-2,5-diphenylpyrrole, 1-(4-carboxyphenyl)-2,5-diphenylpyrrole and CTC 1-(4-nitrophenyl)-2,5-

Table 2
Energies of orbitals calculated by *Gaussian*.

Compound	HOMO (Ev)	LUMO (Ev)	E_g (Ev)
1-(4-Nitrophenyl)-2,5-diphenylpyrrole (**2**)	5.578	2.558	3.02
1-(4-Carboxyphenyl)-2,5-diphenylpyrrole (**3**)	5.363	1.621	3.741
CTC of 1-(4-nitrophenyl)-2,5-diphenylpyrrole (**2**)–TTF (**4**)	9.93	5.33	4.6

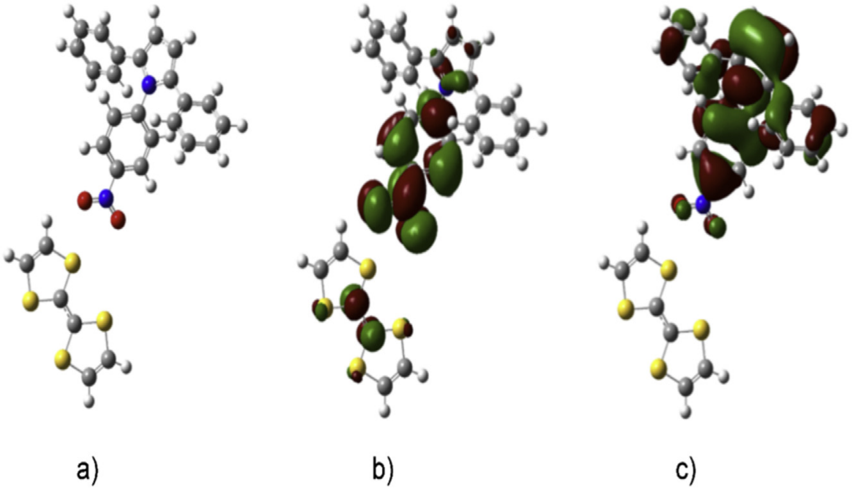


Fig. 19. a) Structure of CTC proposed, b) energetic level of LUMO, c) energetic level of HOMO.

Table 3
Conductivities of obtained compounds.

Compound	Conductivity σ (S/cm)
1-(4-Nitrophenyl)-2,5-diphenylpyrrole (**2**)	3.5×10^{-7}
1-(4-Carboxiphenyl)-2,5-diphenylpyrrole (**3**)	3.94×10^{-7}
1-(4-Nitrophenyl)-2,5-diphenylpyrrole – TTF (CTC **2–4**)	1.07×10^{-9}

diphenylpyrrole–TTF. We found the three compounds to exhibit *band gaps* that place them within the classification of materials with potential semiconducting behavior, and this can be demonstrated by analyzing their electrical properties.

We obtained a good approximation of the theoretical *band gap* compared with the *band gap* obtained experimentally by UV–Visible spectroscopy, which value may be considered among materials with semiconducting behavior.

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