

# Structure simulation and study of electronic and dielectric properties of unfluorinated and fluorinated C-Nitrile derivative

## Abstract

First-principles calculations based on Density Functional Theory have been done on the technologically important organic material C-Nitrile derivative 3-hydroxy-1,2,3-trimethyl-cyclohexane carbonitrile [C<sub>10</sub>H<sub>17</sub>NO]. The triclinic structure of the material has been simulated and the structural parameters are found to be a=6.144Å, b=8.107Å, c=6.163Å, α=111.81°, β=105.69°, γ=109.24°. After fluorination the structural parameters are found to be a=6.722Å, b=8.335Å, c=6.645Å, α=115.09°, β=99.19°, γ=112.99°. Electron Density of States (EDOS) has been computed in the material using the Electronic structure calculation code of Quantum-Espresso which gives a Band gap of 4.4 eV. After fluorination the Band gap is found to be 4.2 eV. The value of dielectric constant in the material comes out to be 2.28, 2.52 and 2.26 along x, y and z axes respectively and the average value comes out to be 2.35. After fluorination the dielectric constant of the compound comes out to be 2.11, 2.28 and 2.05 along x, y and z axes respectively and the average value comes out to be 2.15. The computed phonon modes range from 335cm<sup>-1</sup> to 2802cm<sup>-1</sup>. After fluorination the phonon modes range from 245cm<sup>-1</sup> to 3125cm<sup>-1</sup>. Present study is clearly indicating that this material is having the band gap and dielectric constant exhibited by organic semiconducting materials and NLO materials.

**Keywords:** C-Nitrile, first-principles calculation, electron density of states (EDOS), band gap, dielectric constant, phonon modes

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## Introduction

Metalated nitriles are powerful nucleophiles that are broadly effective in a diverse range of alkylations. The exceptional nucleophilicity stems from the inductively stabilized negative charge density localized on the formally anionic carbon.<sup>1-4</sup> Singh et al., have studied various relaxation processes including the chair-chair transformation in cyclohexane derivatives.<sup>5</sup> Singh and Murthy have studied secondary relaxation in disordered crystals of isocyanocyclohexane, cyanocyclohexane, and 1-cyanoadamantane.<sup>6</sup> Miyanaga et al.,<sup>7</sup> have studied the structure of cobalt containing nitrile hydratase. Nitrile hydratases are found to be unusual metalloenzymes that catalyze the hydration of nitriles to their corresponding amides. It has been found that they are used as biocatalysts in acrylamide production, one of the few commercial scale bioprocesses, as well as in environmental remediation for the removal of nitriles from waste streams.<sup>8,9</sup> Nitriles are used in the manufacture of rubbers. The uses of nitrile rubber include disposable non-latex gloves, automotive transmission belts, hoses, O-rings, gaskets, oil seals, V belts, synthetic leather, printer's form rollers, and as cable jacketing; NBR latex can also be used in the preparation of adhesives and as a pigment binder. A hydrogenated version of nitrile rubber (HNBR) which is also known as HSN (highly saturated nitrile) is commonly used to manufacture O-rings for automotive air-conditioning systems. Koutsantonis et al.,<sup>10</sup> have studied the structure of several crystals of derivatives of nitriles using X-ray diffraction (XRD) studies.<sup>10</sup> Fraser F Fleming et al.,<sup>11</sup> have studied the crystal structure of C-Nitrile derivative 3-hydroxy-1,2,3-trimethyl-cyclohexane carbonitrile [C<sub>10</sub>H<sub>17</sub>NO] using XRD. It has been found that any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material.<sup>12,13</sup> 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<sup>14</sup> has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials.<sup>15,16</sup> With this in view, structure of C-Nitrile derivative 3-hydroxy-1,2,3-trimethyl-cyclohexane carbonitrile [C<sub>10</sub>H<sub>17</sub>NO] 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.<sup>17</sup> 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. Authors have used plane wave self consistent field (PWSCF)<sup>18</sup> implementation of density functional theory (DFT), with a Local density approximation (LDA)<sup>19</sup> to exchange correlation energy of electrons and ultrasoft pseudopotentials,<sup>20</sup> 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<sup>21</sup>

with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme<sup>22</sup> 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 C-Nitrile derivative was first simulated using “Avogadro”.<sup>23</sup> Later, atomic positions of the molecules have been used in the plane wave self consistent field calculations. The structure was relaxed and the optimized values of the unit cell parameters thus arrived at through minimization of energy are;  $a=6.144\text{\AA}$ ,  $b=8.107\text{\AA}$ ,  $c=6.163\text{\AA}$ ,  $\alpha=111.81^\circ$ ,  $\beta=105.69^\circ$ ,  $\gamma=109.24^\circ$ . “scf” calculation was done using the final atomic positions obtained after relaxing the structure using the program ‘pw.x’ of Quantum espresso. Fluorination of C-Nitrile derivative was done by replacing one hydrogen atom by fluorine atom. Again the structure was relaxed to minimize the energy and the lattice parameters thus arrived are;  $a=6.722\text{\AA}$ ,  $b=8.335\text{\AA}$ ,  $c=6.645\text{\AA}$ ,  $\alpha=115.09^\circ$ ,  $\beta=99.19^\circ$ ,  $\gamma=112.99^\circ$ . The completely relaxed structure of the unit cell was visualized using the program “XCrysDen”,<sup>24</sup> and the structure of unit cell of C-Nitrile derivative as seen along X, Y and Z axes are shown in Figures 1 to 6. The bond lengths and bond angles in the relaxed structure of C-Nitrile derivative have been tabulated in Table 1 and Table 2 respectively.

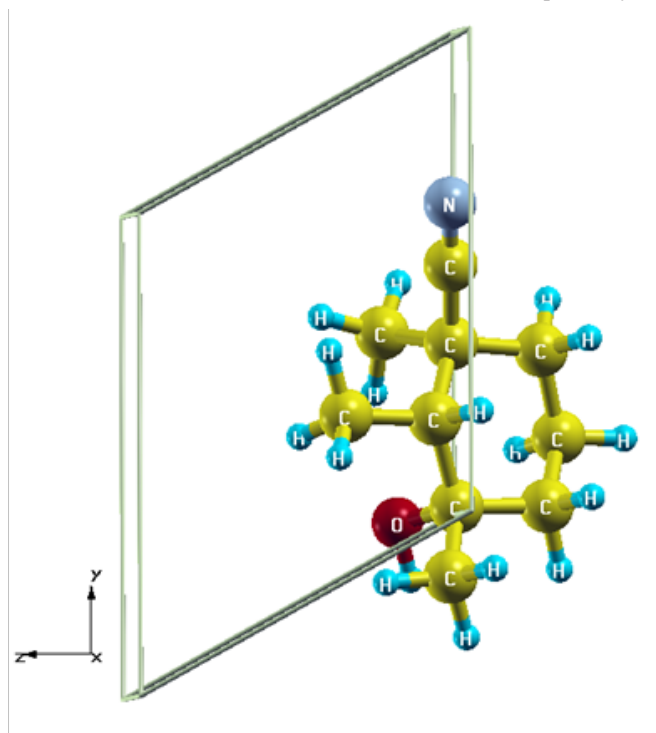


Figure 1 Structure of unit cell of C-Nitrile derivative as seen along x direction.

Table 1 Bond length in C-Nitrile derivative

Bond	Bond length (Å)
C-H	1.1
O-H	1.00
C-O	1.44
C-C	1.53

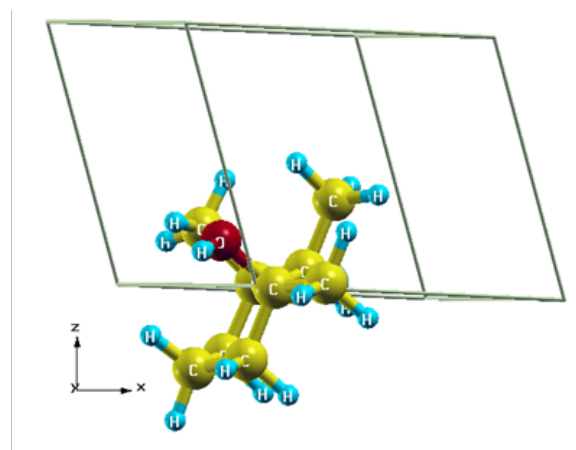


Figure 2 Structure of unit cell of C-Nitrile derivative as seen along y direction.

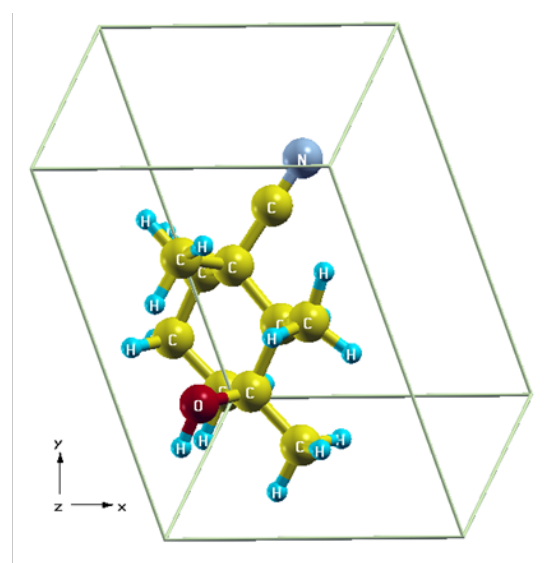


Figure 3 Structure of unit cell of C-Nitrile derivative as seen along z direction.

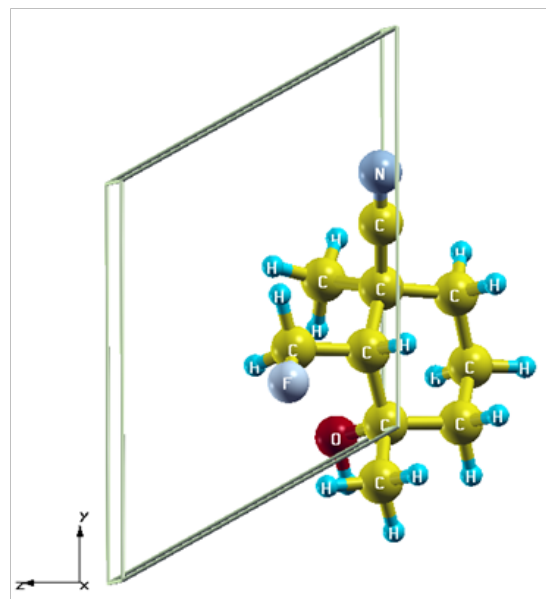
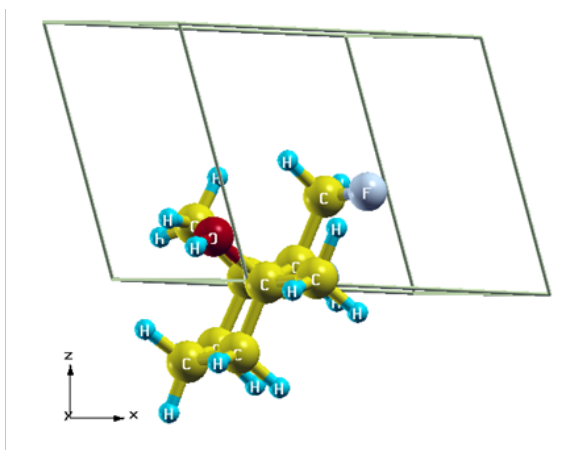
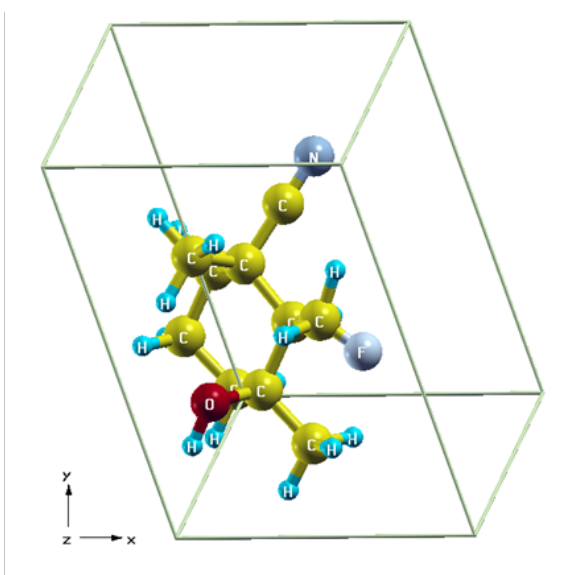


Figure 4 Structure of unit cell of fluorinated C-Nitrile derivative as seen along x direction.



**Figure 5** Structure of unit cell of fluorinated C-Nitrile derivative as seen along y direction.



**Figure 6** Structure of unit cell of fluorinated C-Nitrile derivative as seen along z direction.

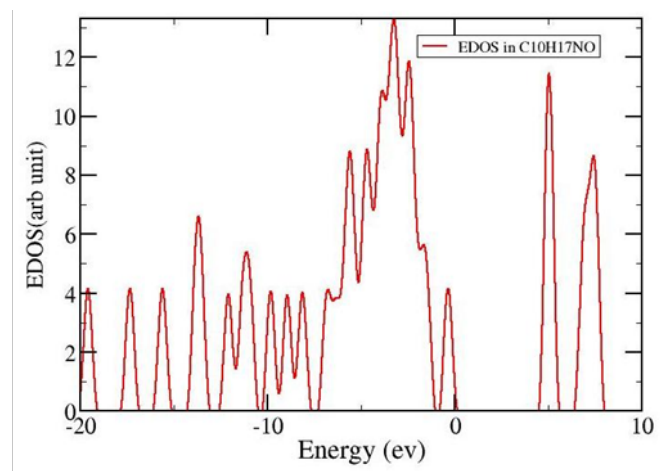
**Table 2** Bond angle in C-Nitrile derivative

Bond	Bond angle (deg)
H-C-H	108
H-C-C	108–111
C-O-H	108
C-C-C	107–118

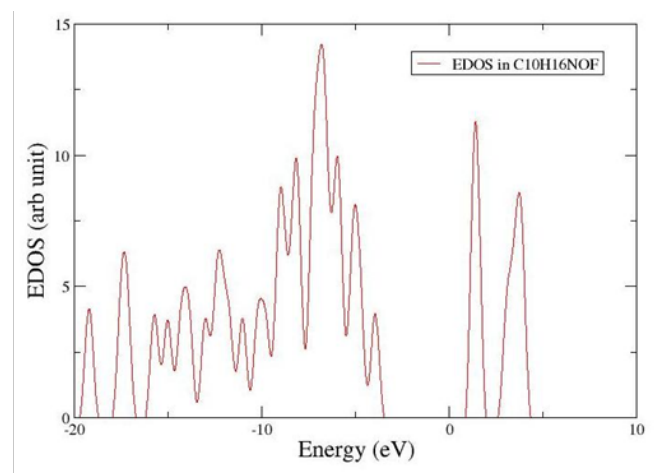
### EDOS calculation

Electron Density of States (EDOS) has been computed in C-Nitrile derivative using Electronic structure calculation code of Quantum espresso. EDOS in C-Nitrile derivative and fluorinated C-Nitrile derivative have been shown in Figure 7 and Figure 8. Band gap in C-Nitrile derivative and fluorinated C-Nitrile derivative is found to be 4.4 eV and 4.2 eV respectively. This value is close to that exhibited by Non-linear optical (NLO) materials<sup>25</sup> and organic semiconducting materials. Presently, the organic semiconducting materials have very much attracted the scientific community owing to their technological advantages over traditional silicon-based semiconductor devices.

Most organic materials are much less expensive to generate than highly crystalline inorganic semiconductors, and also may be used to make devices with inexpensive fabrication methods. Also, most organic materials are soluble in one or more common solvents which allows for the possibility of solution processing which can produce many devices at very low cost.<sup>26,27</sup> Several inorganic NLO materials show a band gap in the range 2eV to 4eV. For example, Lithium niobate shows a band gap of 4eV. Barium titanate shows a value of 3.2eV. BSO crystals show a value of 4.02eV and KTN nanoparticles show a band gap of 3.26eV. The organic NLO material L-Tartaric acid shows an optical band gap of 3.65eV. Tuning of the band gap plays an important role in the field of photonic crystals.



**Figure 7** Electronic density of states in C-Nitrile derivative.



**Figure 8** Electronic density of states in fluorinated C-Nitrile derivative.

### Dielectric constant and phonon modes

The Dielectric constant and Phonon modes of the material have been computed in unfluorinated and fluorinated state using the ph.x code of Quantum espresso. Dielectric constant of the material has been computed. The value of dielectric constant in C-Nitrile derivative comes out to be 2.28, 2.52 and 2.26 along x, y and z axes respectively and the average value comes out to be 2.35. After fluorination the dielectric constant of the compound comes out to be 2.11, 2.28 and 2.05 along x, y and z axes respectively and the average value comes out to be 2.15. This value is in the range exhibited by low k dielectric materials used in the semiconductor industry. For example; Dielectric constant of Fluoropolyimide is 2.8, Benzo-cyclo-butane is

2.7, Black diamond is 2.7, Polyethylene is 2.4, Polypropylene is 2.3, Fluoropolymer is 2.24, Perylene is 2.2 and in Dupont PTFE-based copolymer AF 2400 it is 2.06. They have applications in the fabrication of semiconducting devices.<sup>27</sup> This also shows that the material under study can be used in semiconductor devices. Phonon modes have been computed using the ph.x program of quantum espresso. The computed phonon modes range from  $335\text{cm}^{-1}$  to  $2802\text{cm}^{-1}$ . After fluorination the phonon modes range from  $245\text{cm}^{-1}$  to  $3125\text{cm}^{-1}$ . All the phonon modes are positive and hence they clearly prove that the simulated structures are stable. When one hydrogen atom has been replaced by a fluorine atom which is heavier, the frequency range of phonons has come down in the material. Values of various parameters in unfluorinated and fluorinated C-Nitrile derivative are tabulated in Table 3.

**Table 3** Different parameters in Unfluorinated and fluorinated C-Nitrile derivative

Parameter	Unfluorinated C-Nitrile derivative	Fluorinated C-Nitrile derivative
a (Å)	6.144	6.722
b (Å)	8.107	8.335
c (Å)	6.163	6.645
$\alpha$ (deg)	111.81	115.09
$\beta$ (deg)	105.69	99.19
$\gamma$ (deg)	109.24	112.99
Crystal system	Triclinic	Triclinic
Band gap (eV)	4.4	4.2
Average Dielectric constant	2.35	2.15
Phonon modes $\text{cm}^{-1}$	335-2802	245-3125

## Conclusion

The lattice parameters arrived at by the structural optimization using the first-principles calculations are  $a=6.144\text{Å}$ ,  $b=8.107\text{Å}$ ,  $c=6.163\text{Å}$ ,  $\alpha=111.81^\circ$ ,  $\beta=105.69^\circ$ ,  $\gamma=109.24^\circ$ . After fluorination the structural parameters are found to be  $a=6.722\text{Å}$ ,  $b=8.335\text{Å}$ ,  $c=6.645\text{Å}$ ,  $\alpha=115.09^\circ$ ,  $\beta=99.19^\circ$ ,  $\gamma=112.99^\circ$ . The lattice parameters of the present study are matching well with the experimentally found values in the material. The material shows a band gap of 4.4 eV. After fluorination the band gap of the material reduces to 4.2 eV. These values of band gap tell that this material may behave as NLO material. The material shows an average dielectric constant of 2.35 and after fluorination the average dielectric constant is reduced to 2.15. The computed phonon modes in the material range from  $335\text{cm}^{-1}$  to  $2802\text{cm}^{-1}$ . After fluorination the phonon modes range from  $245\text{cm}^{-1}$  to  $3125\text{cm}^{-1}$ . Thus it is demanding for further investigations in the material to explore the applications of this material in organic semiconductor electronics and NLO applications. Present study of electronic and dielectric properties of the material is clearly indicating that this material is having the band gap and dielectric constant exhibited by organic semiconducting materials and NLO materials. Also, the present study clearly reveals that the band gap of this material can be tuned by the fluorination.

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## Conflicts of interest

The author declares that there are no conflicts of interest.

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