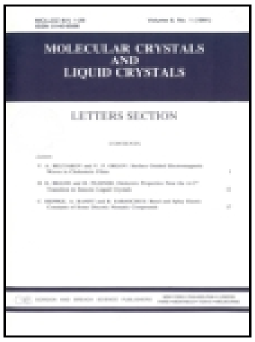

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Structure simulation and study of electronic and dielectric properties of two derivatives of benzamide

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ABSTRACT

First-principles calculations based on density functional theory have been done on the chlorinated phenyl benzamides; 4-chloro-phenyl-benzamide – C13H10ClNO, and 2-chloro-3-chloro-phenyl-benzamide – C13H9Cl2NO. The triclinic structure of 4-chloro-phenyl-benzamide and orthorhombic structure of 2-chloro-3-chloro-phenyl-benzamide have been simulated and the structural parameters have been found out. Electron density of states has been computed in the materials using the electronic structure calculation code of Quantum-Espresso which gives a band gap of 0.74 eV in case of 4-chloro-phenyl-benzamide. This value is close to the value exhibited by semiconducting materials and photonic band gap materials. Band gap in case of 2-chloro-3-chloro-phenyl-benzamide comes out to be 3.08 eV. This value is in the range exhibited by NLO materials. Dielectric constant of the materials has been computed. The value of dielectric constant in 4-chloro-phenyl-benzamide comes out to be 2.78, 3.14, and 3.92 along X, Y, and Z axes, respectively, and the average value comes out to be 3.28. The value of dielectric constant in case of 2-chloro-3-chloro-phenyl-benzamide comes out to be 1.39, 1.53, and 1.34 along X, Y, and Z axes, respectively, and the average value comes out to be 1.42. Thus, additional chlorination is increasing the band gap and decreasing the dielectric constant in phenyl benzamide.

KEYWORDS
2-Chloro-3-chloro-phenyl-benzamide; 4-chloro-phenyl-benzamide; band gap; dielectric constant; electron density of states; first-principles calculation; NLO material

Introduction

Nonsteroidal anti-inflammatory drugs play an important role in the treatment of inflammation and they owe their therapeutic and side effects in large part to the inhibition of cyclooxygenase. The separation of the therapeutic effects from the side effects has been a major goal in the design and synthesis of these drugs. G. Caliendo et al. [1] have synthesized and studied several derivatives of benzamide. It has been found that the N-substituted benzamides can be used as agents for combating pests, in particular as insecticides and nematicides [2].

It is essential to have the knowledge of molecular interactions for the design and synthesis of macromolecules that adopt required conformations. These interactions, being strongly temperature and pH dependent, not only their interplay dominant in the crystallization and stability of macromolecules [3], but also govern conformational properties enabling the pharmacological activity of several molecules [4]. Suryaprakash et. al., have [5] investigated weak

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molecular interactions in isomeric fluorinated benzanilides using 19 F and 1 H-NMR (with 14 N decoupling) spectroscopic techniques together with density functional theoretical (DFT) calculations.

Noncovalent forces play an important role in processes like folding and self-assembly [6]. In recent years, chemists have been engaged in the development of foldamers [7] and artificial molecules that utilize noncovalent forces to modulate folding or helical architectures. In this regard, the strong directional characteristics associated with hydrogen bonds like O–H …O, N–H …O, and N–H …N [8–12] are highly effective in the assembly of supramolecular structures.

T. N. Guru Row and D. Chopra [13] have synthesized and characterized a series of mono- and difluorinated benzanilides to unravel the importance of interactions involving organic fluorine. They have studied the effect of fluorine substitution on the molecular conformation and the solid-state organization of the molecules in the crystalline lattice and have discussed the same in terms of changes in molecular conformation and the supramolecular aggregation. B.Thimmegowda et. al., [14–19] have synthesized and studied several derivatives of benzamide.

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 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 4-chloro-phenyl-benzamide and 2-chloro-3-chloro-phenyl-benzamide 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.

Computational details

Several codes are available for the theoretical structure simulation [25]. The DFT 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 DFT, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF) [26] implementation of DFT, with a local density approximation [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 30 Ry and charge density cutoff of 180 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 triclinic unit cell of 4-chloro-phenyl-benzamide and orthorhombic unit cell of 2-chloro-3-chloro-phenyl-benzamide were first simulated using “Avogadro” [31]. Later, atomic positions of the molecules have been used in the PWSCF calculations.

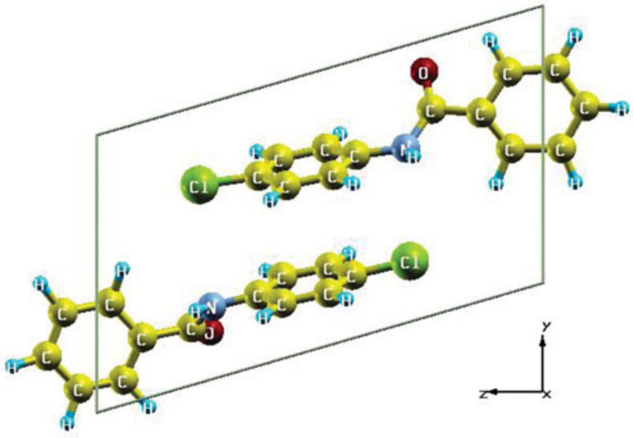

Figure 1. Structure of 4-chloro-phenyl-benzamide as viewed along X axis.

The structure was relaxed and the optimized values of the unit cell parameters thus arrived at through minimization of energy are; a = 5.39 Å, b = 8.00 Å, c = 13.68 Å, α = 105.9 deg, β = 100.8 deg, and γ = 90.02 deg in case of 4-chloro-phenyl-benzamide (triclinic system) a = 11.43 Å, b = 12.21 Å, c = 8.88Å, and $\alpha = \beta = \gamma = 90$ deg in case of 2-chloro-3-chloro-phenyl-benzamide (orthorhombic system), respectively. “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” [32] and the structure of 4-chloro-phenyl-benzamide as viewed along X axis and structure of 2-chloro-3-chloro-phenyl-benzamide as viewed along Z axis are shown in Figs. 1 and 2, respectively. The bond lengths and bond angles in the relaxed structure of 4-chloro-phenyl-benzamide and 2-chloro-3-chloro-phenyl-benzamide have been tabulated in Tables 1 and 2, respectively.

Table 1. Bond lengths in two phenyl benzamide derivatives.

Bond	Bond length in 4-chloro-phenyl-benzamide (Å)	Bond length in 2-chloro-3-chloro-phenyl-benzamide (Å)
C – H	1.09	1.09
C – C	1.38–1.48	1.38–1.48
C – O	1.24	1.22
C – N	1.36, 1.39	1.36, 1.39
C – Cl	1.72	1.72

Table 2. Bond angles in two phenyl benzamide derivatives.

Bond	Bond angle in 4-chloro-phenyl-benzamide (deg)	Bond angle in 2-chloro-3-chloro-phenyl-benzamide (deg)
C – N – C	127	129
O – C – C	121	121
N – C – C	116–122	116–122
N – C – O	123	124
C – C – C	118–123	118–123
C – C – H	119	119
C – C – Cl	121	119
C – N – H	112	116

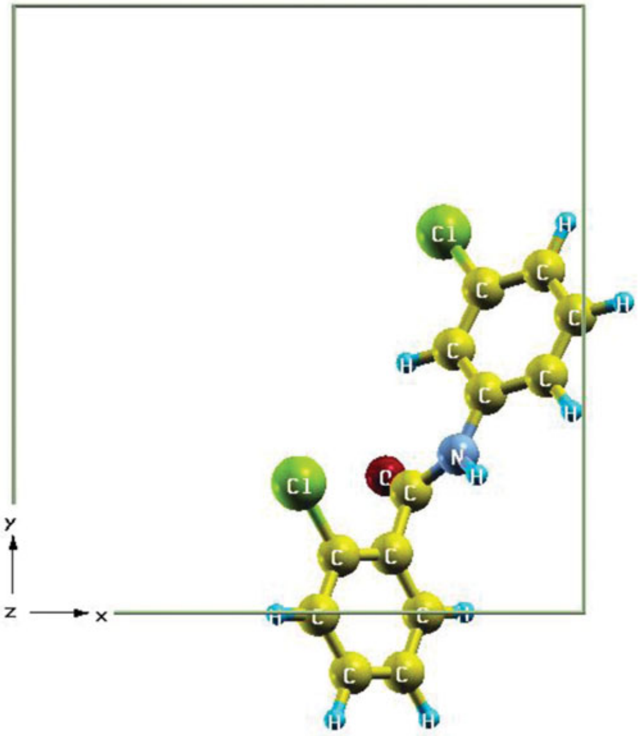

Figure 2. Structure of 2-chloro-3-chloro-phenyl-benzamide as viewed along Z axis.

From the tables, it is clear that bond lengths in most cases are not altered due to additional chlorination. C – O bond length is slightly decreased due to additional chlorination. One can see that few bond angles get slightly altered due to additional chlorination. The structural parameters of both derivatives of phenyl-benzamide are matching well with the XRD studies found in literature [33,34].

EDOS calculation

Electron density of states (EDOS) has been computed in case 4-chloro-phenyl-benzamide andc 2-chloro-3-chloro-phenyl-benzamide using electronic structure calculation code of Quantum espresso. EDOS in 4-chloro-phenyl-benzamide and 2-chloro-3-hloro-phenyl-benzamide have been shown in Figs. 3 and 4, respectively. Band gap in case of 4-chloro-phenyl-benzamide and 2-chloro-3-chloro-phenyl-benzamide are found to be 0.74 and 3.08 eV, respectively. The band gap in case of 4-chloro-phenyl-benzamide is similar to that exhibited by semiconductors and photonic band gap materials. Bang gap in case of 2-chloro-3-chloro-phenyl-benzamide lies in the range of values exhibited by nonlinear optical (NLO) materials [35] and liquid crystalline materials [36]. Several inorganic NLO materials show a band gap in the range 2–4 eV. For example, lithium niobate shows a band gap of 4 eV. Barium titanate shows a value of 3.2 eV. BSO crystals show a value of 4.02 eV and KTN nanoparticles show a band gap of 3.26 eV. The organic NLO material L-tartaric acid shows an optical band gap of 3.65 eV. It can be seen that the additional chlorination is increasing the value of band gap in the phenyl benzamide. Tuning of the band gap plays an important role in the field of photonic crystals.

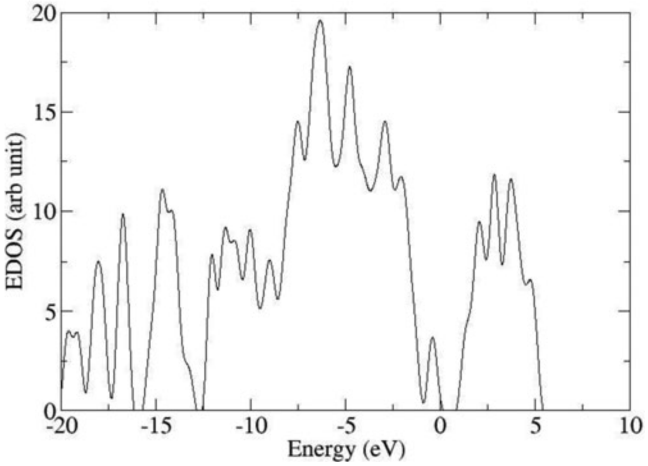

Figure 3. Electron density of states in 4-chloro-phenyl-benzamide.

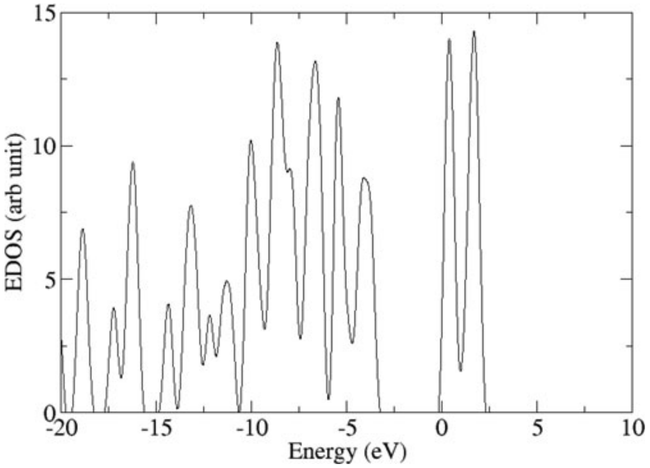

Figure 4. Electron density of states in 2-chloro-3-chloro-phenyl-enzamide.

Dielectric constant

Dielectric constant of the material has been computed in case of 4-chloro-phenyl-benzamide and 2-chloro-3-chloro-phenyl-benzamide. The value of dielectric constant in 4-chloro-phenyl-benzamide comes out to be 2.78, 3.14, and 3.92 along X, Y, and Z axes, respectively, and the average value comes out to be 3.28. In case of 2-chloro-3-chloro-phenyl-benzamide they are found to be 1.39, 1.53, and 1.34 along X, Y, and Z axes, respectively, and the average value comes out to be 1.42. Thus, additional chlorination is found to decrease the dielectric constant of phenyl benzamide.

Conclusions

Band gap in case of 4-chloro-phenyl-benzamide and 2-chloro-3-chloro-phenyl-benzamide are found to be 0.74 and 3.08 eV, respectively. These values are close to the values exhibited by NLO materials and liquid crystalline materials. The average value of dielectric constant in 4-chloro-phenyl-benzamide comes out to be 3.28. In case of 2-chloro-3-chloro-phenyl-benzamide it is found to be 1.42. The additional chlorination is found to increase the value of band gap and decrease the value of dielectric constant of phenyl benzamide.

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