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Theoretical characterization of an all-organic molecular transistor

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Abstract

Recent advances in experimental techniques have led to more stable and reliable all-organic electronic devices as displays, rectifiers and transistors. However, a true molecular device has not yet been realized. In the present work we propose a new type of all-organic transistor with novel properties that is within the feasibility of the present technology for organic materials. Based on molecular modeling techniques, we demonstrate that the conductivity of a conjugated polymer chain may be modulated by a static electric field, without chemical doping. This is the first theoretical characterization of an all-organic molecular transistor based on quantum chemical calculations.

The use of organic conjugated polymers in electronics as active materials is becoming reality. Applications in this field are expected to go beyond the simple replacement of the usual inorganic semiconductors [1]. Light emitting diodes, rectifiers and field effect transistors employing organic conjugated systems as the active materials have recently been reported in the literature [2–5]. These developments, together with modern advanced techniques of molecular deposition should allow in the near future the fabrication of devices in which an individual molecule acts as a device itself.

Since the original proposal by Carter and collaborators [1], the idea of a molecular organic switch has been object of intense theoretical and experimental work [6–9]. A typical Carter switch is based on a polyenic skeleton of *trans*-polyacetylene (*t*-PA) with donor/acceptor groups substituted either at chain ends [9] or laterally added [7]. The structure of *t*-PA is known to support topological solitons as elementary excitations. These conformational defects separate two equivalent alternating patterns of single and double bonds on the chain, the degeneracy of *t*-PA ground state allowing the soliton motion.

In many of the structural models proposed for polyenic Carter switches, the switching mechanism is based on changes in the conformation pattern from ground to excited states (Fig. 1). Whether a real device could work based on this mechanism has been a debated question.

In 1985, Tanaka et al. [7] studied the Carter switch sketched in Fig. 1, where the donor (D) and acceptor (A) groups were taken as NH_2 and NO_2, respectively. Based on molecular orbital calculations they have concluded that such a device would not work. However, in a more recent report (also based on molecular orbital calculations, but with explicit inclusion of an external static electric field to drive

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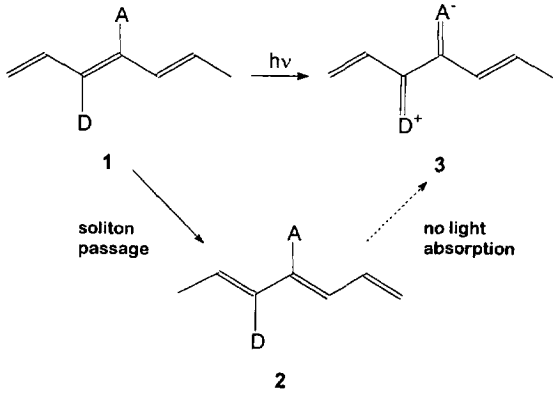

Fig. 1. Typical Carter's switch. D and A are donor and acceptor type molecules to be substituted in the polyene. A molecular switch is defined as a molecule which, under external influence, may switch to a metastable state. It is required to have distinct properties in the two states (states **1** and **3**), permitting a 'read' operation to determine the state of the switch. From ground state **1**, light could be absorbed to produce a charge transfer between D and A, resulting in the excited state **3**. The passage of a soliton converts ground state **1** into ground state **2**, thus blocking light absorption.

the transfer reaction) we have demonstrated [10] that the presence of a spacer (a benzene ring, for example, see Fig. 2) between the D (A) group and the polyenic chain makes the switching process possible. The underlying reason it is that the spacers decrease the overlap between the molecular electronic states of the active groups and the main polyenic chain involved in the charge transfer process, thus allowing the switching function. *It has not been possible to simulate the switching function without the inclusion of spacers.*

In this work we explore further these ideas and propose a new type of organic, quasi one-dimensional, molecular device based on the structural repetition of a unit as shown in Fig. 2. In this new type of device the conductivity (from insulator ↔ conductor ↔ insulator) can be easily modulated via an external, static electric field applied perpendicular to the polyene (gate voltage), without the need of chemical doping. The conduction mechanism does not require the presence of mobile elementary excitations (solitons, polarons or bipolarons), which are the usually assumed charge carriers in conducting polymers [11], though this has been questioned by some authors [12]. We have also noticed a non-linear response of the system as a function of the applied external electric field strength, resembling the behavior of a field effect transistor.

Our studies on molecular conformation and charge transfer reaction were carried out within the well known Austin Method One (AM1) technique [13]. This is a semiempirical technique derived from the Hartree–Fock theory and has been proved to be very successful in reproducing molecular geometries of organic systems. In order to avoid the unphysical polarization effects induced by the use of point charges ('sparkles'), the simulation of charge transfer reactions was performed with a modified version of the AM1 code that contains a static external electric field in the molecular Hamiltonian (Finite Field Approach) [14–17]. Molecular geometries are fully optimized for each value of the external field. A similar treatment, using Hartree–Fock STO-3G Hamiltonian, has been used by Aviram [18] to study

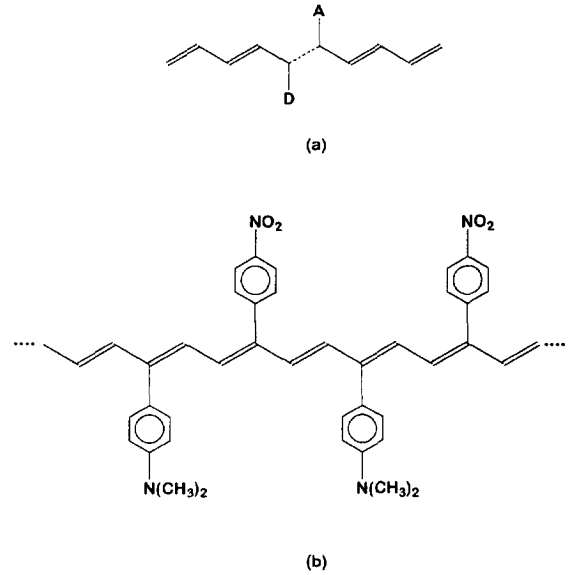

Fig. 2. Molecular models studied: (a) the molecular switch can have one, two or three double bonds between the ligands; if there are more single bonds than double bonds between the ligands, the charge transfer reaction from D to A does not occur; D and A represent active groups for electron transfer plus spacers, as explicitly shown in (b), that represents a model molecule having two switching segments.

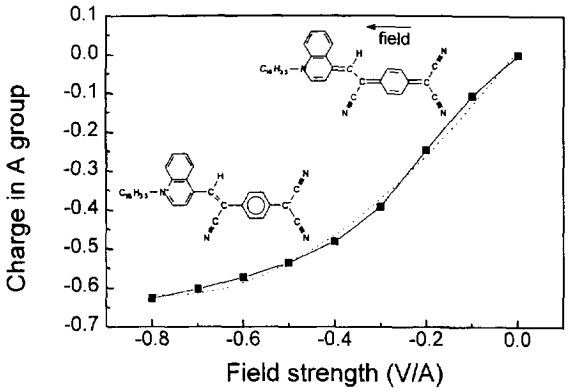

Fig. 3. The molecular rectifier has been used to test the theoretical methodology and to scale the electric field strength used in theory to be compared with the experimental value. The continuous curve shows results for the charge transferred to the acceptor group as a function of the applied field. This curve is nicely fitted by a cubic law (broken line), which is the same power law reported experimentally for the molecular rectifier. The operation voltage of this rectifier is 1 Volt, which is equivalent to an electric field of 10^8 V/m. The structure displayed on top of the figure represents the starting (zero field) molecule that, upon application of the external field represented by the arrow, evolves to the structure displayed on the left corner.

charge transfer rates on molecular systems that are suitable for electronic devices.

We start by investigating the reliability of the above procedure. The properties we wish to discuss are assessed by means of single molecule calculations and a real device will involve a three-dimensional array of interacting molecules. Moreover, the AM1 code used is not the standard one, since the Stark effect is being explicitly treated. We tested our methodology against a real molecular device (molecular rectifier) recently reported in the literature [8]. This device was produced by multi-layer Langmuir–Blodgett deposition technique, and though several layers of the active molecule are present, the authors concluded that the rectifying property has molecular origin. The current density vs. voltage characteristic of this rectifier is experimentally found to follow a cubic dependence on the applied voltage at forward bias, which is the same potential law we found in our model for a single molecule (see Fig. 3). In this case the field was applied along the long axis of the molecule. Since the structure used as a test and the one we are proposing are both organic conjugated systems with the presence of polar groups, we believe the methodology is appropriate.

A last comment should be made on the above results, concerning the order of magnitude of electric fields needed to produce an intramolecular charge transfer. In our model, the molecule is in vacuum and so a real chemical environment is not taken into account. Also, the minimal STO basis set adopted in AM1 calculations together with the approximations made in the semi-empirical Hamiltonian do not allow an accurate description of the molecular polarizability. As a consequence, the field strength at which charge transfer occurs is of the order of few tenths of V/Å ($\approx 10^9$ V/m), thus one order of magnitude higher than the one found experimentally in the molecular rectifier ($\approx 10^8$ V/m) [8]. Similar values of threshold electric fields were obtained in the more accurate Hartree–Fock STO-3G calculations of Aviram (2.829 to 3.343×10^9 V/m) [18]. One could say that these molecular systems are more polarizable and sensitive to the chemical environment than the minimal basis set Hartree–Fock theory (and semi-empirical methods derived from it) is able to describe. Apart from the field strength, the methodology employed in the present work accounted for the molecular behavior, since it also depends upon geometry relaxation (which AM1 technique performs well) that accompanies the charge transfer.

For the structures shown in Fig. 2a, we have investigated the electron transfer from D to A groups as a function of both the electric field strength and the distance (number of bonds) between the lateral groups. In the absence of the external field, the geometries associated to all molecules are similar, with the usual alternating configuration of bonds in the polyene. Both lateral groups present benzene rings (spacers) rotated by 65° relative to the polyenic skeleton and the torsion angle is only slightly sensitive to the number of conjugated bonds between them.

Turning on the external field, applied from the donor to the acceptor and thus perpendicular to the polyene, the geometries and charge distribution are not significantly modified until the field strength reaches a threshold value (~ 0.5 V/Å). The most important modification observed up to this point is the continuous reduction of torsion angles of both benzene moieties. An analysis of the ring torsion

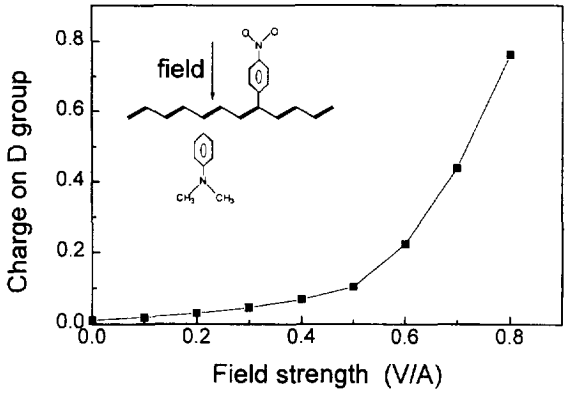

Fig. 4. Net charge (in units of the electron charge, e) on the donor group (D) as a function of the magnitude of external electric field (in V/Å), for the switch shown in the inset. The external field is represented by the arrow. In the present study the D and A groups are $N(CH_3)_2$ and NO_2, respectively.

angles as a function of the field strength indicates that they work like a gate for electron transfer. Above the threshold field strength, charge transfer starts to occur irrespective to the number of bonds between the active groups. Representative results are shown in Fig. 4 for the structure where the ligands are separated by two double bonds, as indicated in the inset.

As can be seen from Fig. 4, charge transfer increases slowly (linear behavior) for fields up to a particular value, above which the process is clearly nonlinear. The net charge on the polyene remains constant. Around the value at which the transfer reaction starts, a small variation of the field induces a large charge transfer between D and A groups.

The polyenic segment between the ligands undergoes a conformational transition at the threshold field. The alternating pattern of single and double bonds disappears and a *metallic* region (equal bond lengths) is created, embedded in the insulating medium. Supposing that, in a multiple array of switching units (a single switch is shown in the inset of Fig. 4) along a polyenic chain, each switch does not destructively interfere with others, a remarkable possibility is opened of building a molecular organic wire with tunable conductivity. In order to verify this point we have investigated, within the same methodology, the structure shown in Fig. 2b, with two switching units. Our calculations have shown the same qualitative behavior illustrated in Fig. 4. Besides that, one interesting new feature is the *collective* rotational behavior of pairs of benzene rings.

In order to show how this effect could lead to the modulation of conductivity, we have performed a numerical simulation to calculate the evolution of the density of electronic states in a long chain, including up to 200 carbon atoms. This chain is built with fifteen randomly distributed D–A segments separated by three double bonds. The electronic structure is assessed by means of a tight-binding Hamiltonian [11]. The parameters of the method were chosen as follows: first, the presence of the external field is only felt by the bonds within the segments, which at certain field strength attain the uniform pattern of bond lengths; the effects on site energies have been neglected since the field is perpendicular to the chain. Hoppings between nearest neighbors were calculated by bond-order–bond-length relationship [11] $\beta(R) = -A \exp(-R/B)$, where R is the bond

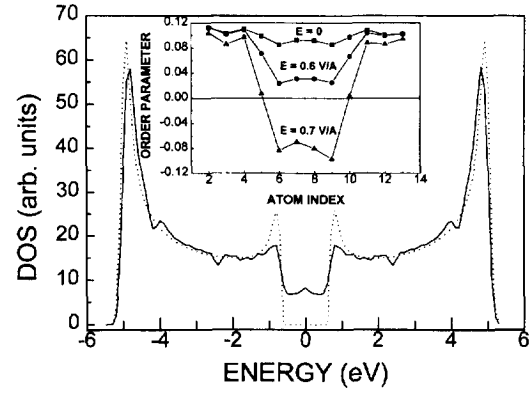

Fig. 5. Density of electronic states (DOS), in arbitrary units, versus one-electron energy, in electronvolts, for the oligomer having 200 carbon atoms and fifteen randomly distributed switching units. Dotted lines represent ground state DOS in the absence of the external field and continuous lines correspond to the DOS at the threshold field. The band gap vanishes at this field strength, with the presence of extended states, thus characterizing a true metallic regime. In the inset it is shown the evolution of the alternating pattern of bonds in the conjugated segment between the lateral A and D groups, in terms of the order parameter $\Delta r_i = (-1)^i (r_{i+1} - r_i)$, where r_i is the bond length of bond i. This shows that at the threshold field a conformational phase transition takes place (a reversal of the Peierls distortion), i.e., a metallic (all equal bond lengths) segment is created.

length and A and B are parameters adjusted to give $\pi-\pi^*$ band gap of 1.6 (eV) and a total π bandwidth of 10.0 (eV), for the ground state geometry having double and single bonds of 1.36 Å and 1.44 Å, respectively. In Fig. 5 are shown the densities of states for two cases: in the absence of the electric field and at the field strength where the bonds within the D–A segments are all of equal length (see inset). Increasing the number of switches in the chain leads to a larger number of electronic states in the original band gap, while the field intensity modulates the gap value. This means that, for a given distribution of switches in the chain, the system will be insulating in the absence of external field. As the perpendicular field is applied with increasing intensity, the band gap gets smaller and closes at some point. The electronic states around the Fermi energy are delocalized over the whole polyenic skeleton, constituting another example of the presence of extended states in disordered one-dimensional systems [19–22].

These results demonstrate the possibility of modulating the conductivity of a molecular wire by an external transversal field and so without the usual chemical doping. Transistor operation is achieved by modulating the source-drain conductance (the polyene) with the gate voltage (the transversal field that produces charge transfer) [23,24].

We would like to stress that the structures we are proposing here are within the feasibility of the present technology for organic materials, since similar structures for operational diode-type devices have been recently synthesized through Langmuir–Blodgett [8] techniques. Moreover, molecular materials are much less sensitive to impurities than inorganic semiconductors since they are held together by weak van der Waals interactions, and their properties are mainly governed by individual molecules [25]. Examples of this have been given by the functionalized polymers for nonlinear optics [26], where the nonlinearities are produced by the large $\chi^{(2)}$ lateral molecules attached to a suitable conventional polymer.

In the present work we have proposed a molecular electronic device with novel properties, that is structurally related to Carter's switch models. The calculations were carried out with the explicit inclusion of a static electric field in the AM1 Hamiltonian, in order to study charge transfer reactions. A non-linear behavior for the charge transfer and order parameter was obtained. We have also demonstrated that a multiple one-dimensional array of structural switches may lead to a new type of molecular device, where the conductivity can be easily modulated by an external electric field without the necessity of chemical doping. This is the first theoretical characterization of a *transistor-like* effect in all-organic molecules based on quantum chemical calculations.

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