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First-principles study of electronic ad dielectric properties of 3-methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole

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ABSTRACT

First-principles calculations based on Density Functional Theory have been done on an important amino acid – 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole. Its structure has been simulated. The unit cell is monoclinic with lattice parameters a=18.122Å, b=7.805Å and c=12.505Å showing a space group of C1c1. Bond lengths and bond angles have been estimated. Electronic Density of States calculations show that the material is an insulator. The dielectric constant has been calculated and its value comes out to be 58.63, 4.25 and 78.2 along X, Y and Z axes respectively and its average value comes out to be 47. Polarizability of the material comes out to be 297.3 $Å^3$, 162.7 $Å^3$ and 301.1 $Å^3$ along X, Y and Z axis respectively with an average of 253.7$Å^3$.

KEYWORDS

3-Methyl-1;
5-diphenyl-4;
5-dihydro-1H-pyrazole;
Dielectric constant;
Electronic density of states;
First-principles calculations;
Polarizability.

INTRODUCTION

The Pyrazoles and their derivatives which are five membered heterocycles have attracted the scientific community with considerable intensity because of their synthetic and biological applications. Pyrazoles have known to exhibit enormous biological activity such as antibacterial, antifungal, anti-inflammatory, anticonvulsant, hypoglycemic and anticancer activities. The pyrazoles possess antipyretic, antitumour, tranquilizing and herbicidal activities. Pyrazole derivatives are reported to exhibit antioxidant and antimicrobial.

Govindaraju, et. Al.,[1] have synthesized a series of 8-[5-aryl-4-octyl-2-phenyl-3,4-dihydro-2H-pyrazol-3-yl]-octanoic acid ethyl esters and have evaluated in vitro for their antibacterial and antifungal activity against different organisms. They have tested the compounds for their antioxidant activity and their reducing power ability. Ajay Kumar at. Al.,[2] discussed the developments in the synthetic strategies, biological activities associated with pyrazole derivatives highlighting the different synthetic methodologies and the diverse pharmacological activities of pyrazole moiety.

Vijay V Dabholkar et. Al.,[3] have synthesized and characterized substituted pyrazoles from p-chlorobenzaldehyde, ethyl acetoacetate as starting materials through azo dye containing 1, 3-diketones as intermediates. They have tested the representative samples for their anti-microbial activity against Gram-negative bacteria, Gram-positive bacteria, Fungi and Yeast using disc diffusion method. Raghavendra et. Al.,[4] have synthesized and char-

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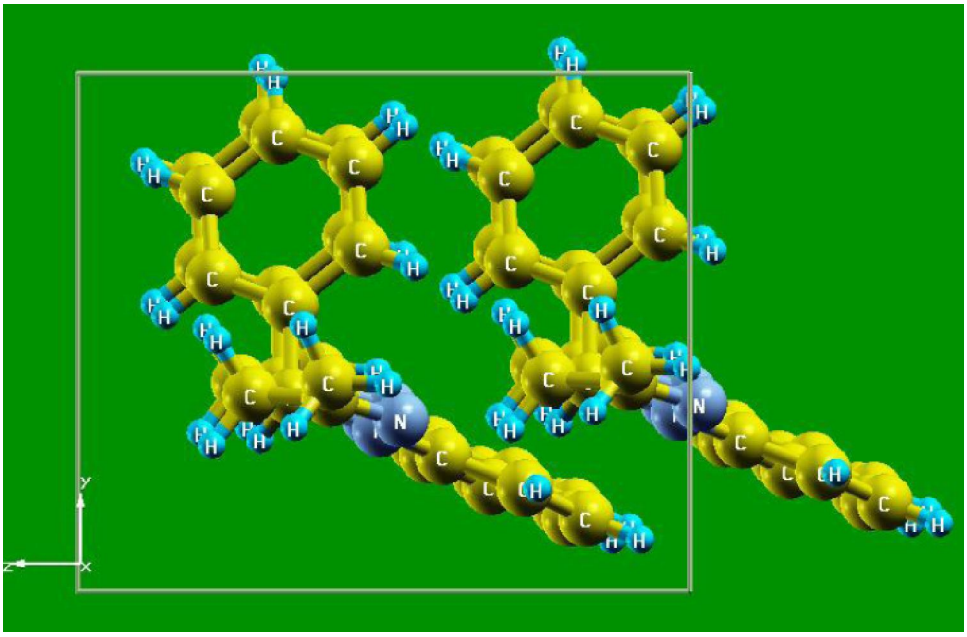

Figure 1 : Structure of unit cell of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole as viewed along X-axis

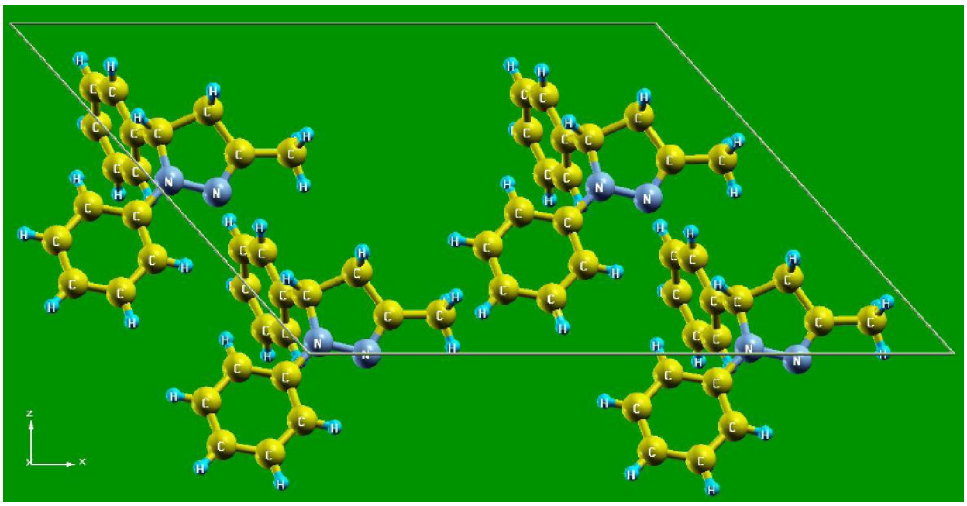

Figure 2 : Structure of unit cell of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole as viewed along Y-axis

acterized some novel azo dyes and have tested them for their resistance against the growth of fungi organisms, antihelmentic properties.

Baktýr et. Al.,[5] have discussed the structure of 3,5-Bis(4-meth¬oxy¬phen¬yl)-1-phenyl-4,5-dihydro-1H-pyrazole. Fun et. Al.,[6] have discussed the structure of 1-Cyclo¬hexyl-5-(4-meth¬oxy¬phen¬yl)-1H-pyrazole-4-carb¬oxy¬lic acid. Kalirajan et. Al.,[7] have synthesized and characterized some novel pyrazole substituted 9-anilino acridine derivatives and have tested them for their antimicrobial activities.

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[8, 9]. 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[10] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials[11, 12]. 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole and such derivatives have attracted the scientific community in various aspects. With this in view, structure of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-

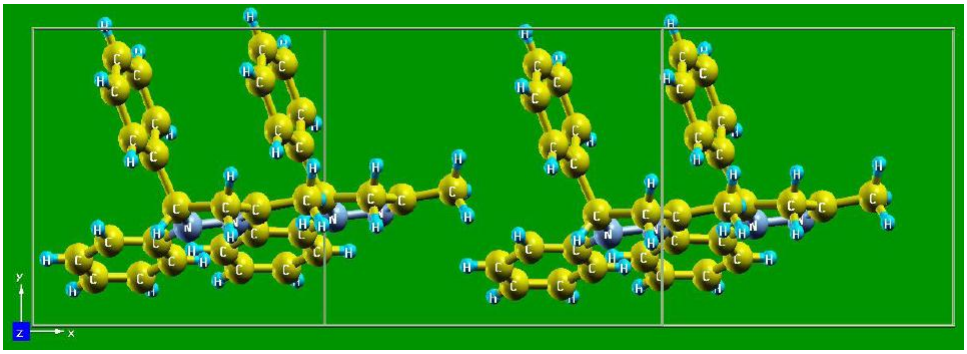

Figure 3 : Structure of unit cell of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole as viewed along Z-axis

TABLE 1 : Bond lengths in 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole

Bond	Bond length (Å)
C – H	0.97
C – C	1.37 - 1.54
C – N	1.28 – 1.38
N – N	1.39

TABLE 2 : Bond angles in 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole

Bond	Bond angle (deg)
C – C – C	102 – 124
C – C – H	109 – 120
H – C – H	109
N – C – C	120 – 121
C – N – C	126.7
C – N – N	120

pyrazole has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant and Polarizability have been done and the results have been reported in the present paper.

COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation[13]. 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)[14] implementation of density functional theory (DFT), with a Local density approximation (LDA)[15] to exchange correlation energy of electrons and ultrasoft pseudopotentials[16], 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[17] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[18] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

RESULTS AND DISCUSSION

In the present study, the monoclinic unit cell of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole was first simulated using "Avogadro"[19]. Later, atomic positions of the molecules have been used in the plane wave self consistent field calculations. The structure was relaxed and "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"[20] and the structure of unit cell of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole as seen along X-axis, Y-axis

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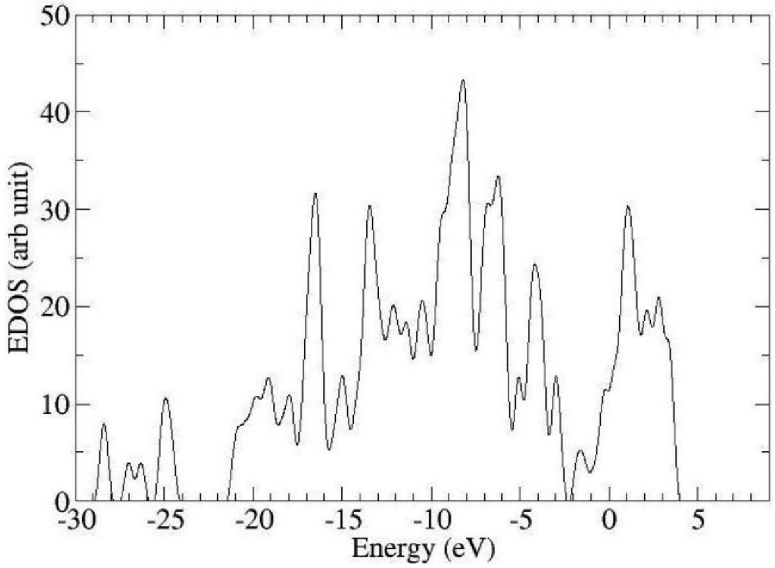

Figure 4 : Electron density of states in 3-methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole

and Z-axis are shown in Figures 1, 2 and 3 respectively. The bond lengths and bond angles in the relaxed structure of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole have been tabulated in TABLES 1 and 2 respectively. The structure is matching well with the XRD studies by Lokanath et. Al.[21].

EDOS Calculation

Electron Density of States (EDOS) has been computed in 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole using Electronic structure calculation code of Quantum espresso. EDOS in 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole has been shown in Figure 3. The EDOS clearly depicts that the material is an insulator.

Dielectric constant and polarizability

Dielectric constant of the material has been computed in case of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole. The value of dielectric constant in 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole comes out to be 58.63, 4.25 and 78.2 along X, Y and Z axes respectively and its average value comes out to be 47. Polarizability of the material comes out to be 297.3 $Å^3$, 162.7 $Å^3$ and 301.1 $Å^3$ along X, Y and Z axis respectively with an average of 253.7$Å^3$.

CONCLUSIONS

The simulated and optimized structure of 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole is matching very well with the structural parameters reported in the literature. EDOS clearly shows that 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole is an insulator. The value of dielectric constant in 3-Methyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole comes out to be 58.63, 4.25 and 78.2 along X, Y and Z axes respectively and its average value comes out to be 47. Polarizability of the material comes out to be 297.3 $Å^3$, 162.7 $Å^3$ and 301.1 $Å^3$ along X, Y and Z axis respectively with an average of 253.7$Å^3$.

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