The molecular rectifier revisited

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Abstract

We present a series of electronic and conformational studies on the push-pull system Z-β-(1-methyl-4-quinolinium)-γ-cyano-4-styryldicyanomethanide, CH_3-Q3CNQ based on semi-empirical calculations to assess solvent, external electric field and correlation effects. The ground state conformation obtained is not of zwitterionic type, and a different interpretation of the rectifying behavior of this system is presented.

Keywords: push-pull molecule, semi-empirical calculations, solvent effects

An experimental demonstration of rectification in LB films of push-pull molecules has been reported recently in the literature by Ashwell and coworkers [1]. The active layers consisted of Z-β-(1-hexadecyl-4-quinolinium)-γ-cyano-4-styryldicyanomethanide ($C_{16}H_{33}$-Q3CNQ) molecules. The current density-voltage curve showed the characteristic rectifying behavior and the current at forward bias followed a cubic dependence on the applied voltage. The proposed mechanism to explain the asymmetric conductance was based on a *zwitterionic* structrure of the active molecule. At forward bias the mechanism responsible for conduction was assumed to be:

$$M_1/D^+\text{-}b\text{-}A^-/M_2 \rightarrow M_1/D^0\text{-}b\text{-}A^0/M_2 \rightarrow M_1/D^+\text{-}b\text{-}A^-/M_2$$
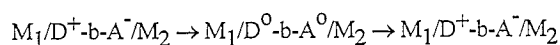
where M_1 and M_2 represent the metal electrodes, D^+-b-A^- stands for the charge separated (*zwitterionic*) structure of the active molecule and D^0-b-A^0 its *neutral* structure (see Fig. 1). At reverse bias, however, the high energy structure D^{2+}-b-A^{2-} has to be invoked, which prevents charge to flow through the electrodes.

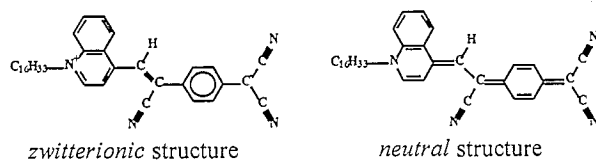*zwitterionic* structure   *neutral* structure

Fig. 1. Two resonance forms of the molecular rectifier $C_{16}H_{33}$ Q3CNQ: *zwitterionic* and *neutral* structures.

In the present work we theoretically investigate the evolution of molecular parameters, such as conformation, dipole moment and optical spectrum, of CH_3- Q3CNQ molecule under the influence of a static electric field applied along the long axis of the molecule. Based on these calculations, and comparing the obtained molecular parameters with experimental data, we discuss the possible structures this system might adopt in different chemical environments. The microscopic mechanism for rectification is then reviewed.

We performed calculations to assess molecular conformations using the Austin Method 1 (AM1) [2,3] technique that has been suitably modified to include the presence of a static electric field in the molecular hamiltonian. At each value of the electric field, the molecular geometry was fully optimized such that its electric dipole is aligned in the direction of the field. The zero-field Hartree-Fock solution gives a *neutral* geometry,. For fields pointing towards the donor moiety, the molecular geometry gradually evolves to a *zwitterionic* structure. On the other hand, fields pointing towards the acceptor group do not significantly affect the geometry until a limiting field strength value is reached.

In Fig. 2 the net charge on the acceptor moiety (ϕ-$(CN)_2$) is displayed as a function of field intensity.
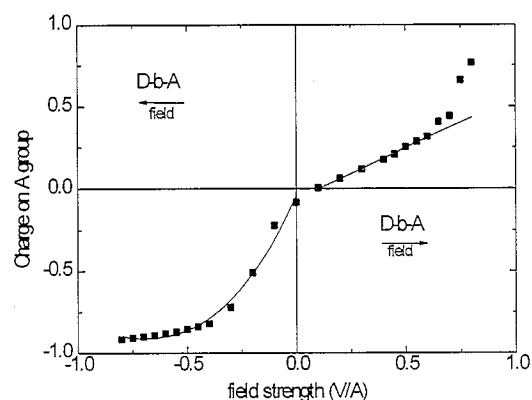

Fig. 2: Net charge in the acceptor group (C_6H_6 -$C(CN)_2$), in units of the electron charge, as a function of the applied field (V/Å). The insets indicate the direction of the field. The continuous lines are fittings to a third power law at forward bias and a linear fitting at the reverse bias.

In order to study the behavior of the heat of formation as the molecular geometry evolves from *neutral* to the *zwitterionic* structure, we have frozen the geometry obtained at a given external field value and performed an AM1 calculation with configuration interaction, including up to 400 lowest energy microstates. In these calculations external field effects are absent.

We found that electronic correlation decreases total energy in 6-8 kcal/mol and displaces the minimum energy geometry to a structure that has some *zwitterionic* character, with the C-C bridging bond shortening from 1.445 Å to 1.431 Å.

Very few experimentally determined structural data are available for this system. For CH_3- Q3CNQ experimental data come essentially from the absorption spectra in acetonitrile and in the LB films [4]. The first absorption peak in acetonitrile solutions of $C_{16}H_{33}$- Q3CNQ is reported to occur at 712 nm, with a halfwidth of 104 nm. A large blue shift and narrowing of the absorption is observed in LB films, where the peak occurs at 565 nm, with halfwidth of 22 nm.. Another interesting feature is the bleaching of the transition in both solutions and LB films. Solutions and films become transparent under illumination, but solutions recolour after some minutes while the films do not recover the initial coloured state [4].

We simulated the absorption spectra of CH_3- Q3CNQ within the INDO/S-CI semiempirical method contained in ZINDO package [5]. Several geometries were employed in order to investigate the nature and wavelength of the transitions.. The curve corresponding to the field strength of -0.1 V/Å is also the absorption spectrum for the zero-field ground state AM1-CI geometry. It is characterized by a strong transition peaking at 564 nm, mainly composed of the HOMO-LUMO transition. The starting molecular dipole is calculated to be 15.3 D and the final state has a dipole of 21.0 D, indicating a charge transfer from donor to acceptor. At the other extreme, the structure corresponding to fields of -0.6 V/Å produces a spectrum having a strong absorption at 780 nm also coming mainly from a HOMO-LUMO transition, but the reference and final dipole moments obtained are 32.0 D and 11.7 D, respectively. This is compatible with a charge transfer from a negatively charged acceptor to a positively charged donor, that is, a charge transfer in the opposite sense as compared to the previous case.

Solvent effects in the molecular geometry were evaluated by means of a continuum solvation model developed by Dixon *et al.* [6], contained in SPARTAN quantum chemistry package [7]. Water has been employed as the solvent. We see that the solvent regarded as a continuum medium changes the geometry from the *neutral* Hartree-Fock solution such that some charge is separated. Solvent effect in this case produced the same geometry that has been obtained by the AM1-CI calculation.

We investigated the effect of conformational changes in the absorption spectrum by performing geometry optimizations in the presence of the external electric field, but constraining the molecule into a planar geometry. For each value of the external field, the resulting geometry was used as input for a INDO/S-CI calculation. The results for two selected geometries are displayed in Fig. 3. The differences in the absorption spectra of Q3CNQ in solution and in the LB films could thus be interpreted as follows: in solution, these molecules strongly interact with the solvent and adopt a charge separated state at several twisted conformations, leading to a broad charge transfer feature in the absorption spectrum. In LB fims the molecules adopt a more neutral structure in order to minimize the repulsion energy among the aligned dipoles. As a consequence, the main absorption peak is blue-shifted, the nature of the transition changes to a charge tansfer from donor to acceptor, and the conformational disorder, if present, does not lead to an important broadening of the absorption. The fact that bleached LB films do not recolour could possibly mean that the molecules do not recover the initial state

due to photodegradation of the films, and that the solvent protects the molecules from this process in solution.
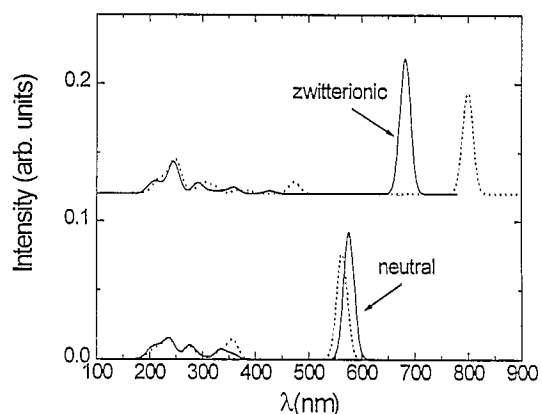

Fig. 3: Comparison between the simulated absorption spectra of planar (continuous line) and twisted (dotted line) molecular conformations, and at the *neutral* (field strength of -0.1 V/Å) and *zwitterionic* (field strength of -0.6 V/Å) structures. Intensities are given in arbitrary units and wavelengths in nm.

We have investigated the influence of chemical environment on the properties of the push-pull system CH_3- Q3CNQ. Our analysis of the relationship between structure and absorption spectrum is consistent with a *neutral* conformation in LB films of this molecule, and a *zwitterionic* structure in solid state and in acetonitrile solutions. We concluded that the first dipole allowed electronic transition of this system corresponds to a charge transfer from a negatively charged acceptor to a positively charged donor in solution, and a charge transfer from donor to acceptor in the LB film. A distribution of twisted conformations is expected in solution that contributes to the broadening of the absorption. In the neutral state, changes in conformation have only a small effect in the absorption wavelength. The mechanism leading to rectification in LB films is rewritten as:

$$M_1/D^o\text{-}b\text{-}A^o/M_2 \rightarrow M_1/D^+\text{-}b\text{-}A^-/M_2 \rightarrow M_1/D^o\text{-}b\text{-}A^o/M_2$$
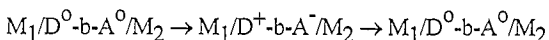
at the forward bias, while at the reverse bias a high energy $D^-\text{-}b\text{-}A^+$ has to be invoked and corresponds to the high resistance state. A full account of this work will be published elsewhere [8].

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