IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 11, Issue 2Ser. I (Mar. – Apr. 2019), PP 10-18
www.iosrjournals.org

Molecular and Electronic Properties of Rubrene and Its Cyanide Derivative Using Density Functional Theory (DFT)

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Abstract:*Rubrene (5, 6, 11, 12-tetraphenyltetracene) is a prototype fluorescent molecule holding the record for the highest field effect mobility of organic semiconductors. It exhibits low stability and delocalization. In comparison with tetracene, both rubrene and tetracene exhibit the same fluorescent backbone, but due to the addition of functional group, the backbone of rubrene is twisted and planar for tetracene. A DFTmethods were carried outusing window version of Gaussian 09 software at B3LYP exchange and 6-311G basis. The work determined the change in the molecular and electronic propertiesof rubrene derivative with addition of cyanide (CN) as functional group. The bond lengths and bond angles were computed, and the results showed the strongest bond was found in CN-RUB formed atR(34,62) with value of (1.0913Å). The weakest bond was found in RUB formed atR(5,13) with value of (1.4756Å). The reorganization energy was evaluated by APS approach and NMA method, the values ofλ_h for 4CN-RUB and RUB in NMA were found to be 0.1590eV and 0.1452eV. Also, λ_e for 4CN-RUB and RUB were found to be 0.2570eV and 0.2150eV. Both values of 4CN-RUB were larger than RUB, and were closed to the experimental values.The HOMO levels of RUB (-4.6624 eV) and 4CN-RUB (-5.4996 eV) were in good agreement with experimental values of -4.94 eV and -5.10 eV. NBO analysis was obtainedwith thehighest value of (E^2)53.940kcal/mol, and was found in the bond bending/deviation C7-C15 interacting with anti-bonding C3-C7 of 4CN-RUB. The value shows that there is an intensive interaction between electron donors and electron acceptors, greater extent of conjugation of the whole system and greater stability of the structure when compared with the value 46.690kcal/molof RUB found in bond bending/deviation C3-C7 interacting with anti-bonding C1. The material demonstratesa potential application in organic light emitting diodes (OLEDs) and organic photovoltaic cells (OPVs) for high performance organic transport materials.*

Keywords*: DFT; NBO;IR-Spectra;Reorganization energy and Rubrene*

Date of Submission: 22-02-2019 Date of acceptance: 08-03-2019

I. Introduction

Interest on organic single crystalmaterials have potentially increased over a decade in space physics, material science and chemistry. This is due to their low cost, flexibility and easy to process which placed them to be accepted as a future technology. Devices such as organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs), flexible devices and organic photovoltaic cells (OPVs) are intensively under investigation in both academic and industrial laboratories (Behzad*et. al*., 2013).

Among organic semiconductors materials, rubrene demonstrateshigh charge carrier mobility and high molecular properties in the solid state physics and material science and this is why it has become a very promising material for various device applications. Rubrene also, exhibits a low stability and delocalization which is affecting device life time. This is due to the molecular packing of π-π interaction. Substitution of foreign atom molecule to rubrene structure may bring about tremendous change in the molecular and electronic properties, such as geometries, electronic structures, reorganization energy, transfer integrals, intermolecular interactions and band structures. In this work, one of the hydrogen atoms of each of the four phenyls in rubrene structure will be replaced by a molecule cyanide(CN) and study their electronic, molecular, vibrational and chemical properties based onDFT. Rubrene holds the distinction of been among the first organic semiconductor with the highest charge carrier of holes mobility(Hsu *et. al*.2007).

Some high mobility organic thin film transistors based on monocrystalline rubrene films is observed to have mobility value as high as 2.4 cm^2/Vs (Chen *et. al*.,2009). Whilethe used of induced crystallization of rubrene in thin film transistors demonstrates a new strategy of using flat thin layers of pentacenequinone (PQ) as a template to induce the crystallization of rubrene in vacuum-deposited thin films have yielded transistors with good field effect mobility. Also, a strategy of using 6,13-pentacenequinone as the template layer to induce the crystallization of rubrene in vacuum deposited thin film transistors show the field effect mobility as high as 0.35cm^2/Vs (Zhefeng*et. al*., 2010).

Moreover, when two phenyls and the tetracene backbone of the rubrene fluorinated, it enhances the rubrene stability and optical properties with less delocalization(Sureeporn*et. al*., 2011).In addition, carrier transport performance can be improved by introducing fluorine into aryl substituted tetracene and parent rubrene. It demonstrates fluorination of phenyl in rubrene change the molecular and electronic properties; just by one phenyl in 5,11-diphenyltetracene (PPT) brings about so tremendous change of the charge carrier mobility as high as 2.49cm^2/V s (Zhang *et. al*., 2013).

Chemical Structure of Rubrene, RUB

Rubrene ($C_{42}H_{28}$; 5,6,11,12-tetraphenylnaphthacene (RUB)) is a small molecule organic semiconductor belonging to the group of polycyclic aromatic hydrocarbons consisting of a tetracene backbone (i.e. four linearly fused benzene rings) with a phenyl ring bonded on each side of the two central benzene rings. The molecules have conjugated structures with alternating single and double bonds of carbon-carbon bonds. The molecules have π-orbital delocalized along the face of a molecule. This orbital delocalization allows electron to move within a molecule. Rubrene has molecular formula given by $C_{42}H_{28}$ and chemical structure given in **Figure1**(Moret*et. al*.,2014).

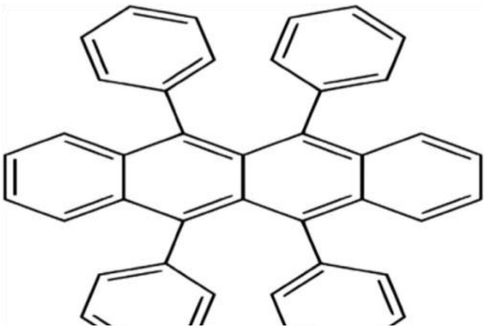

Figure 1.Chemical structure of Rubrene(RUB)

II. Computational Methodology

The work is computational method and is based on Density Functional Theory (DFT) method. It started with the structural building of the RUB and 4CN-RUB from the structural parameter obtained from existing literature using VESTA (Visualization for Electronic and Structural Analysis) and Avogadro software.A full geometry optimizations without symmetry constraints for all compounds were carried out at B3LYP exchange and 6-311G basis set in Gaussian 09 package, in whichthe ground state energies wereevaluated from the density of state of molecules given by the relation (Kohn and Sham 1965):

$$\rho(r) = \sum_{i=1}^{n} \varphi(r)\varphi_j^* \qquad (1)$$

The structure of the most stable conformer was evaluated from the molecular mechanics potential energy given by (Bano *et. al.,* 2013). The stable chemical structure of CN-RUB conformer with minimum energy is given in **Figure 2**:

$$V = V_{str} + V_{bend} + V_{oop} + V_{tors} + V_{cross} + V_{vdw} + V_{es} \qquad (2)$$

Also, the entire quantum chemical calculations wereobtained by DFT-B3LYP at 3-21G, 6-31G, and 6-311G basis sets *(*Frisch *et. al.,* 2009*)*.The total reorganization energies were computed usingAdiabatic Potential Surface (APS) and Normal Mode Analysis(NMA)at DFT and this includes the geometry relaxation when an electron is removed or added from a molecule (inner reorganization) as well as the relaxation energy due to polarization effects. Transfer integral which measures the strength of electronic coupling between the nearest neighbor molecules, depends on the relative position of the molecules. The reorganization energy λ associated with charge transport process in organic solid materials was evaluated using the normal-mode (NM) analysis method, which provided the partition of the total relaxation energy into the contributions from each vibrational mode:

$$\lambda = \sum \lambda_i = \sum \frac{1}{2}(\omega_i^2 \Delta Q_i^2) \qquad (3)$$

The NM analysis was performed with the software program combined with calculation results from Gaussian 09. Also, the Natural Bond Orbital (NBO) calculations were performed using NBO 3.2 program as implemented in the Gaussian 09 package at the DFT/B3LYP level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intermolecular delocalization or hyper-conjugation. The hyper-conjugative interaction energy was calculated from the second-order perturbation approach given as:

$$\mathrm{E}^{(2)} = -n_{\sigma}\frac{\langle\sigma|F|\sigma\rangle^{2}}{\varepsilon_{\sigma^{*}}-\varepsilon_{\sigma}} = -n_{\sigma}\frac{F_{ij}^{2}}{\Delta E} \qquad (4)$$

The harmonic vibrational frequencies have been calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies without imposing any molecular symmetry constraints.

III. Results and Discussion

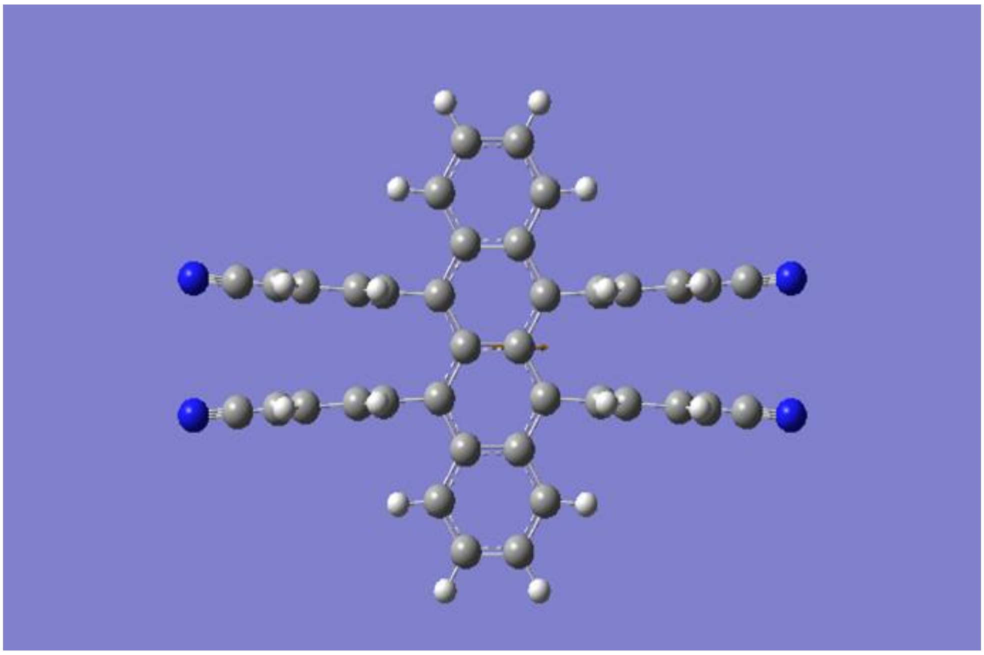

Figure 2. Chemical Structure of CN-RUB Conformer with Minimum Energy

3.1.Optimized Bond Length (Å) of RUB and 4CN-RUB

In molecular geometry, bond length is the average distance between nuclei of two bonded atoms in a molecule. It is transferable property of a bond between atoms of fixed types relatively independent of the rest of the molecule *(*Rosokha*et. al.* 2003*)*. The optimized bond lengths of RUB, CN-RUB and experimental value at DFTwith basis sets were summarized and presented in **Table 1**. The results show that the calculated bond lengths of RUB and 4CN-RUB withB3LYP/6-311G basis set, the R(34,62), R(36,64), R(32,60), R(30,58) and R(29,57) were found to be the least with the values (1.0913Å) and (1.0920Å), (1.0913Å) and (1.0922Å), (1.0921Å) and (1.0923Å) and (1.0924Å) and (1.0933Å) respectively. The bond lengths in R (3, 11) and R (5, 13) were found to be the highest with values (1.4736Å) and (1.4756Å) for RUB and CN-RUB respectively. The strongest bond was found in CN-RUB formed at B3LYP/6-311G level of theory for R(34,62) with value of (1.0913Å) and the weakest bond was found in RUB formed at B3LYP/6-311G level of theory for R(5,13) with value of (1.4756Å). Both values were in agreement with the other experimental values of (1.0909Å) and (1.4676Å) (Alexander et. al., 2012) respectively.

3.2. Optimized Bond Angles of RUB and CN-RUB

Other structural properties that define molecular geometries of an organic material are; bond angles and torsional angles. A bond angle is the angle formed between three atoms across at least two bonds (Alexandros *et. al., 2015).*The optimized bond angles of RUB and CN-RUB at the DFT levels of theory within the basis sets were summarized and presented in **Table 2**. The calculated bond angles for RUB and CN-RUB at B3LYP/3-1G, B3LYP/6-31G and B3LPY/6-311G were found to be in good agreement when compared with the experimental values, and it showed small deviations at some points of the basis sets. The bond angle in CN-RUB formed at B3LYP/6-311G level of theory for A(1,5,9), A(10,9,17), A(18,22,50) and A(38,42,70) with values 120.2060, 118.9013, 119.8359 and 120.3421 respectively were the largest and were in agreement with the other experimental values of 120.4060, 118.6895, 119.5413 and 120.2143 as reported by (Alexander *et. al*., 2012) respectively. This is attributed to large steric hindrance as a result of substitution of one hydrogen atom by functional molecule cyanide in each of the four phenyls in rubrene structure.

Table 1: Optimized Bond Length of RUB and CN-RUB

Bond length(Å)	B3LYP/3-21G		B3LYP/ 6-31G		B3LYP/6-311G		Experimental values [a]
	RUB	CN-RUB	RUB	CN-RUB	RUB	CN-RUB	RUB
R(5,13)	1.3956	1.3847	1.3985	1.3859	1.4756	1.3834	1.4676
R(30,58)	1.0828	1.0932	1.0847	1.0954	1.0923	1.0921	1.0821
R(31,39)	1.3975	1.4040	1.4000	1.4050	1.3915	1.4014	1.3903
R(31,59)	1.0839	1.0939	1.0856	1.0942	1.0919	1.0915	1.0852
R(32,40)	1.3965	1.4004	1.3993	1.4050	1.3903	1.4006	1.4045
R(32,60)	1.0843	1.0937	1.0859	1.0942	1.0922	1.0913	1.0843
R(33,39)	1.3965	1.4004	1.3993	1.4044	1.3901	1.4004	1.4403
R(33,61)	1.0843	1.0937	1.0859	1.0942	1.0922	1.0914	1.0842
R(34,40)	1.3975	1.4040	1.4000	1.4044	1.3914	1.4010	1.8355
R(34,62)	1.0839	1.0939	1.0856	1.0942	1.0920	1.0913	1.0909
R(35,41)	1.3975	1.4040	1.4000	1.4050	1.3915	1.4014	1.3875
R(35,63)	1.0839	1.0939	1.0856	1.0942	1.0919	1.0915	1.0739
R(36,42)	1.3965	1.4005	1.3993	1.4050	1.3903	1.4006	1.3865
R(36,64)	1.0843	1.0937	1.0859	1.0942	1.0922	1.0913	1.0643
R(37,41)	1.3965	1.4004	1.3993	1.4044	1.3901	1.4004	1.3865
R(37,65)	1.0843	1.0937	1.0859	1.0942	1.0922	1.0914	1.0643
R(38,42)	1.3975	1.4040	1.4000	1.4044	1.3914	1.4010	1.3875
R(38,66)	1.0839	1.0939	1.0856	1.0942	1.0920	1.0913	1.0539
R(39,67)	1.0840	1.4105	1.0856	1.4156	1.0919	1.4140	1.0640
R(40,68)	1.0840	1.4105	1.0856	1.4155	1.0919	1.4139	1.0540
R(41,69)	1.0840	1.4105	1.0856	1.4156	1.0919	1.4140	1.0740
R(42,70)	1.0840	1.4105	1.0856	1.4155	1.0919	1.4139	1.0641
R(67,73)	_	1.1721	_	1.1801	_	1.1723	_
R(68,72)	_	1.1721	_	1.1801	_	1.1722	_
R(69,74)	_	1.1721	_	1.1801	_	1.1723	_
R(70,71)	_	1.1721	_	1.1801	_	1.1722	_

[a] Alexander et. al., 2012.

Table 2. Optimized Bond Angles of RUB and CN-RUB

Bond Angles	B3LYP/ 3-21G		B3LYP/6-31G		B3LYP/6-311G		Exp. value,[b]RUB
	RUB	CNRUB	RUB	CN-RUB	RUB	CN-RUB	
A(2,1,3)	118.8701	118.8264	118.9308	118.7906	117.5046	119.9406	118.8564
A(2,1,5)	118.8701	118.8263	118.9308	118.7902	117.5045	119.9407	118.8463
A(3,1,5)	122.2598	122.3474	122.1385	122.4192	124.9908	120.1188	120.2598
A(1,2,4)	118.8693	118.8257	118.9267	118.7904	120.0426	117.2672	118.2672
A(1,2,6)	118.8693	118.8256	118.9267	118.7906	120.0428	117.2671	118.8356
A(4,2,6)	122.2614	122.3487	122.1466	122.419	119.9146	125.4657	124.7657
A(1,3,7)	120.721	121.1434	120.4519	120.0293	120.3128	120.2063	120.0293
A(1,3,11)	123.0049	122.9843	122.7005	119.9431	124.0937	119.8083	119.9432
A(7,3,11)	115.7207	115.6932	116.2123	119.9431	115.5836	119.5867	116.2523
A(26,34,40)	120.2885	120.099	120.2902	119.901	120.2315	120.2285	120.1532
A(26,34,62)	119.7128	120.825	119.6494	120.7239	119.6777	120.4919	120.3619
A(40,34,62)	119.9987	119.0742	120.0603	119.3750	120.0878	119.2793	119.7530
A(27,35,41)	120.2885	120.0989	120.2902	120.0766	120.3355	120.0578	120.5302
A(27,35,63)	119.7129	120.8248	119.6494	120.6025	119.6257	120.5565	120.2657
A(41,35,63)	119.9986	119.0746	120.0603	119.3203	120.0380	119.3830	119.8320
A(28,36,42)	120.0352	119.7257	120.1108	120.0774	120.0532	119.8737	119.3062
A(28,36,64)	119.8465	120.906	119.7533	120.6024	119.8365	120.6853	1203865
A(42,36,64)	120.1154	119.3621	120.134	119.3196	120.1102	119.4385	119.8435
A(29,37,41)	120.0352	119.7259	120.1111	119.9006	119.8983	119.9524	119.9452
A(29,37,65)	119.8464	120.9064	119.7532	120.724	119.8966	120.6532	120.2356
A(41,37,65)	120.1155	119.3614	120.1339	119.3754	120.2045	119.3939	119.3945
A(30,38,42)	120.2886	120.099	120.2902	119.3754	120.2316	120.2285	120.2029
A(30,38,66)	119.7128	120.825	119.6494	120.7241	119.6777	120.4920	120.4127
A(42,38,66)	119.9987	119.0743	120.0603	119.3747	120.0878	119.2792	119.7922
A(31,39,33)	119.6723	119.6902	119.5324	119.4734	119.6932	119.4626	119.2632
A(31,39,67)	120.1167	120.1966	120.1964	120.4264	120.0632	120.4456	120.3206
A(33,39,67)	120.2098	120.1011	120.2709	120.1002	120.2435	120.0908	120.3542
A(32,40,34)	119.6723	119.6902	119.5325	119.4718	119.7277	119.3152	119.4718
A(32,40,68)	120.2097	120.1029	120.2709	120.4274	120.1758	120.3402	120.2043
A(34,40,68)	120.1168	120.1949	120.1962	120.1008	120.0964	120.3421	120.4690
A(35,41,37)	119.6723	119.6902	119.5324	119.4731	119.6932	119.4625	119.2546
A(35,41,69)	120.1167	120.1968	120.1964	120.4264	120.0633	120.4455	120.4545
A(37,41,69)	120.2099	120.1008	120.2709	120.1005	120.2434	120.0910	120.0290
A(36,42,38)	119.6723	119.6902	119.5325	119.4721	119.7277	119.3153	119.7421
A(36,42,70)	120.2097	120.1025	120.2709	120.4274	120.1759	120.3401	120.2754
A(38,42,70)	120.1168	120.1952	120.1962	120.1006	120.0965	120.3421	120.2143

[b] (Alexander et. al., 2012)

3.3. ReorganizationEnergy

Reorganization energy is one of the key parameters influencing the molecular and electronic (such as intrinsic charge transport rates) properties. The reorganization energy was evaluated from the Adiabatic Potential Surface(APS)and the Normal Mode Analysis(NMA) and the resultswere tabulated in **Table 3**. It was observed from the results that the reorganization energy calculated with NM analysis were slightly larger than the ones evaluated from the APS approach, which might originates from a clear deviation of the lattice vibration from the harmonic oscillator model. In comparison of these reorganizations energy associated with intermolecular electron transfer (λ_e) and hole transfer (λ_h) shows that, the introduction of functional molecules cyanide (CN) to phenyls in rubrene causes the increase in electron and hole transfer respectively to be larger than parentRUB. **Table 3** presents calculated reorganizations energy of 4CN-RUB and parent RUB, the values of$\lambda_h$for 4CN-RUB and RUB in NMA were found to be 0.1590eV and 0.1452eV respectively. Also, λ_e for 4CN-RUB and RUB were found to be 0.2570eV and 0.2150eV respectively. Both values for 4CN-RUB were larger than that of RUB and closed to the experimental values.

Table 3. Calculated Reorganization Energy at DFT B3LYP/6-311G Theory

Molecular Crystal	λ_h (eV)		λ_e (eV)	
	NMA	APS	APS	NMA
4CN-RUB	0.1590	0.1665	0.2102	0.2570
Rubrene (RUB)	0.1452	0.1025	0.1360	0.2150
Experimental Value; [c] (RUB)	0.2130	0.1030	0.1700	0.2973

[c] (Huepeng*et. al.,* 2015)

3.4. Electronic Structure (HOMO-LUMO Energy of RUB and 4CN-RUB)

HOMO energy characterizes the capability of electron donating and LUMO energy characterizes the capability of electron accepting. The energy of HOMO and LUMO were evaluated using Local Spin Density Analysis(LSDA) and B3LYP with 6-31G and 6-311G basis sets. The computed HOMO-LUMO energy of the parent RUB and 4CN-RUBat different levels of theories were reported in **Table 4**. The HOMO levels of RUB and 4CN-RUB -4.6624 eV and -5.4996 eV respectively are in agreement with the experimental values -4.94 eV and -5.10 eV respectively as reported by *(*Bing et. *al*., 2013 *and* Huepeng *et. al 20).*

Table 4. HOMO, LUMO Energy and HUMO-LUMO Energy Gap for RUB and 4CN-RUB

Molecules	Basis Sets		HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)
Rubrene (RUB)	B3LYP	6-311G	-5.499	-4.142	1.357
		6-31G	-5.350	-4.054	1.296
	LSDA	6-311G	-5.501	-3.998	1.503
		6-31G	-4.998	-4.250	0.748
4CN-RUB	B3LYP	6-311G	-4.662	-2.029	2.633
		6-31G	-4.542	-2.130	2.412
	LSDA	6-311G	-4.456	-2.038	2.418
		6-31G	-4.386	-2.120	2.266
Experimental value; [d] (RUB)	B3LYP	6-311G	-4.940	-2.340	2.600
	LSDA	6-311G	-5.100	-3.750	2.650

[d] (Bing *et. al.*, 2015)

3.5. Ionization Potentials (IP) and Electron Affinity (EA)

Apart from the charge mobility, the charge injection efficiency is also an important factor that affects the performance of organic materials for the application of organic devices. Other parametersin terms of HOMO and LUMO are; electron affinity and ionization potential which they defines organic semiconductor charge injection efficiency, they allow efficient injection of electrons or holes into empty HOMO-LUMO.

Here, the calculated IPs, EAs, HOMOs, and LUMOs of rubrene (RUB) and 4CN-RUB were shown in **Table 5**. In relation to molecular orbital theory approaches, the HOMO energy is related to the IP and the LUMO energy by Koopmans' theorem, which was used to estimate the electron affinity ($-E_{\text{HOMO}}$ = IP and $-E_{\text{LUMO}}$ = EA).

The chemical hardness (η) of a molecule is a measure of the resistance of a chemical species to changes in it is electronic configuration. It was determined by the relation ($\frac{I-A}{2}$) and was reported in **Table 6**. The softness (S) accounts to measure the chemical reactivity of molecules (Kolandaivel*et. al.*, 2003). It is the reciprocal of the hardness, and was reported in **Table 7**. In addition, the chemical potential (μ) was determined by the relation ($\frac{I+A}{2}$), the results calculated at different levels of theory were reported in **Table 8**.

Table5. Chemical Hardness of RUB and 4CN-RUB

Molecule	Theory/Basis Sets		IP (eV)	EA (eV)	Hardness η(eV)
Rubrene	B3LYP/	6-311G	5.499	4.142	0.678
(RUB)	B3LYP/	6-31G	5.350	4.250	0.550
	LSDA/	6-311G	5.501	3.998	0.752
	LSDA/	6-31G	4.998	4.250	0.374
(4CN-RUB)	B3LYP/	6-311G	4.662	2.029	1.317
	B3LYP/	6-31G	4.542	2.130	1.161
	LSDA/	6-311G	4.456	2.038	1.209
	LSDA/	6-31G	4.386	2.120	1.133

Table 6. Chemical Softness,*S* of RUB and 4CN-RUB

Molecule	Theory/Basis Sets		IP (**eV**)	EA (**eV**)	***S* (eV^{-1})**
Rubrene (RUB)	B3LYP/	6-311G	5.499	4.142	1.4749
	B3LYP/	6-31G	5.350	4.250	1.8181
	LSDA/	6-311G	5.501	3.998	1.3298
	LSDA/	6-31G	4.998	4.250	2.6738
(4CN-RUB)	B3LYP/	6-311G	4.662	2.029	0.7593
	B3LYP/	6-31G	4.542	2.130	0.8613
	LSDA/	6-311G	4.456	2.038	0.8271
	LSDA/	6-31G	4.386	2.120	0.8826

Table 7. Chemical Potential,µ of RUB and 4CN-RUB

Molecule	Theory/Basis Sets		IP(**eV**)	EA(**eV**)	µ(**eV**)
Rubrene (RUB)	B3LYP/	6-311G	5.499	4.142	4.8205
	B3LYP/	6-31G	5.350	4.250	4.8000
	LSDA/	6-311G	5.501	3.998	4.7495
	LSDA/	6-31G	4.998	4.250	4.6240
(4CN-RUB)	B3LYP/	6-311G	4.662	2.029	3.3455
	B3LYP/	6-31G	4.542	2.130	3.3360
	LSDA/	6-311G	4.456	2.038	3.2470
	LSDA/	6-31G	4.386	2.120	3.253

3.6. Natural Bond Orbital (NBO) Analysis

The Natural Bond Orbital (NBO) is an effective mathematical algorithm for analyzing the molecular properties such as electronic wave functions and chemical interpretations in the language of localized Lewis-like chemical bonds*(*Weinhold *et. al.*, 2012*)*.In order to analyze and determine the various second order interaction between the filled orbital of one molecular crystal and vacant orbital, the DFT-B3LYP theory and 6-311G basis set were used to determine the energy (E). The energy interaction was calculated from the second order perturbation approach; the results were summarized and reported in **Table 8** and **Table 9** respectively. The highest value of (E^2)53.940kcal/mol was found in the bond bending/deviation C7-C15 interacting with anti-bonding C3-C7 of 4CN-RUB, the value shows the intensive interaction between electron donors and electron acceptors, greater extent of conjugation of the whole system and greater stability of the structure when compared with the value 46.690kcal/mol for that of rubrene (RUB) found in bond bending/deviation C3-C7 interacting with antibond C1.

Table 8.NBO Energy of 4CN-RUB at B3LYP/6-311G Theory

Donor NBO(i)	Acceptor NBO(j)	E$^{(2)}$ (KJ/mol)	E$_{(j)}$-E$_{(i)}$ (a.u)	F(i,j) (a.u)`
σ(1) (C1- C2)	π*(1) (C3)	0.5100	1.8800	0.0280
σ(1)(C1- C2)	π*(3) (C3)	0.7100	1.5600	0.0300
σ(1)(C7- C15)	σ*(1)(C15-H43)	0.9800	1.0200	0.0280
σ(1)(C7- C15)	σ*(1)(C19-H47)	2.0200	1.0300	0.0410
σ(1)(C7- C15)	σ*(1)(C3-C7)	53.940	0.1200	0.0860
σ(1)(C7- C15)	σ*(1)(C69-N74)	0.9900	0.1200	0.1200
LP(1)(N 71)	σ*(1) (C 70)	19.140	1.0600	0.1280
LP(1)(N 71)	σ*(1)(C42-C70)	9.1700	0.9300	0.0820
LP(1)(N 72)	σ*(1)(C 68)	19.140	1.0600	0.1280
LP(1)(N 72)	σ*(1)(C40-C68)	9.1700	0.9300	0.0820
LP(1)(N 73)	σ*(1)(C 67)	19.140	1.0600	0.1280
LP(1)(N 73)	σ*(1)(C39-C67)	9.1700	0.9300	0.0820

Table 9.NBO Energy of RUB at B3LYP/6-311G Theory

Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (KJ/mol)	$E_{(j)}$-$E_{(i)}$ (a.u)	F(i,j)(a.u)
σ(1) (C1-C2)	σ*(1) (C3)	0.9900	1.7200	0.0370
σ(1) (C3-C7)	σ*(1)(C1-C3)	3.3500	1.2300	0.0570
σ(1) (C3-C7)	σ*(1)(C1-C5)	2.2000	1.2300	0.0460
σ(1) (C3-C7)	σ*(1)(C3-C11)	2.1400	1.1300	0.0440
σ(1) (C3-C7)	σ*(1)(C7-C8)	3.3300	1.2100	0.0570
σ(1) (C3-C7)	σ*(1)(C7-C15)	3.4000	1.2200	0.0580
σ(1) (C3-C7)	σ*(1)(C8-C16)	1.6100	1.2200	0.0400
σ(1) (C3-C7)	σ*(2)(C11-C25)	1.2500	0.7300	0.0290
σ(1) (C3-C7)	σ*(1)(C15-C19)	1.0400	1.3200	0.0330
σ(2) (C3-C7)	LP (1) (C1)	46.690	0.1300	0.0860
σ(2) (C3-C7)	σ*(3) (C15)	0.5300	1.1100	0.0240
σ(2) (C3-C7)	σ*(2)(C4-C8)	17.580	0.2700	0.0620
σ(2) (C3-C7)	σ*(1)(C11-C23)	2.5800	0.8000	0.0450
σ(2) (C3-C7)	σ*(2)(C11-C25)	0.6300	0.2800	0.0120

3.7. Infrared (IR) Spectral

Vibrational frequency analysis is used to determine the vibrational frequencies and intensities of specific molecular structure of a compound (Zhang *et. al.*, 2011). A molecular vibration occurs when atoms in a molecule are in constant periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is the vibrational frequency (Sherwood *et. al.*, 2016). Here, vibrational frequencies of parent RUB and 4CN-RUB were calculated using DFT with B3LYP exchange and 6-311G/6-31G basis sets. The infrared spectra of parent RUB and 4CN-RUB were obtained from the Gauss View of the Gaussian 09 software illustratedin**Figure. 3-6**, respectively. The most intense frequency of 4CN-RUB was found at 3489.876cm^{-1} and that for parent RUB was found at 3434.656cm^{-1}.These frequencies were correspond to a strong CH_2 and CH_3, medium C-C stretch and strong N-O asymmetry stretch modes of vibrations.

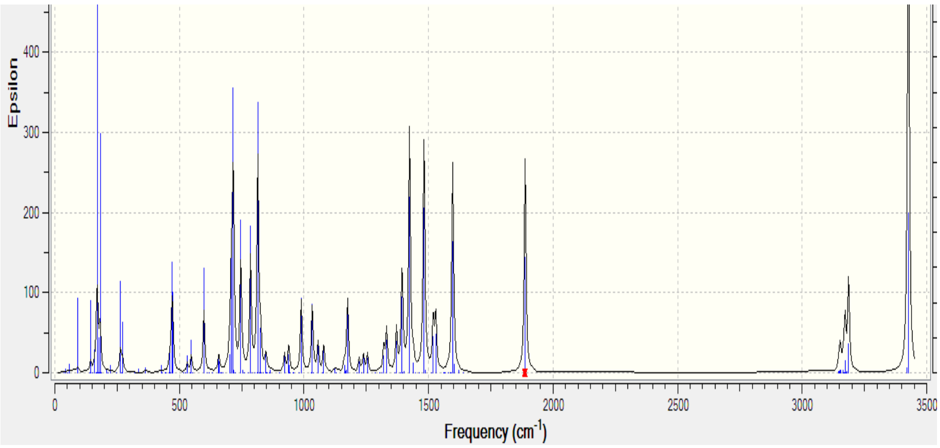

Figure 3. IR Spectrum of 4CN-RUB- at B3LYP/6-311G Theory

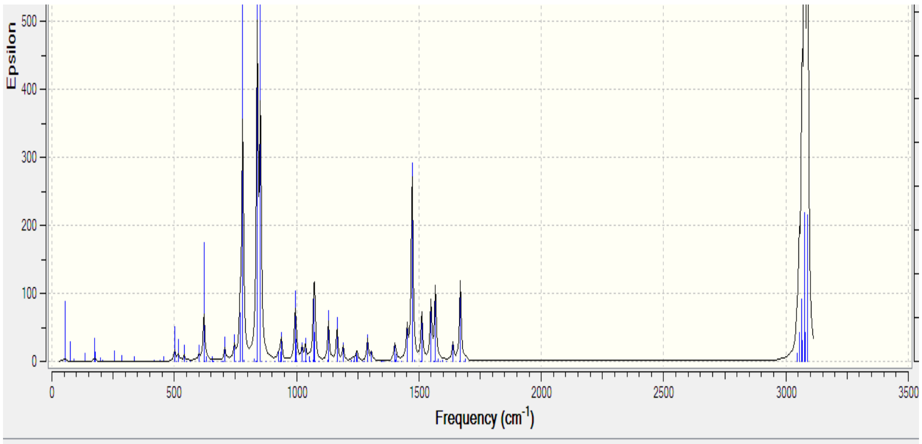

Figure 4.IR Spectrum of RUB at B3LYP/6-311G Theory

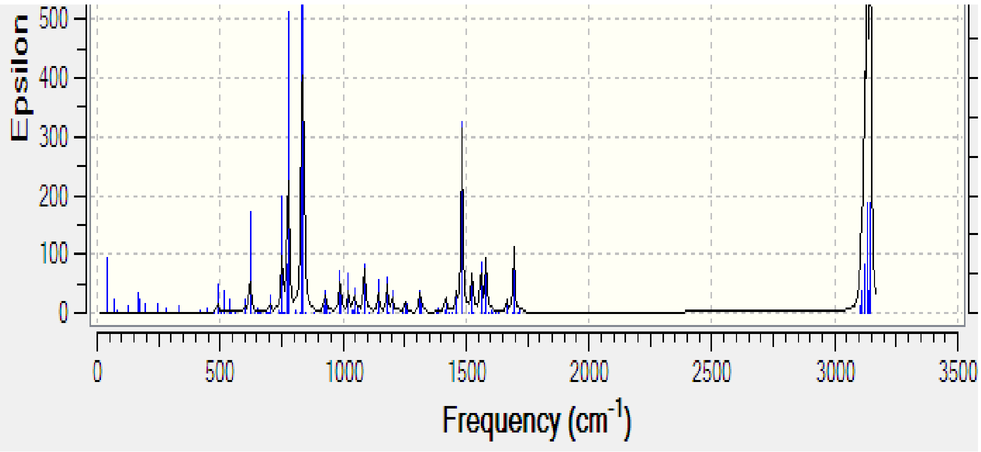

Figure 5.IR Spectrum of RUB at B3LYP/6-31G Theory

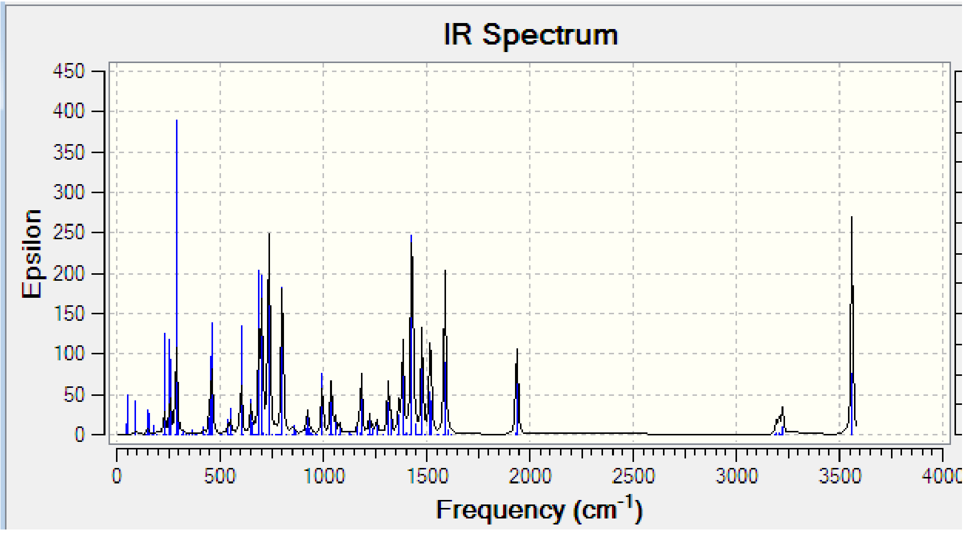

Figure 6.IR Spectrum of 4CN-RUB at B3LYP/6-31G Theory

IV. Conclusion

Among the results obtained for the optimized bond lengths and bond angles of rubrene derivative, CN-RUB have the strongest bond at R(34,62) with value of 1.0913Å, and the weakest bond was found in parent RUB formed at R(5,13) with value of 1.4756Å at DFT-B3LYP/6-311G theory. The cyanide increases the stability of the rubrene and causes increase in delocalization. The reorganization energy with values of (λ_h) for 4CN-RUB and RUB was found to be 0.1665eV and 0.1025eV. Also, (λ_e) for 4CN-RUB and RUB was found to be 0.271eV and 0.150eV.The results shows that the substitution of hydrogen atom with cyanide (CN) functional group in parent RUB can be a way to enhancemolecular stability.In addition, the HOMO, LUMO and HOMO-LUMO energy gaps computed for parent RUB and 4CN-RUB show a good agreement with reported experimental values.

NBO analysis shows hyper-conjugative energy with highest value of (E^2)53.940kcal/mol in the bond bending C7-C15 interacting with anti-bonding C3-C7 of 4CN-RUB. In the vibrational frequencies of RUB and 4CN-RUB, the derivative 4CN-RUB has the most intense frequency at 3426.5 cm^{-1} than that of RUB at 3088.5 cm^{-1} corresponding to a strong CH_2 and CH_3, medium C-C stretch and strong N-O asymmetry stretch modes of vibrations. In conclusion, the material reveals a potential application in organic light emitting diodes (OLEDs) and organic photovoltaic cells (OPVs).

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IOSR Journal of Applied Physics (IOSR-JAP) is UGC approved Journal with Sl. No. 5010, Journal no. 49054.

A. Musa."Molecular and Electronic Properties of Rubrene and Its Cyanide Derivative Using Density Functional Theory (DFT).” IOSR Journal of Applied Physics (IOSR-JAP), vol. 11, no. 2, 2019, pp. 10-18.