

First-principles study of electronic and dielectric properties of 2-azacycloheptanone azine

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ABSTRACT

First-principles calculations based on Density Functional Theory have been done on an important Azine derivative 2-Azacycloheptanone azine. Its structure has been simulated. The unit cell is triclinic with lattice parameters $a=10.80\text{\AA}$, $b=6.00\text{\AA}$, $c=5.41\text{\AA}$, $\alpha=113.2\text{deg}$, $\beta=77.2\text{deg}$ and $\gamma=92.8\text{deg}$. Volume of the unit cell is found to be 313\AA^3 . Band gap in case of 2-Azacycloheptanone azine comes out to be 2.36eV . The value of dielectric constant comes out to be 3.55, 2.96 and 2.31 along X, Y and Z axes respectively and its average value comes out to be 2.94. Polarizability of the molecule comes out to be $34.43(\text{\AA})^3$, $29.63(\text{\AA})^3$ and $22.76(\text{\AA})^3$ along X, Y and Z axis respectively. Phonon modes at gamma point have also been computed in 2-Azacycloheptanone azine and they range from 60cm^{-1} to 3085cm^{-1} . © 2016 Trade Science Inc. - INDIA

KEYWORDS

2-Azacycloheptanone azine;
Dielectric constant;
Electronic density of states;
First-principles calculations;
Polarizability.

INTRODUCTION

Azines are a functional class of organic compounds with the connectivity $RR'C=N=N=CRR'$. Azines may be further classified as aldazines or ketazines, depending on the nature of the carbonyl compound^[1,2]. Ketazines are also important intermediates in the industrial production of hydrazine hydrate by the Peroxide process^[3,4]. C. G. Hamaker and B. P. Oberts^[5] have studied the structure of 2-(Benzyl-sulfanyl) benzaldehyde azine $C_{28}H_{24}N_2S_2$ and have found that it has a crystallographically imposed center of symmetry at the mid-point of the N-N bond and have claimed that it is not planar, due to the steric repulsion between S and H atoms. J. Mo et al.^[6], have studied the complex, $\{[Cu_2(C_{12}H_{10}N_2)(C_{12}H_{10}N_4)(C_{18}H_{15}P)_2](BF_4)_2\}_n$

and claim that the cations form a linear chain, and are bridged by 1,2-bis-(4-pyrid-yl)ethene and pyridine-2-carbaldehyde azine. Also claim that there is a crystallographic centre of symmetry at the mid-point of the N-N bond.

L. Y. Hsu et al^[7], have studied the structures of (E,E)-o-nitroacetophenone azine (I), (E,Z)-o-nitroacetophenone azine (II) and (E,E)-o-nitrobenzaldehyde azine (III). L. Wang et al^[8], have studied the complex, $[Ag_2(C_{10}H_8N_2O_2)_3](PF_6)_2$ and have claimed that it contains two silver cations and three molecules of the new Schiff base ligand furan-2-carbaldehyde azine, accompanied by two charge-balancing PF_6^- anions and there is a centre of inversion at the mid-point of the N-N bond of the central ligand.

M. Lewis et al.^[9] have studied the crystal

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structure of mixed azine, C₁₇H₁₇CIN₂O containing four independent molecules. Qamar Ali et al.,^[10] have studied the structure of 2,3-Dimethoxybenzaldehyde azine, C₁₈H₂₀N₂O₄ and have claimed that weak intermolecular C—H...O hydrogen bonding is present in the crystal structure. R. W. H. Small^[11] has carried out the study of structure of 2-Azacycloheptanone azine and has reported the triclinic lattice with one molecule per unit cell.

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^[12, 13]. 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^[14] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials^[15, 16]. Azines and its derivatives have attracted the scientific community in various aspects. With this in view, structure of 2-Azacycloheptanone azine C₁₂H₂₂N₄ has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant, Polarizability 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^[17]. 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)^[18] implementation of den-

sity functional theory (DFT), with a Local density approximation (LDA)^[19] to exchange correlation energy of electrons and ultrasoft pseudopotentials^[20], 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^[21] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme^[22] 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 2-Azacycloheptanone azine was first simulated using

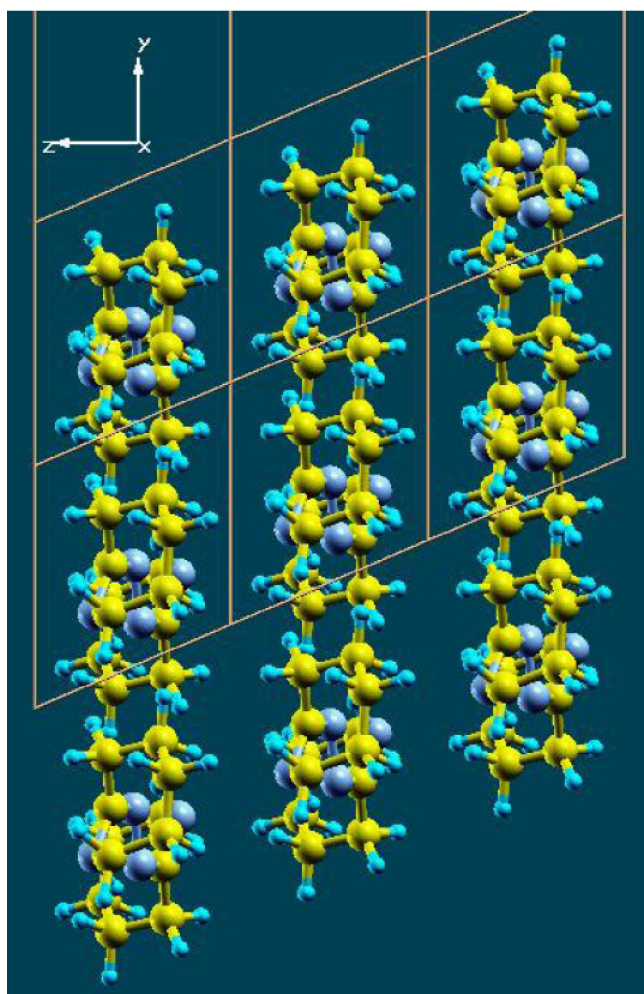


Figure 1 : Structure of unit cell of 2-Azacycloheptanone azine and packing of molecules as viewed along X-axis

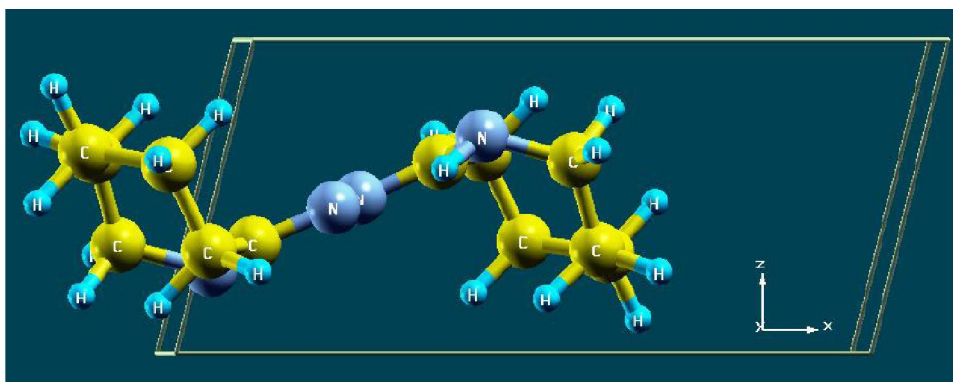


Figure 2 : Structure of unit cell of 2-Azacycloheptanone azine as viewed along Y-axis

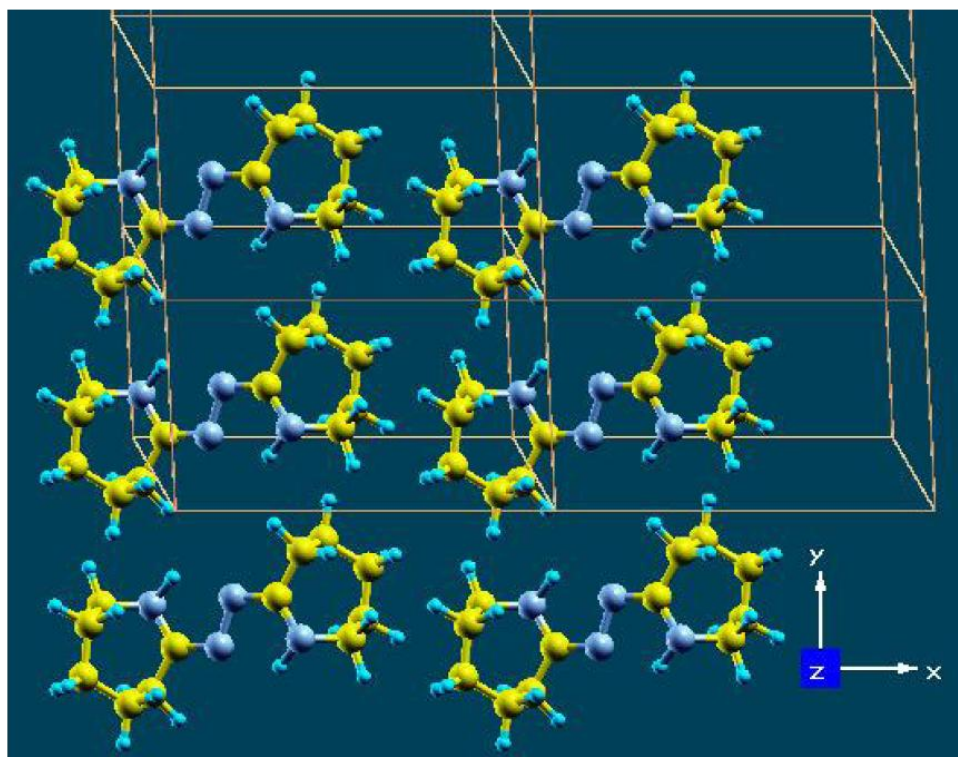


Figure 3 : Structure of unit cell of 2-Azacycloheptanone azine and packing of molecules as viewed along Z-axis

“Avogadro”^[23]. 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; $a=10.80\text{\AA}$, $b=6.00\text{\AA}$, $c=5.41\text{\AA}$, $\alpha=113.2\text{deg}$, $\beta=77.2\text{deg}$ and $\gamma=92.8\text{deg}$. Volume of the unit cell is found to be 313\AA^3 . “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”^[24] and the

structure of unit cell of 2-Azacycloheptanone azine as seen along X-axis, Y-axis and Z-axis are shown in Figures 1, 2 and 3 respectively. The bond lengths and bond angles in the relaxed structure of 2-Azacycloheptanone azine have been tabulated in TABLES 1 and 2 respectively. The structure is matching well with the structure reported in the literature^[11].

EDOS calculation

Electron Density of States (EDOS) has been computed in 2-Azacycloheptanone azine using Electronic structure calculation code of Quantum espresso. EDOS in 2-Azacycloheptanone azine has

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TABLE 1 : Bond lengths in 2-Azacycloheptanone azine

Bond	Bond length (Å)
C – H	1.13 – 1.15
C – N	1.36 – 1.48
C – C	1.48 – 1.50
N – H	1.11

TABLE 2 : Bond angles in 2-Azacycloheptanone azine

Bond	Bond angle (deg)
C – C – C	108 – 114
C – C – H	106 – 112
N – C – C	117 – 119.7
N – C – H	106 – 107
N – C – N	122.5
N – N – C	107.8

been shown in Figure 3. Band gap in 2-Azacycloheptanone azine is found to be 2.36eV.

Dielectric constant, polarizability and phonon modes

Dielectric constant of the material has been computed in case of 2-Azacycloheptanone azine. The value of dielectric constant in 2-Azacycloheptanone azine comes out to be 3.55, 2.96 and 2.31 along X, Y and Z axes respectively and its average value comes out to be 2.94. Polarizability of the molecule has also been estimated and it comes out to be $34.43(\text{Å})^3$, $29.63(\text{Å})^3$ and $22.76(\text{Å})^3$ along X, Y and Z axis respectively. Phonon modes at gamma point have also been computed in 2-Azacycloheptanone azine and they range from 60cm^{-1} to 3085cm^{-1} .

CONCLUSIONS

The simulated and optimized structure of 2-Azacycloheptanone azine is matching very well with the structure reported in the literature. Band gap in case of 2-Azacycloheptanone azine comes out to be 2.36eV. The value of dielectric constant in 2-Azacycloheptanone azine comes out to be 3.55, 2.96 and 2.31 along X, Y and Z axes respectively and its average value comes out to be 2.94. Polarizability of the molecule comes out to be $34.43(\text{Å})^3$, $29.63(\text{Å})^3$ and $22.76(\text{Å})^3$ along X, Y and Z axis respectively. Phonon modes at gamma point have also been computed in 2-Azacycloheptanone azine and they range

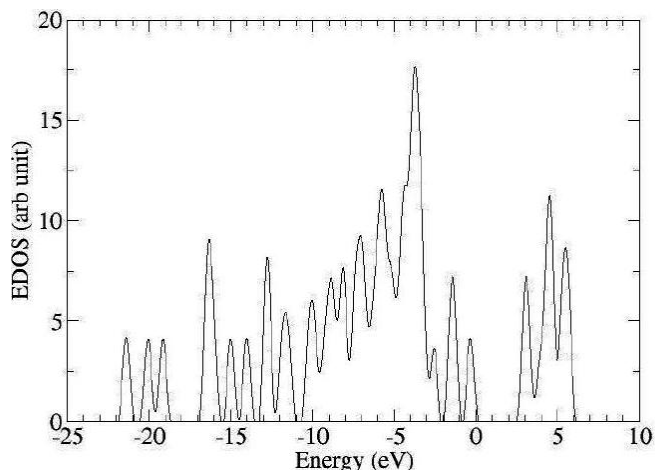


Figure 4 : Electron density of states in 2-azacycloheptanone azine

from 60cm^{-1} to 3085cm^{-1} .

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