ISSN : 0974 - 7443 Volume 11 Issue 3
CHEMICAL TECHNOLOGY
An Indian Journal
Full Paper
CTAIJ 11(3) 2016 [118-121]

First-principles study of electronic and dielectric properties of azoxybenzene

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ABSTRACT

First-principles calculations based on Density Functional Theory employing Plane Wave Self Consistent Field formalism have been done on the technologically important liquid crystalline material Azoxybenzene. The orthorhombic structure with lattice parameters a=10.35Å, b=4.85Å and c=5.5Å has been simulated and the structural parameters have been found out. Electron Density of States (EDOS) have been computed which gives a band gap of 2.52eV that is close to the value shown by NLO materials. Dielectric constant of the material has been computed and it comes out to be 2.61, 2.62 and 2.92 along X, Y and Z axes respectively. The computed phonon modes at the gamma point range from 18cm^{-1} to 1573cm^{-1} showing that the simulated structure is stable.

KEYWORDS

First-principles calculation;
Azoxybenzene;
Electron density of states;
Dielectric constant;
Phonon modes.

INTRODUCTION

Liquid crystals can flow like a liquid, but the molecules in liquid crystal are arranged and/or oriented in a crystal-like manner. There are two specific classes of liquid crystals: one class in which transitions are driven by thermal processes are known as thermotropic liquid crystals and other class that is strongly influenced by solvents are known as lyotropics. Many thermotropic liquid crystals exhibit variety of phases as the temperature is changed[1-3]. For instance, a particular type of liquid crystal molecule may exhibit various smectic and nematic phases as the temperature is changed. Thermotropic liquid crystalline materials have characteristics related to their molecular structure, which consists of two parts, namely the core and side chain. The core part is a rigid body which brings shape anisotropy to the molecule and the side chain part is a flexible region which gives mobility. The liquid crystalline materials are being constantly developed and improved and used industrially in various ways such as in displays, films, drugs and medicines[4-8].

Azobenzene is a chemical compound composed of two phenyl rings linked by a N=N double bond. It has widely attracted the scientific community because of its photo-sensitive nature. It has been found that Azobenzene can be photoswitched selectively from an extended trans to a more compact cis conformation and vice-versa by using light of wavelength 365 nm and 420 nm respectively[9,10]. Azobenzene containing polymers have also attracted the scientific community owing to their potential applications in the field of Photonics as they are used in optical switching devices and diffractive optical elements[11-13]. Azobenzene based Liquid-Crystalline polymers have gained considerable interest[14-16].

Irradiation with polarized light can make an azo-

material anisotropic and therefore optically birefringent and dichroic. This photo-orientation can also be used to orient other materials especially in liquid crystal systems[17]. For example, it has been used to orient liquid crystal domains selectively, and to create nonlinear optical materials[18]. This property of Azo isomerization can also be used to photo-switch the liquid crystal phase of a material from cholesteric to nematic[19,20] or to change the pitch of a cholesteric phase[21].

Any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material[22,23]. Thus it is important to study the structure of the materials and look at the parameters which can be altered to get a better material for technological applications. First-principles calculations based on Density Functional Theory[24] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials[25,26]. With this in view, structure of Azoxybenzene has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant and phonon modes have been done and the results have been reported in the present paper.

COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation[27]. We use plane wave self consistent field (PWSCF)[28] implementation of density functional theory (DFT), with a Local density approximation (LDA) [20] to exchange correlation energy of electrons and ultrasoft pseudopotentials[30], to represent interaction between ionic cores and valence electrons. Kohn-Sham wave functions were represented with a plane wave basis with an energy cutoff of 40 Ry and charge density cutoff of 240 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme[31] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[32] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

RESULTS AND DISCUSSION

In the present study, the orthorhombic unit cell of Azoxybenzene was first built using "Avogadro"[33]. The structure was allowed for geometric optimization. Later, atomic positions of the geometrically optimized structure have been used in the plane wave self consistent field calculations.

The structure was relaxed with different values of lattice parameters. Optimized values of lattice parameters thus arrived at through minimization of energy are; a=10.35Å, b=4.85Å and c=5.5Å. "scf"" calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso. Completely relaxed structure of the unit cell was visualized using the program "XcrysDen"[34] and the structure as viewed along Y and Z axes are given in Figures 1 and 2 respectively.

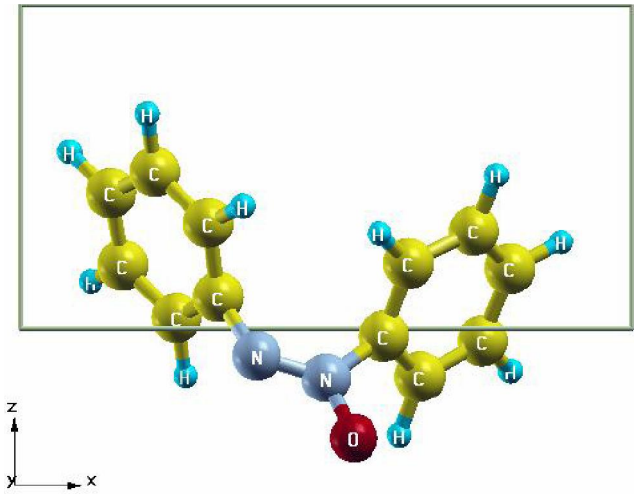

Figure 1: Structure of unit cell of azoxybenzene as viewed along Y-axis

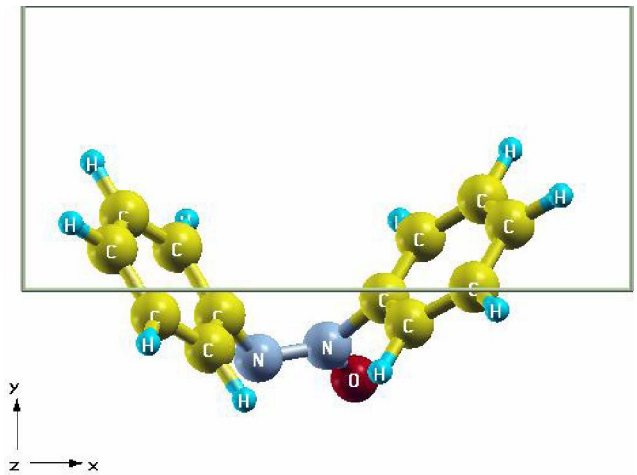

Figure 2 : Structure of unit cell of azoxybenzene as viewed along Z-axis

The bond lengths and bond angles in the relaxed

structure of Azoxybenzene have been tabulated in TABLES 1 and 2 respectively.

TABLE 1 : Bond lengths in Azoxybenzene

Bond	Bond length (Å)
C – C	1.38
C – H	1.09
N – N	1.25
N – O	1.26
C – N	1.39, 1.44

TABLE 2 : Bond angles in Azoxybenzene

	Bond angles (deg)
C – C – H	119, 121
N – N – C	124, 126
C – C – C	119, 121
N – N – O	121
C – N – O	113

EDOS calculation

Electron Density of States (EDOS) have been computed using Electronic structure calculation code of Quantum espresso and is shown in Figure 3. The band gap comes out to be 2.52eV. This value is close to the value shown by NLO materials[26].

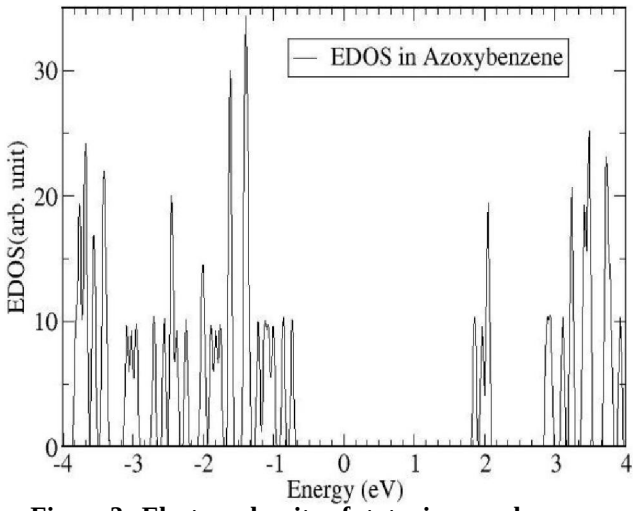

Figure 3 : Electron density of states in azoxybenzene

Dielectric constant and phonon modes

Dielectric constant of the material has been computed and it comes out to be 2.61, 2.62 and 2.92 along X, Y and Z axes respectively and the average value comes out to be 2.72. The computed phonon modes at the gamma point range from 18cm-1 to 1573cm-1 showing that the simulated structure is stable.

CONCLUSIONS

First-principles calculations based on DFT has simulated a stable structure of Azoxybenzene. EDOS calculations show that the polymer has a large band gap of 2.52eV which is close to the values exhibited by NLO materials. The material has an average Dielectric constant of 2.72. Phonon modes at the gamma point range from 18cm-1 to 1573cm-1 showing that the simulated structure is stable. Present study reveals that the First-principles calculations based on DFT can be effectively employed to study the electronic and dielectric properties of the Azoxybenzene. Also, the present study indicates that Azoxybenzene can be used for NLO applications and for the preparation of NLO materials and several liquid crystalline materials.

ACKNOWLEDGMENTS

Author thanks the Department of Collegiate Education, Government of Karnataka for permitting to carry out the research work. Also, author acknowledges the necessary facilities provided by the Government College (Autonomous), Mandya (Affiliated to University of Mysore), India.

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