The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2019

Volume 6, Pages 68-73

ICRES 2019: International Conference on Research in Education and Science

Investigation of Electronic Properties of Substituted Pyrimidine Derivatives with Density Functional Theory

Erdem ERGAN
Yuzuncu Yil University

Esvet AKBAS
Yuzuncu Yil University

Abstract: Quantum chemical calculations are widely used in the reactivity of organic compounds. The configuration in the methodology reached a point where the reasonably predicted properties could be obtained from the density functional theory (DFT) calculations. The geometry and molecular orbitals of organic compounds are characterized by their activities. The electronic properties of the compounds are related to the frontier orbital energy of highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), and energy gap ($\Delta E_{LUMO\text{-}HOMO}$). In this study, compounds of pyrimidine have been researched the electronic properties using density functional theory.

Keywords: Pyrimidine compounds, DFT, HOMO, LUMO

Introduction

Substituted pyrimidines attracted synthetic organic chemistry interest very much because of their biological and chemotherapeutic importance. The pyrimidine compounds and related fused heterocycles are interesting classes of heterocyclic compounds that exhibit a wide spectrum of biological activities such as anticancer, antiviral, antioxidant, antibacterial, anxiolytic, antidepressant, anti-inflammatory and analgesic activities (Addepalli, at al., 2018; Gokhale, at al., 2017).

Quantum chemical calculations are widely used in the reactivity of organic compounds. The configuration in the methodology reached a point where the reasonably predicted properties could be obtained from the density functional theory (DFT) calculations. The geometry and molecular orbitals of organic compounds are characterized by their activities. The properties of the components, the highest molecular orbital energy (E_{HOMO}), the lowest empty molecular orbital energy (E_{LUMO}) and energy deficit ($\Delta E = E_{LUMO} - E_{HOMO}$) are related to the use of the boundary orbital (Kanmazalp, 2017).

The high E_{HOMO} value has a molecule tendency to give electrons, while a low E_{LUMO} value indicates the ability of the molecule to accept electrons. The difference between E_{LUMO} and E_{HOMO} energies is called energy gap. Larger values of the energy gap will provide low reactivity to a chemical interaction and inhibition efficiency. But the lower values of the ΔE will render good reactivity to a chemical interaction and inhibition efficiency (Karzazi, at al., 2014).

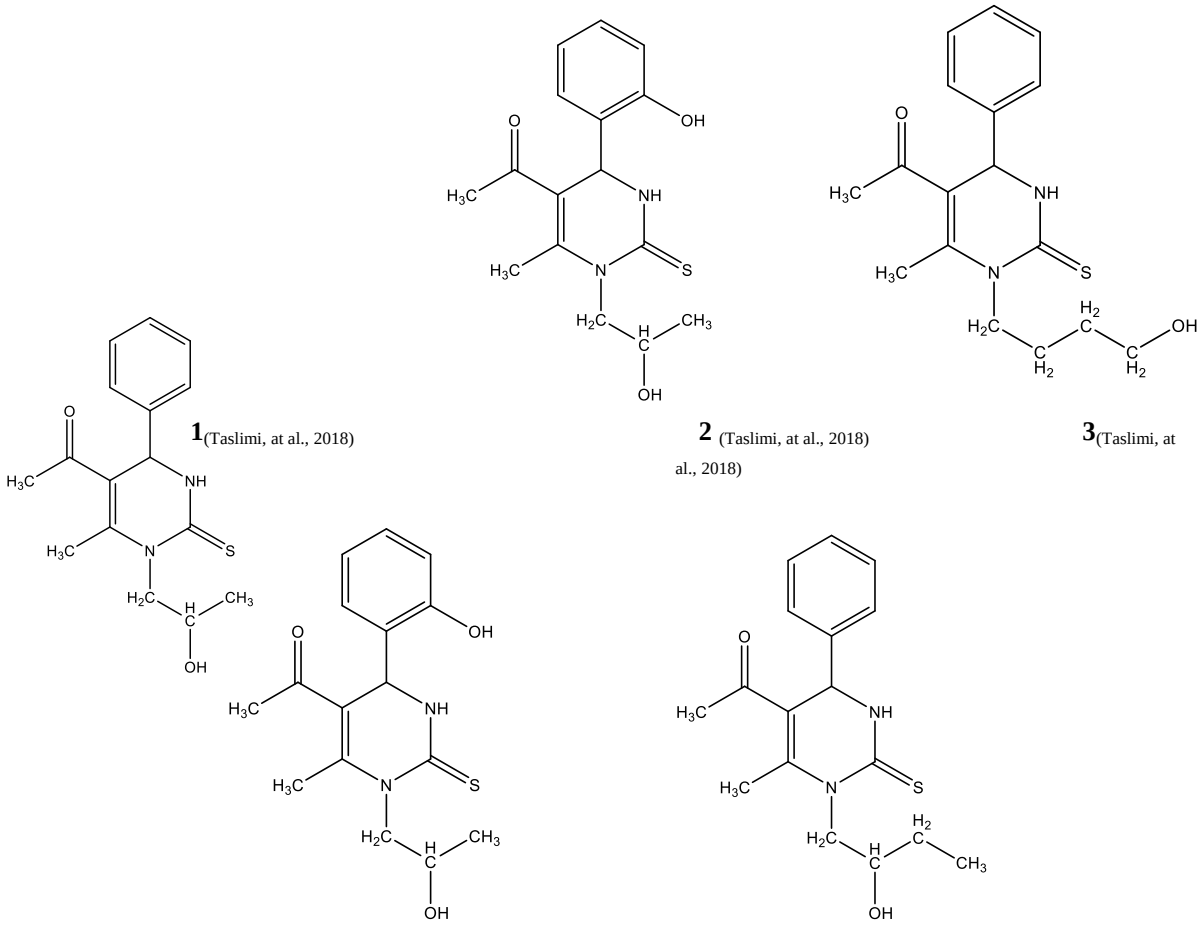
Method

Calculation Analysis

The quantum chemical parameters of the earlier synthesized pyrimidine compounds **1-5** (Taslimi, at al., 2018) (Fig. 1.) have been investigated as electronic properties using density functional theory. Full geometry optimizations of pyrimidine derivatives were performed using DFT based on Beck's three parameter exchange

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) and the 6-31G (d, p) orbital basis sets in Gaussian09 program (Becke,1993; Lee, at al., 1988; Frisch, at al., 2009).



1(Taslimi, at al., 2018)

2 (Taslimi, at al., 2018)

3(Taslimi, at al., 2018)

4 (Taslimi, at al., 2018)

5 (Taslimi, at al., 2018)

Figure 1. Molecular structures of the compounds

Results and Discussion

The highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy and the energy gap of HOMO and LUMO are calculated at the B3LYP/6–31G(d,p) level in order to evaluate the energetic behavior of earlier synthesized molecules 1-5. The energies and pictorial illustration of HOMO and LUMO frontier molecular orbitals are shown in Fig. 9. The positive and negative phases are represented in red and green color, respectively. It is very important to know the energy gap of synthesized molecules and see the contribution of functional groups on frontier molecular orbitals because HOMO and LUMO play an important role in the electrical and optical properties, as well as in UV–vis spectra and chemical reactions (Cinar, at al., 2011). The bio- and chemical-activity of the molecules depend on the eigen value of HOMO which represents the ability to donate an electron, LUMO which represents the ability to obtain an electron as an electron acceptor and $\Delta E_{HOMO–LUMO}$ energy gap (Shukla, at al., 2014). If the molecules have a large energy gap, they are more stable molecules in terms of a chemical activity. The graphs show that HOMOs are generally formed in the pyrimidine ring and that LUMOs are localized in the benzoyl group attached to the pyrimidine ring shown in Figure 2.

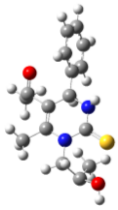
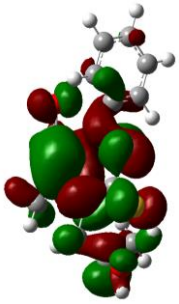
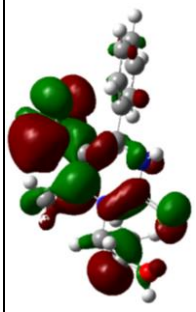
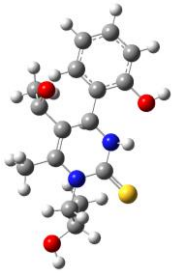
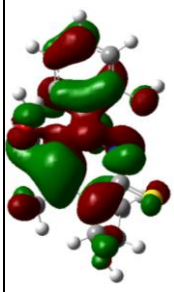
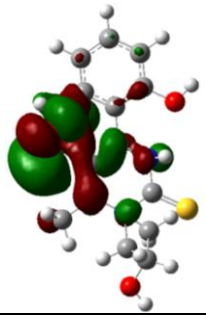
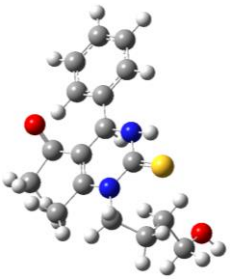
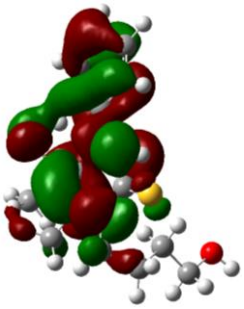
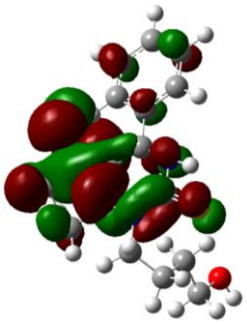
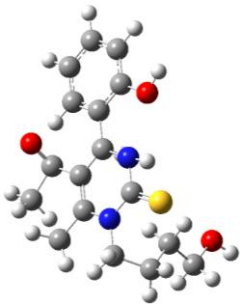
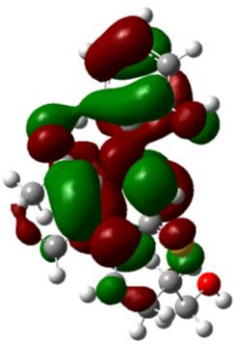
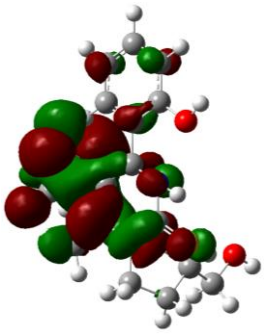
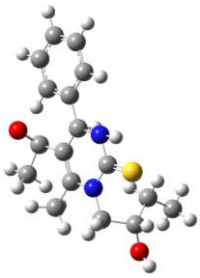
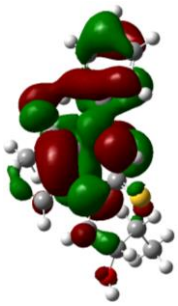
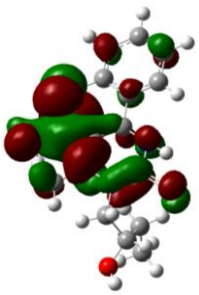
Compounds	Molecular structure	HOMO	LUMO
1			
2			
3			
4			
5			

Figure 2. The optimized structures of molecules 1-5 obtained at B3LYP/6-31 G (d, p)

By using HOMO and LUMO energy values for a molecule, the global chemical reactivity descriptors of molecules such as hardness (η), chemical potential (μ), softness (S), electronegativity (χ) and electrophilicity index (ω) have been defined. Where A is the ionization potential and I is the electron affinity of the molecule. All the calculated values of ionization potential, electron affinity, hardness, potential, softness and electrophilicity index are shown in Table 1.

Table 1. Calculated quantum chemical parameters of the studied molecules

Compounds	**1**	**2**	**3**	**4**	**5**
E_{HOMO} (eV)	-5.0956	-5.0080	-5.0056	-4.8347	-5.0507
E_{LUMO} (eV)	-2.0836	-2.5565	-2.6012	-2.5312	-2.6325
Ionization potential: I (eV)	5.0956	5.0080	5.0056	4.8347	5.0507
Electron affinity: A (eV)	2.0836	2.5565	2.6012	2.5312	2.6325
Electronegativity: χ(eV)	3.5896	3.7823	3.8034	3.6830	3.8416
Chemical hardness: η(eV)	3.012	2.4515	2.4044	2.3035	2.4182
Chemical softness: S	0.3320	0.4079	0.4159	0.4341	0.4135
Dipole moment: $\mu_{(debye)}$	3.6072	1.5520	6.2170	4.6906	4.6787
Electrophilicity index: (ω)	2.1600	0.4913	8.0376	4.7757	4.5261
Transferred electrons fraction: (ΔN)	0.5661	0.6563	0.6647	0.7200	0.6530
Energy gap: $\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	3.012	2.4515	2.4044	2.3035	2.4182
$\Delta E_{back\ donation}$	-0.753	-0.6129	-0.6011	-0.5759	-0.6046

As presented in Table 1, the compound which have the lowest energetic gap is the compound 4 (ΔE = 2.3035 eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **1**(ΔE = 3.012 eV). The compound that has the highest HOMO energy is the compound 4 (E_{HOMO} = - 4.8347 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **5** (E_{LUMO} = -2.6325 eV) which signifies that it can be the best electron acceptor.

The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electro negativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound 4 has lowest value of the potential ionization (I =4.8347 eV), so that will be the better electron donor. Compound **5** has the largest value of the affinity (A = 2.6325 eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules.

Chemical hardness (softness) value of compound 4 (η = 2.3035 eV, S = 0.4341 eV) is lesser (greater) among all the molecules. Thus, compound 4 is found to be more reactive than all the compounds. Compound **5** possesses higher electro negativity value (χ = 3.8416 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 3 (ω = 8.0376 eV) indicates that it is the stronger electrophiles than all compounds.

Compound 4 has the smaller frontier orbital gap so, it is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

Molecular Electrostatic Potential (MEP) Surface

MEP is a protocol of mapping electrostatic potential onto the iso electron density surface. Red color shows electron rich regions which are partially negatively charged. Blue color shows electron deficient regions which are partially positively charged. Light blue shows slightly electron deficient regions. Yellow color shows slightly electron rich regions and green color represents neutral regions. The MEPs have been used for interpreting and predicting relative reactivities of sites for electrophilic and nucleophilic attack, investigation of biological recognition, hydrogen bonding interactions, studies of zeolite, molecular cluster and crystal behavior and the correlation and prediction of a wide range of macroscopic properties (Ravikumar at al., 2008). In this study, 3D plots of MEP for 1-5 have been drew in Figure. 3.

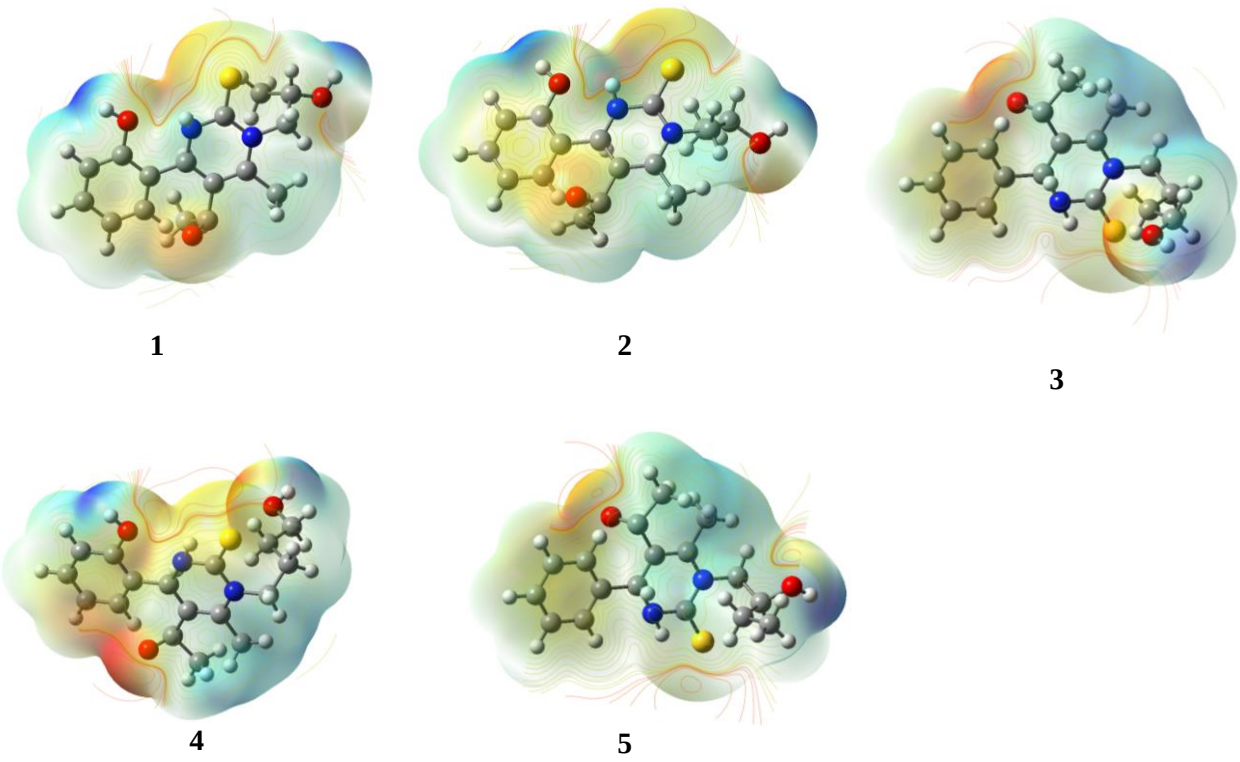


Fig. 3. Molecular electrostatic potential for 1-5

Conclusion

The calculated HOMO–LUMO energy gaps showed that eventual charge transfer took place within the compound. The predicted MEPs revealed the negative regions of the molecules, subjected to the electrophilic attack of these compounds and positive regions of the molecules which are attacked by nucleophiles. To sumup, the calculated data, molecular orbital diagrams and Molecular Electrostatic Potential (MEP) maps provided information about the electronic properties of pyrimidine compounds.

References

Addepalli, Y., Yang, X., Zhou, M., Reddy, D. P., Zhang, S.L., Wang, Z., He, Y. (2018). Synthesis and anticancer activity evaluation of novel azacalix[2]arene[2]pyrimidines. *Eur. J. Med. Chem.*, 151, 214-225.

Becke, A.D. (1993) A new mixing of Hartree–Fock and local density-functional theories. *The Journal of Chemical Physics*, 98, 1372.

Cinar, M., Coruh, A., Karabacak, M. (2011). FT-IR, UV–vis, ^{1}H and ^{13}C NMR spectra and the equilibrium structure of organic dye molecule disperse red 1 acrylate: A combined experimental and theoretical analysis *Spectrochim. Acta A*, 83, 561–569.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, N.J., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels,

A.D., Farkas, Ö., Foresman, J.B., Ortiz, J.V., Cioslowski, J., Fox, D.J. (2009). Gaussian, Inc., Wallingford CT.

Gokhale, N., Dalimba, U., Kumsi, M. (2017). Facile synthesis of indole-pyrimidine hybrids and evaluation of their anticancer and antimicrobial activity *J. Saudı Chem. Soc.,* 21, 761-775.

Kanmazalp, S.D. (2017). nvestigation of Theoretical Calculations of 2-(1-Phenylethylideneamino)guanidine Compound: NBO, NLO, HOMO-LUMO and MEP Analysis by DFT Method. *Karaelmas Science and Engineering Journal*, 7(2), 491-496.

Karzazi, Y., Belghiti, M.E.A., Dafali, A., Hammouti, B. (2014). A theoretical investigation on the corrosion inhibition of mild steel by piperidine derivatives in hydrochloric acid solution. *Journal of Chemical and Pharmaceutical Research*, 6(4), 689.

Lee, C., Yang, W., Parr, R.G. (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37(2), 785.

Ravikumar, C., Joe, I.H., Jayakumar, V.S. (2008). Charge transfer interactions and nonlinear optical properties of push–pull chromophore benzaldehyde phenylhydrazone: A vibrational approach. *Chem. Phys. Lett.*, 460, 552–558.

Shukla, V.K., Al-Abdullah, E.S., El-Emam, A.A., Sachan, A.K., Pathak, S.K., Kumar, A., Prasad, O., Bishnoi, A., Sinha, L. (2014). Spectroscopic (FT-IR, FT-Raman, and UV–visible) and quantum chemical studies on molecular geometry, Frontier molecular orbitals, NBO, NLO and thermodynamic properties of 1-acetylindole. *Spectrochim. Acta A*, 133, 626–638.

Taslimi, P., Sujayev, A., Turkan, F., Garibov, E., Huyut, Z., Farzaliyev, V., Mamedova, S., Gulçin, İ. (2018). Synthesis and investigation of the conversion reactions of pyrimidine-thiones with nucleophilic reagent and evaluation of their acetylcholinesterase, carbonic anhydrase inhibition, and antioxidant activities. *Journal of Biochemical and Molecular Toxicology*, 32(2), 1-12.

Author Information

Erdem Ergan
Van Yuzuncu Yil University,
Van Vocational School Of Security,
Department of property protection and security,
65080 Van/Turkey
Contact E-mail: *erdemergan@yyu.edu.tr*

Esvet Akbas
Van Yuzuncu Yil University,
Faculty of Science, Department of Chemistry,
65080 Van / Turkey