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DFT Studies on 2-amino-7-bromo-5-oxo-[1]benzopyrano [2,3-b]pyridine-3 carbonitrile

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Abstract: The molecular structure of 2-amino-7-bromo-5-oxo-[1]benzopyrano [2,3-b]pyridine-3-carbonitrile (ABOBPC) was optimized by the DFT/B3LYP method with 6-311G (d,p), 6-311++G (d,p) and cc-pVTZ basis sets using the Gaussian 09 program package. The most stable, optimized structure of the molecule was predicted by the DFT/B3LYP method with cc-pVTZ basis set. The Mulliken atomic charge distribution, nonlinear optical (NLO), Frontier molecular orbitals (FMOs) and natural bond orbital (NBO) analysis were carried out for the optimized structure of ABOBPC molecule. The NLO analysis shows that the nonlinear optical activity of ABOBPC molecule was 16 times higher than the urea. The NLO activity of the molecule was confirmed by the FMOs and NBO analysis. The vibrational modes were assigned on the basis of Potential Energy Distribution and their corresponding infrared and Raman spectra were also simulated.

Keywords: DFT studies; 2-amino-7-bromo-5-oxo-[1]benzopyrano[2,3-b]pyridine-3-carbonitrile.

Introduction

The novel and more efficient nonlinear optical (NLO) materials are having vast applications in photonic and optoelectronic technologies. Recently, many research articles appeared in the designing and synthesis of NLO materials, which improved optical transparency and good thermal stability [1]. The organic NLO materials are generally more efficient than inorganic materials, which is due to high optical nonlinearities, fast response time and structural variations [2]. The organic molecules such as aminopyridine nitro derivatives act as a building blocks of NLO materials. The density functional theory (DFT) approach has been used to understand and design the NLO properties of a molecule before synthesis as an inexpensive way, which has become a very active area of research [3]. In the present investigation, DFT studies were carried out for 2-amino-7-bromo-5-oxo-[1]benzopyrano [2,3-b]pyridine-3-carbonitrile (ABOBPC) molecule.

Computational Details:

The molecular structure of ABOBPC molecule was optimized by the DFT/B3LYP method with 6-311G (d,p), 6-311++G (d,p) and cc-pVTZ basis sets [4]. The most stable, optimized structure of the molecule was predicted by the DFT/B3LYP method with cc-pVTZ basis set, which is shown in figure 1. The NLO activity,

FMOs analysis, NBO analysis, Mulliken atomic charge distribution and vibrational frequency calculations were carried out.

Results and Discussions:

NLO activity:

The first order hyperpolarizability of ABOBPC molecule was obtained as 6.908×10^{-30} esu, which was 16 times greater than that of urea. The obtained value of the first order hyperpolarizability of ABOBPC molecule confirms the higher NLO activity.

Frontier Molecular Orbitals (FMOs) analysis:

The FMOs analysis of ABOBPC molecule shows the delocalization of charges occur within the molecule, which increases the molecular reactivity of the molecule. The HOMO-LUMO energy gap was calculated as 4.29 eV. The lower energy gap indicates that the strong hydrogen bonding between the charged species reduces the energy gap considerably with the formation of the charge transfer axis, which leads to the higher value of β_{tot} [5].

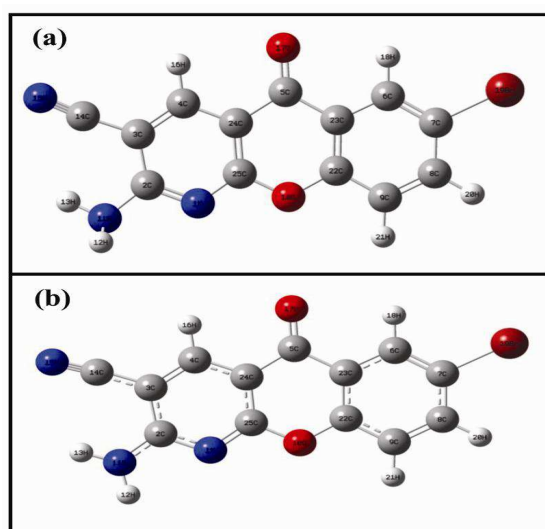


Figure 1. The optimized structure of ABOBPC molecule. (a) Before optimization, (b) After optimization.

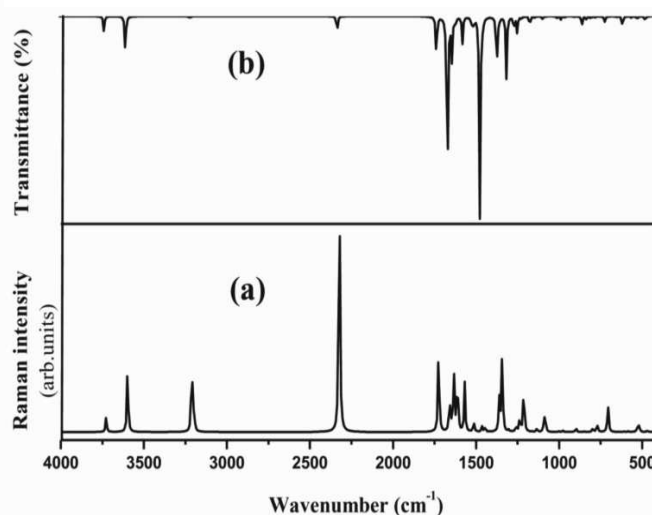


Figure 2. The vibrational spectra of ABOBPC molecule. (a) Raman spectrum, (b) IR spectrum.

NBO analysis:

The NBO calculations were performed using NBO 3.1 program as implemented in the Gaussian 09 program package. The NBO analysis is used to understand the interaction among the bonds, intra and intermolecular interaction of the ABOBPC molecule. The stabilization energy $E_{(2)}$ values of the ABOBPC molecule were calculated on the basis of second-order Fock matrix perturbation theory. The larger $E_{(2)}$ value of a lone pair of C24 to π^* of N1-C25 ($E_{(2)} = 124.85$ kcal/mol) and lone pair N11 to antibonding lone pair of C2 ($E_{(2)} = 120.74$ kcal/mol) indicates the presence of ICT of the ABOBPC molecule. The intermolecular interaction leads to the conjugated bond within the ABOBPC molecule, which plays an important role in the stabilization of the molecule. In the benzene ring, the ICT occurs by transfer of π electron cloud from donor to acceptor ($\pi \rightarrow \pi^*$), which leads to the polarization of the molecule. This polarization phenomenon is responsible for the NLO activity of the molecule [3].

Mulliken atomic charge distribution:

In ABOBPC molecule, all Hydrogen atoms have a positive charge and all electro negative atoms N, Br and O have negative charges, but carbon atoms have both positive and negative charges, which shows that the delocalization of charges mainly arises via the carbon atoms.

Vibrational Studies:

Figure 2 shows the simulated IR and Raman spectra of ABOBPC molecule. The vibrational assignments were made with a high degree of accuracy on the basis of Potential Energy Distribution (PED) calculation with the aid of VEDA 4.0 program [6] and visualized by GaussView 05 program. The strongest vibrational modes were appeared at 1725, 1633, 1568, 1501, 1463, 1366, 1359, 1304 and 1240 cm^{-1} in the IR spectrum and the corresponding modes were appeared in the Raman spectrum at 1725, 1659, 1633, 1612, 1568, 1359, 1343 and 1213 cm^{-1} . These modes are assigned as in-phase symmetric stretching vibrations of single CC bonds, C=O bonds and shrinking of CC double bonds, $\nu(\text{C}=\text{C}/\text{C}-\text{C})$. These vibrations spread over the whole π -conjugated path with relevant amplitudes from almost all the constituent parts of the molecule, which involves the ICT from the donor to the acceptor and gives rise to a large variation of the dipole moment, thus gaining a strong IR activity. These strong IR peaks are due to the electron-phonon coupling. The π -electron cloud movement from donor to acceptor can make the molecule highly polarized, which causes the more intense Raman lines [3].

Conclusion

The stable optimized structure of ABOBPC was predicted by the DFT/B3LYP method with cc-pVTZ basis set. The NLO analysis reveals that the NLO activity of the ABOBPC molecule was 16 times higher than the urea. The FMOs of the ABOBPC shows that the NLO activity arises due to the ICT of the molecule. The NBO analysis also confirms the ICT occurs within the molecule. The Mulliken atomic charge distribution indicates that the ICT occurs within the molecule via the carbon atoms. The lower energy gap of the molecule indicates the strong hydrogen bonding between the charged species. The vibrational analysis was used to predict the electron-phonon coupling and π electron cloud movement of the ABOBPC molecule.

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References

1. Manimaran D., Jesintha John C., Rastogi V.K., Hubert Joe I., Growth and vibrational spectral investigation of nonlinear optical crystal L-Argininum Perchlorate-DFT study, *Spectrochim. Acta.*, 2013, 109A, 173–178.
2. Ikeda H., Sakai T., Kawasaki K., Nonlinear optical properties of cyanine dyes, *Chem. Phys. Lett.* 1991, 179, 551-554.
3. Sajan D., Vijayan N., Safakath K., Reji Philip, Hubert Joe I., Intramolecular Charge Transfer and Z-Scan Studies of a Semiorganic Nonlinear Optical Material Sodium Acid Phthalate Hemihydrate: A Vibrational Spectroscopic Study, *J. Phys. Chem. A* 2011, 115, 8216–8226.
4. Gaussian 09, Revision A.1, M. J. Frisch et al, Gaussian, Inc., Wallingford CT, 2009.
5. Moreno Castro C., Ruiz Delgado M. C., Hernández V., Hotta S., Casado J., Lopez Navarrete J. T., Efficiency of the π conjugation in a novel family of α,α' -bisphenyl end-capped oligothiophenes by means of Raman spectroscopy, *J. Chem. Phys.* 2002, 116, 10419-10427.
6. M.H. Jamroz, Vibrational Energy Distribution Analysis VEDA 4.0 Program, Warsaw, 2004.
