Journal University of Kerbala , Vol. 15 No.4 Scientific . 2017

Study of Some benzylidene aniline Derivatives Using Density Function theory (DFT, B3LYP/6-32G)

الدراسة النظرية لبعض مشتقات البنزلدين انلين باستخدام نظرية دالة الكثافة DFT, B3LYP/6-32G

Nedaa . A . Jassim
Chemistry Dep ., Science College. *University* of Karbala

Abstract

The research involves the application of the Gaussian program (Gaussinan 09) utilizing density function theory (DFT) with B3LYP/6-32G of quantum mechanical calculations on a several of N-benzylidene aniline derivatives that containing substitutes (CH_3, NO_2). The calculations leads to find out electronic densities, ionization energies , geometries optimization, dipole moment , energies of HOMO , LUMO orbital , and also the vibrational modes were investigated using Chemchraft program .Spectra of Ultraviolet and standard thermodynamic functions (U^0 ,H^0 , S^0 ,G^0 ,A^0)for each substituted benzlidene aniline was additionally explored .The impact of substituted groups on stabilition of each examined molecule is explored. Data obtained of benzylidene aniline derivatives are compared with the benzylidene aniline.

الخلاصة

تضمنت الدراسة تطبيق برنامج كاوسين (Gaussinan 09) باستخدام نظرية دالة الكثافة DFT مع B3LYP/6-32G في حسابات ميكانيك الكم لعدد من مشتقات البنزلدين ألأنلين المشتملة على المعوضات الآتية (NO_2, CH_3) توصلت الحسابات الى ايجاد الكثافة الالكترونية ،طاقات التأين ،الشكل الهندسي المتوازن ،عزم ثنائي القطب(طاقات المدارات HOMO , LUMO) وكذلك تم التوصل الى الانماط الاهتزازية ، باستخدام برنامج كيم كرافت . بالاضافة الى ذلك تم تشخيص طيف الاشعة الفوق البنفسجية والدوال الثرموداينميكـية (U^0 ,H^0 ,G^0 ، S^0 ، A^0) لكل من جزئيات البنزلدين انلين المعوضة. وتم دراسة تأثير المجاميع المعوضة على استقراريـه كل من المركبات المدروسة . ،البيانات التي تم الحصول عليها لمركبات البنزولدين الانلين المعوضة تم مقارنتها مع مركب البنزلدين انلين .

Introduction

N-benzylideneaniline is a category of vital compounds in medicinal and pharmaceutical field. N-benzylideneaniline represents a model aromatic Schiff base and it is also a conventional bioisoster of stilbene and resveratrol [1,2].Benzylidene aniline derivatives as well as benzylidene aniline are widely found in herbal products, proteins, vitamins and in the generation of dyes and insecticides and are getting used as an antioxidants[3,4] . Although these chemical substances are harzardous to the human body and natural environment , alongside intense toxicity[5], reproductive, neurotoxic , and formative poisonous[5],. 4-bromoaniline and Aniline were utilized as an intermediary substances in the combination and synthesis of various medication pills (pamaquine , plasmochin) antioxidants , cancer prevention agents (octyl diphenylamine, p-phenylenediamine),and disinfectant marketers[6]. Aniline is a harmful natural compound organic compound with the system $C_6H_5NH_2$, For example as a phenyl group linked to an amino organization, aniline is the prototypical aromatic amine. Its principal use is inside the manufacture of precursors to polyurethane and other commercial chemical substances. Like maximum volatile amines, it possesses the odor of rotten fish .It ignites easily burning with a smoky flame feature of fragrant compounds[7]. The stableness trouble related with the essential properties of fragrant amine derivatives can be tended by means of an alternative condition . These days the application of medical care in bio field is comprehended to change the Nowadays bio field treatment is fathomed to change the diverse properties of living and non-living matters characterizes . Bio fields as “strength fields that purportedly encompass and infiltrate the human body”. Human body has the

outfit the power from environment and may transmit into any protest over the universe . The protest dependably get the energy and replied into gainful way. This method is known as field therapy [7-11] . Utilization of numerous new investigative gadgets requires the presence of organic reagents critical compounds of the measuring device. some of the natural reagents genuinely utilized. Schiff bases have excellent attributes, auxiliary similitudes with herbal organic compounds, quite easy coaching strategies and the artificial flexibility that empowers plan of reasonable structural properties . Activity of antibacterial is reliant on the molecule shape of the chemical substances, the dissolvable utilized and the bacterial species[12,13] .

Computational method

One of the important methods in quantum chemistry is Density functional theory method and that we can thusly begin via utilizing presenting or better reviving a few main principles from essential atomic quantum mechanics. focused on the classical Hartree-Fock approximation. when you consider that contemporary density practical thought is as often discussed in relation to the Hartree-Fock variant and the comparing expansions to it, a capable valuation for the related physics is an important component for a profound information of the issues to return. build up the red line that connects the seminal theorems of Kohn and Hohenberg by the conclusion of this via utilizing Sham and Kohn to the right now famous approximate alternate-correlation deliberate[14] . The idea of the alternate-correlation hole, that's not regularly discussed in standard quantum chemical textbooks, keeps an extraordinary area inside our composition . Contributions of Ferm and Thomas in addition to Slater, who utilized the electron density as easy variable additional out of impulse than out of stable substantial contentions. We trust that getting an handle on its attributes allows a great deal with motivation to obtain more pictorial and less outline understanding of the theory[15] .

Solution of this equation yields vibration frequencies ($\lambda = 4\pi^2 \nu^2 C^2$) and vibration mode eigen vector coefficients, L_j .These coefficients are used in evaluating the atomic partial contribution values (APP) (the partial contribution of each atom to the molecular vibration), the IR absorption intensities in addition to doing the graphic representation of each of vibration mode. Sham DFT schemes for open-shell systems, which imply different meanings of the exchange–correlation energy functional and lead to different exact conditions with this functional

The ground-state electronic energy (E) of a N-electron systemcan be distinctively dependent on the electron charge density[16]

$Ep = E$ [ρ (r)] .....(1)

$$\left[-\frac{1}{2}\nabla^2 + V^{KS}(r) \right] \Phi_i(r) = E_i \Phi(r) \quad \text{..... (2)}$$

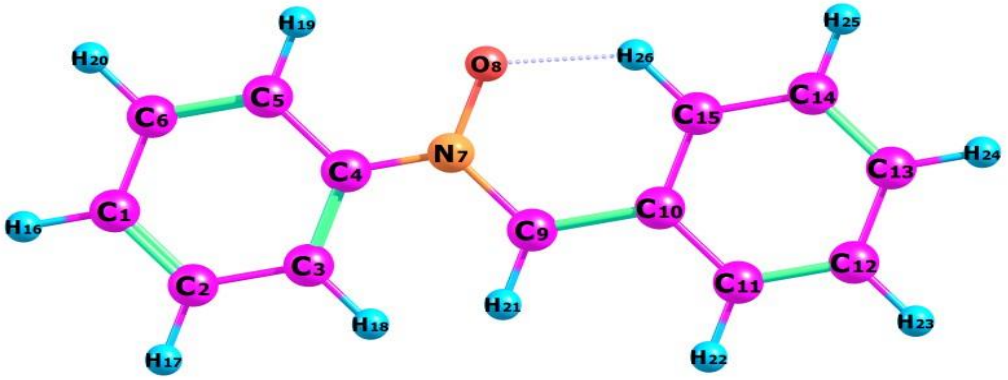
$$V^{KS} = V_{ext}(r) + \int \frac{\rho(r^-)}{(r - r^-)} dr^- + V_{xc}(r) \quad \text{.....(3)}$$

$$V_{xc}(r) = \frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)} \quad \text{.....(4)}$$

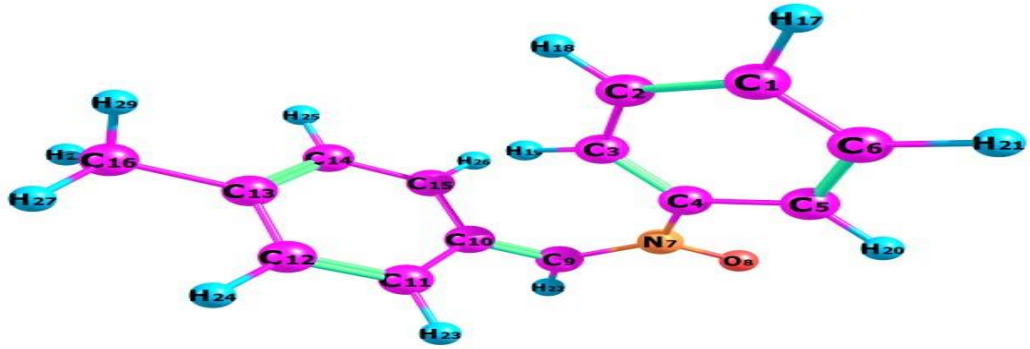
$$\rho(r) = \sum_i^N [\Phi_i(r)]^2 \quad \text{.....(5)}$$

Kohn-ShamV^{Ks} V_{xc} = exchange – correlation potential P(r) = electron density V_{ext}=external potential

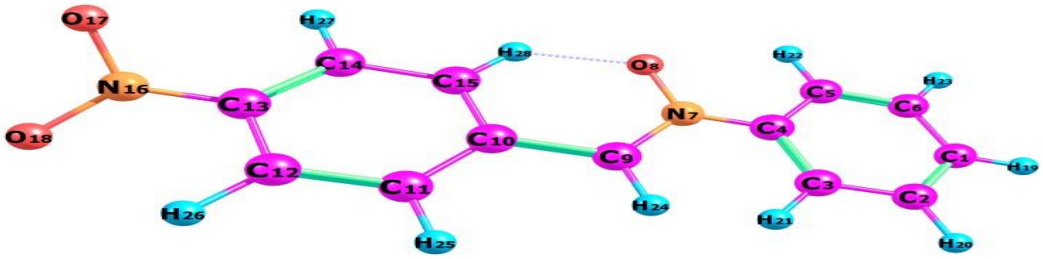
Fig 1 : Structures of benzylidene aniline Derivatives (3D)



N- benzylidene aniline oxide



N-(4-methylbenzylidene)aniline oxide



N-(4-nitrolbenzylidene)aniline oxide

Results and discussion

The benzylidene aniline Derivatives investigated in the present work are:

Compound 1 N-bnzylideneaniline oxide
Chemical Formula: $C_{13}H_{11}NO$

Comopound 2 N'-(4- Methylbnzyliden)aniline oxid
Chemical Formula: $C_{14}H_{14}NO$

Comopound 3 N'-(4- Nitrobnzyliden)anilin oxid
Chemical Formula: $C_{13}H_{10}N_2O_3$

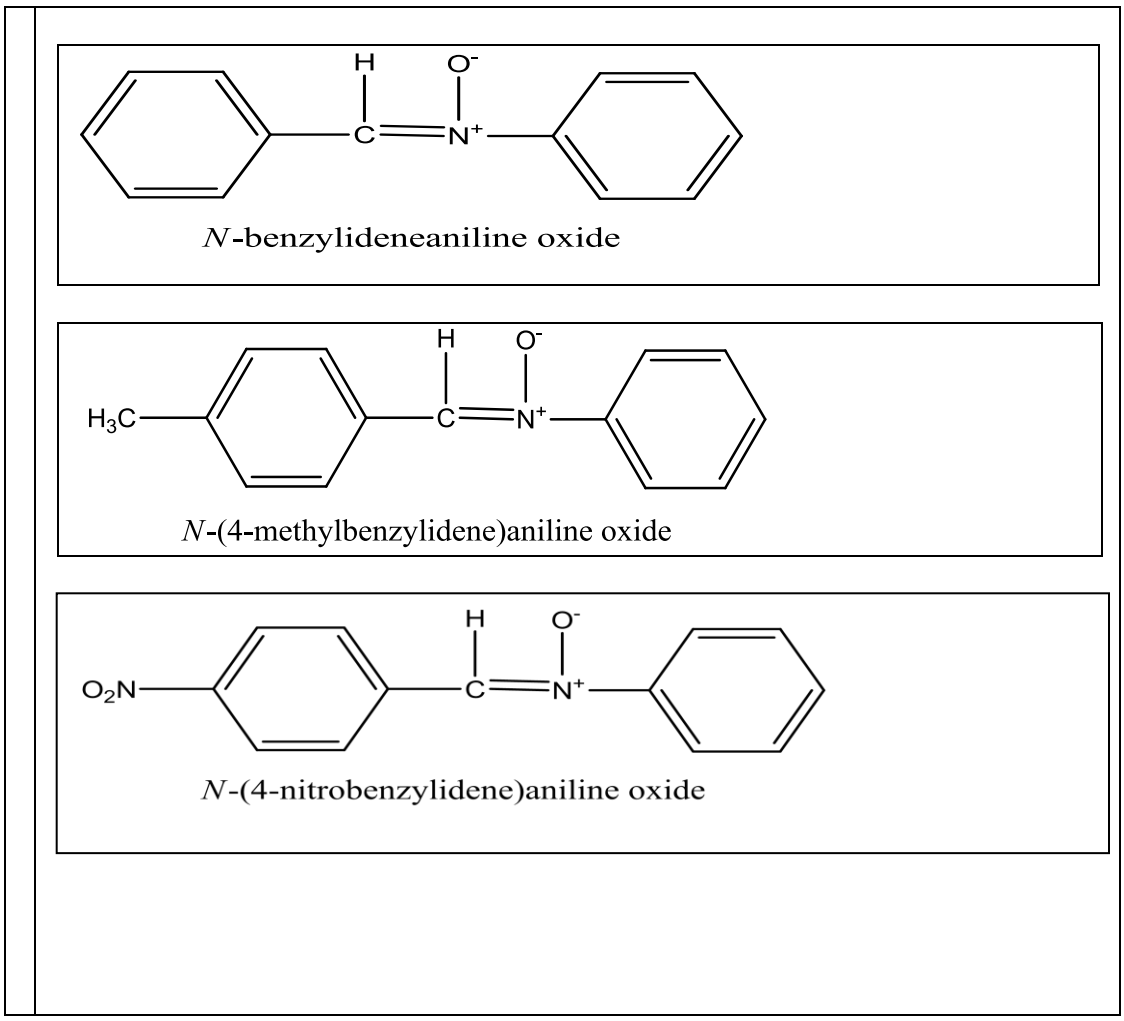


Fig 2: The geometric equilibrium for N'-(bnzylidenaniline oxide) , N'-(4- Methylbnzyliden)anilin oxide , N'-(4- Nitrobnzyliden)anilin oxid

*M*ethods of calculation (DFT)

This study involves application of DFT (B3LPY /6-32-G) approach by the Gaussian **09** program which became evolved and the treatment of organic molelcule [20 .21]. Many of these programs , values can be obtained for the equilibrium geometry energy

of the molecules in the further with their IR absorption intensities and fundamental vibration frequencies (3N-6). Solution of this equation yields vibration frequencies $\lambda=4\pi^2\ \upsilon^2\ c^2$ [22,23] . Depending on DFT method a few physical properties were calculated according to these equations $E_A = - E_{LUMO}$, $\eta=1/2\ (E_{HOMO} - E_{LUMO})$, $(G^0 = H^O - ST)$, $(A^0 = G^0 - ST)$.

G09 program of J. Frisch, G. W. Trucks, et al[24,25] was applied throughout .

Results and Discussion

In this research calculated the vibrational spectra and electronic spectra of three molecules **N'-(bnzylidenaniline oxide) , N'-(4- Methylbnzyliden)anilin oxide , N'-(4- Nitrobnzyliden)anilin oxid .** Result show that vibrational stretching frequencies of (NO) is less for substituted bnzyliden aniline with CH_3 and is larger for NO_2 compared with non-substitu bnzyliden aniline with CH_3 is larger compared with non-substituted bnzyliden aniline and substituted aniline with NO_2. This is theoretical analysis has shown effecting of electron donating group CH_3 and with drawing group NO_2 ,it is because increasing of conjugated system effect . Results of a study theoretical UV transitions energies showing the appearance of three bands for each of the substituted bnzyliden aniline compounds. The first band of ultraviolet transitions due to (N-O) group that caused by electronic transitions including n-π and π-π^*, while the second and third band is due to electronic transitions in the aromatic ring and the aromatic system, respectively .substituted bnzyliden aniline with NO_2 have long wavelength of electronic absorption bands compared with bnzyliden aniline and substituted bnzylidenaniline with CH_3 . This difference in band values results from the increase in the conjugated system
(table 1, table 2).

Table 1: Comparison of the energies of theoretical UV transitions studied benzylidne aniline derivatives in nm

NO. Of Comp.	Substituted group	First Excited State (nm)	Second Excited State (nm)	Third Excited State (nm)
1	—	244	212	211
2	$-CH_3$	235	207	204
3	$-NO_2$	283	260	236

Table 2: Vibrational frequencies of the studied benzylidne aniline derivatives in cm^{-1}

NO. Of COMP.	Substituted group	N—O St.	=C—H ben .	C=N St.	=C–H St.	C—H Ar. St.
1		1164	1419	1620	3226	3246-3168
2	$-CH_3$	1149	1418	1605	3224	3247- 3186
3	$-NO_2$	1170	1422	1660	3229	3269-3187

The Physical Properties and Thromdynamic functions ;

The end result show that dipole moment of benzyliden aniline derivatives has higher value when comparison with non-substituted bnzyliden aniline compounds due to that a lot of groups raise the negative charge while others reduce the positive charge on the C atom (**Table 4)**. HOMO of benzyliden aniline linked to the electron donating group CH_3 is large when compared with non-substituted aniline, consequently that is lose electrons (oxidation). this is may be due to the hyperconjunction impact , while , the electron – with drawing group NO_2 have the opposite impact LUMO of benzyliden aniline connected to the electron – with drawing group NO_2 is less in comparison with non-substituted benzyliden aniline, consequently they are accept electron (Reduction) . even as , the electron donating group have the opposite impact. This change in the behavior of molecules is due to the characteristics of organizations linked to C atom (**Table 4)** Ionization energies (IP) of benzyliden aniline linked to the electron donating institution CH_3 is much less contrast to non-substituted benzyliden aniline , so that they have ionize without difficulty . even so the electron with - drawing organization NO_2 have the opposite effect **(Table 4).** Substituted benzyliden aniline have less total energy as compared with non-substituted benzyliden aniline so they are more stable because of an increase in conjugated system **(Table 3**). Thermodynamic functions (G^o , H^o , U^o , A^o) of benzyliden aniline attached with the electron donating group (CH_3) is larger when compared with non-substituted benzyliden aniline . Alternatively, The electron- with drawing group (NO_2) have the inverted effect , All substituted benzyliden aniline compounds have large Entropy function (S^o) as compared with non-substituted benzyliden aniline compound **(Table 3)**

Table 3: Standard thermodynamic function for benzylidene aniline Derivatives at 298.15 K

NO. Of Comp.	Substituted groups	U^0 KJ mol $^{-1}$	H^0 KJ mol $^{-1}$	G^0 KJ mol $^{-1}$	A^0 kJ mol $^{-1}$	S^0 kJmol $^{-1}$
1	—	660 .987	663.466	516.478	513.999	0.493
2	$-CH_3$	738.472	740.951	582.037	579.558	0.533
3	$-NO_2$	652.127	644.606	509.133	506.654	0.555

Table 4:Calculatated dipole momonts (debye) , Orbital energies HOMO,LOMO(in a.u) Total enrgy (in a.u) for the difference aniline compounds

No. of comp.	Point groups	Substituted Groups	Dipole momen t	E_{HOMO} (a.u)	E_{LUMO} (a.u)	Δ (E_{HOMO} - E_{LUMO}) (a.u)	IP (a.u)	Total energy (a.u)
1	C_1	—	4.022	- 0.203	- 0.052	- 0.151	0.203	- 671.053
2	C_1	$-CH_3$	4.562	- 0.200	- 0.049	- 0.152	0.201	-710.363
3	C_1	$-NO_2$	4.030	- 0.204	- 0.055	- 0.148	0.204	- 671.050

Aim of Research

N-benzylidene aniline derivatives are a type of vital chemical molecules in pharmaceutical and medicinal field [26,27]. Study of this compounds show biological activities including anticancer, , herbicidal activities and antibacterial antifungal [28] .
So the aim of reaserch

1. To help solve problem and hind solution before doing experiments .
2. To predict properties of N-benzylidene aniline derivatives and quantities that are difficult or even impossible to observe experimentally
3. To help with analysis and interpretation of experimental data of N-benzylidene aniline.
4. To know the best structure – on for which the energy is minimum of N-benzylidene aniline
5. To know the best compound have more biological activities.

Conclusions

information of infrared spectral of N-benzylidene aniline and its derivatives are comparative roughly to the normal range . A band at 1605-1660 cm^{-1} belongs to C=N vibration. The bands that appeared for every studied chemical molecules show at about max 204 - 236 nm belong to n- π^* of conjugated arrangement of molecules . **(Table 1**).

The conduct of these chemical substances have answered to the high electron density thusly , it can be inferred that the conjugation system have solid impact as antibacterial action , because the electrons are delocalized along the entire of the conjugated molecules can comes about having antibacterial activity and become end up plainly troublesome toss the body cell off the microscopic organisms .

Recommendations

Almost half of these chemical substance (bnzylidenaniline) demonstrated reasonable sensible action up against the bacterial types ,Tuse future reviews ought to regard for on N-benzylidene aniline to comprehend the best compound utilizing as antibacterial

References

[1] Merchant J.R. , Chothia D.S, 1970 , [4-(Dimethylamino)benzylidene]-3-hydroxybenzohydrazide synthesis , J .Amer .Chem .Soc , 13: pp.335-336.

[2] Travis A.S. , 2007, Manufacture and uses of the anilines: A vast array of processes and products. Patai's Chemistry of Functional Groups. Wiley, New York, USA.

[3] Kavitha E , Sundaraganesan N ., 2010 ,Molecular structure, vibrational spectroscopic and HOMO, LUMO studies of 4-nitroaniline by density functional method. Indian. J .Pure. Appl .Phys ,48: pp.20-30 .

[4] More P G., Bhalvankar R B. and Pattar S C., 2001, 4-phenyldiazenyl 2-(phenylimino methyl) phenols; synthesis and in-vitro biological evaluation as potential antibacterial agents , J .Indian. Chem. Soc., 2001, 78(9) , pp. 474-475.

[5] Shanker V ., Rayabandla S.M , Kumavath R.N., Chintalapati S ., 2006 , Light-dependent transformation of aniline to indole esters by the purple bacterium Rhodobacter sphaeroides OU5. Curr. Microbiol 52: pp. 413-417.

[6] Himaja M . , Das P., Rout P.K , Sharma S ., et al., 2012, Synthesis docking and antioxidant activity of some NSAID derivatives of amines. Int. J. res. Ayurveda .pharm , 3: pp. 548-551 .

[7] Fierz-David H.E ., Blangey L ., 1995, Fundamental processes of dye chemistry. (5^{th} edn), Interscience publishers, Inc., New York.1995

[8] Kasthuri J ., Santhanalakshmi J ., Rajendiran N . , 2008, Antipyrilquinoneimine dye formation by coupling aniline derivatives with 4-aminoantipyrine in the presence of ruthenium nanoparticles. J. Iran. Chem .Soc ,3: pp. 436-444 .

[9] Kareem M.T ., Ibrahim K.A. , 2011, Synthesis and characterization of some

[10] Shinde V., Sances F., Patil S., Spence A. , 2012 , Impact of biofield treatment on growth and yield of lettuce and tomato. Aust .J .Basic & Appl .Sci , 6: pp. 100-105.
[11] Trivedi M.K., Patil S ., Shettigar H ., 2015, Antimicrobial sensitivity pattern of Pseudomonas fluorescens after biofield treatment . J .Infect. Dis. Ther, 3: pp. 222-226
[12] Parekh J., Inamdhar P., Nair R ., Baluja S and Chanda S., 2005, Synthesis and antibacterial activity of some Schiff base complexes , J .Serb .Chem. Soc., 70(10), pp. 1155-1161
[13] Jarrahpour A. A., Motamedifar M., Pakshir K., Hadi N. and Zarei M. , 2004, Synthesis of Novel Azo Schiff Bases and Their Antibacterial and Antifungal Activities, J. Molecules, 9, pp. 815-824 .
[14] Trevor J. D ., 2007, Computational Chemistry Using Modern Electronic Structure Methods, J. Chem. Educ , 84 ,8 , pp. 1364-1370.
[15] David Y., 2001 ,"Appendix A. A.2.4 Gaussian". Computational Chemistry. Wiley-Interscience , 336 -339.
[16] Hehre W. J., Lathan W. A., Ditchfield R., Newton M. D., and Pople J. A., 1970 , Gaussian 70 Quantum Chemistry Program Exchange, Program No. 237.
[17] Bereket G, Ogretir C, Ozsahin C. , 2003, Quantum chemical studies on the inhibition efficiencies of some piperazine derivatives for the corrosion of steel in acidic medium. J. Mol .Struct: Theochem ; 663 , PP. 39-46 .
[18] Obot I .B., Obi-Egbedi N.O., 2009 , HSAB descriptors of thiadiazole derivatives calculated by DFT: possible relationship as mild steel corrosion inhibitors. Der Pharma Chemica. 1, pp. 106-123.
[19] Michael J. S. Dewar , Walter T. , 1977, Ground states of molecules. 38. The MNDO method. Approximations and parameters J. Am. Chem. Soc. , 99 , pp. 4899-4907 .
[20] Frisch M. J .et al, 2004, Gaussian 03, Revision B.03, Gaussian Inc., Wallingford, CT .
[21] James J. P. S., 1989, Optimization of parameters for semiempirical methods , J. Comp. Chem**.,** 10 , pp. 209 -216.
[22] Stewart J.J .P, Csaszar P., Pulay P., 1982 ,"Fast Semiempirical Calculations, ***J.*** Comp. Chem. , 4, 3, pp. 227-228.
[23] Dewar J. S., Walter T. , 1977 , Ground states of molecules. 38. The MNDO method. Approximations and parameters , J. Am. Chem. Soc., 99 , pp. 4899-4907 .
[24] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., M. A. Robb M. A., Cheeseman J. R ., Mennucci B., Petersson G. A ., 2009, Gaussian 09, Revision E.01 .
[25] Young D., 2001, "Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems" ; John Wiley & Sons, inc: USA.
[26] Karia F. D., and Parsania P. H. , 1999, Asian .J Chem., 11(3),pp. 991-995.
[27] More P .G. , Bhalvankar R B and Pattar S C, 2001,*J Indian Chem Soc*., 78(9), pp. 474-475.
[28] El-masry A. H., Fahmy H H .and Abdelwahed S H A., 2000, Molecules, 5, pp.1429- 1438.
[26] Baseer M. A., Jadhav V. D., Phule R. M., Archana Y .V. and Vibhute Y .B., 2000.,*Orient J Chem*., 16(3), pp.553-556.