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First-principles study of fluorination of azobenzene

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ABSTRACT

First-principles calculations based on density functional theory have been done on the technologically important liquid crystalline material azobenzene. The orthorhombic structure of azobenzene has been simulated and the structural parameters have been found out. Structures of Ortho-fluorinated and Para-fluorinated azobenzene have also been simulated. Electron density of states (EDOS) have been computed in all the three cases which exhibits a narrow band gap and are looking similar to that of a semiconductor in all the three cases. Dielectric constant of the material has been computed and it has been observed that the value of dielectric constant decreases due to fluorination. Phonon modes computed in all the three cases show that the structure is very much stable in all the three cases.

KEYWORDS

Azobenzene; band-gap; electron density of states; first-principles calculation; 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 [4–6].

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 and 420 nm, respectively [7, 8]. Azobenzene containing polymers have also attracted the scientific community owing to their potential applications in the field of photonics as they are used in

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optical switching devices and diffractive optical elements [9–11]. Azobenzene based liquid-crystalline polymers have gained considerable interest [12–14].

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 [15]. For example, it has been used to orient liquid crystal domains selectively, and to create nonlinear optical materials [16]. This property of azo isomerization can also be used to photo-switch the liquid crystal phase of a material from cholesteric to nematic [17, 18] or to change the pitch of a cholesteric phase [19].

Any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material [20, 21]. 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 calculation based on density functional theory(DFT) [22] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [23, 24]. With this in view, structures of un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene have been simulated using First-principles calculations based on DFT and computation of electronic density of states and Dielectric constant have been done and the results have been reported in the present paper. An effort has been done to look at the effect of fluorination in azobenzene.

Computational details

Several codes are available for the theoretical structure simulation [25]. We use plane wave self consistent field (PWSCF) [26] implementation of DFT, with a local density approximation (LDA) [27] to exchange correlation energy of electrons and ultrasoft pseudopotentials [28], 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 [29] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [30] 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 azobenzene was first built using "Avogadro"[31]. 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; $a = 10.5$ Å, $b = 5.14$ Å, and $c = 6.48$ Å. "scf"" calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso. The H atom at the ortho position (attached to 6th C atom) has been replaced by F atom in both benzene rings. The structure was again relaxed and optimized. The lattice parameters are not altered by ortho-flourination. Later, substitution of the F atom was done at the para position and again the structure was relaxed and optimized. Optimized values of lattice parameters thus arrived at through minimization of energy in case of para-fluorinated azobenzene are; $a = 10.75$ Å, $b = 5.14$ Å and $c = 6.48$ Å.

Completely relaxed structure of the unit cell was visualized using the program "XcrysDen" [32] and the structure of un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene

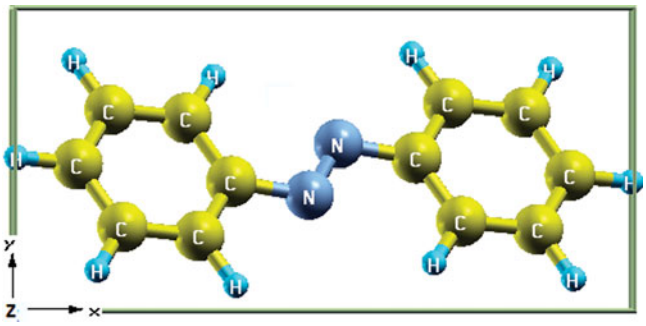

Figure 1. Structure of unit cell of un-fluorinated azobenzene as viewed along Z-axis.

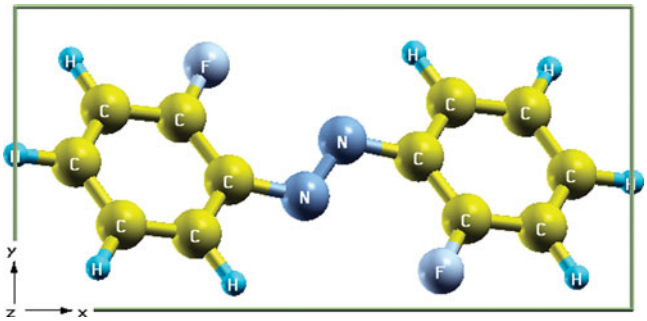

Figure 2. Structure of unit cell of ortho-fluorinated azobenzene as viewed along Z-axis.

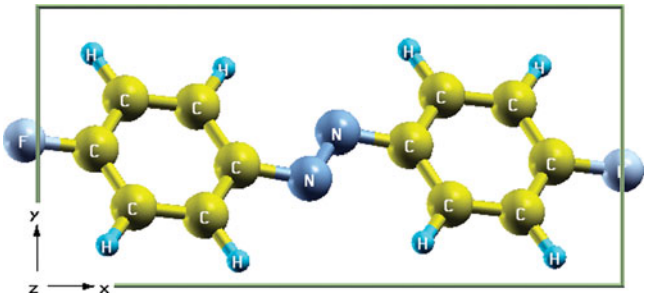

Figure 3. Structure of unit cell of para-fluorinated azobenzene as viewed along Z-axis.

as viewed along Z axis are given in Figs. 1, 2, and 3, respectively. The bond lengths and bond angles in the relaxed structure of un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene have been tabulated in Tables 1 and 2, respectively. From the tables it is clear that C – H, N = N and C = N bond lengths are not altered due to fluorination whereas the C – C bond length gets altered due to fluorination. Almost all the bond angles get slightly altered due to fluorination.

Table 1. Bond lengths in azobenzene.

Bond	Bond length in un-fluorinated azobenzene (Å)	Bond length in ortho-fluorinated azobenzene (Å)	Bond length in para-fluorinated azobenzene (Å)
C – C	1.38	1.38, 1.40	1.37, 1.38, 1.39
C – H	1.09	1.09	1.09
N = N	1.25	1.25	1.25
C – N	1.39	1.39	1.39

Table 2. Bond angles in azobenzene.

	Bond angles in un-fluorinated azobenzene (deg)	Bond angles in ortho-fluorinated azobenzene (deg)	Bond angles in para-fluorinated azobenzene (deg)
C – C – H	118, 120	118, 120, 122	118, 120, 122
N – N – C	115	116	116
C – C – C	120	117, 120, 122	118, 119, 120, 123
N – C – C	116, 124	115, 127	116, 124

EDOS calculation

Electron density of states (EDOS) have been computed in case of un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene using electronic structure calculation code of Quantum espresso. EDOS in un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene have been shown in Figs. 4, 5, and 6, respectively – from which it is clear that the material is showing a narrow band gap of 0.67 eV, 0.64 eV, and 0.77 eV in case of un-fluorinated, ortho-fluorinated, and para-fluorinated samples respectively and are looking similar to that

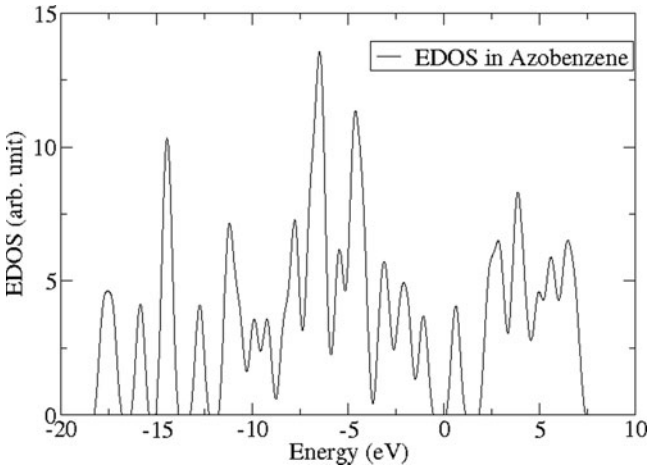

Figure 4. Electron density of states in un-fluorinated azobenzene.

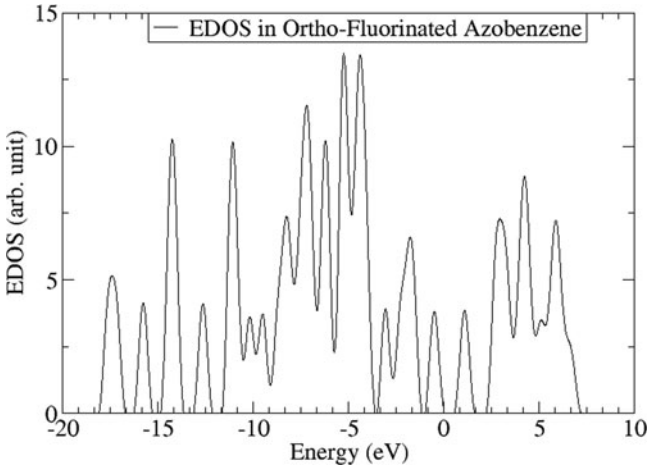

Figure 5. Electron density of states in ortho-fluorinated azobenzene.

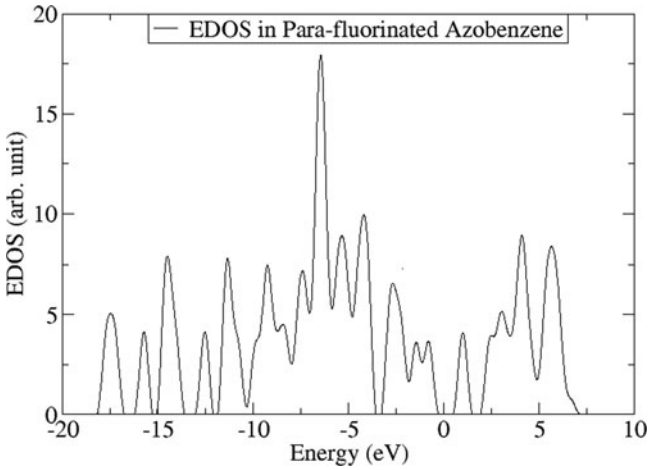

Figure 6. Electron density of states in para-fluorinated azobenzene.

of a semiconductor. But the band gap shown by its derivative azoxybenzene is 2.52 [33] which is equal to that exhibited by NLO materials [34]. It can be seen that the fluorination is causing modification in the EDOS. EDOS in case of ortho-fluorinated material is different from that in the para-fluorinated azobenzene.

Dielectric constant and phonon modes

Dielectric constant of the material has been computed in case of un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene. The value of dielectric constant in un-fluorinated case comes out to be 3.56, 2.29, and 1.97 along X, Y, and Z axes, respectively, and the average value comes out to be 2.6. In case of ortho-fluorinated azobenzene they are found to be 3.38, 2.22, and 1.97 along X, Y, and Z axes, respectively, and the average value comes out to be 2.52, whereas in case of para-fluorinated azobenzene they are found to be 3.35, 2.21, and 1.91 along X, Y, and Z axes, respectively, and the average value comes out to be 2.49. Thus fluorination of azobenzene is found to decrease the dielectric constant of the material. Phonon modes range from 18 to 3093 cm^{-1} in case of un-fluorinated sample. They range from 19 to 3095 cm^{-1} in case of ortho-fluorinated sample and from 34 to 3239 cm^{-1} in case of para-fluorinated sample. These modes show that the structure is very much stable in all the three cases.

Conclusions

EDOS calculations in un-fluorinated, ortho-fluorinated, and para-fluorinated azobenzene show that the all the three show a very narrow band gap and look similar to that of a semiconductor. The material has an average Dielectric constant of 2.6 in case of the un-fluorinated case, whereas the average value of dielectric constant in ortho-fluorinated and para-fluorinated cases are found to be 2.52 and 2.49, respectively, indicating that the value of dielectric constant decreases due to fluorination. Present study reveals that the first-principles calculations based on DFT can be effectively employed to study the electronic and dielectric properties of azobenzene and fluorinated azobenzene.

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