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Density Functional Theory Investigation of The Physical Properties of Dicyano Pyridazine Molecules

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Abstract: ***Quantum calculations of the physical properties (electronic and vibrational), based on density functional theory (DFT) method at B3LYP/6-31G** level of theory, were performed, by means of the Gaussian 09 set of programs, to investigate the effect of the addition of the radical CN on pyridazine molecules. The best geometry, the total energy, frontier molecular orbital energies (HOMO and HUMO), energy gap, ionization potential, electron affinity, electronegativity, chemical hardness, chemical softness, electrophilicity, dipole moment and the harmonic vibration frequencies were calculated and discussed for the study molecules. The electronic properties are computed by two different methods, a finite difference approximation and Koopman's theorem. The study clearly shows that adding the radicals CN cause decreased the energy gap and the chemical hardness, and increase the electrophilicity. Therefore, the presence of these radicals improves the conductivities and enhances the solubility and reactivity. All the results indicate that the molecule 2,4-(CH)*** $_4N_2$ ***(CN)*** $_2$ ***is the best option for n-type organic semiconductors.***

Keywords: DFT, B3LYP, Koopman's theorem, HOMO, energy gap, IR spectra.

1. Introduction

Density functional theory is a quantum mechanical method used in physics and chemistry to investigate and calculate the physical properties of atoms, molecules and solids [1, 2]. It is today one of the most important tools for calculating the ground state properties of semiconductors, and to investigate the electronic structure of many electron systems [3-5]. DFT methods have been very popular for calculations in solid state physics since the 1970s [6, 7]. However, this method was not considered accurate enough for calculations in quantum physics until the 1990s, when the approximations employed in the theory were greatly refined to better model the exchange and correlation interactions. In many studies, the results of DFT calculations for solid state systems agree quite satisfactorily with experimental data [1, 3, 8].

The organic semiconductor materials have been widely used as active materials for optoelectronic devices such as field effect transistor, solar cells and light emitting diodes [9]. The organic transistors are one type of the organic devices, in which they fabricated by using the organic semiconductors. These materials have advantages of easy fabrication, mechanical flexibility and low cost [9, 10]. The most important methods for the preparation of organic compounds are the substitution reactions on organic compounds. The effect of substituent groups depends on the type of this substituent, atoms or groups of atoms way serve to make the organic ring either more reactive [11]. The cyano radical is a radical with molecular formula CN. The cyano anion is a potent ligand for many transition metals. The very high affinities of metals for this anion can be attributed to its negative charge, compactness, and ability to engage in π-bonding [12].

The objective of this study is the theoretical investigation of the effect of the radical CN on the electronic and vibrational properties of pyridazine molecules by using DFT/B3LYP method with 6-31G** basis set, and comparison our results with experimental data.

2. Quantum Computational Methods Details

The quantum calculations of the physical properties (electronic and vibrational) were performed on an Intel(R) Core(TM) i7-3632QM CPU(2.20 GHz and 8.0 GB RAM) computer using standard Gaussian 09W software package [13, 14] to optimize the molecular structures and to calculate the electronic and vibrational properties of the study molecules. The geometry optimizations were carried out at the DFT level using the hybrid functional B3LYP based on Becke's three-parameter functional including Hartree Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke together with the nonlocal correction for the correlation energy provided by Lee et al. [15]. Indeed, DFT method are often the method of choice for many calculations because of their ability to overcome one of the main disadvantages of ab-initio methods by including some of it at greatly reduced computational cost. Thus, all the parameters presented in this study: the best geometry, the total energy, frontier molecular orbital energies (HOMO and HUMO), energy gap, ionization potential, electron affinity, electronegativity, chemical hardness, chemical softness, electrophilicity, dipole moment and the harmonic vibration frequencies were calculated at B3LYP with 6-31G** basis set [2, 16-18]. Figure 1, right panel represents the study molecules.

The partitions the electronic energy in DFT as

$$E = E_T + E_V + E_J + E_{XC} \quad (1)$$

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 wave function and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [19].

The energy needed to remove one or more electrons from a neutral molecule to form a positively charged ion is a physical property that influences the chemical behavior of the molecule. By definition, the ionization energy of an element is the energy needed to remove the outermost, or highest energy, electron from a neutral molecule in the gas phase [20]. In this investigation, the ionization potential IP is calculated as the energy difference between the energy of the molecule derived from electron-transfer and the respective neutral molecule [21, 22],

$$IP = E_{cation} - E_n \quad (2)$$

while electron affinity EA refers to measure the tendency of a neutral molecule to resist the loss of electrons. It takes a considerable amount of energy, where the electron affinities were computed as the energy difference between the neutral molecule and the anion molecule,

$$EA = E_n - E_{anion} \quad (3)$$

Within the framework of DFT, one of the global quantities are chemical potential μ, which is measures the escaping tendency of an electronic cloud, and the electronegativity χ, which is characterizes the escaping tendency of electrons from the equilibrium system (e.g., atoms or molecules). Let $E(N)$ be a ground-state electronic energy as a function of the number of electrons N. As is well-known, the derivative of $E(N)$ with respect to N at a constant external potential $V(\vec{r})$, is the chemical potential or the negative of the absolute electronegativity, where [21, 22]

$$\mu \approx \left(\frac{\partial E}{\partial N}\right)_{V(\vec{r})} \approx -\chi \quad (4)$$

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 at a constant external potential $V(\vec{r})$ [21-23].

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{V(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{V(\vec{r})} \quad (5)$$

Eq. 5 shows that chemical hardness is the resistance of the chemical potential to change in the number of electrons.

There are two different methods to calculate the electronic properties: the first one being energy-vertical (a finite difference approximation) is based on the differences of total electronic energies when an electron is added or removed in accordance with the neutral molecule. The second one is based on the differences between the energies of the highest occupied and lowest unoccupied molecular orbital (HOMO and the LUMO energies) of the neutral molecule and is known as orbital-vertical (Koopman's theorem) [24]. Using a finite difference approximation, a working equation for the calculation of electronegativity and chemical hardness can be given by [21, 23]

$$\chi = (IP + EA)/2 \quad (6)$$

$$\eta = (IP - EA)/2 \quad (7)$$

then the above equations can be rewritten using Koopman's theorem as

$$\chi = (E_{HOMO} + E_{LUMO})/2 \quad (8)$$

$$\eta = (E_{HOMO} - E_{LUMO})/2 \quad (9)$$

The chemical softness is a property of molecules that measures the extent of chemical reactivity. It is the reciprocal of chemical hardness. Since always, zero chemical hardness constitutes maximum chemical softness, and maximum chemical softness means (as it should) no energy change associated with the disproportionation reaction [21, 23],

$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_{V(\vec{r})} = \left(\frac{\partial N}{\partial \mu}\right)_{V(\vec{r})} \quad (10)$$

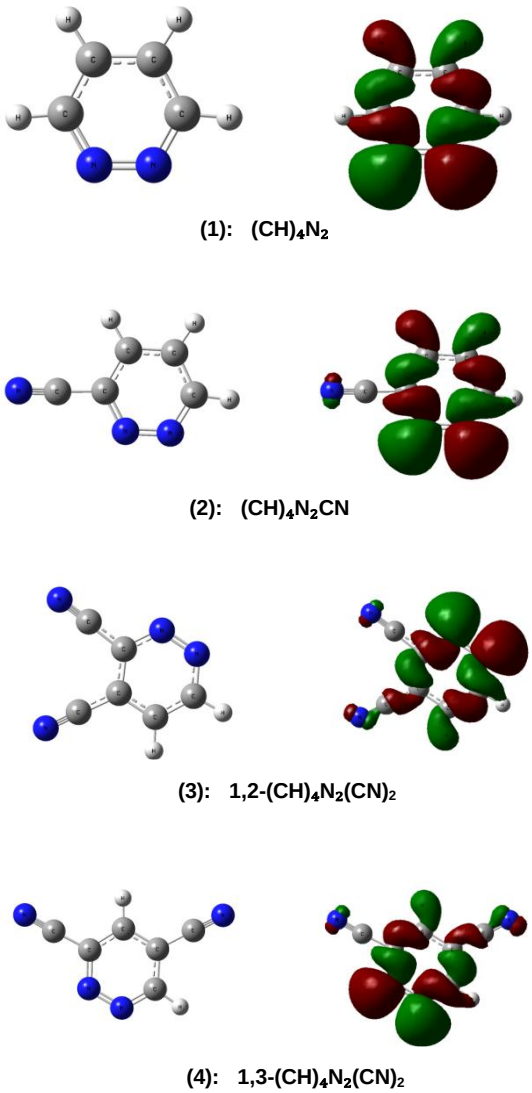
Electrophilicity is a measure of energy lowering of the chemical species due to maximum electron flow between donor and acceptor. Electrophilicity (ω) is defined as [21],

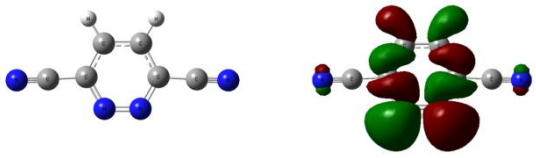
$$\omega = \mu^2/2\eta \quad (11)$$

3. Results and Discussion

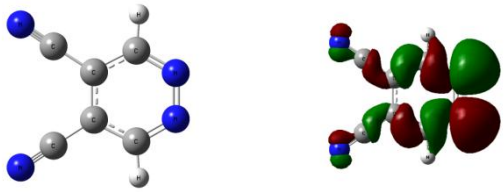
3.1 Molecular Geometry

Before proceeding in physical properties calculation, it is necessary to find out the geometry optimization of the study molecules, as we see in Fig. 1, left panel. The equilibrium geometries for all study molecules were fully optimized at the DFT level of theory using a B3LYP functional together with the standard 6-31G** basis set in gaseous phase and for a better approach of the experimental parameters. Figure 1, right panel shows the shapes of the highest occupied and lowest unoccupied molecular orbital (HOMO and the LUMO) for these structures, drawn by Gaussian View 5.0 using B3LYP/6-31G** method.





(5): 1,4-$(CH)_4N_2(CN)_2$



(6): 2,4-$(CH)_4N_2(CN)_2$

Figure 1: (Left): Optimized structures of study molecules. (Right): The shapes of HOMO and LUMO for study molecules.

3.2 Energies

Table 1 represents the results of the ground state total energy and electronic states HOMO and LUMO of the study molecules. It is clear that from Table 1, the total energy depends on the number of side groups adding to the ring. The total energy is decreasing with the increase of the radicals CN number as a linear relationship, this indicates that the addition gives the molecule more stability. On the other hand, the total energy is independent of the position of the radicals CN in the ring, as we see in Fig. 1. The energy of HOMO is often associated with the electron donating ability of the molecules, whereas the energy of LUMO is associated with the electron accepting ability of the molecules. Therefore, high value of HOMO indicate high tendency to donate electrons to appropriate acceptor molecule with low empty molecular orbital energy. Likewise, low value of LUMO indicate high tendency to accept electrons from the metal surface [25, 26]. The results presented in Table 1 show that molecule (5) has the higher energy of HOMO, whereas the molecule (6) has the lower energy of LUMO.

The gap between the HOMO and LUMO energy levels of the molecules is another important descriptor that should be studied. Large values of the energy gap imply high electronic stability and then low reactivity, when low values imply that it will be easier to remove an electron from the HOMO orbital to LOMO one which can result in good reactivity [25, 26]. The results in Table 1 show that adding the radicals CN cause decreased the energy gap. Therefore, the presence of radical CN improves the conductivity and also enhances the reactivity of these molecules [26,25]. This effect was the largest in molecule (6) it has the lowest energy gap (3.916 eV), therefore, its higher conductivity and reactivity. The energy gap of pyridazine molecule (4.723 eV) is agreements with experimental value (4.9 eV) [27].

Table 1: Total energy, electronic states (HOMO and LUMO) and energy gap for study neutral molecules, in electron volt unit.

Mol.	Total Energy	Electronic States		Energy Gaps	
		HOMO	LUMO	Our data	Expt.
1	-7189.552	-6.695	-1.972	4.723	4.9
2	-9698.667	-7.396	-2.751	4.645	-
3	-12207.614	-7.978	-3.735	4.243	-
4	-12207.674	-8.023	-3.801	4.223	-
5	-12207.680	-8.030	-3.700	4.329	-
6	-12207.616	-7.970	-4.054	3.916	-

3.3 The Global Chemical Indexes

B3LYP functional used in this study has a high efficient to calculate the electronic properties of the study molecules, such as the ionization potential IP, electron affinity EA, electronegativity χ, chemical hardness η, chemical softness S, electrophilicity ω. All the global chemical indexes are summarized in Table 2 for each variable are computed by two different ways, the first is energy-vertical and the second is orbital-vertical method which are explained in the above. Table 2 displays clearly reveal that the ionization potential and the electron affinity for molecules (2-6) are higher than that for the original molecule (1). The calculated values of the ionization potential and electron affinity for original molecule (1) are a good agreement with the experimental values 8.640 eV and 0.012 eV, respectively [27]. Therefore, we think that Koopman's theorem is a crude but useful and fast approach [28]. It is observed that the molecules (2-6) show little tendency for electrons to escape from the equilibrium density.

The chemical hardness and softness are very important parameters to describe the reactivity and stability of the molecules. Soft molecules are more reactive than hard ones because they can easily offer electrons [25, 28]. Hence, pyridazine molecule with the highest values of chemical softness (the least value of the chemical hardness) are expected to be good corrosion inhibitors for bulk metals in acidic media. The calculations indicate that the molecule (6) has the highest softness value compared to study molecules.

The molecules (2-6) have a large value of electronegativity and electrophilicity, therefore, they are more reactive because they have a large measuring value of the electronic transfer that the compound may accept. The behavior of electronegativity, chemical softness and electrophilicity for the study molecules show the magnitude larger than those for the original molecule, where adding the radicals CN give the molecule more chemical softness and reactive.

Table 2: The electronic properties for study neutral molecules, in electron volt unit.

Mol.	Ionization Potential		Electron Affinity		Electronegativity		Hardness		Softness		Electrophilicityity	
	E	O	E	O	E	O	E	O	E	O	E	O
1	8.555	6.695	0.057	1.972	4.306	4.334	4.249	2.361	0.118	0.212	2.182	3.977
2	9.142	7.396	0.953	2.751	5.047	5.073	4.094	2.322	0.122	0.215	3.111	5.540
3	9.613	7.978	1.985	3.735	5.799	5.857	3.814	2.122	0.131	0.236	4.409	8.084
4	9.650	8.023	2.076	3.801	5.863	5.912	3.787	2.111	0.132	0.237	4.539	8.277
5	9.664	8.030	1.983	3.700	5.824	5.865	3.840	2.165	0.130	0.231	4.416	7.945
6	9.600	7.970	2.308	4.054	5.954	6.012	3.646	1.958	0.137	0.255	4.861	9.231

E: energy-vertical method and O: orbital-vertical method

The results in Table 3 display that values of electric dipole moment are independent on the number of radicals CN added to the original molecule, but depend on the positions of these radicals in the molecule. The electric dipole moment of molecule represents a generalized measure of bond properties and charge densities in a molecule. The calculations clearly show that the molecule (2) has higher dipole moment (6.513 Debye), this mean better charge distribution and increasing distance of bonds. The molecules have a low dipole moment may accept less electronic charge than the molecules of the high dipole moment. The localized molecules have a large dipole moment and they are more electrophilic systems, this is a main feature result and refer to that conductivity at these localized molecules might be improved through oxidation processes [21, 28].

Table 3: The dipole moments for study neutral molecules.

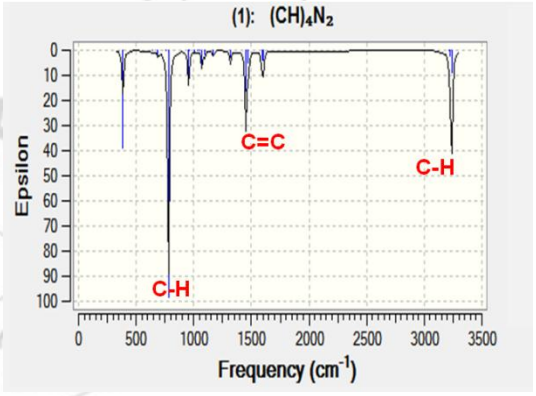
Molecule	1	2	3	4	5	6
Dipole Moment (Debye)	4.930	6.513	5.959	2.461	5.173	1.460

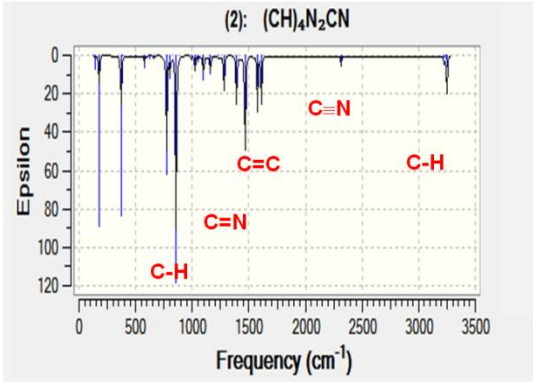
3.4 Infrared Spectra

The harmonic vibration frequencies calculated for study molecules at B3LYP level using the 6-31G** basis set. There are two types for stretching vibration are symmetric and asymmetric, the symmetric stretching is happening when the bonds of the same atoms vibrate in the same phase, and the asymmetric stretching is happening when the bonds vibrate in different phases. The number of vibrational frequency modes was calculated by the relation $3N-6$, where N is the number of atoms in the structure [20, 29].

The **C-H** stretching vibrations of aromatic molecules in the region (2900-3250) cm^{-1} which is a characteristic region for ready identification of **C-H** stretching vibrations and particularly the region (3100-3250) cm^{-1} for asymmetric stretching and (2900-3100) cm^{-1} for symmetric stretching modes of vibration [28]. While the vibration frequencies of **C-H** bending, **C=C** bending, **C=N** stretching and **C≡N** stretching in the regions (680-860) cm^{-1}, (1475-1700) cm^{-1}, (1250-1335) cm^{-1} and (2220-2260) cm^{-1}, respectively [19, 28].

Figure 2 displays the vibration frequencies calculated of the study molecules (1-6) using B3LYP/6-31G** method. The strong peaks observed due to **C-H** bending, **C=N** stretching, **C=C** bending and **C-H** stretching, as in Fig. 2. These results have been found in good agreement with experimental data and our results supplied new data about the vibration frequencies of molecules (2-6). It is clear from Fig. 2 that the IR spectra of molecules (2-6) characters by multiply the vibration mode due to existing of **C-N** bond, the stretching and bending of these bonds caused to new peaks or a band of peaks to be appeared. The torsion vibrations appear at very low frequency for (2-6) molecules at below 60 cm^{-1} [25].





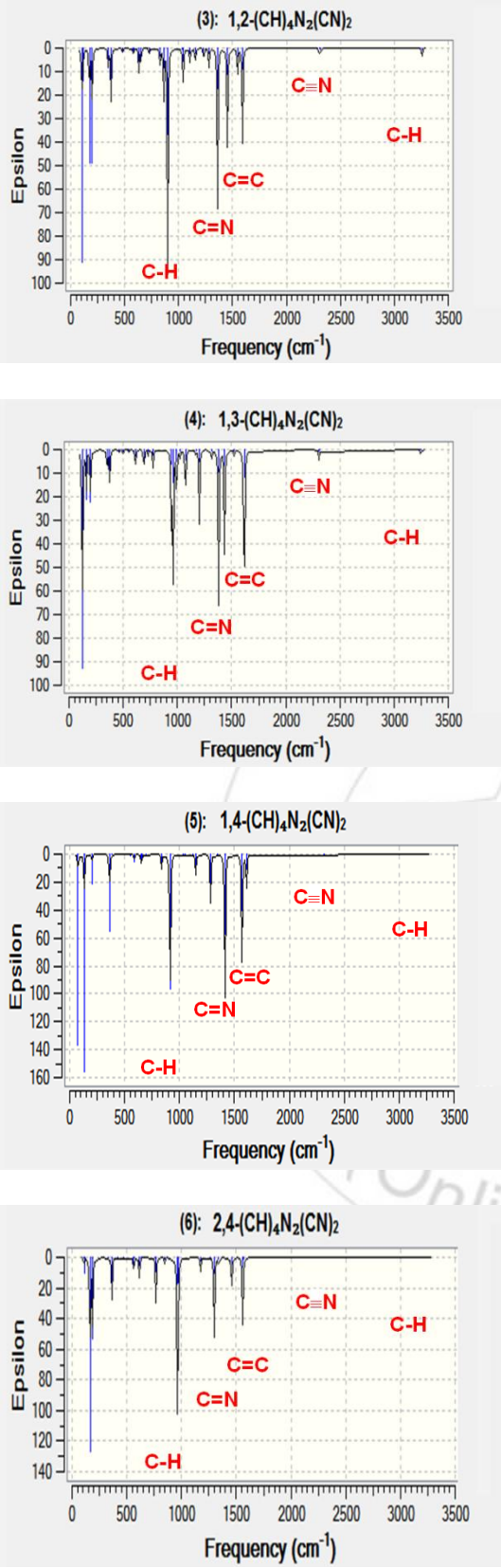


Figure 2: The IR spectra of study neutral molecules, where Epsilon is the Intensity in unit Km/mol.

4. Conclusions

Using the DFT/B3LYP method with the 6-31G**, the molecular geometry and physical (electronic and vibrational) properties of pyridazine derivatives were investigated. Depending on our results, the following points are noteworthy: geometry optimization for pyridazine molecule has been found in a good agreement with experimental data, while for other dicyano pyridazine molecules it has not been found a reference data. The total energies of dicyano pyridazine molecules found not dependent on the position of the radical CN in the ring, and adding the radicals CN causes decreasing energy and more stability. The presence of these radicals decreases the energy gap of the molecules; this is one of the important properties obtained in this work. Small energy gap means small excitation energies of the manifold of the excited states.

The electronic properties IP, EA, χ, η, S and ω are calculated by two different ways, the first is energy-vertical and the second is orbital-vertical method. The results from first method is a good agreement with experimental data and better than the second method, thus Koopman's theorem is not satisfied accurately. The chemical softness and electrophilicity for the new molecules group are large values as comparing with the original molecules. These new molecules are soft with small energy gaps, while it has small values of the dipole moment. Therefore, they have an electron density changed more easily and more reactive in charge transfer process. All results indicate that the molecule 2,4-$(CH)_4N_2(CN)_2$ is the best option for n-type organic semiconductors because of its better physical properties.

In IR spectra calculations, it gives a good agreement with experimental data for pyridazine molecule. Adding the radicals CN lead to increasing the vibration modes and highest stretching vibration wave numbers.

5. Acknowledgements

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