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Structure simulation and study of electronic and dielectric properties of 1, 3-dimethyl urea

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ABSTRACT

First-principles calculations based on Density Functional Theory have been done on the 1, 3-Dimethyl Urea - *[C2H8N20]*. The Orthorhombic structure of Urea has been simulated and the structural parameters have been found out. Electron Density of States (EDOS) has been computed in the materials using the Electronic structure calculation code of Quantum-Espresso which gives a Band gap of 3.3 eV. This value is close to the value exhibited by NLO materials. Dielectric constant of the materials has been computed. The value of dielectric constant comes out to be 2.11, 2.06 and 2.05 along X, Y and Z axes respectively and the average value comes out to be 2.07. Phonon modes have also been computed.

KEYWORDS

1, 3-dimethyl urea;
First-principles calculation;
Electron density of states;
Band gap;
Dielectric constant;
NLO material;
Liquid crystalline material.

INTRODUCTION

Dimethylurea (DMU) is a urea derivative and it is used as an intermediate in organic synthesis. It is usually obtained as a colorless crystalline powder[1,2]. 1,3 - Dimethylurea is used for synthesis of caffeine, theophylline, pharmachemicals, textile aids, herbicides and others. In the textile processing industry 1, 3-Dimethylurea is used as intermediate for the production of formaldehyde free easy care finishing agents for textiles.

Pratik M. Wankhade and Gajanan G. Muley[3] have used 1,3-dimethyl urea as a dopant and studied the effect of its doping in growing l-arginine phosphate monohydrate (LAP) crystals and have found that the doping with 1, 3-dimethyl urea increases optical transparency. They have also found increase in the second harmonic generation (SHG) efficiency of the doped crystal.

Thus, Urea and its derivatives have wide number of applications in several fields[4-6]. Any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material[7, 8]. 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[9] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials[10, 11]. With this in view, an attempt has been made to look into the structural aspects, Electronic and Dielectric properties of Dimethyl Urea using the First-principles calculations.

Computational details

Several codes are available for the theoretical structure simulation[12]. The density functional theory approach has emerged as a well established computational method. It has been widely employed to arrive at the conformations of a large number of molecular systems. The practical applicability and sophistication of DFT is strongly sensitive to the good choice of exchange–correlation function along with the appropriate basis set.

Quantum espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modelling. It is based on density-functional theory, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF)[13] implementation of density functional theory (DFT), with a Local density approximation (LDA)[14] to exchange correlation energy of electrons and ultrasoft pseudopotentials[15], 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 15 Ry and charge density cutoff of 70 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme[16] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[17] 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 Dimethyl Urea was first built using "Avogadro"[18]. 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=10.85Å, b=4.91Å and c=5.50Å. "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"[19] and the structure as viewed along X, Y and Z axes are given in Figures 1, 2 and 3. The bond lengths and bond angles in the relaxed structure of Urea have been tabulated in TABLES 1 and 2.

Similar values of structural parameters have been

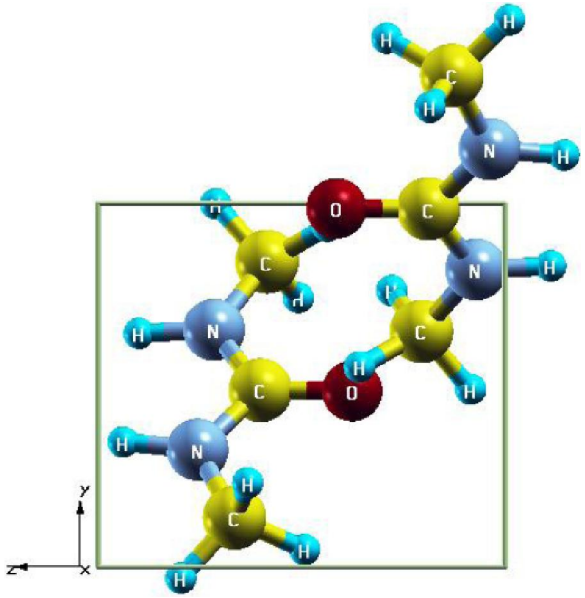

Figure 1 : Structure of 1, 3-dimethyl urea as viewed along X axis

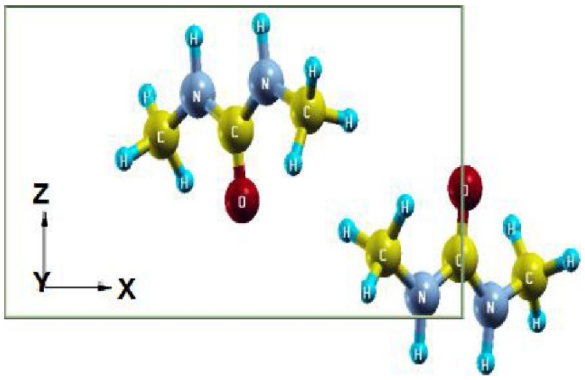

Figure 2 : Structure of 1, 3-dimethyl urea as viewed along Y axis

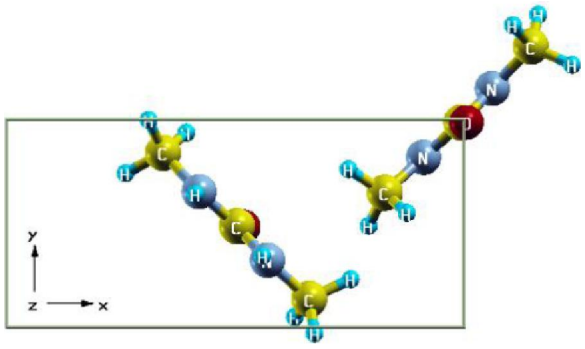

Figure 3 : Structure of 1, 3-dimethyl urea as viewed along Z axis

TABLE 1 : Bond lengths in 1,3-dimethyl urea

Bond	Bond length (Å)
O-C	1.25
C-N	1.37, 1.44
N-H	1.02
C-H	1.01

TABLE 2 : Bond angles in 1,3-dimethyl urea

	Bond angle (Deg)
O-C-N	123
H-C-H	108
H-C-N	110
C-N-C	121, 123

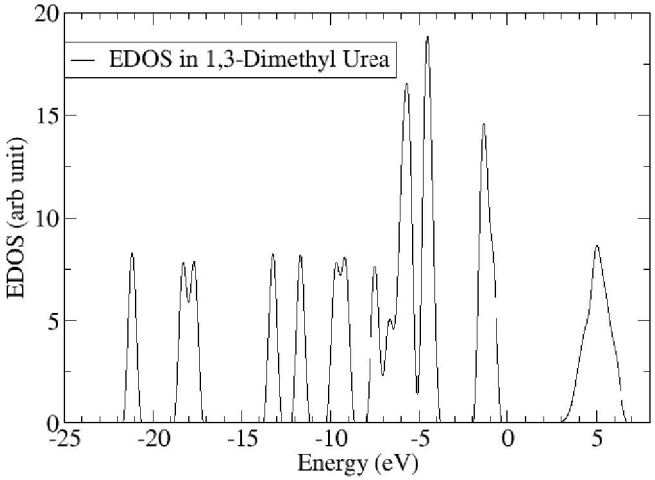

Figure 4 : EDOS in 1, 3-dimethyl urea

found by C. Näther et. al.,[20]. They have studied two polymorphs of Dimethyl Urea at lower temperature. Pérez-Folch et al.[21] and Marsh[22] have studied a polymorph of this compound having 8 molecules per orthorhombic unit cell. Martins et al.[23] have studied a polymorph having 2 molecules per orthorhombic unit cell. 1,3-Dimethyl urea is an organic compound derived from urea by replacing two hydrogen atoms of two -NH2 groups by -CH3 groups. It has one H-donor site and two acceptor sites. It is capable of forming multiple hydrogen bonds. It is expected that, it can form multiple hydrogen bonds and modify the properties of the host crystal when used as a dopant. It has been found that, doping of 1,3-dimethyl urea improves optical properties of the KDP crystal[24].

EDOS calculation

Electron Density of States (EDOS) have been computed using Electronic structure calculation code of Quantum espresso and is shown in Figure 4. The band gap comes out to be 3.3 eV. This value is close to the value shown by NLO materials[25] and liquid crystalline materials[26, 27]. It has been found that Urea is an organic compound having very large NLO properties. It has good optical and mechanical properties but its crystallization and handling is rather difficult as it is highly hygroscopic. Other urea derivatives like monomethylurea (H2NCONHCH3), 1,1-dimethylurea (H2NCON (CH3)2), 1,3-dimethylurea (CH3HNCONHCH3) and phenylurea (H2NCONHCH5) have been investigated in the light of NLO applications and few of them have been found suitable for NLO applications[28].

Dielectric constant and phonon modes

The value of dielectric constant comes out to be Dielectric constant of the material has been computed and it comes out to be 2.11, 2.06 and 2.05 along X, Y and Z axes respectively and the average value comes out to be 2.07. The computed phonon modes at the gamma point range from 105 cm^{-1} to 2568 cm^{-1} showing that the simulated structure is stable.

CONCLUSIONS

Band gap in case of Dimethyl Urea is found to be 3.3 eV. This value is close to the value shown by NLO materials and liquid crystalline materials. Hence the possibility of finding liquid crystalline nature in mixtures containing Urea can be explored. The value of estimated Band gap is confirming that the material can be used for NLO applications. The average value of dielectric constant in Urea comes out to be 2.07. The computed phonon modes at the gamma point range from 105 cm^{-1} to 2568 cm^{-1} showing that the simulated structure is stable.

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