MUSLIM ARTS COLLEGE

ISO 9001:2008 CERTIFIED

(Affiliated to Manonmaniam Sundaranar University, Tirunelveli)
Azhagiamandapam, Thiruvithancode - 629 174, Kanyakumari District, Tamilnadu
Ph: 04651 248842, 248841, 248803 e-mail : muslimartscollege@gmail.com

ISO 9001 : 2008
Reg.No. RQ91 3688

DEPARTMENT OF PHYSICS & RESEARCH CENTRE

NATIONAL SEMINAR ON

FUNCTIONAL MATERIALS AND ITS APPLICATIONS

CERTIFICATE

This is to certify that Mr./Ms./Dr./Prof. Dr. A. Rathika Asst. Prof affiliated to Muslim Arts College has participated/ presented paper in National Seminar On Functional Materials And Its Applications (NSFMA –2022), organized by the Department of Physics & Research Centre on 14th October 2022 at Muslim Arts College, Thiruvithancode, Kanyakumari District.

Lion Dr. H. Mohamed Ali
Secretary / Correspondent

Dr. G. Edwin Sheeba
Principal

Dr. J. R. Sheeba
Convener

PROCEEDINGS OF NATIONAL SEMINAR ON

FUNCTIONAL MATERIALS AND ITS APPLICATIONS

(NSFMA–2022)

EDITED BY

Dr. J.R.Sheeba
Dr. A. Iren Sobia

14th OCTOBER, 2022

DEPARTMENT OF PHYSICS
&
RESEARCH CENTRE

MUSLIM ARTS COLLEGE
Thiruvithancode - 629174
Kanyakumari District
Tamil Nadu, India

RAJ PATHIPPAKAM
3E, North Street
Kurusady
Nagercoil - 4

ISBN : 978-93-84737-37-5

The author of the book is fully responsible for the facts and figures presented in this book.

Further it is stated that the publisher is not responsible for the statements or opinions expressed by the author of the book.

ISBN 978-93-84737-37-5

Published by

Raj Pathippakam,
3E, North Street,
Kurusady,
Nagercoil - 4

Synthesis, Electronic (Homo-Lumo) Properties and Topology Exploration (Elf, Lol) Of Diethylenediamine 4-Hydroxynitrobenzene

R.Suja[a], A. Rathika[b]*

[a]Reg. No: 21213092132004, Research Scholar, Department of Physics and Research Centre, Muslim Arts College, Tiruvithancode.

[b]Assistant Professor, Department of Physics and Research Centre, Muslim Arts College, Thiruvithancode.

Affiliated to Manonmaniam Sundaranar University, Tirunelveli - 627 012.

*e-mail:rathikarthi87@gmail.com

Abstract

Diethylenediamine 4-hydroxynitrobenzene is an organic compound. Diethylenediamine consist of a six-membered ring containing two opposing nitrogen atoms. 4-Hydroxynitrobenzene is a phenolic compound that has a nitro group at the opposite position of the hydroxyl group on the benzene ring. The molecular structure of D4HB was optimized by B3LYP method with 6-311 G (d. p). The frontier molecular orbital energy gap probably indicates a compound's strong chemical reactivity. Electrophile LUMO value is perceived squat on the 4-hydroxynitrobenzene imputable to the electro absorbing capacity of but the nucleophile HOMO value is spotted on the Diethylenediamine upsurges ascribed to the presence of electron donating capacity. The topological analyses of the electron localization function (ELF) and the localized orbital locator (LOL) were completed using Multiwfn program.

1.Introduction

Piperazines, the six membered nitrogen-containing heterocyclic ring, are certainly an established important pharmacophore in medicinal chemistry [1,2]. Piperazine itself is a respectable hydrogen-bond acceptor and their metal complex capability makes it an interesting moiety for supra molecular complex chemistry [3]. The molecular architecture heterocyclic piperazine derivatives have produced a lot of interest due to owing to many reasons, particularly their biological properties as anti-inflammatory, anti-bacterial, anti-cancer, cardio-protective agents, anti-viral, antituberculosis, anti-diabetic, and antihistamine profiles [4,5]. Diethylenediamine4-Hydroxynitrobenzene (D4HB) has 4-hydroxy nitro benzene that is connected to hydroxyl group. There are two benzene rings that are connected to D4HB compound. The important aim of the present study is to give detailed description of the molecular structure of D4HB. HOMO and LUMO analysis were executed to intend the molecular stability and charge transfer of D4HB. MEP surface is extremely useful for determining probable electrophilic and nucleophilic reaction sites. Colour map of ELF and LOL gives information about electron density charge distribution. Repulsive, attractive, and van der Waals strong and weak interactions in D4HB were investigated by RDG (Reduced Density Gradient) analysis.

2. Synthesis

The calculated amount of the reactants containing, Anhydrous 98% for synthesis Diethylenediamine were purchased from (Loba chemie) and GLC 99% grade of 4-Hydroxy nitro benzene were purchased from (Nice) in the equimolar ratio 1:1 is taken and dissolved in methanol as solvent. 0.8614g of Diethylenediamine was dissolved in 20ml of methanol and mixed with 1.3911g of 4-Hydroxy nitro benzene. To get homogeneous mixture, the solutions were mixed and stirred well using magnetic stirrer for 6hr and filtered with Whatman filter paper and taken in a beaker. The beaker was closed with perforated polythene cover and placed in dust free atmosphere for slow evaporation at room temperature. The growth period of 6 days, transparent yellow-coloured single crystals are harvested. The photographs of grown D4HB single crystal are depicted in Figure 1.

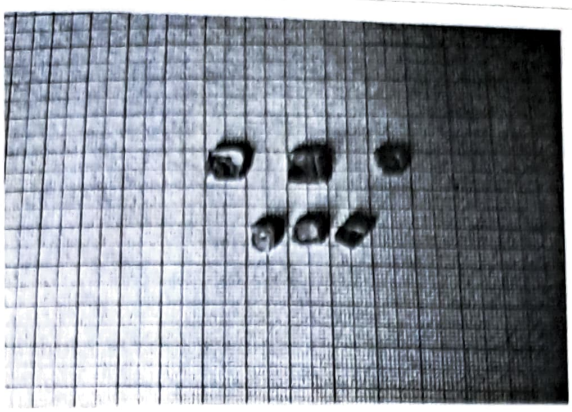

Figure. 1. Photograph of D4HB Single crystals

3. Optimized geometry

Optimized molecular geometry of D4HB was optimized using the B3LYP/6-311++G (d.p) level of theory. Optimized geometry clearly shows that N-H-----O hydrogen bonding interactions act as bridge for electronic delocalization between Diethylenediamine and 4-Hydroxy nitro benzene. The D4HB molecular system has two polar ends, in which N atom act as an electron withdrawing end and hydroxyl group acts as an electron pushing end. These two push pull ends make an easy oscillation of electrons within the system creating molecular asymmetry. The existence of N-H-----O hydrogen bonding interactions facilitates the flow of electronic charge generating molecular hyper polarizability in the system.

The optimized molecular structure reveals the presence of hydrogen bonding interaction. The inter molecular contacts N11-H26 with N----H distance 1.7781A^o which is meaningfully shorter than the Van der walls separation between N and H atoms. Bond angle C4-C1-N11 (122.23°) and C3-C2-N11(122.1871°) significantly deviate from the expected trigonal angle (120°) as an effect of attaching the electron donating group (N-H) instead of hydrogen atom. The bond length of N22-O23 and N22-O24 bond in the nitro group is 1.23664 A^o and 1.2359 A^o which clearly reveals the delocalization of electrons in N-O bond.

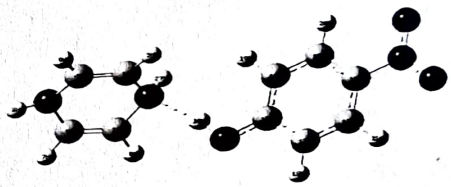

Figure. 2. Optimized structure of D4HB

4. Homo Lumo Analysis

The HOMO energy characterizes the electron donating ability while the LUMO characterizes the electron accepting ability and the gap between HOMO and LOMO characterizes the molecular chemical stability [6]. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity [7]. 3D plots of highest occupied molecular orbitals (HOMOs) and lower unoccupied molecular orbital (LUMOs) are shown in (fig.3). The HOMO is located on the Diethylenediamine but the LUMO is located on the 4-Hydroxy nitro benzene. According to B3LYP/6-31 (d.p) calculation, the energy band gap (ΔE) (translation from HOMO to LUMO) of the molecule to the first excited states is

HOMO energy: –7.33455 eV

LUMO energy: – 4.762994 eV

HOMO – LUMO energy gap ΔE: – 2.5725 eV

The HOMO LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. This small energy gap is responsible for intermolecular charge transfer, which confirms the biological activity of the molecule.

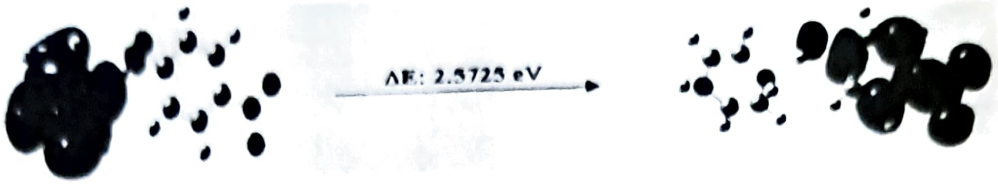

Figure. 3. HOMO-LUMO plot of D4HB

5. ELF and LOL analysis

Topological analysis of Electron Localization function (ELF) and Localized orbital locator (LOL) are tools used for enacting covalent bonding analysis as they reveal regions of molecular space where probability of finding an electron pair is lofty. ELF and LOL reveal high probability of finding an electron pair on molecular structure are carried out by Multiwfn software package.

ELF and LOL have homogenous chemical content because they hinge on kinetic energy density. ELF explains the electron pair density whereas LOL explains maximum localized orbitals overlapping due to gradient of orbitals [8]. ELF map is designed in the range 0.0 to 1.0; however region below 0.5 shows delocalized electronic region [9] and the LOL attains large values > 0.5 in regions where electron density is dominated by electron localization [10].

Colour shades of ELF and LOL maps confirm the existence of bonding and nonbonding electrons, where the red colour around hydrogen atoms with maximum value bespeak the presence of bonding and nonbonding electrons. High ELF or LOL values indicated by red colour around hydrogen atoms shows high localization of electrons due to the ubieties of covalent bond, a lone pair of electrons or a nuclear shell in that region. Blue colour around carbon atoms in Diethylenediamine and p-hydroxy nitrobenzene rings evinces the delocalized electron cloud around it whereas blue circle around nitrogen and atoms bespeak the region of electronic depletion between the inner layer and valence layer. whilst the chemical bonds C-N are described by irregular localization domains (orange) with smaller values of electron localization (0.8-0.9). The covalent regions are seen between hydrogen and nitrogen atoms indicated by red color with high ELF value, the electron depletion regions between valence shell and inner shell are shown by the blue circles around the nitrogen and hydrogen nuclei then conveys a more decisive and clear picture than LOL.

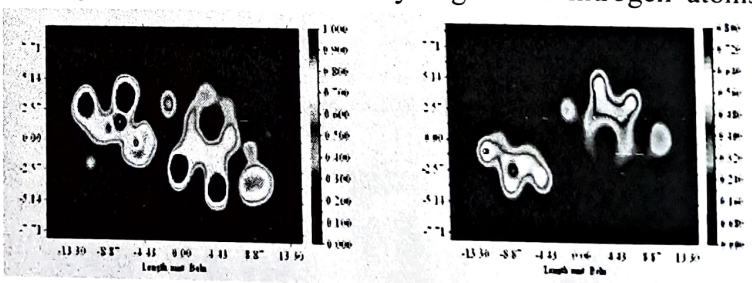

Figure. 4 Colour filled ELF and LOL map of D4HB

Conclusion

In the present work a complete study using quantum chemical computation along with spectroscopic technique. D4HB was synthesized by slow evaporation method and there structural optimization conceded out by B3LYP method. The energy gap as per HOMO-LUMO calculations is 2.5725 eV signifying that the molecule would be both stable and bio active in nature. Electron distribution and reactive sites on the surface were analyzed using ELF and LOL analysis the weak attractive interaction, strong attraction and steric repulsion existed in the title compound.

References

[1] G.G. Zhanel, A. Walkty, L. Vercaigne, J.A. Karlowsky, J. Embil, A.S. Gin, D.J. Hoban, The new fluoroquinolones: A critical review, Canad. J. Infect. Dis. – J. Canad. Malad. Infect. 10 (1999) 207–238.

[2] R.S. Upadhayaya, N. Sinha, S. Jain, N. Kishore, R. Chandra, S.K. Arora, optically active antifungal azoles: synthesis and antifungal activity of (2R,3S)-2-(2,4-difluorophenyl)-3-(5-{2-[4-aryl-piperazin-1-yl]-ethyl}-tetrazol-2-yl/1-yl)-1- [1,2,4]- triazol-1-yl-butan-2-ol, Bioorg. Med. Chem. 12 (2004) 2225–2238. Pamplin B.R. (1979), 'Crystal Growth', Pergamon Press, Oxford.

[3] H. Keypour, M. Mahmoudabadi, A. Shooshtari, M. Bayat, F. Mohsenzadeh, R.W. Gable, Cadmium (II) macrocyclic Schiff-base complexes containing piperazine moiety: Synthesis, spectroscopic, X-ray structure, theoretical and antibacterial studies, Journal of Molecular Structure 1155 (2018) 196–204.

[4] L.R. Chiang, M.L. Jones, S. Ferreira, T.T. Storr, Multifunctional ligands in medicinal inorganic chemistry-current trends and future directions, Cur topics in med chem 12 (3) (2012) 122–144.

[5] Rathi, K. Anuj, Riyaz Syed, Han-Seung Shin, V. Rahul Patel, Piperazine derivatives for therapeutic us.e: a patent review (2010-present), Expert opinion on therapeutic patents. 26 (7) (2016) 777-797.

[6] K. Fukui, Science 218 (1982) pp.747-754.

[7] G. Gece, Corros, Sci.50 (2008) pp. 2981-2992.

[8] Silvi B. Savin A. (1994), 'Classification of chemical bonds based on topological analysis of electron localization functions',Nature, 371 (6499) , pp. 683-686.

[9] Fathima Rizwana B. Prasana J.C. Muthu S. Abraham C.S. (2019), 'Molecular docking studies, charge transfer excitation and wave function analyses (ESP, ELF, LOL) on valacyclovir: A potential antiviral drug Comput', Biol. Chem., 78 , pp. 9-17.

[10] Heiko Jacobsen (2008), 'Localized-orbital locator (LOL) profiles of chemical bonding',Can. J. Chem., 86 (7) (2008), pp. 695-702.

[11] G. Saleh, C. Gatti, L.Lo Presti, Non-covalent interaction via the reduced density gradient: independent atom model vs experimental multipolar electron densities, Comput. Theor. Chem. 998 (2012) 148–163, doi: 10.1016/j.comptc.2012.07. 014.

[12] E.R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A.J. Cohen, W. Yang, Revealing noncovalent interactions, J. Am. Chem. Soc. 132 (2010) 6498–6506, doi:10.1021/ja100936w.