**Theoretical determination of NLO, Chemical reactivity and TD parameters of (1S\*,4R\*,7S\*)-(E)-7-(2,5-Dimethoxyphe nyl)-3,3-dimethoxy-5-(2nitrovinyl)bicyclo[2.2.2]oct-5-en-2-**

**one using DFT method**

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**Abstract**. FMO (Frontier molecular orbital) method was used to understand the stability of the (1S\*,4R\*,7S\*)-(E)-7-(2,5-Dimethoxyphenyl)-3,3-dimethoxy-5-(2nitrovinyl)bicycle [2.2.2] oct-5-en-2-one (DNB) molecule. Non-linear optical properties like dipole moment and hyperpolarizability were calculated, and common thermodynamic parameters also estimated for DNB.

1. **Introduction**

(1S\*,4R\*,7S\*)-(E)-7-(2,5-Dimethoxyphenyl)-3,3-dimethoxy-5-(2nitrovinyl)bicycle [2.2.2] oct-5-en-2-one (DNB) molecule was synthesized by Sharma et al[1]. It belongs to hypervalent iodine chemistry, and acts as good reagents in synthesis of organic molecules [2]. To generate the masked o-benzoquinones and benzoquinone monoamines, hypervalent molecules plays a vital role [3]. Diels-Alder reaction of o-benzoquinones and benzoquinone monoamines is identified as key step of producing biologically dynamic molecules [4] and many natural products [5-6]. However, the calculations of Non-linear optical properties, chemical reactivity and thermodynamic parameters are yet to appear in literature. We computed such quantum chemical calculations recently [7-15] and now extended the investigations to the selected molecule DNB, in this article.

1. **Computational Information**

Computational quantum chemical estimations carried out by using DFT, incorporated in 09 Gaussian window package [16,17] with 6-311++G(d,p) basis set. NLO properties of the DNB calculated by DFT method of finite field [18]. The Chemical reactivity of the selected molecule also determined using the methods [19-23]. By assuming a rigid-rotor harmonic approximation [24], we estimated the thermodynamic parameters for the chosen molecule.

1. **Results and Discussions**
   1. *Molecular geometry*

DNB molecule is optimized with above said method. The geometry parameters were excellent agreement with the experimental values [1]. By the calculation the DNB molecule has been belongs to C1 symmetry and its optimized molecular structure as shown in figure.

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Figure**.** Optimized structure of DNB

* 1. *NLO properties*

When Electromagnetic radiation interacts with NLO material, then change occurse in phase, amplitude, frequency, or gives the new propagation field characteristics [25]. If this change is significant then the NLO material used in signal processing, optical inter-connections telecommunications and optical memory [26-29]. Using DFT techniques, expansively investigate organic NLO materials [30-34].

The NLO behavior of selected compound is judged by comparing the related quantities of Urea. For Urea, hyper polarizability (βt)and dipole moment(µt) are 372.8 × 10-33 cm5/esu and 1.3732 Debye, respectively. For DNB, these values are βt = 8272.174 × 10-33 cm5/esu and µt = 2.415 Debye. The estimated values are very high compared with that of Urea; hence DNB is a sturdy contender for the enlargement of novel NLO materials. βt components are very helpful to identify the delocalization of charge in the DNB.

* 1. *Chemical reactivity*

The parameters of FMO were calculated for the molecule DNB. From the calculations we observed that the energy gap, linking the LUMO and HOMO orbital energies is 2.340 eV. It is comparatively small, worth to characterize a conjugated molecule. The chemical potential (µ) is negative for DNB, and is stable [35, 36].

* 1. *Thermodynamic parameters*

Thermodynamic parameters such as entropy, Cv, Cp were determined (183.955, 101.541 and 103.526) in cal mol-1 K-1. ZPV energy and TT energy (256.040 and 273.100 kcal mol-1), SCF energy -1357.486 Hartree were calculated for chosen molecule. Further, the rotational constants were A, B and C also calculated as (0.201, 0.138 and 0.088 GHz) for the selected molecule.

1. **Conclusion**

The following inferences are drawn from the calculations:

1. DNB molecule has the non-planar structure acquiring point group of C1 symmetry. Theoretically calculated geometric parameters of DNB are excellent agreement with the values of experimental.
2. DNB is a good candidate for NLO materials.
3. References
4. Sharma S, Ram Tilak N and Peddinti R. K, 2015 Expedient synthesis of nitrovinyl substituted bicyclo[2.2.2]octenone scaffolds RSC Adv. 5 100060-100069.
5. Wirth T, 2003 Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis, Topics in Current Chemistry, Springer, Berlin, Heidelberg, New York, NY, vol. 224
6. Stang P. J. and Zhdankin V. V 1996 Organic Polyvalent Iodine Compounds Chem. Rev., 96, 1123– 1178
7. Magdziak D, Meek S. J and Pettus T. R. R, 2004 Cyclohexadienone Ketals and Quinols:  Four Building Blocks Potentially Useful for Enantioselective Synthesis Chem. Rev., 104, 1383–1429
8. Hsu D.-S., Hsu P.-Y. and Liao C.-C, 2001 The First Total synthesis of **(±)-**Eremopetasiodine Org. Lett., 3, 263–265
9. Dong S, Hamel E, Bai R, Covell D. G, Beutler J. A. and Porco J. A. 2009 Enantioselective Synthesis of (+)‐Chamaecypanone C: A Novel Microtubule inhibitor Jr., Angew. Chem., Int. Ed., 48, 1494–1497.
10. Srishailam K, Venkata Ramana Rao P, Ravindranath L, Venkatram Reddy B, Ramana Rao G 2019 Experimental and theoretical determination of structural and vibrational properties of pentachlorophenol and pentachlorothiophenol J. Mol. Struct. 1178 142-154.
11. Venkata Ramana Rao P, Srishailam K, Ravindranath L, Venkatram Reddy B, Ramana Rao G 2019 Structural and vibrational properties of pentabromophenol and pentafluorophenol: A spectroscopic investigation using density functional theory. J. Mol. Struct. 1180 665-675.
12. Ramaiah K, Srishailam K, Laxma Reddy K, Venkatram Reddy B, Ramana Rao G 2019 Synthesis, crystal and molecular structure, and characterization of 2-((2-aminopyridin-3- yl)methylene)-N-ethylhydrazinecarbothioamide using spectroscopic (1H and 13C NMR, FT-IR, FT-Raman, UV-Vis) and DFT methods and evaluation of its anticancer activity J. Mol. Struct. 1184 405-417.
13. Srishailam K, Venkatram Reddy B, Ramana Rao G 2019 Investigation of torsional potentials, hindered rotation, molecular structure and vibrational properties of some biphenyl carboxaldehydes using spectroscopic techniques and density functional formalism J. Mol. Struct. 1196 139-1**61.**
14. Padmaja G, Devarajulu G, Deva Prasad Raju B, Turpu G R, Srishailam K , Venkatram Reddy B, Pavan Kumar G 2020 Synthesis of Sr1-xBaxBi2B2O7 glass ceramics: A study for structure and characterization using experimental techniques and DFT method J. Mol. Struct. 1220 128660.
15. Venkata Ramana Rao P, Srishailam K, Ramesh G, Venkatram Reddy B, Ramana Rao G 2020 NMR & Electronic Spectra, NLO, FMO, NBO and Thermodynamic Properties of Pentachlorophenol: An Experimental and Theoretical Investigation, Asian Journal of Chemistry; 32, 12 , 3057-3062
16. Venkata Ramana Rao P, Srishailam K, Rajesh A 2020 Electronic, NLO, and thermodynamic parameters and frontier molecular orbital investigation of pentafluoro phenol and pentachloro thiophenol with DFT approach. Mater.Sci.Eng.981.022087.
17. Srishailam K, Ramaiah K, Laxma Reddy K, Venkatram Reddy B and Ramana Rao G, 2021 Synthesis and evaluation of molecular Structure from torsional scans, study of molecular characteristics using spectroscopic and DFT methods of some thiosemicarbazones, and investigation of their anticanceractivity. Chem. Pap.Chemical Papers, 75(7), 3635-3647.
18. Venkata Ramana Rao P, Srishailam K, Venkatram Reddy B, Ramana Rao G 2021 Theoretical (DFT) and experimental (FT-IR & FT Raman) approach to investigate the molecular geometry and vibrational properties of 2,5- and 2,6-dihydroxytoluenes J. Mol. Struc. 1240, 130617
19. Gaussian 09, Revision B.01, M.J. Frisch M. J et al 2010 Gaussian, Inc., Wallingford CT
20. Becke A. D 1993 Density-functional thermochemistry. III. the role of exact exchange J. Chem. Phys. 98 5648-5652
21. Lee C, Yang W. T, Parr R. G 1988 Development of the colle-salvetti correlation-energy formula into a functional of the electron density Phys. Rev. B 37 785-790
22. Scalmani G, Frisch M. J 2010 Continuous surface charge polarizable continuum models of solvation. I. General formalism J. Chem. Phys. 132 1-15
23. Improta R, Barone V, Scalmani G, and Frisch M. J 2006 A state-specific polarizable continuum model time dependent density functional method for excited state calculations in solution J. Chem. Phys. 125 1-9
24. Improta R, Scalmani G, Frisch M. J, and Barone V 2007 Toward effective and reliable fluorescence energies in solution by a new State Specific Polarizable Continuum Model Time Dependent Density Functional Theory Approach, J. Chem. Phys. 127 1-9
25. Gece G 2008 The use of quantum chemical methods in corrosion inhibitor studies, Corros. Sci. 50 2981–2992
26. Parr R. G, Szentpa´ly L. V, Liu S 1999 Electrophilicity Index, J. Am. Chem. Soc.121 1922-1924
27. Ö zdemira N, Erenb B, Dinc¸era M and Bekdemir Y 2010 Experimental and ab initio computational studies on 4-(1H-benzo[d]imidazol-2-yl)-N,N-dimethylaniline, Mol. Phys. 108 13-24
28. Sun Y-X, Hao Q-L, Wei W-X, Yu Z-X, Lu L-D, Wang X, Wang Y-S, 2009 Experimental and density functional studies on 4-(3,4-dihydroxybenzylideneamino) antipyrine and 4-(2,3,4-trihydroxybenzylideneamino)antipyrine, J. Mol. Struct. Theochem 904 74-82.
29. Andraud C, Brotin T, Garcia C, Pelle F, Goldner P, Bigot B, Collet A, 1994 Theoretical and Experimental Investigations of the Nonlinear Optical Properties of Vanillin, Polyenovanillin, and Bisvanillin Derivatives, J. Am. Chem. Soc. 116 2094-2102.
30. Geskin V.M, Lambert C, Bre´das J-L, 2003 Origin of High Second- and Third-Order Nonlinear Optical Response in Ammonio/Borato Diphenylpolyene Zwitterions: the Remarkable Role of Polarized Aromatic Groups, J. Am. Chem. Soc. 125 15651-15658.
31. Nakano M, Fujita H, Takahata M, Yamaguchi K,2002Theoretical Study on Second Hyperpolarizabilities of Phenylacetylene Dendrimer: Toward an Understanding of Structure-Property Relation in NLO Responses of Fractal Antenna Dendrimers, J. Am. Chem. Soc. 124 9648-9655.
32. Sajan D, Joe H, Jayakumar V.S, Zaleski J, 2006 Structural and electronic contributions to hyperpolarizability in methyl *p*-hydroxy benzoate, J. Mol. Struct. 785 43-53.
33. Sun Y-X. Hao Q-L, Yu Z-X, Wei W-X, Lu L-D, Wang X, 2009 Experimental and density functional studies on 4-(4-cyanobenzylideneamino)antipyrine, Mol. Phys. 107 223-235.
34. Ahmed A.B, Feki H, Abid Y, Boughzala H, Minot C, Mlayah A, 2009 Crystal structure, vibrational spectra and theoretical studies of L-histidinium dihydrogen phosphate-phosphoric acid, J. Mol. Struct. 920 1-7.
35. Abraham J.P, Sajan D, Shettigar V, Dharmaprakash S.M, Neˇmec I, Joe I.H, Jayakumar V.S, 2009 Efficient p-electron conjugated push–pull nonlinear optical chromophore 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one: A vibrational spectral study, J. Mol. Sruct. 917 27-36.
36. Sagdinc S.G, Esme A, 2010 Theoretical and vibrational studies of 4,5-diphenyl-2-2 oxazole propionic acid (oxaprozin), Spectrochim. Acta A 75 1370-1376.
37. Ahmed A.B, Feki H, Abid Y, Boughzala H, Minot C, 2010 Crystal studies, vibrational spectra and non-linear optical properties of l-histidine chloride monohydrate, Spectrochim. Acta A 75 293-298.
38. Fukui K 1982 Role of frontier orbitals in chemical reactions, Science 218 747-754.
39. Koopmans T. A, 1933 Ordering of wave functions and eigen energies of the individual electrons of an atom, Physica 1 (1933) 104-113.