Theoretical Study of Donor - Spacer - Acceptor Structure Molecule for Stable Molecular Rectifier

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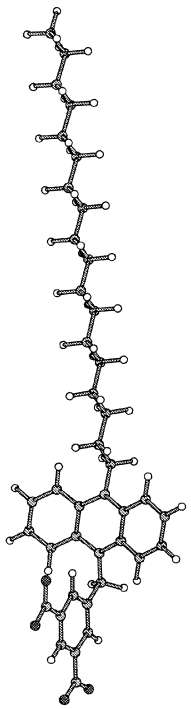
ABSTRACT

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 alkyl derivative $C_{37}H_{50}N_4O_4$ (PNX), (donor - spacer - acceptor), a leading candidate for a molecular rectifying device, has been investigated theoretically using *ab initio* quantum mechanical calculations. The results suggest that in such donor-acceptor molecular complexes, while the lowest unoccupied orbital is concentrated on the acceptor subunit, the highest occupied molecular orbital is localized on the donor subunit. The approximate potential differences for the optimized PNX molecule have been estimated at the HF/6-311g++(d,p) level of theory, which achieves quite good agreement with experimentally reported results.

Keywords: molecular electronics; molecular device; nanotechnology; simulation; donor - spacer - acceptor structure.

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 a 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. 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 purposes of this is to explore a little further the role of the spacer in the operation of the rectifier.



Recently, Mikayama *et al.* [8] proposed the novel long-chain alkyl derivative $C_{37}H_{50}N_4O_4$ (PNX, Fig. 1) as a molecular rectifier. This molecule, which has a Donor-sigma-Acceptor structure is composed of a dinitrobenzene moiety for the acceptor with a dihydrophenazine moiety providing the donor function. In this present work, the geometric and electronic structure of the PNX molecule is studied in order to examine its rectifying function.

Figure 1: Stable structure of the $C_{37}H_{50}N_4O_4$ Molecule (PNX).

Aslo, in this work, we optimized the structure of this molecule, which is composed of a donor and acceptor sub-unit and a long-chain alkyl. In the next section, we explain in detail the numerical method used and the results for the PNX 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 [9] 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 [9, 10]. To save computational time, we made the calculations for the PNX without taking the alkyl chain into account, having

confirmed that this chain has no effect at the molecular level using the HF/6-311g method. All the calculations were performed using the Gaussian98 program [11] at the B3LYP theory level. The B3LYP/6-31(d) was used to obtain the stable structure of the PNX 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

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 PNX 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. From Fig. 2, it is clear that the LUMO+3 is delocalized on the PNX 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]. Figure 2 suggests that the potential drop ΔE_{LUMO} across the PNX molecule is determined by the difference between E_{LUMO} and the E_{LUMO+K} for an unoccupied orbital localized on the opposite (donor) side of the molecule from the LUMO. A detailed description of the definition of ΔE_{LUMO} is provided elsewhere [5].

(a)

(b)

(c)

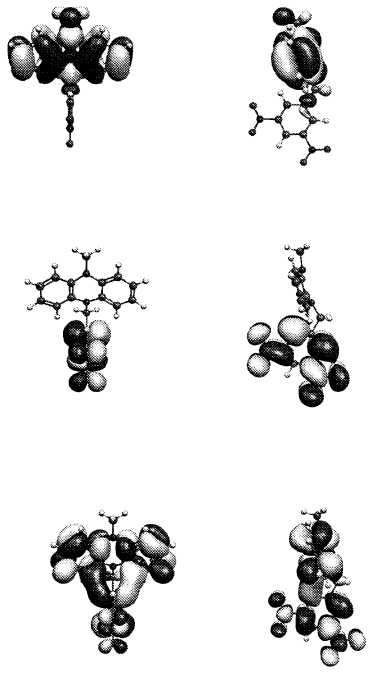
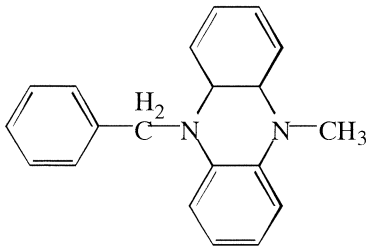


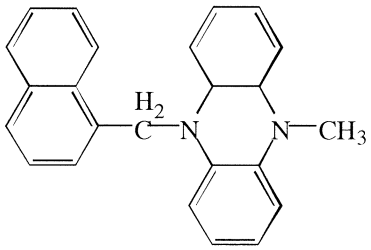
Figure 2: Orbital spatial orientation of (a) HOMO, (b) LUMO, and (c) LUMO+3 for the PNX molecule. Left: Front view. Right: Side view.

We examined the effect of a substituent group on the acceptor (See Table 1). From these results electron withdrawing groups produce a strong localized LUMO and increase ΔE_{LUMO}, while stronger than hydrogen donating groups produce a delocalized LUMO. Moreover we examined the effect of various donors (See Table 2). With a dihydrophenazine moiety providing the donor function, an electron donating group has almost no influence on ΔE_{LUMO} ,whereas and an electron withdrawing group decrease ΔE_{LUMO}. Finally we explored the effect of various fused moieties on the acceptor. Generally speaking, anthracene and phenanthrene have a stronger acceptor function than benzene. From Fig. 3, we can see that a strong acceptor makes a large potential difference. The order of the values of ΔE_{LUMO} for AP1, 2AP1, and PP1 molecules is in quite good agreement with experimentally reported results [12].

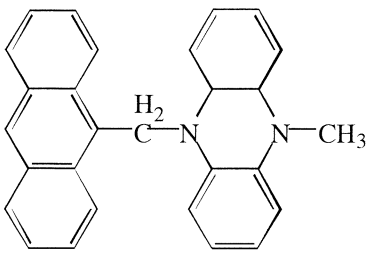
BP1



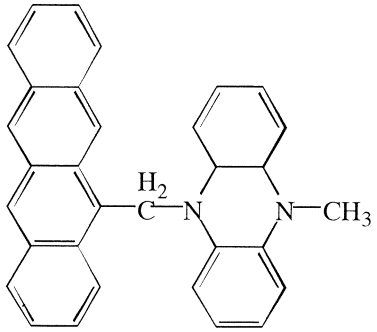
NP1



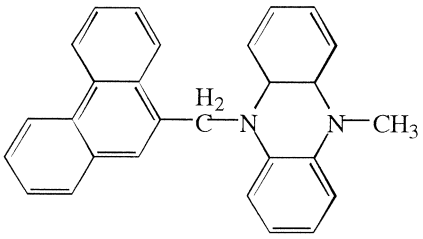
AP1



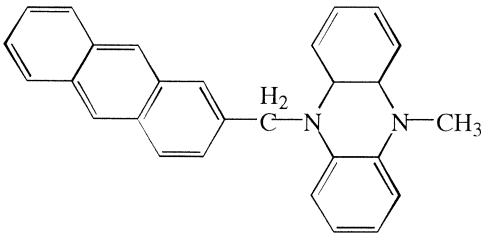
CP1



PP1

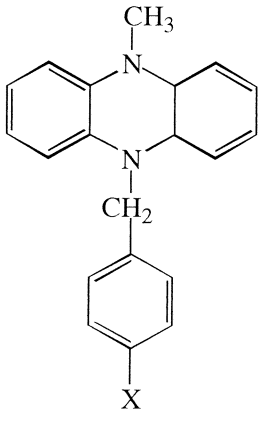


2AP1



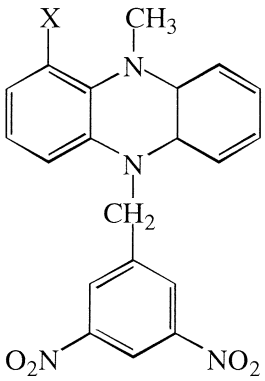
Molecule	ΔELUMO	$E_{HOMO-LUMO}$
BP1	0.205 eV	3.945 eV
NP1	1.062 eV	3.135 eV
AP1	1.772 eV	3.074 eV
CP1	1.978 eV	2.190 eV
PP1	0.969 eV	3.191 eV
2AP1	1.630 eV	2.548 eV

Figure 3: Acceptor moieties for the PNX derivative and ΔE_{LUMO} using B3LYP/6-311++g(d,p).



Substituent(X),	ΔELUMO
-CN	1.15 eV
-NO2	2.17 eV
-CHO	1.56 eV
-COCH3	1.38 eV
-COOC2H5	1.12 eV
-COOH	1.26 eV
-Br	0.49 eV
-Cl	0.48 eV
-OH	0.29 eV
-H	0.21 eV
-CH3	delocalized
-SCH3	delocalized
-OCH3	delocalized
-NH2	delocalized
-NHCH3	delocalized

Table 1: Substituent on the acceptor and ΔE_{LUMO} using B3LYP/6-311++g(d,p): this "delocalized" molecule has a delocalized LUMO.



Substituent(X),	ΔELUMO
-NO2	0.96 eV
-CHO	1.60 eV
-COCH3	1.73 eV
-COOC2H5	1.94 eV
-COOH	1.81 eV
-Br	2.56 eV
-Cl	2.57 eV
-OH	2.64 eV
-H	2.68 eV
-CH3	2.69 eV
-SCH3	2.49 eV
-OCH3	2.69 eV
-NH2	2.69 eV
-NHCH3	2.70 eV

Table 2: Substituent on the donor and ΔE_{LUMO} using B3LYP/6-311++g(d,p).

4 CONCLUSION

The geometry and electronic structure of neutral PNX 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. The localization of the unoccupied orbital state on the acceptor moiety depends on the substituents group both for the acceptor and donor moieties.

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