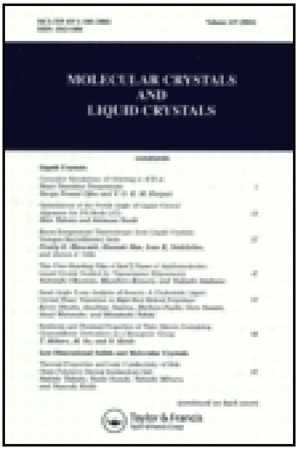

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THEORETICAL STUDY OF DONOR-SPACER-ACCEPTOR STRUCTURE MOLECULE FOR STABLE MOLECULAR RECTIFIER

H. Mizuseki [a] , K. Niimura [a] , C. Majumder [a] , R. V. Belosludov [a] , A. A. Farajian [a] , Y. Kawazoe [a] & C. Majumder [b]

[a] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

[b] Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Center, Mumbai 400 085, India

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THEORETICAL STUDY OF DONOR–SPACER–ACCEPTOR STRUCTURE MOLECULE FOR STABLE MOLECULAR RECTIFIER

H. Mizuseki, K. Niimura, C. Majumder, R. V. Belosludov,*
A. A. Farajian, and Y. Kawazoe
Institute for Materials Research, Tohoku University,
Sendai 980-8577, Japan

C. Majumder
Novel Materials and Structural Chemistry Division,
Bhabha Atomic Research Center, Mumbai 400 085, India

Recently, field of molecular electronics has attracted strong attention as a "post-silicon technology" to enable future nanoscale electronic devices. To realize this molecular device, unimolecular rectifying function is one of the most fundamental requirements using nanotechnology. In the present study, the geometric and electronic structures of alkyl derivative $C_{37}H_{50}N_4O_4$ (PNX) molecule, (donor – spacer – acceptor), a 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 concentrates on the acceptor subunit, the highest occupied molecular orbital is localized on the donor subunit. After the optimization of the structure by B3LYP/6-31(d), the approximate potential differences for the optimized PNX molecule have been estimated at the B3LYP/6-311++G(d,p) level of theory, which achieves quite good agreement with experimentally reported results.

Keywords: donor – spacer – acceptor structure; first principles calculations; molecular electronics; molecular device; nanotechnology

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*Corresponding author. Tel.: +81-22-215-2054, Fax: +81-22-215-2052. E-mail: mizuseki@imr.edu

INTRODUCTION

Molecular electronic devices have attracted much 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 and fundamental requirements in molecular device. A quarter of a century ago, Aviram and Ratner [2] first proposed molecular rectifying function using a single molecule. This work has been further supported 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, which it is required to induce an effective charge separation and transfer. For a spacer, σ and π bonds have been introduced. σ bonds have a potential of a strong charge separation. On the other hand, π bonds have delocalized orbitals and a good conductivity.

Recently, Mikayama et al. [8] proposed the novel long-chain alkyl derivative $C_{37}H_{50}N_4O_4$ (PNX, Figure 1) as a molecular rectifier. This molecule is composed of a dinitrobenzene moiety for the acceptor with a dihydrophenazine moiety providing the donor function. In the present study, the geometric and electronic structures of PNX molecule are calculated to examine the rectifying function and the effect of the substituent on this donor – spacer – acceptor structure. We explain in detail the numerical method that we used in next section and the results for the PNX molecule and the effect of substituents on the acceptor and donor moieties of the PNX molecule.

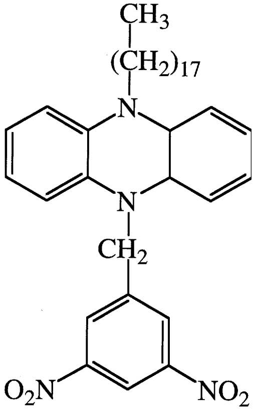


FIGURE 1 Chemical structure of the $C_{37}H_{50}N_4O_4$ molecule (PNX).

MODEL AND NUMERICAL METHOD

The total energy calculations were performed using density functional theory [9] formalism. The exchange and correlation energies were calculated using a hybrid functional. In the present calculation, we use the hybrid functional better than the Hartree-Fock (HF) method. This is because accurate descriptions of the unoccupied molecular orbitals states are very important, since the incoming electrons are assumed to pass through these states of the molecule. Therefore, the use of a hybrid function in the DFT formalism 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 PNX molecule. After the optimization of the structure, the 6-311++G(d,p) basis set was used, augmented by appropriate polarization functions.

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, while the lowest unoccupied orbital is localized around the acceptor part, the highest occupied molecular orbital is localized on the donor part. From Figure 2, it is clear that the LUMO+3 is delocalized on the whole PNX molecule. This can be attributed to the localization of the HOMO 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. 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 a donor and an acceptor was used to estimate a criterion (potential drop) of a rectifying function. 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 ($\Delta E_{LUMO}(\infty) = E_{LUMO}(\text{donor}) - E_{LUMO}(\text{acceptor})$) [5]. We analyzed the effect of a substituent group on an acceptor (See Table 1). From these

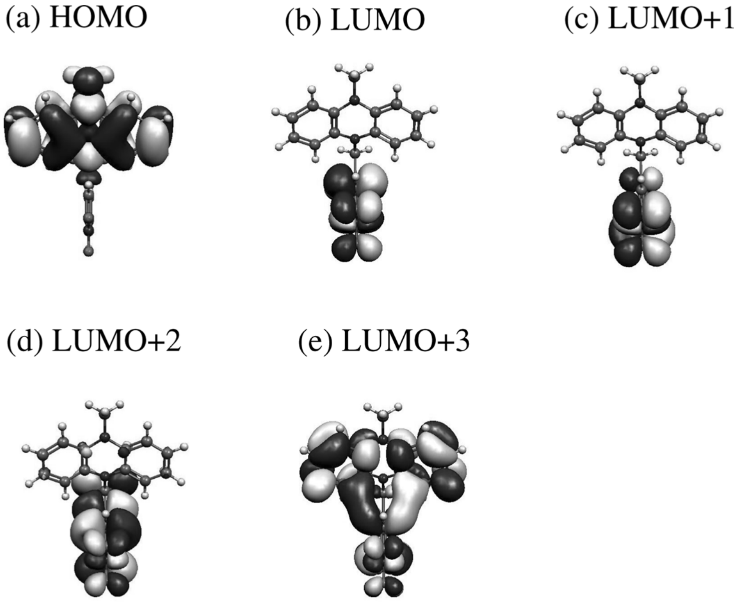


FIGURE 2 Orbital spatial orientation of (a) HOMO, (b) LUMO, (c) LUMO+1, (d) LUMO+2, and (e) LUMO+3 for the PNX molecule, respectively.

TABLE 1 Effect of Substituent Group on the Acceptor and ΔE_{LUMO} Using B3LYP/6-311++G(d,p). "Delocalized" Means this Molecule has a Delocalized LUMO. Namely, these Molecules did not Show the Rectifying Function

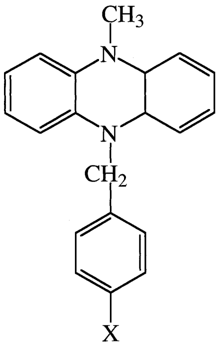
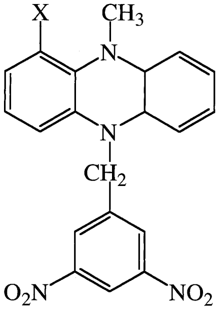
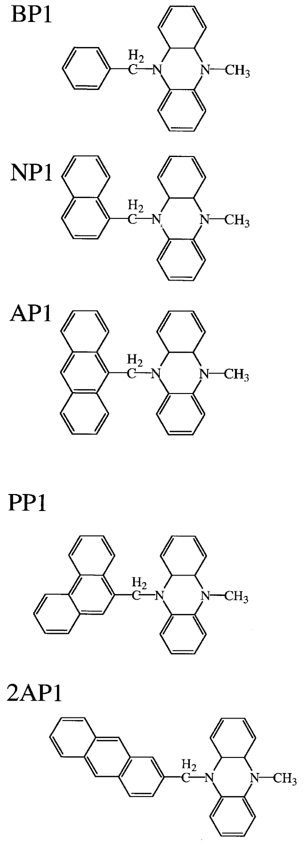
	Substituent(X)	ΔE_{LUMO}
 CH_3 N N CH_2 X	-CN	1.15 eV
	$-NO_2$	2.17 eV
	-CHO	1.56 eV
	$-COCH_3$	1.38 eV
	$-COOC_2H_5$	1.12 eV
	-COOH	1.26 eV
	-Br	0.49 eV
	-Cl	0.48 eV
	-OH	0.29 eV
	-F	0.33 eV
	-H	0.21 eV
	$-CH_3$	delocalized
	$-SCH_3$	delocalized
	$-OCH_3$	delocalized
	$-NH_2$	delocalized
	$-NHCH_3$	delocalized

TABLE 2 Effect of Substituent Group on the Donor. ΔE_{LUMO} and HOMO-LUMO Gap Obtained by Using B3LYP/6-311++G(d,p) Level of Theory



Substituent(X),	ΔE_{LUMO}	$\Delta E_{HOMO\text{-}LUMO}$
$-NO_2$	0.96 eV	1.85 eV
-CHO	1.60 eV	1.72 eV
$-COCH_3$	1.73 eV	1.65 eV
$-COOC_2H_5$	1.94 eV	1.66 eV
-COOH	1.81 eV	1.71 eV
-Br	2.56 eV	1.65 eV
-Cl	2.57 eV	1.64 eV
-OH	2.64 eV	1.49 eV
-H	2.68 eV	1.56 eV
$-CH_3$	2.69 eV	1.50 eV
$-SCH_3$	2.49 eV	1.62 eV
$-OCH_3$	2.69 eV	1.46 eV
$-NH_2$	2.69 eV	1.35 eV
$-NHCH_3$	2.70 eV	1.27 eV

results electron withdrawing group make a strong localized LUMO and increase of ΔE_{LUMO}, while more strong donating group than hydrogen make a delocalized LUMO. Moreover we examine the effect of various donors (See Table 2). A dihydrophenazine moiety providing the donor function, therefore, an electron donating group have an almost no influences on ΔE_{LUMO} and an electron withdrawing group decrease of ΔE_{LUMO}. Finally we explore the effect of a various fused moieties for an acceptor. Generally speaking, anthracene and phenanthrene have a stronger acceptor function than benzene. From Figure 3, we can observe a strong acceptor makes a large potential difference. AP1, PP1, and 2AP1 have a same size of fused ring, however, these molecules show a different ΔE_{LUMO}. The order of values of ΔE_{LUMO} for AP1, 2AP1, and PP1 molecules is in quite good agreement with experimentally reported results [12].



Molecule	ΔE_{LUMO}	$\Delta E_{HOMO\text{-}LUMO}$
BP1	0.21 eV	3.95 eV
NP1	1.06 eV	3.14 eV
AP1	1.77 eV	3.07 eV
PP1	0.97 eV	3.19 eV
2AP1	1.63 eV	2.55 eV

FIGURE 3 Effect of fused ring as acceptor moieties for PNX derivative. ΔE_{LUMO} and HOMO-LUMO gap obtained by using B3LYP/6-311++G(d,p) level of theory.

CONCLUSION

Molecular device is a potential candidate and would make it possible to realize a new paradigm shift beyond the silicon technology. In this paper, the geometry and electronic structures of neutral PNX molecules have been calculated using density functional theory. The effect of substituents in these molecules has been analyzed, based on 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 a substituent both of the acceptor and of the donor moieties.

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