Study of The Electronic Properties For Cyanobenzene Molecules group: B3LYP Density Functional Theory Calculations

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Abstract

In this work, B3LYP density functional theory was employed to calculate the effect of cyano substituent group on the electronic properties of benzene molecule. These properties include the total energy, electronic states, energy gap, ionization potential, electron affinity, electronegativity, hardness, softness and electrophilic index. As a result, the total energy for the studied molecules was decreased linearly with increasing the cyano groups number and the cyanobenzene molecules are more soft with small energy gap in comparison with benzene. Increasing the cyano substituent added to the ring give the molecule more electrophilicity and more reactivity.

Keywords: DFT, ionization potential, HOMO, LUMO, energy gap and electrophilicity.

الخلاصة

في هذا البحث تم استخدام نظرية دالة الكثافة لحساب تاثير مجاميع السيانو المضافة في الخصائص الالكترونية لجزيئة البنزين . حيث تم دراسة بعض الخصائص ,منها الطاقة الكلية, الحالات الالكترونيه, فجوه الطاقة, الجهد الايوني, الالفة الالكترونيه, السالبيه الكهربائيه, الصلادة, المرونه, والتالف مع الوسط. حيث وجد ان الطاقة الكليه تزداد خطيا بزيادة مجاميع السيانو CN المضافة كما ان الجزيئه الناتجة هي اكثر مرونه مع فجوه طاقة قليله مقارنه مع جزيئه البنزين الاصلية.ان زيادة عدد المجاميع الجانبيه المضافة من الCN الى حلقة البنزين يعطي الجزيئه الجديدة الناتجه اكثر تالف مع الوسط واكثر تفاعلا.

Introduction

Aromatic compounds are important in industry and play key roles in the biochemistry of all living things [K. J. Denniston, J. Topping and T. M. Dwyer,(2007) , K. Kefa Onchoke, M. Christopher,(2006)]. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [H. Klauk, D. J. Gundlach, M. Bonses, C. C. Kuo and T. Jackson,(2000), T. W. Kelley, D. V. Muyres, P. F. Baude, T. P. Smith, T. P. Jones,(2003)]. Many studies on cyclic oligomers have been reported both experimentally and theoretically [M. D. Curtis, J. Cao, J. W. Kampf, J. Am,(2004), S.E. Koh. C. Risko, D.A. de Sliva Filho, O. Kwon, A. Facchefti, J. L. Bredas,(2008)], in [G. R. Hutchison, M. A. Ratner, T. J. Marks, J. Am,(2005)] the substituent effects of oligomers such as oligothiophene, oligopyrrole and oligofuran are discussed in terms of reorganization energy. Also, [R. G. Parr, W. Yang,(1989)] studied the geometric and electronic properties for cynothiophene oligomers as a prototype of an organic conducting polymer using ab initio and Density function theory [M. A. De Oliveira, H. F. De Almeida, In. J. Quan,(2002)], they showed that the cyano group generally reduced the band gap with variation of the substitution position.

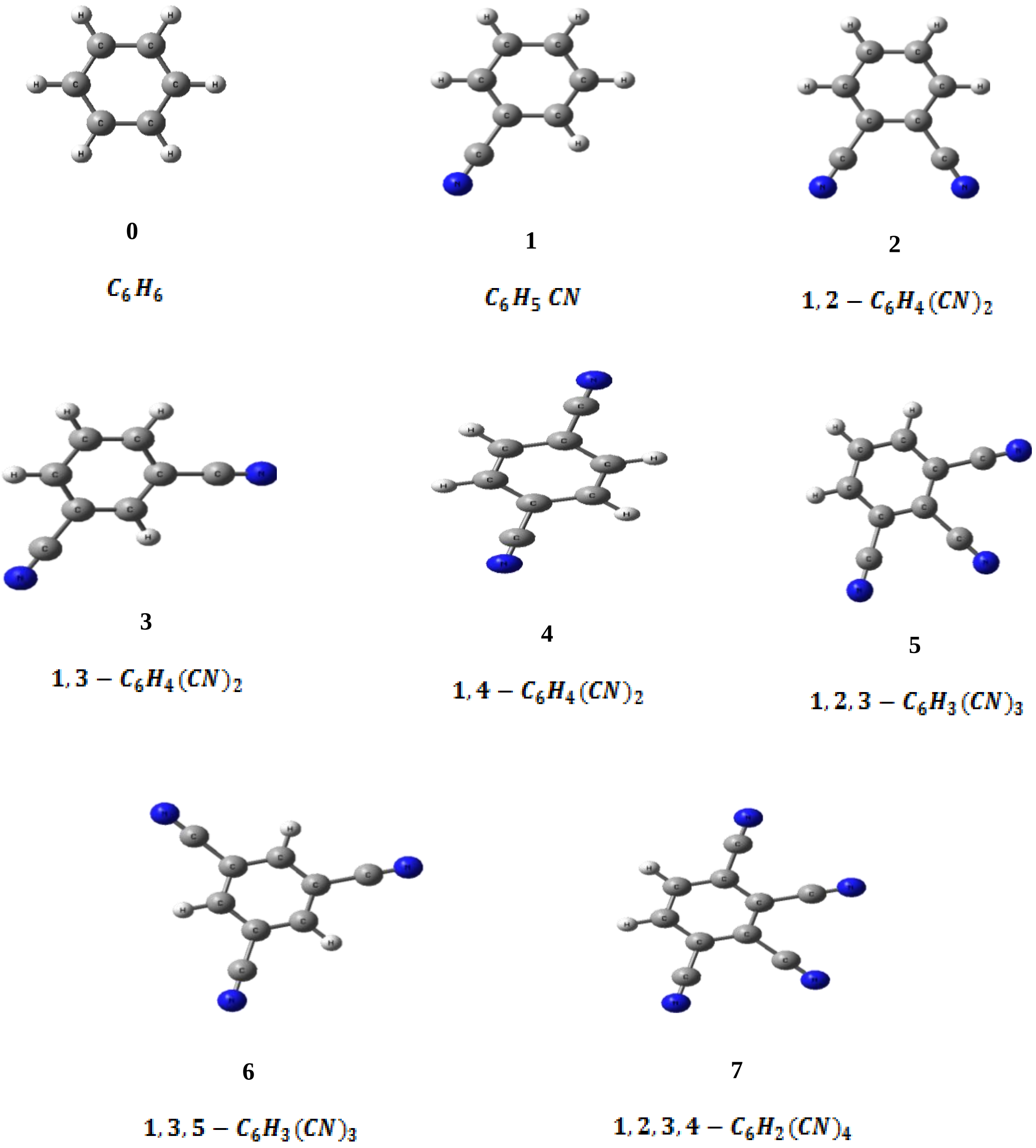
Cyanobenzene molecules group are aromatic compounds possessing the ring structure of benzene or other molecular structures that resemble benzene in electronic configuration and chemical behavior. These compounds are manufactured on a large scale for use in high octane gasoline and in the production of polymers, insecticides, detergents, dyes and many miscellaneous chemicals[T. Balaban, P. v. R. Schleyer and H. S. Rzepa,(2005)]. There are many compounds that, at first appearance, bear little resemblance to benzene, but have a basic similarity in electronic configuration, and they are aromatic, too[P. v. R. Schleyer,(2005), O. Kwon, V. Coropceanu, N. E. Gruhn, J. C. Durivage, J. G. Laquindanum, H. E. Katz, J. Cornil, and J. L. Bredas, J. Chem,(2004)]. Benzene was formed from a six member carbon ring with alternating single and double bonds, was developed by Kekule [Robert Thornton Morrison, Robert Neilson Boyd,(2007)]. The model for benzene consists of two resonance forms, which corresponds to the double and single bonds switching positions[Peter R.S. Murray,(2005)].

In present work, density functional theory has been performed to study the electronic properties of the cyanobenzene molecules to determine the effects of the substituent groups.

Computational details

Figure 1 represents the molecules under study. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 03 suite of programs [M. J. Frisch, G. W. Trucks, H. B. Schlegel,(2009)]. The molecular properties of the compounds have been computed by DFT using the standard 6-31G(d, p) basis sets. In the DFT calculations the Lee, Yang and Parr correlation functional [C. Lee, W. Yang, R.G. Parr,(1988)] is used together with Becke's three parameters [A.D. Becke,(1988)] exchange functional B3LYP. Conformational analysis of the molecules has been performed to have an idea about the lowest energy structures of the species.

The geometry optimization was performed at the B3LYP density functional theory with the same basis sets [C. Lee, W. Yang, R.G. Parr,(1988), A.D. Becke, J. Chem,(1993)]. Harmonic vibrational frequencies were computed at the same level of theory. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [J. Engelberts, R. Havenith, J. Van Lenthe, L. Jenneskens, P. Fowler,(2005) - J. C. Santos, J. Andres, A. Aizman, P. Fuentealba, J. Chem,(2005)].The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms, respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC}, which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [P. Udhayakala, T. V. Rajendiran, S. Seshadri, and S. Gunasekaran, J. Chem,(2011)]. The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction, and vibrational analysis for some structures does not yield any imaginary frequencies, which indicates that these structures of the molecules correspond to at least a local minimum on the potential energy surface [S. Gümüs, Turk,(2011)].



0

C_6H_6

1

$C_6H_5\,CN$

2

$1,2-C_6H_4(CN)_2$

3

$1,3-C_6H_4(CN)_2$

4

$1,4-C_6H_4(CN)_2$

5

$1,2,3-C_6H_3(CN)_3$

6

$1,3,5-C_6H_3(CN)_3$

7

$1,2,3,4-C_6H_2(CN)_4$

Figure 1. Optimized Structures of benzene and its derivatives discussed in this work

In this investigation, the more relevant electronic potential (IP), electron affinities (EA), chemical potential (μ) [it is the negative of electronegativity (χ)], hardness (η), softness (S), electrophilic index (ω) and the electric dipole polarizability (α) were calculated. The HOMO and LUMO energy was used to estimate the IP and EA in the framework of Koopmans' theorem [A. Demetrio Da Silva, V. Coropceanu, D.Fichou,(2007)]:

$$IP = -\varepsilon_{HOMO} \quad \text{and} \quad EA = -\varepsilon_{LUMO}$$

Within the framework of the density functional theory (DFT), one of the global quantities is chemical potential (μ), which is measures the escaping tendency of an electronic cloud, and equals the slope of the energy versus N(number of electrons) curve at external potential ν(r) [M. Oftadeh, S. Naseh, M. Hamadanian,(2011)]:

$$\mu = \left[\frac{\partial E}{\partial N}\right]_{\nu(r)} \qquad (1)$$

Finite difference approximation to Chemical Potential gives,

$$\mu \approx -\chi = -(IP + EA)/2 \qquad (2)$$

The theoretical definition of chemical hardness has been provided by the density functional theory as the second derivative of electronic energy with respect to the number of electrons N, for a constant external potential ν(r) [M. Oftadeh, S. Naseh, M. Hamadanian,(2011)]:

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_{\nu(r)} = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right]_{\nu(r)} \qquad (3)$$

Finite difference approximation to Chemical hardness gives,

$$\eta = (IP - EA)/2 \qquad (4)$$

For insulator and semiconductor, hardness is half of the energy gap ($\varepsilon_{HOMO} - \varepsilon_{LUMO}$), and the softness is given as [A. Demetrio Da Silva, V. Coropceanu, D. Fichou ,(2007)]:

$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_{\nu(r)} = \left(\frac{\partial N}{\partial \mu}\right)_{\nu(r)} \qquad (5)$$

Electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index (ω) is defined as [] P. Udhayakala, T. V. Rajendiran, S. Seshadri, and S. Gunasekaran,(2011)],

$$\omega = \frac{\mu^2}{2\eta} \qquad (6)$$

Results and discussion

I. Total energy and symmetry

Table (1) shows the result of geometrical optimization for studied molecules includes the total energy and symmetry group. It is obvious from table (1) that the total energy for all mentioned molecules is less than that for the reference molecule (benzene), the total energy is decreased.

Table 1: Total energy and symmetry for molecules

Species		E_T (a.u)	Symmetry
0	C_6H_6	-232.2778818	D_{6h}
1	C_6H_5CN	-324.5287197	C_{2v}
2	$1,2-\ C_6H_4(CN)_2$	-416.7719841	C_{2v}
3	$1,3-C_6H_4(CN)_2$	-416.7750177	C_{2v}
4	$1,4-C_6H_4(CN)_2$	-416.7756352	D_{2h}
5	$1,2,3-C_6H_3(CN)_3$	-509.0118235	C_{2v}
6	$1,3,5-C_6H_3(CN)_3$	-509.0172568	D_{3h}
7	$1,2,3,4-C_6H_2(CN)_4$	-601.2489769	C_{2v}

The addition of cyano groups gives that the benzene molecule becomes more stable with increase CN groups number. As a result, the total energy for any of cyanobenzene molecule is given by: $E_{tot} \approx E_{tot}(benzene) + nE_{tot}\ (CN)$

Where n is the number of CN group.

The total energy for all di-cyanobenzene molecules is approximately the same. Also, the total energy for all tri-cyanobenzene molecules is approximately the same, as we see in figure (2).

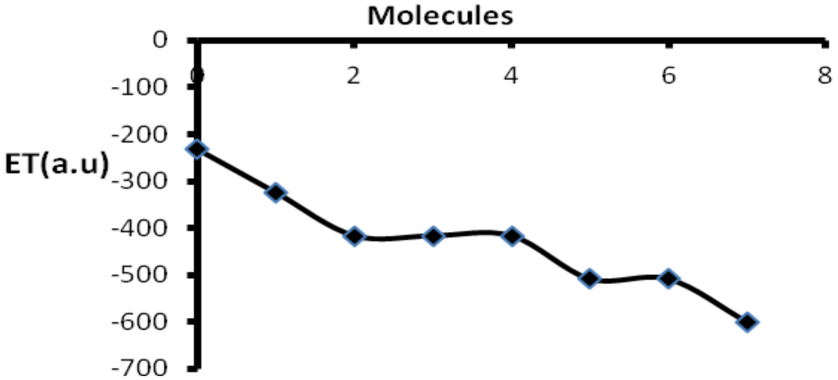


Figure (2): Total energy for studied molecules

II. Electronic states and energy gap

Figure (3) shows the HOMO and LUMO levels for studied molecules. The carbon-carbon single bonds are formed in the cyano benzene molecules, the lobes of the HOMO are largest on the terminal carbon atoms, and it is these atoms that become bound to the carbon atoms in the ring. The HOMO and LUMO are close in energy to a number of molecular orbitals, because these molecular orbitals will contribute to the reactivity.

Figure (4) shows the (LUMO – HOMO) energy gap behavior for the studied molecules group, it is less than that for benzene.. Adding the CN substituent to the ring was the lowering the energy gap, tetra-cyanobenzene molecule has the lowest value of energy gap (4.889 eV).

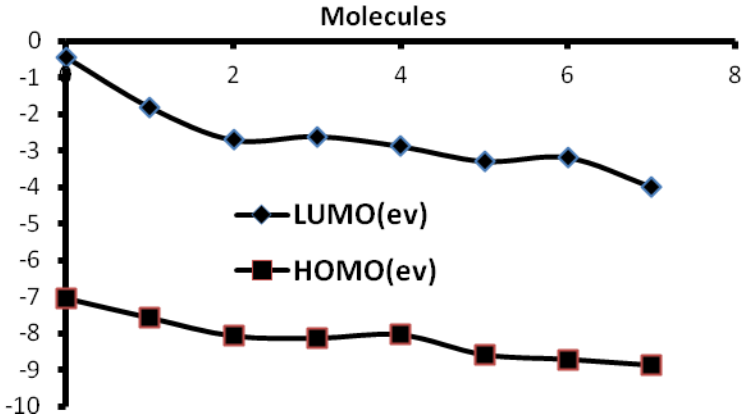


Figure (3): HOMO and LUMO for studied molecules

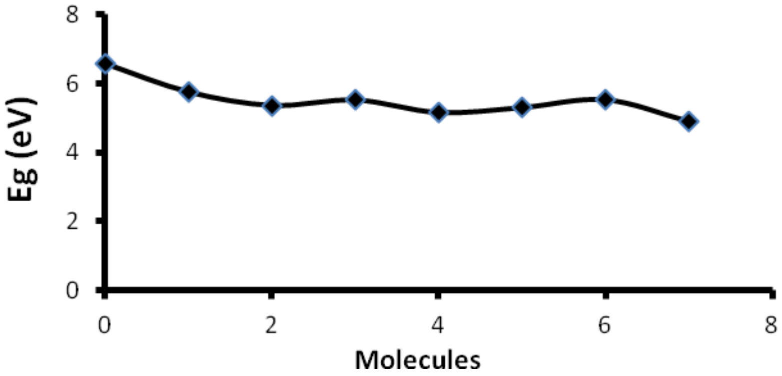


Figure (4): Energy gap for studied molecules

III. Electronic properties

The results of ionization potential as shown in figure (5)clearly that these cyanobenzene molecules have a tendency to capture electrons instead of donating them. IP for all cyanobenzene molecules group is greater than that for benzene, tetr-cyanobenzene molecule has the largest value of IP, this refers to that this molecule needs high energy to become cation comparing with others. The electron affinity is a measure of the strength of an acceptor molecule in which it has a high EA. Adding the CN substituent groups to the ring leads to increasing the ability of EA for the molecule. EA was slightly increasing with increase the CN groups number, the electron affinity for tetra-cyanobenzene is the largest (9.053 eV). Figure (6) shows the increasing of EA with increase CN groups to the ring.

The behavior of electronegativity, softness and electrophilic index for the studied molecules shows large magnitudes than these for benzene. Adding the cyano groups to the ring lead to decrease the hardness of the molecule and give it more softness. Figure (7) shows the relation between the electronegativity and the number of CN groups, it is obvious from this figure that all cyanobenzene molecules have an electronegativity greater than (a chemical potential less than) that for benzene, that means the electrons in cyanobenzene molecules have a large escaping tendency.

Figures (8) to (10) show the behavior of softness, chemical hardness and electrophilic index for studied molecules, it is clear that the softness was increased from (0.152 eV) for benzene to

(0.187 eV) for tetra-cyanobenzene molecule. This increasing of softness is the main future as a sign for that band gap goes to be rather soft. This behavior gives these molecules more electrophilicity than benzene, tetra-cyanobenzene has (ω=7.672 eV) , while benzene has (ω=2.134 eV).

Figure (5):Ionization potential for studied molecules

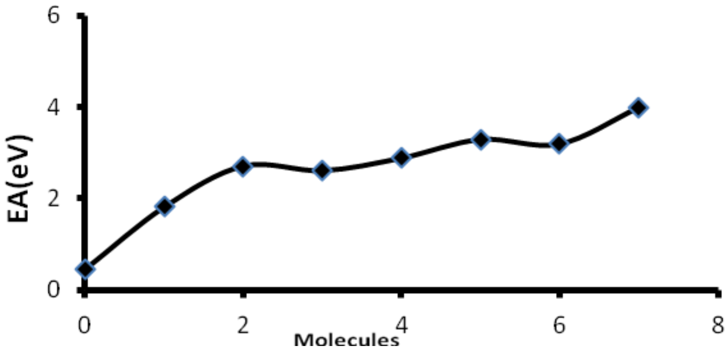


Figure (6):Electron affinity for studied molecules

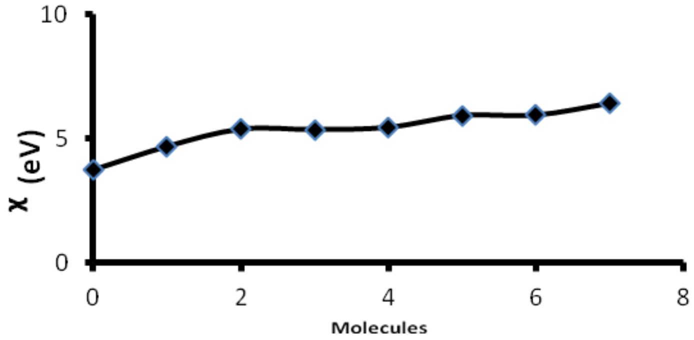


Figure (7): Electronegativity for studied molecules

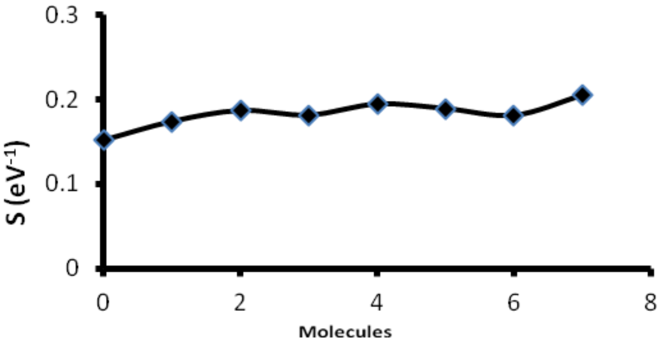


Figure (8): Softness for studied molecules

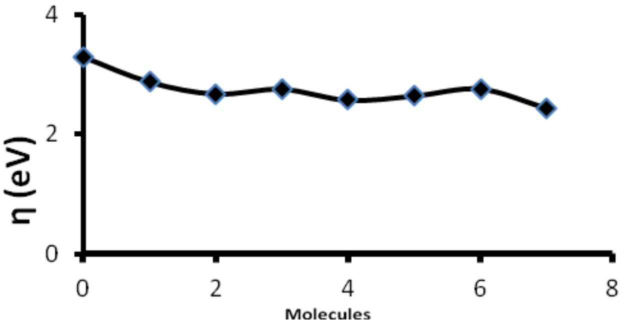


Figure (9): Chemical hardness for studied molecules

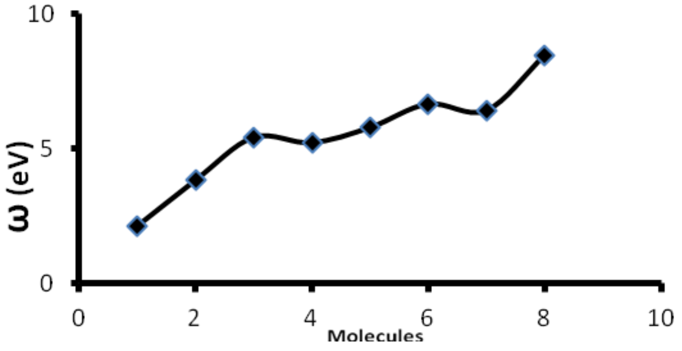


Figure (10): Electrophilic index for studied molecules

Conclusions:

important conclusions are:

1- Geometry optimization for molecule **1** has been found in a good agreement with experimental data, while for other studied molecules it has not been found a reference data.

2- The total energies for dicyanobenzene and tri-cyanobenzene found not dependent on the position of the cyano radical in the ring and substitution causes decreasing energy .

3- The presence of the substituent decreases the energy gap of the studied molecules, a small energy gap means small excitation energies of manifold of the exited states.

4- Tetra-cyanobenzene molecule is the best option for n-type organic semiconductors because of its better HOMO – LUMO ratio and other electronic properties.

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