

SEMICONDUCTOR BEHAVIOR OF 2, 5-AROMATIC DISUBSTITUTED PYRROLLES, AN EXPERIMENTAL AND THEORETICAL STUDY

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ABSTRACT

Theoretical calculations were performed on 2, 5-aromatic substituted pyrroles which have a nitro-benzene or a cyano-benzene link to the nitrogen atom of the pyrrol fragment. The molecules manifested interesting semiconductor behavior that was confirmed when thin films were prepared and their corresponding electrical characterization undertaken. The reason for this behavior is discussed, with reference to the electron withdrawing feature of the substituents in the benzene chain.

INTRODUCTION

Recently, organic materials have started to play an important role in electronic and photonic technologies. Organic semiconductors are very useful because they have electrical properties similar to those of inorganic semiconductors, but manifest the same properties as plastic (low cost, easily processed, flexibility and versatility of chemical synthesis). Until now, π -conjugated oligomers and polymers have attracted considerable interest because of their potential applications in optoelectronic devices [1]. One of the most widely investigated π -conjugated polymers is polypyrrole, due to its optical properties and electrical conductivity [2]. Investigations concerning the substitution effects of polypyrrole oligomers, using quantum mechanical calculations have provided an understanding of the conducting and optical properties of these materials [3]. Most systems being researched comprise semiconductors with band gaps ranging from 2 to 4 eV [4]. Extensive research [1, 5], using both experimental and theoretical approaches has been carried out in an attempt to endow a low HOMO/LUMO gap to organic materials. One strategy employed in order to decrease the band gap in organic molecular materials consists of substitution with electron-withdrawing groups [6]. In this work, nitro and cyano 2,5-disubstituted pyrroles were synthesized, electrically characterized and theoretically studied to explain the origin of their semiconducting behavior. The theoretical calculations were compared to the experimental results of the synthesized systems that were obtained using a modification of the Schulte-Reisch reaction, as previously described [7, 8].

EXPERIMENTAL DETAILS

Reagents were provided by Aldrich Chemical Company and used as purchased. FT-IR spectra were taken, using Nicolet 510p spectrophotometer. NMR ^1H and ^{13}C spectra were recorded using a Bruker Avance 400 MHz spectrometer. The chemical shifts are reported in ppm, scaled relative to TMS. Melting points are uncorrected. Thermogravimetric analyses (TGA) were carried out in air at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ on a TGA 2950 Instrument and Differential Scanning Calorimetry (DSC) was carried out on a DSC 2910 instrument. Gel Permeation Chromatographic Analysis was carried out on a Varian 9012, columns (TSK-gel 64008H8), detector (Varian RI-4) and integrator (Varian 4400), software GPC-plus. THF and DMF were employed as eluents at $25\text{ }^\circ\text{C}$ and flux speed of 1.0 mLmin^{-1} after calibration with polystyrene standards.

Synthesis of 2,5-disubstituted pyrroles

These compounds were produced, according to a modified version of a previously described procedure [8] (Fig. 1).

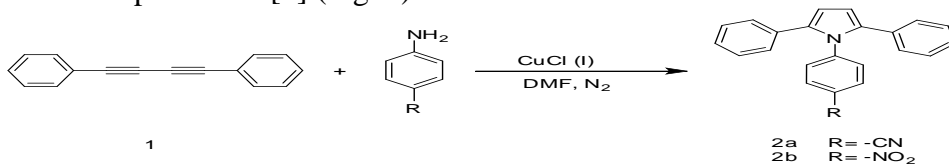


Fig. 1 Chemical reaction of 1,4-diphenylbuta-1,3-diyne with electron-withdrawing amines, used to obtain the pyrrole derivatives.

Polymer reactions with amines: general procedure

The preparation of polymer 3 has been reported previously [8, 9]. The same technique was followed in the present case (Fig. 2).

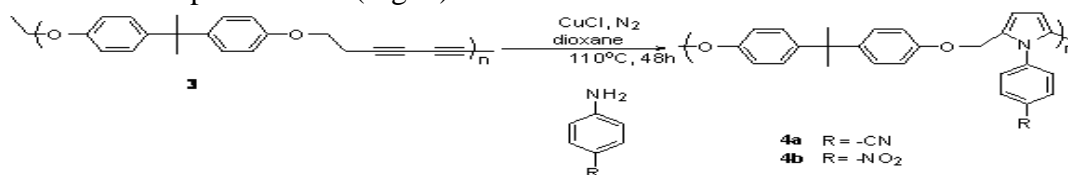


Fig. 2 Reactions of polymer 3 with electron-withdrawing amines.

Deposition and electrical characterization of NO₂- and CN-derivatives thin films

NO₂- and CN-derivatives solids were used to produce thin films of these materials, by means of vacuum evaporation. The films were deposited on Pyrex glass substrates that had been ultrasonically cleaned, using trichloroethylene, acetone and methanol. Chromium electrodes were evaporated onto the substrates, prior to the NO₂- or CN- compounds deposition, in order to make electrical measurements. The resulting NO₂-monomer films were uniform, yellow in color, with thicknesses of approximately 400 nm, measured with a Sloan Dektac IIA profilometer, and the CN-monomer films were almost white in color and around 480 nm thick. In contrast, the NO₂-polymer was only 180 nm thick and has a light brown color. The deposition conditions were not sufficient to obtain good quality CN-polymer films, because the deposition temperature was close to the decomposition temperature of the polymer. NO₂- and CN- monomer and NO₂-polymer films were

characterized electrically, by the two probe test current-voltage measurements, using a Keithley K-230 DC voltage source and a Keithley K-485 picoammeter. Both instruments were automatically controlled using a personal computer. Temperature dependent measurements were made by applying a voltage ramp to the electrodes and measuring the surface current, at room temperature up until 90 °C, with stepped increases of 10 °C.

Theoretical calculations

All density functional (DFT) calculations were carried out, using full geometry optimizations, without symmetry constraints. Becke's gradient corrections [10] for the exchange and Perdew-Wang's for the correlation [11] were used for optimization and total energy evaluation. Thus, BPW91 represents the corresponding functional which has given an excellent performance for this kind of system [12]. All calculations were carried out using the 6-31-G** basis set. The version used was that included in the Gaussian03 code [13]. The bond lengths for the optimized structures were employed for the HOMA (Harmonic Oscillator Model of Aromaticity) method [14] used for studying the aromaticity.

DISCUSSION

It has been reported that the reaction of diacetylene with amines depends strongly on the reaction conditions [15]. Model reactions to find conditions for selective formation of 2,5-disubstituted pyrrole units were carried out. The 1,4-diphenylbuta-1,3-diyne (1) obtained through a modification of Hay's oxidative coupling using copper (I) chloride as a catalyst was reacted with different aromatic amines with electron-withdrawing group in the *p*-position (Fig. 1). The products (2a, 2b [8]) were obtained with the yield 30 and 34%, respectively, and characterized by NMR and IR spectroscopy. The preparation of polymer 3 has been reported previously [9], but its structural characterization was very limited. Therefore, the polymer 3 thus obtained was characterized by NMR, IR, GPC and thermal analysis before chemical modification by amines [8]. Polymer 3 was reacted with aromatic amines with electron-withdrawing group (Fig. 2).

The most important factor, which must be taken into account in order to explain the electronic behavior of this kind of molecules (nitro-derivative and cyano-derivative), refers to the electron-withdrawing nature of the substituents linked to the six-member aromatic ring. The final effect is the narrowing of the gap between the frontier orbitals, but the secondary effects related to these features are fundamental (i.e. the nature and form of the pair HOMO-LUMO) when addressing this phenomenon. In our case, the electron withdrawing is used to explain the semiconductor behavior manifested by the monomers of the species in question, because only the substitution of these groups (NO₂ and CN) yields semiconductor monomers. The nitro-benzene fragment as well as the entire nitrile group manifests a well known capacity for withdrawing electron density. In the case of molecule 2b this effect is so strong that even the pyrrol fragment is involved, generating a real electronic current and a dipole molecule. This dipole manifests a negative electronic charge around the NO₂- fragment and a delocalized positive region around the pyrrol fragment. This effect precludes the electronic current, as indicated by the high polarizability volume α , also evident in the result from the theoretical calculation ($\alpha=119.21 \text{ \AA}^3$) shown in Table 2.

The CN-monomer behaves different; it seems to show semiconductor properties, but the magnitude of the electronic current is very small.

The semiconductor behavior of NO₂- and CN- derivative films was measured as a function of temperature. In both cases, conductivity increased with rising temperature. It was possible to deduce the activation energy (E_a) of the monomers of NO₂- and CN- derivative and the NO₂-polymer films (Table 1).

Table 1. Activation energy of the different compounds

Sample	E _a (eV)
NO ₂ -monomer	1.05
CN-monomer	0.88
NO ₂ -polymer	1.91

The NO₂-derivative presented a semiconductor behavior with raising temperature for both the monomer and the polymer.

A comparison of the conductivities manifested by the two monomers shows that the NO₂- derivative represents a better semiconductor than the CN-monomer. However, the activation energy obtained for the NO₂-derivative (1.05eV) is greater than that for the CN-monomer (0.88 eV). These results may be related to the conduction mechanisms inherent in these compounds and to their electronic structure. The conduction mechanisms of these materials are commonly complicated because more than two conduction processes are present. These materials probably present localized states within the band gap, giving apparently a smaller gap (that is, that the electrons can easily pass to the localized states within the gap and then jump a lower barrier to reach the conduction band).

The frontier orbitals, calculated using the BPW91 method in the case of the NO₂-derivative are presented in figure 3. The corresponding eigenvalues are presented in Table 2. The HOMO-LUMO gap variation in the case of the CN-compound is 3.807 eV, whereas in the case of the NO₂-compound is only of 3.02 eV. Besides, several calculations were carried out in the same fashion in order to get the HOMO-LUMO gap values for analogue molecules in which the substituents are not electron withdrawing or even -H, the results are also shown in Table 2. Clearly all of them are larger than those values obtained in our molecules under study addressing our proposition. A narrow gap between the HOMO and the LUMO is one of the most important characteristics that a molecule should have to be applied in semiconductor devices, and it is also expected that this gap falls within the visible light spectrum (1.59-3.18 eV), as it already is in the most efficient commercial devices. The NO₂-compound manifests this behavior in terms of its HOMO-LUMO gap. In contrast, as the gap of the CN-compound was over 3.8 eV –a higher energy than the visible light– a lower conductivity was expected, in agreement with the results shown in the graph of figure 7, which shows that the conductivity of the CN-monomer is one order of magnitude smaller than the conductivity of the NO₂-monomer. Furthermore the shape of the frontier orbitals reveals the dipole nature of the molecule, as the LUMO is localized completely in the region of the NO₂- substituent and manifests a negative electronic density, whereas the HOMO is localized exclusively in the region of the pyrrol fragment

and its substituents. This arrangement is ideal for an electronic transfer from head to tail, in the bulk of a monomer sample.

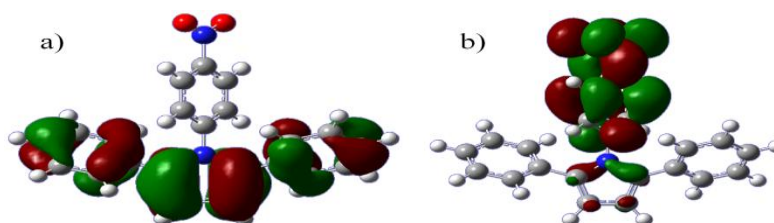


Fig. 3 a) HOMO of nitro-derivative; b) LUMO of nitro-derivative. Calculated at BPW91/6-31-G**//BPW91/6-31-G** level of theory.

Table 2. Calculated frontier orbital energy of the compounds being studied and the energy gap between each pair (energy values in eV)

Compound	HOMO	LUMO	Gap	α (Å ³)
NO ₂ -derivative	5.578	2.558	3.02	119.21
CN-derivative	5.535	1.728	3.807	80.1

Besides its semiconductor capacity, the nitro-derivative presents the photoluminescence phenomenon as it was illuminated using a He-Cd laser source, with a wavelength of 325 nm. The emission spectrum presents a broad band, centered at 558 nm, giving an orange-red emission. This revelation confirms the applicability of this material in specific semiconductor devices, such as the organic light emitting diodes, OLEDs. In contrast, the CN-monomer film did not show photoluminescence, as it was expected due to the large bandgap presented.

CONCLUSIONS

The monomers and polymers containing 2,5-aromatic substituted pyrroles with electron-withdrawing substituents were successfully synthesized, fully characterized by NMR, IR, GPC and thermal analysis and spectroscopically and theoretically analyzed. Thin films of the obtained NO₂- and CN-derivatives were deposited and electrically characterized. The presence of the electron-withdrawing groups induced a change in the conduction properties of the studied systems, which is more evident for the nitro-derivative. The nitro-derivative presents a higher conductivity and a smaller bandgap than the cyano-derivative. However, the activation energy of NO₂-derivative exceeds slightly that of the CN-derivative, therefore it was stated that the lack of available electrons hinders the conduction of the latter. In addition, the NO₂-monomer presented a strong photoluminescence band, while no signal was observed for CN-monomer. In the analysis of π -conjugated polymers, the presence of electron-withdrawing groups favors the charge separation that is necessary to improve the conductivity of this kind of materials. The present study exhibits that promising monomers that can be used to produce good semiconductor materials are those

who have strong electron-withdrawing groups, and by changing those groups it is possible to tune the energy bandgap for semiconductor devices applications.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Caroline Sarah Karlslake, Ms. Teresa Vázquez, Ms. Oralia Jiménez and Mr. Victor Gómez for technical help. Thanks are also due to Gerardo Cedillo for the assistance in NMR- and GPC- analysis, to Miguel Angel Canseco for thermal analysis and to Salvador Lopez Morales for GPC- analysis. This research was supported by projects PUNTA-UNAM and Consejo Nacional de Ciencia y Tecnología CONACYT-57432.

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