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Theoretical Study of Electronic Properties of Pyridine, Pyrimidine, Pyrazine and Pyridazine via Density Functional Theory

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Abstract
Theoretical studies on pyridine, pyrimidine, pyrazine and pyridazine molecules were performed using DFT. Based on B3LYP with 6-31(d, p)basis sets was used to investigate the effect of different position of nitrogen atom on the electronic and structure properties of benzene. The optimized structure, total energies, electronic states, energy gaps, ionization potentials, electron affinities, chemical potential, global hardness, softness, global electrophilicity, dipole moment and dipole polarizability were calculated. The harmonic vibration frequencies calculated and compared with available experimental data. The results showed a decrease in gap energies and improve the electronic properties.
Keywords: B3LYP, DFT, optimization, energy gap, and vibration frequency.

Introduction

Aromatic compounds are important in industry and play key roles in the biochemistry of all living things [1], atoms and subgroups substituted on aromatic molecules are members of a class of environmental contaminants found in airborne particulate matter, fossil fuel combustion products, coal fly ash, cigarette smoke, and vehicular emissions, formed by reactions of aromatic molecules with nitrogen oxide [2]. The organic thin film are one type of the so called organic devices, in which they fabricated by using the organic compounds such as semiconductors [12]. These materials have advantages of easy fabrication, mechanical flexibility and low cost. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [13, 14].
Many studies on cyclic oligomers have been reported both experimentally and theoretically [15, 16], in [17] the substituent effects of oligomers such as oligothiophene, oligopyrrole and oligofuran are discussed in terms of reorganization energy. Also, [18] studied the geometric and electronic properties for cynothiophene oligomers as a prototype of an organic conducting polymer using ab initio and DFT [19], they showed that the cynogroup generally reduced the band gap with variation of the substitution position.
Benzene and its derivatives have attracted considerable interest since they have interesting applications. Therefore the purpose of this work is to examine the effect of nitrogen atoms added to the ring on benzene molecule.
In present work, density functional theory has been performed to study the electronic properties of the benzene and their sdducts molecules to determine the effects of the nitrogen atoms on the original ring and evaluation of their dipole polarizability and comparison with available experimental results.

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 09 suite of programs [21]. The molecular properties of the compounds had been computed by DFT using the standard 6-31G(d, p) basis sets. In the DFT calculations, Lee, Yang and Parr correlation functional [22] is used together with Becke's three parameters[23]exchange functional B3LYP. Conformational analysis of the molecules had 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 [22,24]. Harmonic vibration 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 [25-27].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 anti-symmetry 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 [28].
The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction, and the vibration analysis for each structure does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface[29].

In this investigation, the more relevant electronic potential (IP), electron affinity (EA), chemical potential (μ) (the negative of electro-negativity (χ)), hardness (η), softness (S),electrophilic index (ω) and the electric dipole polarizability (□) were calculated. The ionization potential is calculated as the energy difference between the energy of the molecule derived from electron-transfer and the respective neutral molecule; $IP_v = E_{cation} - E_n$. The EA was computed as the energy difference between the neutral molecule and the anion molecule: $EA = E_n - E_{anion}$ [30]. The HOMO and LUMO energy was also used to estimate the IP and EA in the framework of Koopmans' theorem: $IP = -\varepsilon_{HOMO}$ and $EA = -\varepsilon_{LUMO}$ [31].

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 the number of electrons(N) curve at external potential ν(r)[32]:

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

The 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) [32]:

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

And the 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 [31] :

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

The electrophilic index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilic index (ω) is defined as [28]:

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

One of the important global properties is the electric dipole polarizability, which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field (F) and represents a second-order variation in energy [32] :

$$= -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right) \text{a,b = x, y, z} \qquad (7)$$

If some of applied molecules are planar and some are not, it will be useful to report polarizability quantities that are invariant to the choice of coordinate system. One of them is the mean polarizability< >is evaluated using the equation [28].

$$< >= \frac{1}{3}(_{xx} + _{yy} + _{zz}) \qquad (8)$$

Results and discussion

Molecular optimization geometry

The optimized structure parameters of molecules under study calculated by DFT-B3LYP levels with the 6-31G(d, p) basis sets are listed in table 1. This table shows the calculated bond lengths and angles for benzene and its adducts. From the theoretical values obtained in this work, we can find that the optimized bond lengths and angles for benzene molecule are in good agreement with the experimental values, but for other compounds we have not found experimental data, the bonds are change due to the adding nitrogen atoms in the ring and the theoretical calculations are belong to isolated molecules in gaseous phase.

Total energy and electronic states

Table 2 shows the values of the total energy and electronic states for the analyzed structures and the energy gap ($\mathcal{E}_{LUMO} - \mathcal{E}_{HOMO}$)of the studied molecules. The total energy for the molecules as a linear function of nitrogen atoms number (n) adding to the ring. The final total energy of the product is approximately the collection of total energy of all small molecules which build the product molecule, that means:

$$E_{tot} \approx E_{tot}(benzene) + nE_{tot}(N\ atom) \qquad (9)$$

It is clear that from Table 2, the total energy for pyridizine, pyrimidine and pyrizine molecules is approximately the same in which this refers to that the total energy is independent on the position of the nitrogen atoms in the ring, and it is observed that adding the nitrogen atoms in place of carbon atoms causes decreasing the HOMO energy [34],and energy gap decreased. Therefore, the presence of adding the nitrogen atoms decreases the

energy gaps improves the conductivity and also enhances the solubility of these molecules.
The LUMO-HOMO energy gaps of all new molecules are less than that of the original ring, with decreasing energy gap, electrons can be easily excited from the ground state [35,36]. This effect of adding was the largest in pyrizine it has energy gap of(3.120eV). The energy gap of benzene (*6.79* eV) is agreements with experiment value (6.89 eV). Table 2 shows also the symmetry of studied molecules, benzene molecule is a planar with high D_{6h} symmetry and have higher electronegativity, while pyrizine molecule is a planer and have C_{2h} symmetry (high symmetry), and have lower electronegativity (40.316).

Some important electronic properties
Present method used in this study has a high efficient to calculate the electronic properties for the studied molecules, such as ionization potentials(IP), electron affinities(EA), electro-negativity (χ), absolute hardness(η), absolute softness (S), electrophilic index (ω). The properties that are displayed in Table 3 for each variable are computed by two different ways: The first one being energy-vertical (E-V) is based on the differences of total electronic energies when an electron is added or removed in accordance with the neutral molecule. The second is based on the differences between the HOMO and the LUMO energies of the neutral molecule and is known as (O-V) orbital-vertical (Koopmans' theorem).
The calculated properties for each variable as shown in table 3 clearly reveal that these compounds have a tendency to capture electrons instead of donating them. The ionization potentials for pyridene, pyridizine, pyrimidine and pyrizine molecules are greater than that for the original molecule (benzene), but the pyrizine molecule has the largest value of ionization potential, this indicates that the this molecule needs high energy to become cation comparing with the others. The strength of an acceptor molecule is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the nitrogen atoms to the ring leads to increasing the ability of the electron affinity for the molecule, EA for pyrizine molecule is the largest, as we see in Table 3. The calculated value of IP, EA and energy gaps for benzene is a good agreement with experimental value.
Few interesting observations have been made from the results that are shown in table 3 obtained through the energy-vertical and orbital-vertical methods. The electron affinity (EA) computed from the energy of the lowest unoccupied molecular orbital (LUMO) are higher for all studied molecules than that of the energy-vertical method. The ionization potential (IP) that results from the highest occupied molecular orbital is smaller for all studied molecules than that of the energy-vertical method. From the previous investigations, it has been found that for almost all the commonly used exchange-correlation functional such as B3LYP, B3PW91, Koopman's theorem is not satisfied accurately [30]. The two results obtained by the calculation of electro-negativity and electrophilicity also agreed very well with the difference in the result. This could be the reason for the low hardness values obtained from the orbital-vertical method than from the method of energy-vertical. Koopman's theorem neglects the relaxation effect by using the frozen-orbital approximation. However, this error is frequently compensated by the oppositely directed error due to the electron correlation effect, neglected in the Hartree-Fock (HF) method. Therefore, the Koopmans' theorem is a crude but useful and fast approach [38].The behavior of electro-negativity, softness and electrophilic index for the studied molecules shows the magnitude large than these for the original ring, adding the nitrogen atoms give the molecule more softness.
The molecules dipole moment represents a generalized measure of bond properties and charge densities in a molecule [30]. Molecule with electron accepter group due to better charge distribution and increasing distance have higher dipole moment[32], from Table 4 pyridizine molecule has higher dipole moment (4.6739 Debye) .
The results of the calculated polarizability for molecules in table 4 showed that adding the nitrogen atoms leads to change the average polarizability, all the four last molecules have large values of dipole polarizability and they are more reactive than the original molecules. The pyrizine and pyridine molecules have average dipole polarizability equal 112.316 and 93.872 a.u, respectively. they have the highest polarizability and have highest reactivity. This due to the ring delocalizing π electron resonance from the benzene ring [32].

IR Vibration frequencies
The IR spectra of studied molecules are provided in figure (2). The harmonic vibration frequencies calculated for these molecules at B3LYP level using the 6-31(d, p) basis sets. The (C – H) stretching vibrations of aromatic molecules in the region (2900 – 3250) cm^{-1} which is characteristic region for ready identification of (C – H) stretching vibrations and particularly the region (3250 – 3100) cm^{-1} for asymmetric stretching and (3100 – 2900) cm^{-1} for symmetric stretching modes of vibration [30].
This work gives the frequency values at (692, 1066.3, 1528.28 and 3202.34) cm^{-1} for benzene which are consistent with experimental results of (673, 1038, 1469 and 3210) cm^{-1}. the aromatic molecules frequency has both in-plane (1100 – 1700) cm^{-1} and out-of-plane (below 1000 cm^{-1}) (C – H) bending vibrations, the strong peak computed by B3LYP/6-31G(p, d) observed at 691 cm^{-1} and weak peak at 1066 cm^{-1} are due to the bending of (C - H) bond, the peak observed at 1528 Cm^{-1} is due to the stretching of (C- C) bond, the peak at 3202 Cm^{-1}

is due to the stretching of (C – H) bond.
It is clear from fig. (2) that the IR spectra for the other molecules characters from that of benzene by multiply the vibration mode due to existing of (N – N) , (C – N) bonds, (C = C) stretching and (C – H) stretching. For the last four molecules the stretching of (C – N) bond has been observed at (1600 – 1720) cm^{-1}, the (C – H) stretching stay in the region (3150 – 3360) cm^{-1}, the stretching of (C – N) bond has been observed at (1310 – 1425) $cm^{-1}$and the stretching of (C=C) bond at the range (1505 – 1590) cm^{-1},while the bending of (N – N) bond appeared at (1635 – 1795)cm^{-1}. The πelectron density on the aromatic ring was delocalized in the presence of the nitrogen atoms which reduced the strength of (C = C) bond and depending on the position of nitrogen.

Conclusions
in this study, we have used B3LYP-DFT to compute geometry optimization and electronic properties of benzene and its adducts by adding the nitrogen atoms in place of carbon in the ring. The calculated electronic properties such as ionization potential, electron affinity, electro-negativity, hardness, softness and electrophilic index by using two different ways: energy-vertical method and orbital-vertical method.
The geometry optimization for benzene molecule has been found in a good agreement with experimental data, while for other studied molecules it has not been found a reference data. The total energies for all di-nitrogen atom found not dependent on the position of the nitrogen in the ring and adding the nitrogen causes decreasing energy and more stability.
The presence of the nitrogen atoms in the ring decreases the energy gap of the molecules under study, this is one of the important properties obtained in this work, where a small energy gap means small excitation energies of manifold of the exited states. The other electronic properties were calculated by using energy-vertical method are a good agreement with experimental result and better than was calculated by using orbital-vertical method, thus Koopman's theorem is not satisfied accurately.
Adding the nitrogen atoms to the ring leads to increase the average polarizability and dipole moment and cause to more reactive than original molecule. The vibration frequencies calculations showed a good agreement with experimental data for benzene, adding the nitrogen leads to increasing the vibration modes, and highest stretching vibration wave numbers and its gave suitable positions for nitrogen with carbon atoms in the ring. pyrizine molecule is the best option for organic semiconductor because of its better LUMO – HOMO ratio, dipole polarizability and other electronic properties.

References
[1] K. J. Denniston, J. Topping and T. M. Dwyer,"General Organic and Biochemistry", 5th Edition, Towson University, 2007.
[2] K. KefaOnchoke, M. Christopher /Hadad, and K. PrabirDutta, J.Phys. Chem. A 110, 76-84, 2006.
[3] O. Kwon, V.Coropceanu, N. E. Gruhn, J. C. Durivage, J. G. Laquindanum, H. E. Katz, J. Cornil, and J. L. Bredas, J. Chem. Phys., 120, 8186, 2004.
[4] H. Geng, Y. Niu, Q. Peng, Z. Shuai, V. Coropceanu, and Jean-Luc Bredas, J. Chem. Phys.135, 04703, 20111.
[5] J. R. Sheats, H. Antoniadis, M. hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, science, 273, 884, 1996.
[6] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, Science, 265, 1648, 1994.
[7] G. Horowitz, D. Fichou, X. Z. Peng, Z. G. Xu, F. Gamier, Solid State Commun, 72, 381, 1989.
[8] G. Horowitz, Adv. Mater, 10, 365, 1998.
[9] H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y. Y. Lin, A. Dodabalapur, Nature (London), 404 , 478, 2000.
[10] G. Yu, J. Wang, J. McElvain, A. Heeger, Adv. Mater, 10 (1998)1431.
[11] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, Adv. Funct. Mater, 11, 15, 2001.
[12] H. E. Katz, J. Mater. Chem, 7, 369, 1997.
[13] H. Klauk, D. J. Gundlach, M. Bonses, C. C. Kuo, T. Jackson, Appl. Phys. Lett, 76, 1692, 2000.
[14] T. W. Kelley, D. V. Muyres, P. F. Baude, T. P. Smith, T. P. Jones, Mater. Res. Soc. Symp. Proc, 717, 169, 2003.
[15] M. D. Curtis, J. Cao, J. W. Kampf, J. Am. Chem. Soc, 126, 4318, 2004.
[16] S. E. Koh, C. Risko, D. A. de Silva Filho, O. Kwon, A. Facchefti, J. L. Bredas, T. J. Marks, M. A. Ratner, Adv. Funct. Mater, 18, 332, 2008.
[17] G. R. Hutchison, M. A. Ratner, T. J. Marks, J. Am. Chem. Soc., 127, 2339, 2005.
[18] R. G. Parr, W. Yang, "Density- Functional Theory of Atoms and Molecules", Oxford University Press: New York, 1989.
[19] M. A. De Oliveira, H. F. De Almeida, In. J. Quan. Chem, 90, 603, 2002.
[20] Y. H. Park, Yun-Hi Kim, I. Sun Koo, and K. Yang, Bull. Korean Chem. Soc.,Vol.31, 1649 – 1656, 2010.

[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 09, Revision A.02, Gaussian, Inc., PA, Wallingford CT. 2009.
[22] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 , 785, 1988.
[23] A.D. Becke, Phys. Rev. A 38 , 098, 19883.
[24] A.D. Becke, J. Chem. Phys. 98, 5648, 1993.
[25] J. Engelberts, R. Havenith, J. Van Lenthe, L. Jenneskens, P. Fowler, Inorg. Chem, 44, 52266, 2005.
[26] J. C. Santos, W. Tiznado, R. Contreras, P. Fuentealba, J. Chem. Phys, 120, 1670, 2004.
[27] J. C. Santos, J. Andres, A. Aizman, P. Fuentealba, J. Chem. Theory Comput, 1, 83, 2005.
[28] P. Udhayakala, T. V. Rajendiran, S. Seshadri, and S. Gunasekaran, J. Chem. Pharm. Res., 3, 610-625, 2011.
[29] S. Gümüs, Turk. J. Chem., 35, 803-808, 2011.
[30] K. Sadasivam, R. Kumaresan, Computational and Theoretical Chemistry 963, 227-235, 2011.
[31] A. Demetrio Da Silva, V. Coropceanu, D. Fichou et al., Phil. Trans. R. Soc. A, 365, 1435-1452, 2007.
[32] M. Oftadeh, S. Naseh, M. Hamadanian, Computational and Theoretical Chemistry 966,20-25, 2011.
[33] N. Ketkar et al., J. Mol. Struc. 77, 127, 1981.
[34]P. Ravi, G. M. Gory, S. P. Tewari, and A. K. Sikder, Journal of Energetic Materials, 29, 209-227, 2011.
[35] X. Ming-Hua, SU Ning-Hai, S. WU, Chinese J. Struct. Chem., 27, 421-425, 2008.
[36] Z. Wang, S.WU, J.Serb. Chem. Soc. 73, 1187-1196, 2008.
[37] A.V. Kuhta, I. N.K. Kuhta, N. A. Kuhta, O. L. Neyra, E. Meza, J. Phys. B: At. Mol. Opt. Phys. 41, 205701, 2008.
[38] U. Salzner, J. B. Lagowski, P.G. Pickup, and R. A. Poirier, J. Comput. Chem. 18, 1934, 1997.
[39] A. L. Mattiode, D. M. Hudgins, C. W. Bauschlicher Jr. L. J. Allamandola, Advances in Space Reseaich, 36,156 – 165, 2005.
[40] Hai-Bo Yi, Han Myoung Lee, Kwang S.Kim, Journal of Chemical Theory and Computation (JCTC), Vol.5, P.1709-1717, 2009.

Table1: Optimized geometrical parameters of molecules, bond length R (Å), Interaxial angles (°).

Molecules	bond length	Our data	Expt.[1]	Interaxial angles	Our data	Expt. [1]
Benzene	*C–C*	*1.396*	*1.390*	*C – C – C*	*120*	*120*
	C – H	*1.086*	*1.10*	*C – C – H*	*120*	*120*
Pyridene	*C–C*	*1.3825*		*C – C – C*	*120.7419*	
	C – H	*1.0705*		*C – C – H*	*118.5375*	
	C – N	*1.3307*		*C – C – N*	*121.1446*	
Pyridizine	*C–C*	*1.395*		*C – C – C*	*120.8594*	
	C – H	*1.069*		*C – C – H*	*117.3555*	
	C – N	*1.316*		*C – C – N*	*123.2558*	
Pyrimidine	*C–C*	*1.3286*		*C – C – C*	*121.5052*	
	C – H	*1.0671*		*C – C – H*	*116.9717*	
	C – N	*1.3818*		*C – C – N*	*124.5996*	
Pyrizine	*C–C*	*1.3809*		*C – C – C*	*120.9725*	
	C – H	*1.0689*		*C – C – H*	*117.7131*	
	C – N	*1.3313*		*C – C – N*	*121.3144*	

Table2: Total energy, electronic states and energy gap for molecules

Structure	Energy(a.u)	Symmetry	Electronic States(eV)		Energy Gaps (eV) Our data	Energy Gaps(eV) Expt.
			HOMO	LUMO		
Benzene	-232.27788	D_{6h}	-0.07	6.72	6.79	6.89
Pyridene	-245.31200	C_{2v}	-3.536	9.686	3.589	
Pyridizine	-261.19968	C_{2v}	-2.634	10.759	3.409	
Pyrimidine	-261.20619	C_{2v}	-3.057	0.560	3.124	
Pyrizine	-261.19749	D_{2h}	-2.876	10.210	3.120	

Table 3: The electronic properties for studied molecules.

Mol.	IP (eV)		EA (eV)		χ (eV)		η (eV)		S /(eV)		ω (eV)	
	E-V	O-V	E-V	O-V	E-V	O-V	E-V	O-V	E-V	O-V	E-V	O-V
1	9.24	9.24	0.35	2.48	3.68	3.38	3.32	5.86	0.15	1.22	2.03	0.97
2	7.75	6.28	1.58	3.90	4.66	4.45	3.08	1.52	0.162	4.24	3.53	6.95
3	7.64	6.26	1.75	3.76	4.74	4.33	2.99	1.52	0.167	4.32	3.76	7.22
4	7.78	6.32	1.85	4.86	4.78	4.89	3.00	1.58	0.168	4.85	3.81	7.45
5	7.72	5.85	1.88	5.07	4.80	5.65	2.92	1.36	0.171	5.12	3.94	7.65

Table 4:calculated dipole moment μ(debye), components and average of the dipole polarizability< > in (a. u) for studied molecules.

molecules	μ	α_{zz}	α_{yy}	α_{xx}	< >
Benzene	0.000	81.403	81.4	44.74	69.181
Pyridene	2.3968	61.813	55.215	14.590	93.872
Pyridizine	4.6739	56.507	48.965	14.592	90.021
Pyrimidine	2.5115	54.449	49.460	14.802	89.570
Pyrizine	0.0000	59.515	46.410	15.024	112.316

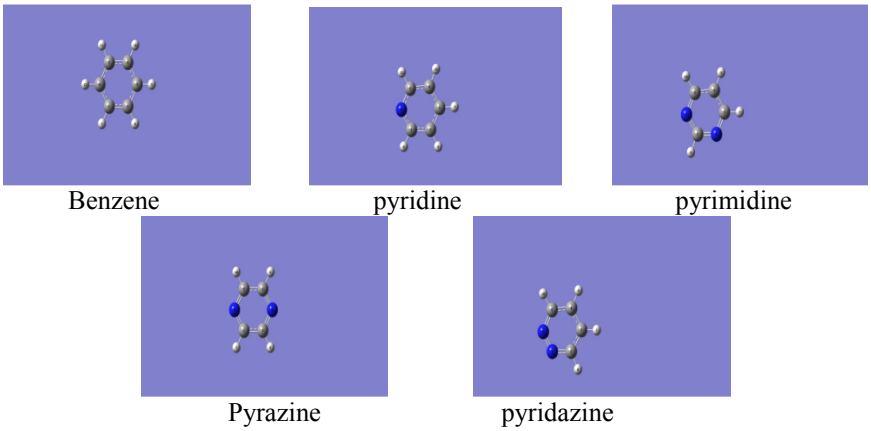
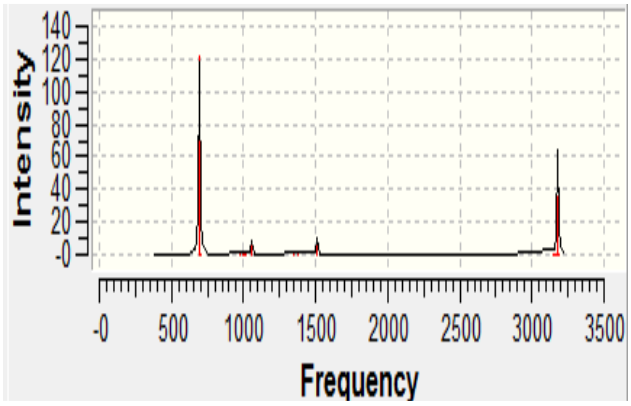


Figure 1: optimized structures for studied molecules



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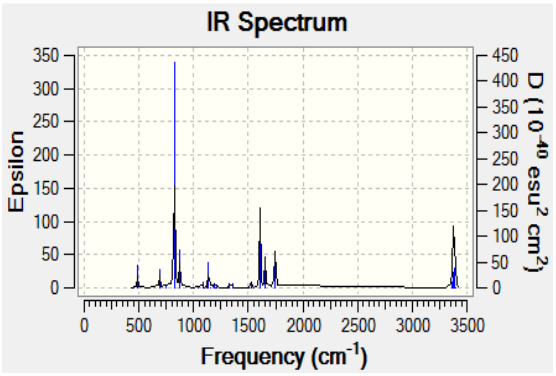

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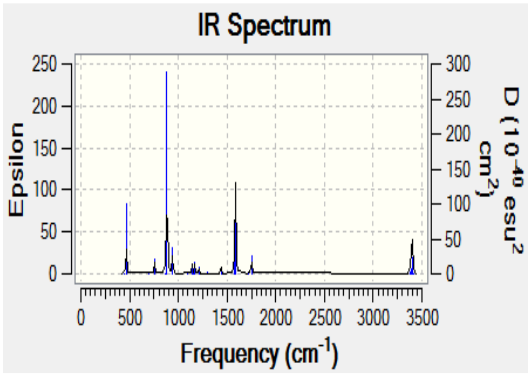

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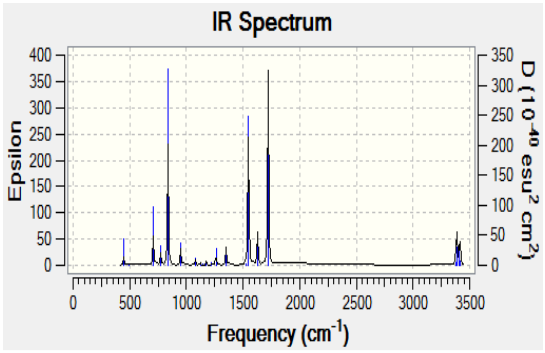
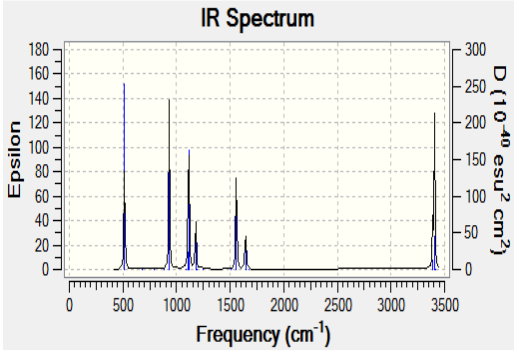


pyrimidine



pyrizine

Figure 2: The IR spectra of molecules under study, Epsilon ≡ Intensity (Km/mol).