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Theoretical study of the alkyl derivative $C_{37}H_{50}N_4O_4$ molecule for use as a stable molecular rectifier: geometric and electronic structures

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Abstract

The realization of a molecular device with a unimolecular rectifying function is one of the most important requirements in nanotechnology. In the present study, the geometric and electronic structure of the alkyl derivative molecule $C_{37}H_{50}N_4O_4$ has been investigated theoretically using ab initio quantum mechanical calculations. This molecule has a donor–spacer–acceptor structure, and is a leading candidate for the creation of a molecular rectifying device. The results suggest that in donor–acceptor molecular complexes such as this, while the lowest unoccupied orbital is concentrated around the acceptor sub-unit, the highest occupied molecular orbital is localized on the donor sub-unit. The approximate potential differences for an optimized PNX molecule have been estimated to be 2.683 eV at the B3LYP/6-311g++(d,p) level of theory.

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Keywords: Molecular electronics; Molecular device; Nanotechnology; Simulation; Donor–spacer–acceptor structure

1. Introduction

Recently, the field of molecular electronics has attracted strong attention as a “post-silicon technology” to enable future nanoscale electronic devices. A quarter of a century ago, Aviram and Ratner [1] first demonstrated how an organic molecule could function as a molecular device. This work has been further supported by a number of experimental results [2–4] and several theoretic

cal studies have been published [5–10]. Many rectifier molecules are comprised of electron donor and electron acceptor sub-units connected by a methylene tunneling bridge. In order to realize an efficient unimolecular rectifier and photoelectric device composed of a D (donor sub-unit)–spacer (sigma bond)–A (acceptor sub-unit) molecule, it is necessary to induce an effective charge separation and transfer. Thus, careful selection of each sub-unit is important for the regulation of the potential between the donor and the acceptor sub-units.

From the viewpoint of practical applications, Mikayama et al. [11–13] proposed the novel long-chain alkyl derivative $C_{37}H_{50}N_4O_4$ (PNX, Fig. 1(a) and (b)) as a molecular rectifier. This molecule is

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composed of a dinitrobenzene moiety for the acceptor with a dihydrophenazine moiety providing the donor function. These moieties are connected by a methylene group, while a long alkyl chain is bonded to the donor part. A well ordered monolayer of these molecules has been constructed by the Langmuir–Blodgett (LB) method. Scanning tunneling spectroscopy (STS) was used to characterize the conductivity of the PNx molecular monolayer on Au(1 1 1) and the rectifier function was reported [13].

In the present work, we optimized the structure of this molecule to examine the rectifying function of the PNx molecule, which is composed of a donor and acceptor sub-unit and a long-chain alkyl. We explain in detail the numerical method that we used (Section 2) and the results for the PNx molecule (Section 3) and the effect of the acceptor on the PNx molecules (Section 4).

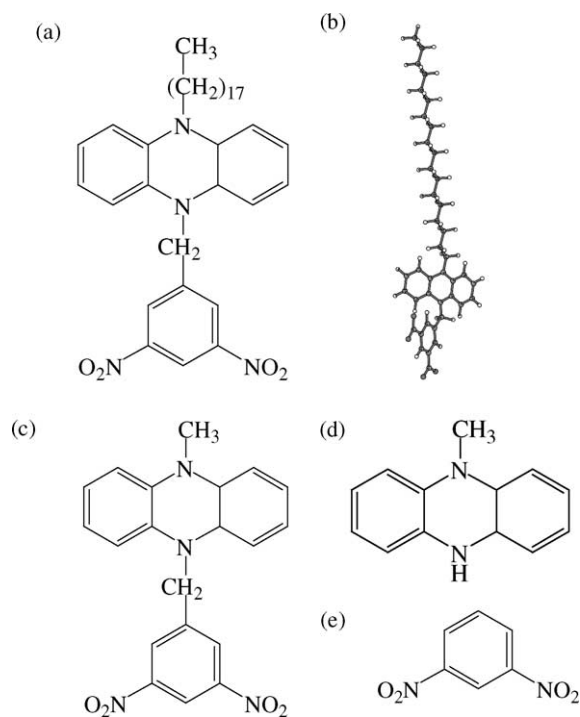


Fig. 1. (a) Chemical structure and (b) stable structure of C₃₇H₅₀N₄O₄ molecule (PNx) optimized at the HF/6-311g level of theory. (c) Chemical structure used in this study. (d) Donor moiety. (e) Acceptor moiety for PNx molecule.

2. Model and numerical method

The total energy calculations were performed using density functional theory [14] 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 LUMO states are very important, since the incoming electrons are assumed to pass through the molecule. Therefore, the use of the hybrid function in DFT formalism is fully justified. Several successful applications of molecular devices using hybrid functions have been reported [14–16]. To save computational time, we make 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 [17] at the B3LYP theory level. The B3LYP/6-31(d) was used to obtain the stable structure of PNx molecule. After the structure optimization, the 6-311++g(d,p) basis set was used, augmented by appropriate polarization functions.

3. Results

To understand the rectifying behavior of the PNx molecule, we calculate the HOMO, LUMO and HOMO–LUMO gaps of the structure for optimized donor and acceptor moieties independently. Fig. 1(c)–(e) show the chemical structure of the molecule as the whole molecule, the donor sub-unit, and the acceptor sub-unit, respectively.

Fig. 2 shows a comparison of the five highest occupied (HOMO) and five lowest unoccupied orbital levels (LUMO), using HF/6-311g for the donor sub-unit without the alkane chain, the donor sub-unit with the alkane chain and the whole PNx molecule with the chain and acceptor sub-unit. It is clear from Fig. 2 that a long alkane chain has advantages for a molecular device, because the energy levels both with the alkane chain and without the chain are almost the same, and therefore the chain has no effect on the molecular state. Thus, it was used to give stability to the

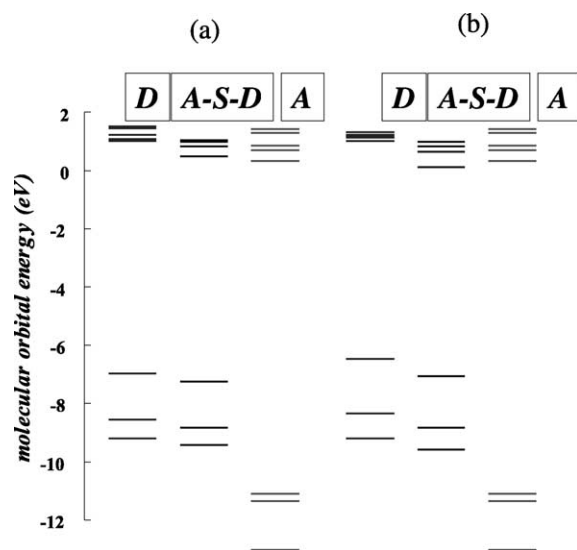


Fig. 2. Comparison of the five highest occupied and five lowest unoccupied orbital levels for the donor sub-unit, the PNx molecule, and the acceptor sub-unit. D, A-S-D, and A stand for donor, donor-spacer-acceptor structure, and acceptor, respectively. (a) Donor has no alkyl chain. (b) Donor has a long alkyl chain. The chain has no effect on the molecular state.

rectifying moiety so that the metal atoms of the electrode would not have much influence on the electronic structure of the PNx molecule. Therefore, again to save computational time, we calculate the molecular state without the alkane chain using the more accurate (B3LYP/6-311++g(d,p)) method to evaluate the frontier orbitals.

Fig. 3 shows the frontier orbitals for the donor sub-unit without the alkane chain, for the whole PNx molecule, and for the acceptor sub-unit using B3LYP/6-311++g(d,p). It is interesting to note here that while the LUMO energy levels of the PNx molecule compare well with the LUMO energy level of the dinitrobenzene group (acceptor moiety), the HOMO energy level of the PNx is close to the HOMO energy level of the dihydrophenazine group (donor moiety).

To estimate the electron transport through this molecule, we have analyzed the spatial extent of the frontier orbitals (HOMO and LUMO), providing a strategy by which the rectifying properties of the PNx molecule can be understood. Fig. 4 shows the HOMO and LUMO + K ($K = 0, 1, 2, 3$), plots of the PNx molecule. From Fig. 4, it is

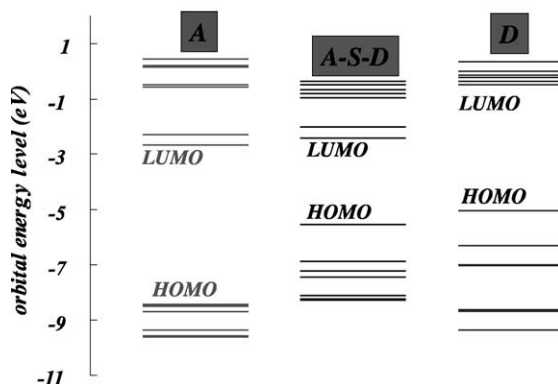


Fig. 3. Comparison of the frontier orbital levels using B3LYP/6-311++g(d,p).

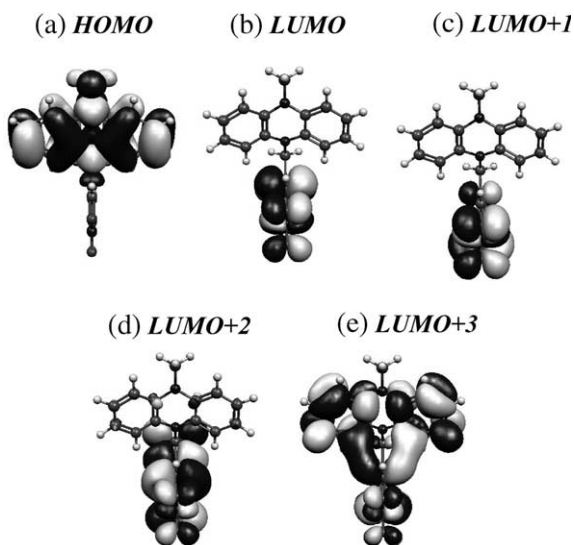


Fig. 4. Orbital spatial orientation of HOMO and LUMO + K ($K = 0, 1, 2$) for the PNx molecule: (a) HOMO, (b) LUMO, (c) LUMO + 1, (d) LUMO + 2, and (e) LUMO + 3.

clear that for the PNx molecule, the LUMO is localized on the acceptor, while 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 D-Sigma-A molecular complex, respectively [5]. Figs. 3 and 4 suggest that the potential drop ΔE_{LUMO} across the PNx 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. A detailed description of the definition of ΔE_{LUMO} is provided elsewhere [5]. The approximate potential differences for an optimized PNX molecule have been estimated to be 2.683 eV at the B3LYP/6-311g++(d,p) level of theory. From Fig. 8 in Ref. [13], we can see this molecule has a rectifier function and good conductivity around 0.8 V on forward biased direction.

4. Discussion

To investigate the effect of the chemical structure of the PNX molecule with regard to its rectifying functionality, we examined the use of various functional groups as the acceptor and various spacer lengths for the PNX molecule, as synthesized by Uehara et al. [11]. Namely, benzene, anthracene and phenanthrene were investigated as the acceptor, and methylene and dimethylene were investigated as the spacer (see Table 1). Generally speaking, anthracene and phenanthrene have a stronger acceptor function than benzene. From Table 2, we can see a strong acceptor makes a large potential difference. From these series of acceptor calculations, we derived the effect of the acceptor moiety. On the other hand, dimethylene has a wider sigma bond length than methylene, so its functional separation ability is stronger than one sigma bond. It is clear that their ΔE_{LUMO} are affected by the length of a spacer.

Table 1
Length of alkane chain for spacer and ΔE_{LUMO} using B3LYP/6-311++g(d,p)

Length	ΔE_{LUMO} (eV)
$n = 0$	2.627
$n = 1$	2.683
$n = 2$	2.841
$n = 3$	2.856
$n = 4$	2.901
$n = 5$	–
$n = 6$	–

$n = 0$ means that acceptor and donor is connected directly. In $n = 5, 6$ case, LUMO is not delocalized on whole molecule due to a long alkane chain.

Table 2

Acceptor moieties for PNX molecule and ΔE_{LUMO} using B3LYP/6-311++g(d,p)

Acceptor	ΔE_{LUMO} (eV)
Benzene	0.205
Naphthalene	1.062
Anthracene	1.772
Naphthacene	1.978

5. Conclusions

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 electron transport 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 both the excess electron and the acceptor group. Finally, we can examine the effect of a various acceptor and the length of σ bridge.

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