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Theoretical study of donor–spacer–acceptor structure molecule for use as stable molecular rectifier: geometric and electronic structures

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Abstract

Recently, molecular electronics has attracted much attention as a ‘post-silicon technology’ for future nanoscale electronic devices. One of the most important elements in molecular electronic devices is the realization of a unimolecular rectifier. In the present study, the geometric and electronic structure of the TTF-derivative (donor)–sigma-bond–TCNQ-derivative (acceptor), a leading candidate for a molecular rectifying device has been investigated theoretically using ab initio quantum mechanical calculations.

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Keywords: Molecular electronics; Molecular device; Nanotechnology; Unimolecular rectifier

1. Introduction

Molecular electronic devices have attracted considerable attention as a ‘post-silicon technology’ for future applications in advanced computer electronics [1]. The realization of a unimolecular rectifying function is one of the most important requirements in molecular device. A quarter of a century ago, Aviram and Ratner [2] first proposed rectification using a single molecule. This work has been followed by a number of experimental results [3,4] and several theoretical studies have been published [5–7]. In order to realize an efficient unimolecular rectifier D (donor sub-unit)–Spacer–A (acceptor sub-unit) structure has been proposed with which it is required to induce an effective charge separation and transfer. A molecule should have roughly the properties of a bulk-effect solid-state p–n junction diode. For the spacer, σ and π bonds have been introduced. σ bonds have the potential for strong charge separation. On the other hand, π bonds have delocalized orbitals and good conductivity. One of the purposes of this study is to explore a role of the spacer in the operation of the rectifier.

From this viewpoint of practical applications, Metzger et al. [8–10] reported the novel TTF- σ -TCNQ molecule

as a molecular rectifier. This molecule, which has a Donor-sigma-Acceptor structure is composed of a TCNQ derivative for the acceptor with a TTF derivative providing the donor function. In this present work, the geometric and electronic structure of the TTF- σ -TCNQ molecule (see Fig. 1a) is studied in order to examine its rectifying function.

Also, in this work we optimized the structure of this molecule, which is composed of a donor and acceptor sub-unit. In the next section, we explain in detail the numerical method used and the results for the TTF- σ -TCNQ molecule and the effect of substituents on the acceptor and donor moieties of the molecule.

2. Model and numerical method

The total energy calculations were performed using density functional theory [11] and the exchange and correlation energies were calculated using a hybrid functional, which we used in preference to the Hartree–Fock (HF) method. This is because accurate descriptions of the LUMO states are very important, since the incoming electrons are assumed to pass through the molecule. Therefore, the use of a hybrid function in the DFT is fully justified. Several successful applications of molecular devices using hybrid functions have been reported [11–14]. All the calculations were performed using the Gaussian98 program [15] at the B3PW91

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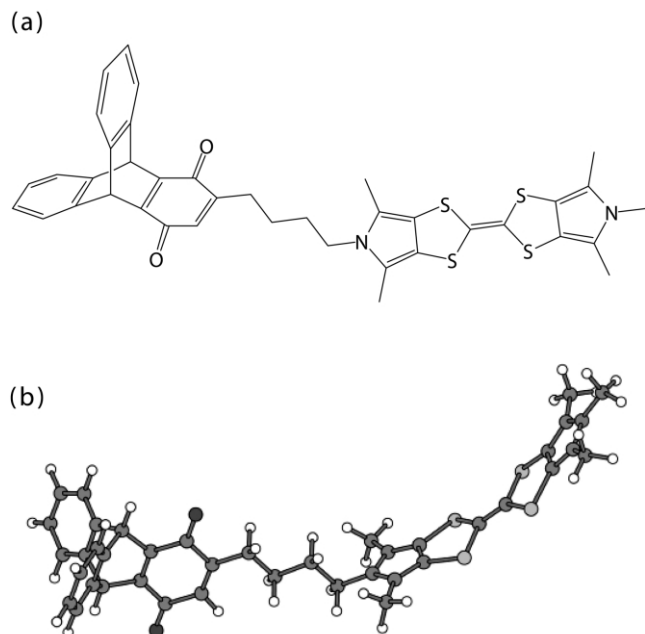


Fig. 1. (a) Chemical structure of the TTF- σ -TCNQ molecule. (b) Stable structure obtained by B3PW91/6-31(d).

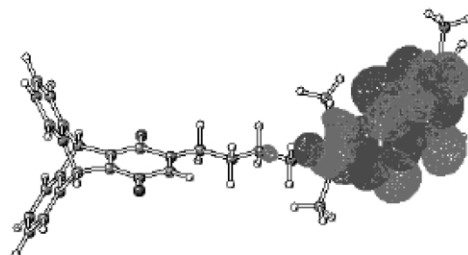
theory level. The B3PW91/6-31(d) was used to obtain the stable structure of the TTF- σ -TCNQ molecule. After optimization of the structure, the 6-311++G(d,p) basis set was used, augmented by appropriate polarization functions.

3. Results and discussion

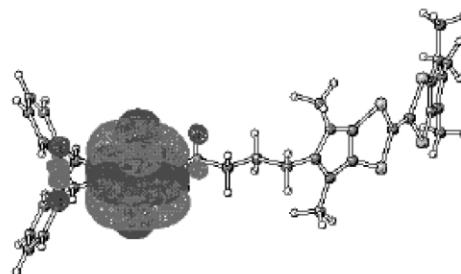
Fig. 1a,b show the chemical and optimized structures of the TTF- σ -TCNQ molecule as the whole molecule. To estimate the electron transport through this molecule, we analyzed the spatial extent of the frontier orbitals (HOMO and LUMO), providing a strategy by which the rectifying properties of the D (donor sub-unit)–Spacer–A (acceptor sub-unit) structure molecule could be understood. The results suggest that in donor–acceptor molecular complexes such as this, the lowest unoccupied orbital is concentrated around the acceptor sub-unit, while the highest occupied molecular orbital is localized on the donor sub-unit. In a recent review, article by Ellenbogen et al. [16], a number of monosubstituted and disubstituted polyphenyl compounds were chosen to study the rectification behavior in this class of molecules. It is assumed that the unoccupied orbitals provide channels for electron conduction through the molecules. The difference in the energy of the lowest unoccupied levels between the isolated substituted benzene molecules was used to estimate the approximate value of potential drops (P.D.) across the molecule and thereby the effectiveness of the combined molecule to behave as a molecular rectifier. However, for a chemi-

cally bonded D–S–A (donor–spacer–acceptor) molecular complex, the potential drop is measured as the difference between the unoccupied orbitals localized on the donor and acceptor sides. From Fig. 2, it is clear that the LUMO+1 is delocalized on the TTF- σ -TCNQ molecule. This can be attributed to the localization of the HOMO and LUMO energy levels on the donor and acceptor sides of the Donor–Sigma–Acceptor molecular complex, respectively [5,6]. Fig. 2 suggests that the potential drop ΔE_{LUMO} across the TTF- σ -TCNQ molecule is determined by the difference between E_{LUMO} and the $E_{\text{LUMO}+K}$ for an unoccupied orbital localized on the opposite (donor) side of the molecule from the LUMO. The potential drop in a vacuum can be explained as the difference in the LUMO energies between the donor and acceptor molecules when they are widely separated ($\Delta E_{\text{LUMO}}(\infty) = E_{\text{LUMO}}(\text{donor}) - E_{\text{LUMO}}(\text{acceptor})$) [5].

(a) HOMO



(b) LUMO



(c) LUMO+1

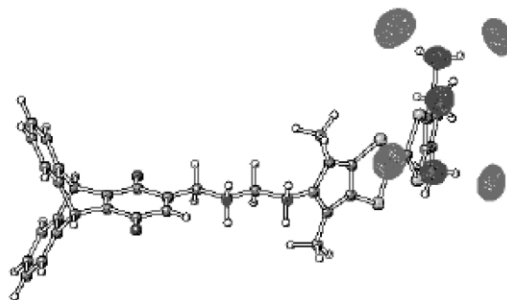


Fig. 2. Orbital spatial orientation of (a) HOMO, (b) LUMO, and (c) LUMO+1 for the TTF- σ -TCNQ molecule.

The feature and the difference of the energy levels have been affected by the functional group of the donor and we can see the same strategy in rectifier molecules with the same reported localization [17].

4. Conclusion

The geometry and electronic structure of neutral TTF- σ -TCNQ molecules have been calculated using density functional theory. A Gaussian software package has been used for all the calculations. The effect of substituents in these molecules has been analyzed based on the spatial distribution of the frontier orbitals. It is seen that while the occupied orbitals are localized on the donor sub-unit, the unoccupied orbitals are localized on the acceptor sub-unit. It has been previously reported that the tendency for localization of the frontier orbitals of other donor–spacer–acceptor supramolecular system is the same [5].

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