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SYNTHESIS, SPECTRAL, THERMAL, NLO AND DFT STUDIES ON *N*-NITROSO-2,6-BIS(4-METHOXYPHENYL)- 3, 3-DIMETHYLPIPERIDIN-4-ONE: EXPERIMENTAL AND THEORETICAL APPROACH

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ABSTRACT

An organic NLO material *viz.*, *N*-nitroso-2, 6-bis(4-methoxyphenyl)-3, 3-dimethyl-piperidin-4-one (NPM3DMPO), is synthesized and single crystals are grown by adapting the technique of slow evaporation using methanol. Solubility study is used to find out the appropriate solvent for crystal growth. The absorption range of the crystals is studied by UV-Vis spectroscopy. FT-IR spectrum is used to confirm the functional groups. Thermal studies (TG/DTA) are used to determine the stability of the material. To find out the suitability of this crystal for NLO applications, a second-order nonlinear optical property of NPM3DMPO has been ascertained by Kurtz and Perry technique. Quantum chemical studies are done by B3LYP/6-311 g(d,p) basis set using Gaussian'09. Done

Keywords: Crystal Growth, UV-Vis, FTIR, TG/DTA, NLO, SHG, DFT

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INTRODUCTION

Emerging NLO (nonlinear optical) materials exhibit a wide range of optical and optoelectronic properties, making them attractive for optoelectronics and photonic technologies.[1-5] In the recent past, researchers from various fields related to material chemistry are encouraged to discover a new group of NLO materials satisfying the needs of the above fields. Copious efforts have been already made to find out new and improved NLO materials with a good transparent window in the visible region and superior SHG conversion efficiency. In this perspective, a range of organic and inorganic NLO materials has been discovered.[6-9] In general, high and fast nonlinearities are established by organic chromophores compared to that of their inorganic ones. Very importantly, a non-centrosymmetric material[10-15] is known to demonstrate the frequency doubling of light (SHG).

In continuation of our effort on the finding of a new organic NLO material with piperidone skeleton,[16–18] in this paper, growth of a new organic NLO crystal *viz.*, of *N*-nitroso-2,6-bis(4-methoxyphenyl)-3, 3-dimethylpiperidin-4-one (Fig.-1)[19, 20] has been reported. Crystal's absorption range is tested by UV- VIS spectrum. Functional groups are established using the FT-IR spectrum. TG/DTA analyses are used to ascertain the thermal stability of the organic material. Second-harmonic generation (SHG) using Nd: YAG laser is employed to confirm the NLO optical property of the crystal. DFT studies are completed by B3LYP/6-311 g(d,p) basis set using Gaussian'09 software package.[21] NPM3DMPO crystal posses a non-centosymmetric space group $P2_12_12_1$ with orthorhombic crystal system.[20a]

EXPERIMENTAL

Synthesis of NPM3DMPO

3,3-Dimethyl-2,6-bis(4-methoxyphenyl)piperidin-4-one (1.69g 5 mmol) was dissolved in 10 ml of chloroform. To this solution, a mixture of 1.5 ml of the con. HCl (1.5) and 1.5 ml of water were added with stirring and immediately sodium nitrite (0.84g, 12 mmol) was added in small part for 30 min.

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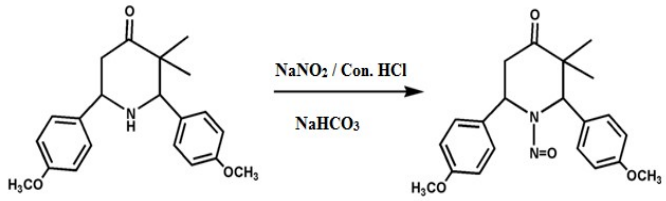
Stirring was continued for an extra 30 min at RT. The chloroform layer was separated, washed with water and saturated aq.$NaHCO_3$. The resulting solution was dried above anhydrous sodium sulfate and concentrated. The obtained NPM3DMPO solid was purified by recrystallization using ethanol to get a pure material[19] (Scheme-1).



Scheme-1: Schematic Representation for the Preparation of NPM3DMPO

Crystal Growth of NPM3DPO

A slow evaporation technique was employed to obtain large crystals. Methanol was used as a solvent to prepare a saturated solution of NPM3DMPO at 40°C based on solubility studies. The resulting solution was filtered (Whatman 41) and allowed to evaporate slowly at RT. Large crystals of NPM3DMPO were formed after 7-8 days and are exposed in Fig.-1.

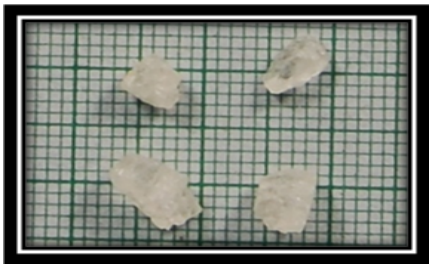


Fig.-1: *N*-Nitroso-2, 6-bis(4-methoxyphenyl)-3, 3-dimethylpiperidin-4-one (NPM3DMPO)

Solubility

Suggestions on the nucleation and ease of use of the material (solute) for the growth of a crystal can be obtained through solubility measurement in a given solvent besides measuring the cooling rate. The driving power for the crystallization is supersaturation which also affects the quality of the crystal. Solubility was measured at different temperatures using the recrystallized material of NPM3DMPO by dissolving it in an airtight container maintained at a stable temperature with constant stirring. . Benzene and methanol were used as solvents for this study. The equilibrium concentration of the material was determined gravimetrically after reaching saturation. Based on this study (Fig.-2), methanol is chosen as a solvent for the crystal growth of NPM3DMPO.

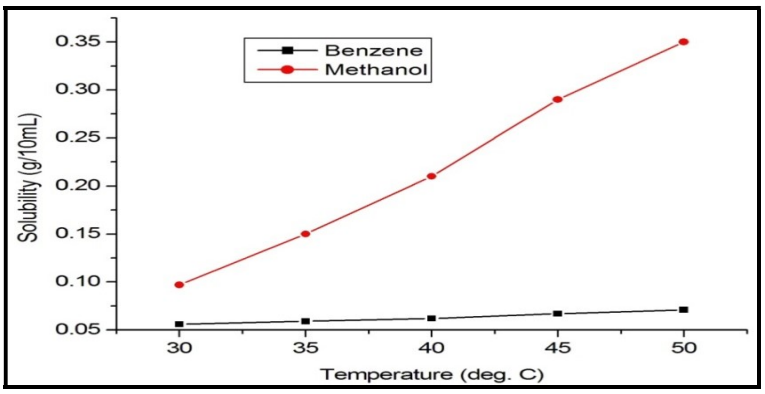


Fig.-2: Solubility Test for NPM3DMPO

RESULTS AND DISCUSSION

UV-VIS Spectrum

The electronic spectrum of NPM3DMPO was recorded in ethanol employing Systronics double beam UV-VIS spectrometer 2202 and in the range of 200 - 800 nm (Fig.-3). It shows strong absorption bands in the near UV-region owing to π-π* and n-π* transitions. The title material does not demonstrate any absorption band in the whole visible region up to 800 nm. This transparency strongly implies that the material may be suitable for NLO applications.

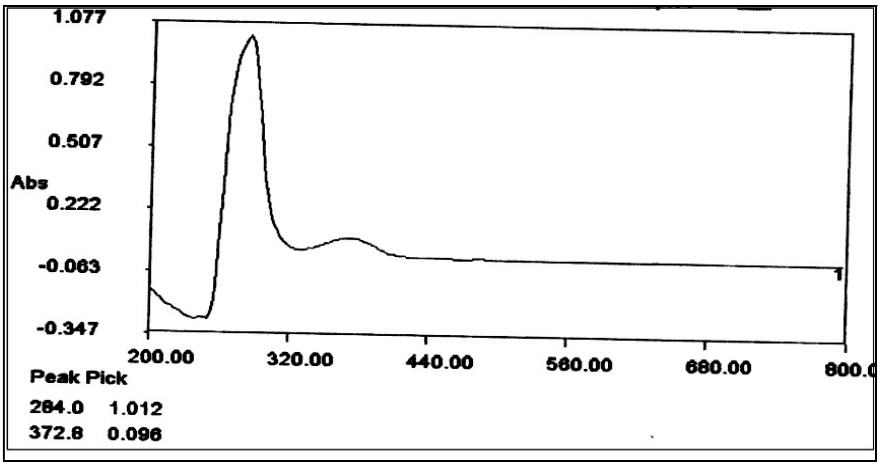


Fig.-3: UV-Vis Absorption Spectrum of NPM3DMPO

IR Spectrum

Bruker (alpha-model) FT-IR spectrometer was employed to record the IR spectrum of NPM3DMPO by KBr pellet method between 400 and 4000 cm^{-1} (Fig.-4). A Peak at 3061 cm^{-1} is due to aromatic C–H stretching and the peaks at 2971 and 2938 cm^{-1} are attributable to aliphatic C–H stretching vibrations. A sharp and strong band emerged at 1713 cm^{-1} is due to the carbonyl (>C=O) stretching. The strong absorptions at 1511 and 1394 cm^{-1} are ascribed to stretching vibrations of NO.

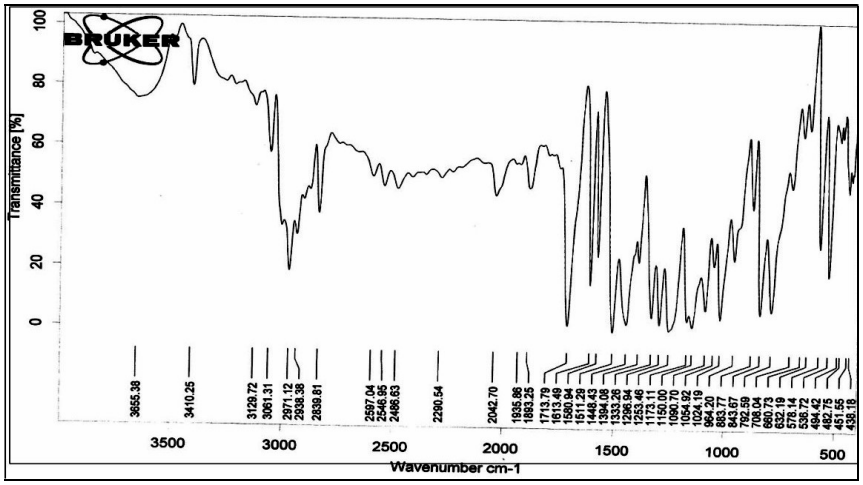


Fig.-4: FT-IR Spectrum of NPM3DMPO

Thermal Properties

Thermal analysis of the title material was performed between 25ºC and 500ºC with a heating rate of 10 ºC under nitrogen atmosphere (Model: NETZSCH STA 409) and the TG/DTA trace of NPM3DMPO is depicted in Fig.-5. Weight loss of 0.66% between 25 ºC and 170ºC may be accounted for occluded water during the reaction. Possible fragmentation that would occur is the initial methoxy group detachment followed by benzene moieties. The residual mass accounting for about 26% may be due to piperidone breakdown with subsequent release of N_2, O_2 and leftover carbons. An endothermic shoulder between 200

and 275 ºC opens up for a rearranged product and it extends the possibilities of stable compounds up to 400ºC. Hence, based on these investigations, it is inferred that NPM3DMPO can be used as NLO material up to 151.6 º C. Further, a good level of crystallinity with purity has been revealed from the sharpness of the peak (endothermic).

SHG Measurement

Kurtz and Perry technique[15] was employed to measure the SHG efficiency of the powdered crystals of NPM3DMPO and a Q-switched Nd: YAG laser was utilized as a source of light. A laser beam with fundamental wavelength 1064, the pulse width of 8 ns and 10 Hz pulse rate was allowed to fall usually on sample cell and the input energy incident on it is 8.1mj/pulse. Powdered KDP (Potassium dihydrogen orthophosphate) crystal was used as reference material. The emanation of bright green rays confirmed the SHG and a photomultiplier tube was monochromated for the collection of 532 nm radiation as an output. For the same input energy, NPM3DMPO showed an SHG signal of 5.1 mv and that of KDP was 11 mv.

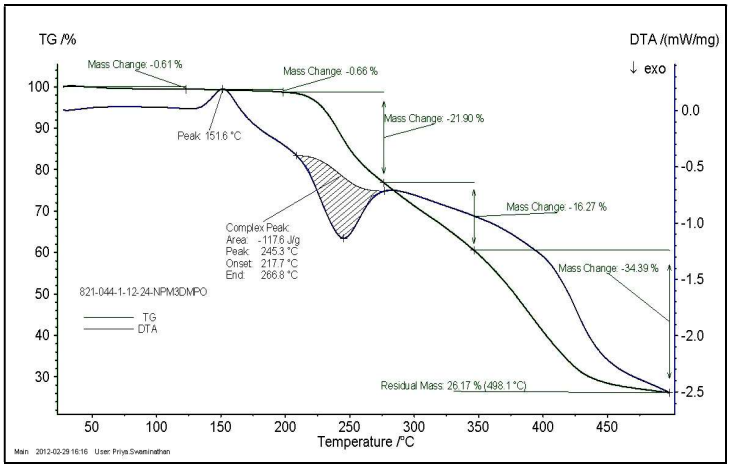


Fig.-5: TG/DT Analysis of NPM3DMPO

Optimized Structure of NPM3DMPO

The structure of NPM3DMPO was optimized at B3LYP/6-311g (d,p) level of theory. The C-C bond lengths of both phenyl rings match with the reported normal bond length values[22]. N_1-N_{11} bond length is decreased by 0.11 Å due to the attachment of nitroso group. The torsional angles obtained for C_9–N_1–C_2–C_4 and C_9–C_6–C_5–C_4 are 47.66º and 22.91º, respectively, which conform to the reported distorted boat conformation[19, 20] of NPM3DMPO (Fig.-6). Further, the observed dihedral angles of C_{30}-C_9-N_1-N_{11} and C_{12}-C_2-N_1-N_{11} are -73.87º and 113.64º, respectively, which indicates the deviation of phenyl rings from the average plane of piperidone ring. This distortion leads to the C_{31}-C_{32}…..π interaction between the two rings which is supported by the fact that H_3 possesses the highest positive charge among other aromatic hydrogens in Mulliken atomic charge analysis. Also, an intramolecular C_9-H_{10}…..O_{49} hydrogen bond interaction is observed for NPM3DMPO with donor…acceptor distance of 2.382 Å which arises due to the interaction between the polar nitroso oxygen with the neighboring hydrogen (C_9-H_{10}).

Analysis of FMO

The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are termed as Frontier molecular orbital's (FMO). HOMO and LUMO signify their capacity to donate and accept electrons, respectively. Further, this orbital also has a crucial role in deciding the optical properties of the material[22, 23]. The energy gap of HOMO-LUMO in NPM3DMPO has been computed at B3LYP/6-311g (d,p) levels and is 4.73 eV (Fig.-7). The calculated value exposes that the title material is a soft one with high reactivity. It is also noted that the HOMO of NPM3DMPO is localized on one of the methoxy substituted benzene rings while the LUMO is confined on the piperidine-4-one ring in addition to on another methoxy substituted phenyl ring.

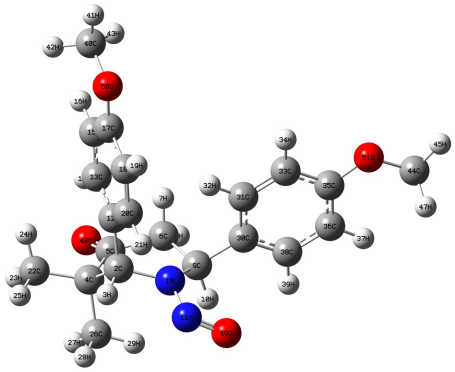


Fig.-6: Optimized Structure of NPM3DMPO

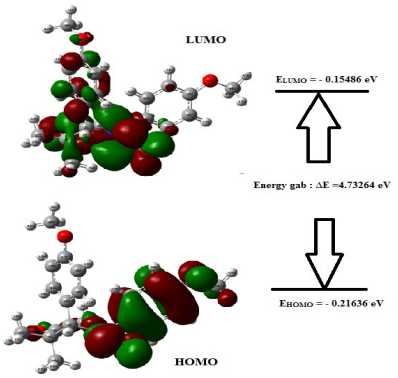


Fig.-7: HOMO-LUMO Plot for NPM3DMPO

Study of Mulliken Atomic Charges

Calculation of Mulliken atomic charges has an imperative role in the investigation of properties such as molecular dipole moment and electronic structure. The charge distribution over various atoms of NPM3DMPO obtained from Mulliken population analysis is shown in Fig.-8. The results prove that the presence of methyl group at C_3 of the piperidone ring leads to the redistribution of electron density. All H atoms in NPM3DMPO display a positive charge in which H_3 of piperidone moiety has the highest. The piperidone hydrogens show higher values than any other hydrogen in NPM3DMPO. The carbons C_{17} and C_{35} (attached with methoxy groups) and the piperidine ring carbon C_5 exhibit a high positive charge due to the neighboring electronegative oxygen. The remaining carbons show negative charge[22,23]. Further, N_{11} nitrogen of nitroso group possesses a positive charge (+ 0.143 e) while another nitrogen attached to the nitroso group exhibits a negative charge (-0.285e). Oxygen atoms display a negative charge which reveals the availability of these atoms for the electrophilic attack.

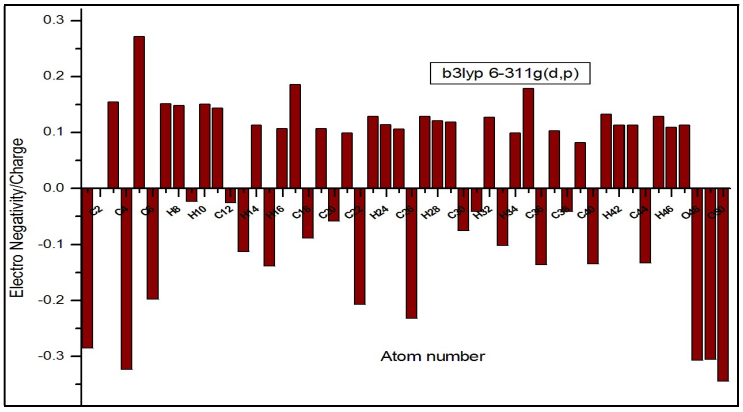


Fig.-8: Mullikan Populations of NPM3DMPO

Hyperpolarizability of NPM3DMPO

Superior values of hyperpolarizability besides dipole moment and molecular polarizability are required for a molecule to act as a better NLO material. The value of hyperpolarizability is computed using B3LYP /6-311g(d, p) method based on the finite field approach. Dipole moment (μ) and polarizability of NPM3DMPO are calculated to be 5.0434 D and 1.6618 x10^{-24}esu, respectively. Component μ_x shows the highest value of dipole moment. A key aspect for an NLO system is the magnitude of molecular hyperpolarizability β, which is found to be 1.666 x10^{-30}esu (Table-1). Thus, NPM3DMPO may be useful as a material for NLO applications.[23]

CONCLUSION

The slow evaporation method is used to grow the good optical quality crystals of NPM3DMPO material using methanol. UV-Visible & FT-IR spectra and thermal studies are recorded. Furthermore, NLO studies

reveal that the title material shows a significant SHG efficiency. Computational (DFT) calculations were performed on NPM3DMPO at B3LYP/6-311g(d, p) level of the basic set. A smaller HOMO-LUMO energy difference of 4.73 eV reveals the reactive nature of the material. The computed first-order hyperpolarizability value (1.6618 X 10^{-24} esu) indicates that NPM3EPO is a good candidate for NLO applications. Among the H and carbon atoms of piperidine-4-one, the highest positive charge is exhibited by H_3 and C_5, respectively. Further, the oxygen atom O_{51} possesses the maximum negative charge.

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REFERENCES

1. D.S. Chemla, J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, (1987), **DOI:**10.1063/1.353217
2. P.N. Prasad, D.J. Williams, Non-linear Optical Effects in Molecules and Polymers, Wiley, USA,(1991), **DOI:**10.1007/978-1-4899-0112-5_29
3. P.V. Dhanaraj, N.P. Rajesh, G. Bhagavannarayana, *Physica B*, **405**, 3441(2010), **DOI:**10.1016/j.physb.2010.05.020
4. G. Anandha Babu, G. Bhagavannarayana, P. Ramasamy, *Journal of Crystal Growth*, **310**, 1228(2008), **DOI:**10.1016/j.jcrysgro.2007.12.024
5. R. Ezhil Vizhi, S. Kalainathan, *Materials Letters*, **62**, 791(2008), **DOI:**10.1016/j.matlet.2007.06.083
6. A. Chandramohan, R. Bharathikannan, V. Kandavelu, J. Chandrasekaran, M.A. Kandhaswamy, *Spectrochimica Acta, Part A*, **71**, 755(2008), **DOI:**10.1016/j.saa.2008.01.036
7. K. Nakamoto, IR Spectra of Inorganic and Coordination Compounds, Second Ed., Wiley, New York(1978)
8. S. Senthil, S. Pari, P. Sagayaraj, J. Madhavan, *Physica B*, **404**, 1655(2009), **DOI:**10.1016/j.physb.2009.01.042
9. K. Kirubavathi, K. Selvaraju, R. Valluvan N. Vijaya, S. Kumararaman, *Materials Letter*, **62**, 7 (2008), **DOI:**10.1016/j.matlet.2007.01.082
10. R.N. Rai, P. Ramasamy, C.W. Lan, *Journal of Crystal Growth*, **235**, 499,(2002), **DOI:**10.1016/S0022-0248(01)01796-1
11. V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikoyosyan, Third Ed., Springer, Berlin, 1999.
12. S.A.Martin Britto Dhas, S. Natarajan, *Optical Communication*, **278**, 434(2007), **DOI:**10.1016/j.optcom.2007.06.052
13. G.Anandha Babu, P. Ramasamy, *Current Applied Physics*, **10**, 214(2010), **DOI:** 10.1016/j.cap.2009.05.026
14. R. Uthrakumar, C. Vesta, M. Jose, K. Sugandhi, S. Krishnan, S. Jerome Das, *Physica B: Condensed Matters*, **405**, 3371(2010), **DOI:**10.1016/j.physb.2010.06.030
15. S.K. Kurtz, T.T. Perry, *Journal of Applied Physics*, **39**, 3798(1968), **DOI:**10.1063/1.1656857
16. P.Sakthivel, S. Ponnuswamy, *Journal of Molecular Structure,* **1074**, 349(2014), **DOI:**10.1016/j.molstruc.2014.05.053
17. S. Ponnuswamy, V. Mohanraj, P. Sakthivel, A. Chandramohan, *Optik*, **125**, 5550(2014), **DOI:**10.1016/j.ijleo.2014.07.064
18. S. Ponnuswamy, V. Mohanraj, s.s. Ilango, M. Thenmozhi, M.N. Ponnuswamy, *Journal of Molecular Structure*, **1081**, 449(2005), **DOI:**10.1016/j.molstruc.2014.10.063
19. P. Sakthivel, Ph.D. Thesis, Bharathiar University (2014).
20. (a) T. Kavitha, S. Ponnuswamy, P. Sakthivel, K. Karthik and M.N. Ponnuswamy, *Acta Crystallographica Section E Structure Reports Online*, **E65**, o1420, (2009), **DOI:**10.1107/S1600536809019357; (b)V. Mohanraj, P. Sakthivel, S. Ponnuswamy, International Conference on Advances in New Materials (ICAN 2014) , University of Madras, Chennai, India.
21. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato,

X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C.Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 Revised E01, Gaussian, Inc., Wallingford CT, 2013.

22. T. Joselin Beaula, P. Muthuraja, M. Sethuram, M. Dhandapani, V. Bena Jothy , V.K. Rastogi, *Journal of Molecular Structure*, **1128**, 290(2017), **DOI:**10.1016/j.molstruc.2016.08.060
23. K. Sathya., P. Dhamodharan, M. Dhandapani, *Journal of Molecular Structure*, **1130**, 414(2017), **DOI:**10.1016/j.molstruc.2016.10.018

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