A theoretical study of charge transport properties of trifluoromethyl (-CF\textsubscript{3}) substituted naphthalene (TFMNA) molecule

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Abstract. We present a density functional (DFT) study of the charge transport properties of CF\textsubscript{3}-naphthalene. Nature of charge transport is investigated using parameters such as reorganization energy (λ), transfer integral (t), ionization potential (IP), electron affinity (EA), and carrier mobility (µ) computed through electronic structure calculations. We observe a decrease in λ and IP from 2,6-DTFMNA to 1,5-DTFMNA, whereas, the EA is found to be enhanced, as a result p-type characteristics, with mild n-type signature, in the organic semiconductor gets increased. In addition, the HOMO-LUMO gap also gets reduced inferring more charge injection through the potential barrier. The maximum hole and electron mobility values for the substituted compound are obtained to be 2.17 cm\textsuperscript{2}/Vsec & 0.20 cm\textsuperscript{2}/Vsec, respectively.

1. Introduction

Since last many years, organic conjugated materials have attracted much attention due to their potential applications such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), solar cells, etc. [1-3] The efficiency of these devices basically depends on the charge transport properties. However, the major problems with organic semiconductors (OSC) are their instability, moisture sensitivity, etc. Many authors were reported to have substituted electron withdrawing groups (EWGs) such as halogens (-X), cyano (-CN) and trifluoromethyl (-CF\textsubscript{3}) etc. to overcome these problems and to increase the stability as well. For example, Bao et al. and Wudl et al. reported their works on pentacene derivatives and found mobility as high as 0.23 cm\textsuperscript{2}/Vsec. [4, 5] Further, Tsuzuki and his co-workers investigated F- and CF\textsubscript{3}-substituted oligomers and observed the electron mobility to be up to 0.55 cm\textsuperscript{2}/Vsec, whereas the single crystal transistors exhibited high electron mobilities up to 3.1 cm\textsuperscript{2}/Vsec. [6] In order to achieve high air stability and to develop a high performance n-type organic semiconductors, a series of oligomers containing -CF\textsubscript{3} and -CN groups were synthesized by Shoji et al. [7] In addition, Yu and coworkers also experimentally developed two air stable n-type CF\textsubscript{3}-triphenodioxazines. [8] In this report, we have investigated the influence of trifluoromethyl (-CF\textsubscript{3}) on the charge transport properties of naphthalene.
2. Theory

In the present context, Marcus-Levich-Jortner theory for the dimer system has been used to explain the charge transport in terms of electron transfer rate from one molecular site to another and is stated as [9-11]:

\[
\lambda_S \approx 0.4 \text{ eV}, K_B \text{ is the Boltzmann's constant, } T \text{ is the absolute temperature, and } n \text{ denotes the number of vibration levels. The factor } S \text{ represents the Huang-Rhys factor and } \Delta G^0 \text{ is a change in Gibb's free energy due to the electric field. For the calculation, the Huang-Rhys factor is defined as } S = \lambda S / \hbar \omega. \text{ The Gibb's free energy of the molecule is given as } \Delta G^0 \approx e. F. d, \text{ where } F \text{ is electric field and } d \text{ is interplanar spacing between the dimer system [9-11]. The charge carrier mobility (\mu) can be computed using the following formula;}
\]

\[
\mu = (d. K) / F \quad \text{(2)}
\]

where \(d, K, \) and \(F\) are defined in the above paragraph.

The total reorganization energy is a sum of internal and external reorganization energy. Here we only focus on the internal reorganization energy and for holes & electrons it is calculated by:

\[
\lambda_i = (E^+ - E^+) + (E^- - E^-) \quad \text{(3)}
\]

Here '+' for holes and '-' for electrons respectively. And here \(E^+\) (or \(E^-\)) represents the energy of cation (or anion) at the neutral geometry, \(E^+\) (or \(E^-\)) represents the energy of cation (or anion) respectively, \(E^+\) represents the energy of neutral at charged state and \(E\) represents the energy of neutral at neutral geometry [1].

3. Computation

All the structures of trifluoromethyl substituted naphthalene molecules (TFMNA) have been optimized using the basis set 6-311G (d, p) with Becke's three exchange parameter and Lee-Yang-Parr correlation functionals, within the framework of Density Functional Theory (DFT). All the structures of different charge states were optimized without any imaginary harmonic frequencies. Value of transfer integral (\(t\)) was calculated using semi-empirical intermediate neglect of differential overlap (INDO) Hamiltonian. All the calculations were performed using the computational chemistry software GAUSSIAN 09 and the graphical user interface CHEMCRRAFT. [12, 13]

4. Result and Discussion

The trifluoromethyl (-CF\(_3\)) groups are substituted to both \(\alpha\)- and \(\beta\)-positions of naphthalene molecule such as 1,5-DTFMNA and 2,6-DTFMNA and the optimized structures are presented in Fig.1. The calculated values of reorganization energy, ionization potential & electron affinity and HOMO/LUMO gap are provided in Table 1 and the HOMO/LUMO orbitals of the CF\(_3\)- substituted naphthalene are presented in Fig. 2. In order to avoid the clustering between the molecules, the interplanar orientation of the molecules at a distance range from 3.7 Å to 5.0 Å is considered. The calculation has been performed by an external electric field of 5x10\(^{6}\) V/cm and a fixed temperature of 300K. It can be seen from Table 1 that both hole and electron reorganization energy get decreased while going from 2,6-DTFMNA to 1,5-DTFMNA. Further, the hole reorganization energy is computed to be smaller in 1,5-DTFMNA as compared that in 2,6-DTFMNA indicating a predominance of p-type characteristics of the former. The fact is supported also by the decrease in value of IP value in 1,5-DTFMNA by 0.016 eV. However, the increase in EA values in 1,5-DTFMNA also marks the n-type characteristics, inferring an increased ambipolar signature 1,5-DTFMNA as compared to 2,6-DTFMNA. The above fact is also reflected in the FMOs of both isomers and it can be
found that -CF$_3$ group has a comparatively larger contribution to 1,5-DTFMNA than FMOs of 2,6-DTFMNA. Moreover, reduction of HOMO-LUMO gap by an amount of 0.10 eV in 1,5-DTFMNA also indicate the case to be comparatively more favorable for the charge transport.

![Figure 1](image1.png)  
**Figure 1.** Optimized neutral structures of CF$_3$-naphthalene (a) 2,6-DTFMNA (b) 1,5-DTFMNA.

![Figure 2](image2.png)  
**Figure 2.** Frontier molecular orbitals (FMOs) of the CF$_3$-naphthalene (TFMNA) conjugate molecule.

Figure 3 defines the evolution of the transfer integral in terms of HOMO/LUMO splitting as a function of normal unidirectional translation in the dimer system. The transfer integral is observed to decay exponentially with the increase of the inter planar spacing being maximum of 0.35 eV and 0.179 eV (for HOMO and LUMO respectively) for 2,6-DTFMNA and 0.38 eV and 0.18 eV, for 1,5-DTFMNA, at an inter planar spacing of 3.7 Å inferring larger mobility for the spacing. The exponential decay in the value of the transfer integral is supposed to due to diminishing overlapping of
the $\pi$-molecular orbitals between the stacked molecules. From calculations, we observed the transfer integral tends to vanish after the inter molecular separation of 5.0 Å.

Further, the carrier mobility of molecules has been calculated by means of transfer integral and charge transfer rate, and are shown in Fig. 3. As expected, the carrier mobility is also observed to decay exponentially with the inter molecular separation. Even though, the hole mobility is found to be very large, in TFMNA molecule, however, a noticeable electron mobility is also observed in the computed system which is found to be enhanced from 2,6-DTFMNA to 1,5-DTFMNA, respectively. The maximum hole mobilities of 2,6-TFMNA and 1,5-TFMNA are observed to be 1.17 cm$^2$V$^{-1}$s$^{-1}$ and 2.17 cm$^2$V$^{-1}$s$^{-1}$, at the inter planar separation of 3.7 Å, respectively, whereas the electron mobility are calculated to be 0.10 cm$^2$V$^{-1}$s$^{-1}$ & 0.20 cm$^2$V$^{-1}$s$^{-1}$ for the respective cases.

### Table 1. Calculated H-L gap, ionization potential, electron affinity and reorganization energy of the observed molecule.

| Compounds    | H-L gap (eV) | IP (eV) | EA (eV) | Reorganization Energy |
|--------------|--------------|--------|--------|-----------------------|
|              | Hole (eV)    | Electron (eV) |
| 2,6-DTFMNA   | 4.80         | 8.757  | 0.437  | 0.376                 | 0.601                 |
| 1,5-DTFMNA   | 4.70         | 8.741  | 0.508  | 0.291                 | 0.471                 |

### Figure 3. Variation of the transfer integral and hole mobility of the CF$_3$-napthalene (TFMNA) molecule.

5. **Conclusion**

We report our theoretical study, within the framework of density functional theory, of the charge transport properties of the CF$_3$-naphthalene molecules (TFMNA) using the dimer model. We found that the hole reorganization energy was smaller in 1,5-DTFMNA as compared that in 2,6-DTFMNA indicating a predominance of p-type characteristics of the former and the fact is reflected in the computed values of IP and transfer integrals. Though the investigated molecule can be primarily considered to be a p-type OSC, however, a signature of electron mobility of the order of 0.20 cm$^2$ V$^{-1}$s$^{-1}$ could be traced in 1,5-DTFMNA, which explains the n-type characteristics of the conjugated molecule.
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